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ELEMENTS OF CHEMISTRY,

INCLUDING THE

HISTORY OF THE IMPONDERABLES AND THE INORGANIC CHEMISTRY

OF THE LATE

EDWARD TURNER, M.D., F.R.S. L. & E.

SEVENTH EDITION.

AND THE

OUTLINES OF ORGANIC CHEMISTRY,

BY WILLIAM GREGORY, M.D., &c.

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WITH NOTES AND ADDITIONS,

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PREFACE.

The present blended re-publication embraces the whole of the Imponderables and Inorganic Chemistry of Dr. Turner's well known Elements, together with the Organic Chemistry of Professor Gregory's Outlines, and the separate treatises on Mineral and Organic Analysis by Mr. Parnell and Professor Liebig. In the first plan of the work it was proposed simply to re-edit the seventh edition of Turner's Elements, making such additions and emendations as the progress of the science required, and at the same time re-moulding the part devoted to Organic Chemistry in an abridged and systematic shape. The opportune appearance of Professor Gregory's Outlines greatly aided the accomplishment of this plan by furnishing ready prepared, just such a condensed and methodical treatise on Organic Chemistry as was originally proposed, and the publishers availing themselves of so valuable an aid, at once determined upon substituting the second part of the Outlines in place of the intended abridgment of the Organic Chemistry of Dr. Turner's work. Of the propriety and utility of this change, the editors believe no doubt will be entertained, when it is remembered that the Outlines are from the same pen that drew up a large part of the Organic Chemistry in the seventh edition of Turner, that they are in reality compiled of the same materials with the addition of some more recent results, all very skilfully recast, and that they conform in notation and general method with the inorganic portion of Dr. Turner's work.

In the department of Analytical Chemistry, the closing division of the work, the editors conceive that the present publication will be admitted to present a very important improvement. This portion of the Elements though enriched in the seventh edition by an able sketch of Inorganic

Analysis, written expressly for it by Mr. Parnell, contains no account of the methods of *Organic Analysis*, a subject of peculiar and perhaps leading interest in its connection with modern Chemical research. To remedy this defect the editors have gladly introduced Liebig's outline of the processes for analyzing organic bodies, a treatise of the highest authority with all who are engaged in this department of science, and one happily adapted to the wants of the practical student.

In the first and second parts, treating respectively of the Imponderables and of Inorganic Chemistry, the editors have not felt at liberty to alter the arrangement, and except where some new fact or view derived from recent researches rendered a correction or interpolation necessary, they have uniformly adhered to the lucid language and illustrations of the text. In the department of the Imponderables, and especially under the head of Caloric, they have thought it expedient to make large additions, many of them relating to new determinations on points of much practical, as well as theoretical interest; and in doing so, they think they have not given to this branch of the subject greater relative importance than is assigned to it in the usual course of chemical studies in this country. So long as these subjects continue to be embraced in systematic treatises on Chemistry, and to form a part of the regular oral instructions of the chemical teachers in our medical and other schools, it is thought that a comprehensive and somewhat detailed account of them will be deemed an essential part of every Text book of Chemical Science.

Under the head of Inorganic Chemistry many additions have been made of facts and processes discovered since the publication of the text, and every effort has been used to render this as well as the other portions of this work, a faithful picture of the present condition of the science.

In the Organic Chemistry no important change has been made beyond the introduction at the beginning of many of the distinct sections, of short tabular views of the principal compounds of each of the leading radicals. This it is thought will prove useful as a means of immediate comparison, and will help to remove the seeming confusion arising from a great multiplicity of details.

Most of the additions are incorporated in the text, and are indicated by enclosing brackets; a few are in the form of notes with the editor's initial.

In labouring to correct the numerous typographical errors of the London work, the editors have been greatly assisted by the American reprints of the former edition of Turner's Elements, the great accuracy of which reflects so much credit on the industry and attainments of their accomplished editor. In spite of the care that has been used, many errors have no doubt escaped detection, some of which have been discovered in time to be included in the list of errata. For others which it is feared the reader will detect, the editors must claim his indulgence on the plea of the very short time allowed them for the performance of their task.

Without claiming any merit in the present work, beyond that of a selection of materials already furnished to their hands, and some labour in incorporating matters of recent discovery, the editors indulge the hope that the compilation now offered to the public will be found well suited to the wants of the chemical student, and especially adapted as a *comprehensive text book* and work of reference to those who are pursuing their scientific studies in our medical and other schools. Founding their opinion upon the acknowledged merits of the distinguished authors whose separate treatises they have ventured to unite in one work, they think that the present volume will be found to embrace a larger body of the facts and principles, the processes and applications of the science than any other elementary work which has yet been published in our language. They may be permitted to add, that an experience of many years in teaching Chemistry has convinced them that, though not without faults, the method and scope of Dr. Turner's work are better suited to the use of the student and even for general reference, than the more original, and at the same time speculative modes of presenting the science, adopted in the very able treatises which have more recently issued from the press; and if they may judge from the great demands evinced for a republication of the seventh edition of the Elements, a demand in which the present work originated, they would infer that a large number of the chemical teachers of this country share with them in this preference.

(R.)

PHILADELPHIA, NOVEMBER, 1845.

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CONTENTS.

		Page
	Introduction	1

PART I.

IMPONDERABLE SUBSTANCES.

Sect. I.	Heat	7
	Communication of Heat	8
	Conduction	9
	Radiation	11
	On the Cooling of Bodies	18
	Effects of Heat	19
	Expansion	20
	Thermometer	25
	Specific Heat	31
	Liquefaction	37
	Vaporization	41
	Ebullition	42
	Evaporation	46
	Constitution of Gases with respect to Heat	52
	Sources of Heat	53
Sect. II.	Light	55
Sect. III.	Electricity	67
Sect. IV.	Galvanism	82

PART II.

INORGANIC CHEMISTRY. 111

Sect. I.	Affinity	115
	On the changes that accompany Chemical Action	118
	On the Circumstances that modify and influence the operation of Affinity	120
	On the Measure of Affinity	125
Sect. II.	On the Proportions in which Bodies unite, and on the Laws of Combination	126
	On the Atomic Theory of Dalton	135
	On the Theory of Volumes	138
	Table of Equivalent Weights and Volumes	144
	Chemical Symbols	146
	Isomeric Bodies	150
Sect. III.	Oxygen	150
	Theory of Combustion	154
Sect. IV.	Hydrogen.—Water	156

		Page
	Binoxide of Hydrogen	162
Sect. V.	Nitrogen	165
	On the Atmosphere	166
	Compounds of Nitrogen and Oxygen.—Protoxide	174
	Binoxide of Nitrogen	175
	Hyponitrous Acid	178
	Nitrous Acid	179
	Nitric Acid	181
Sect. VI.	Carbon	185
	Carbonic Acid	188
	Carbonic Oxide	190
Sect. VII.	Sulphur	192
	Compounds of Sulphur and Oxygen.—Sulphurous Acid	194
	Sulphuric Acid	195
	Hyposulphurous Acid	199
	Hyposulphuric Acid	200
	Sulphuretted Hyposulphuric Acid	201
	Bisulphuretted Hyposulphuric Acid	201
Sect. VIII.	Phosphorus	201
	Hypophosphorous Acid	204
	Phosphorous Acid	204
	Phosphoric Acid	205
	Pyrophosphoric Acid	207
	Metaphosphoric Acid	207
Sect. IX.	Boron.—Boracic Acid	208
Sect. X.	Silicon	210
Sect. XI.	Selenium	212
	Oxide of Selenium, and Selenious and Selenic Acids	213
Sect. XII.	Chlorine	215
	Hydrochloric Acid	219
	Compounds of Chlorine and Oxygen	222
	Chloric and Perchloric Acids	226
	Chloride of Nitrogen	228
	Chlorides of Carbon	229
	Chloride of Sulphur	230
	Chlorides of Phosphorus	231
	Chloro-carbonic Acid	230
	Terchloride of Silicon	232
	Chloride of Boron, and Chloro-nitrous Gas	232
	Nature of Chlorine	233
Sect. XIII.	Iodine	235
	Hydriodic Acid	237
	Oxide of Iodine, Iodous and Iodic Acids	239
	Periodic Acid	241
	Chlorides of Iodine	241
	Iodide of Nitrogen, &c.	242
Sect. XIV.	Bromine	243
	Hydrobromic Acid	245
	Bromic Acid	247
	Chloride of Bromine	247
	Bromide of Sulphur and Phosphorus	248
	Terbromide of Silicon	249
Sect. XV.	Fluorine	249
	Hydrofluoric Acid	250
	Fluoboric Acid	252
	Fluosilicic Acid	253

ON THE COMPOUNDS OF THE SIMPLE NON-METALLIC ACIDIFIABLE COMBUSTIBLES WITH EACH OTHER.

Sect. I.	Hydrogen and Nitrogen.—Ammonia	255
Sect. II.	Hydrogen with Carbon.—Light carburetted Hydrogen, &c.	258

		Page
Sect. III.	Compounds of Hydrogen and Sulphur.—Hydrosulphuric Acid	263
	Persulphuretted Hydrogen	265
Sect. IV.	Hydrogen and Selenium.—Hydroselenic Acid	267
Sect. V.	Hydrogen and Phosphorus	267
Sect. VI.	Nitrogen and Carbon.—Cyanogen	271
	Mellon	272
Sect. VII.	Compounds of Phosphorus and Nitrogen	273
Sect. VIII.	Compounds of Sulphur with Carbon	273
	Compounds of Sulphur with Phosphorus	274
	Compounds of Selenium with Sulphur and Phosphorus Compounds of Selenium with Nitrogen	275

METALS.

	General properties of Metals	276
Sect. I.	Potassium and its Compounds with Oxygen, Chlorine, Sulphur, &c.	291
Sect. II.	Sodium and its Oxides, Chloride, &c.	299
Sect. III.	Lithium and its Oxides, &c.	302
Sect. IV.	Barium and its Oxides, &c.	303
Sect. V.	Strontium, and its Oxide, Chloride, Sulphuret, &c.	306
Sect. VI.	Calcium and its Oxides, Chloride, &c.	308
Sect. VII.	Magnesium and its Oxide, &c.	311
Sect. VIII.	Aluminium.—Alumina	314
Sect. IX.	Glucinium, Yttrium, Thorium, Zirconium, and their Oxides	318
Sect. X.	Manganese, and its Compounds with Oxygen, Chlorine, &c.	323
Sect. XI.	Iron, and its Compounds with Oxygen, Chlorine, Sulphur, &c.	331
	Carburets of Iron.—Steel, Cast Iron, Graphite	339
Sect. XII.	Zinc, and its Compounds with Oxygen, Chlorine, Sulphur, &c.	341
	Cadmium and its Oxide	343
Sect. XIII.	Cobalt, Nickel	345
Sect. XIV.	Tin, and its Compounds with Oxygen, Chlorine, &c.	350
Sect. XV.	Copper, and its Compounds with Oxygen, Chlorine, &c.	354
Sect. XVI.	Lead and its Oxides, &c.	358
Sect. XVII.	Arsenic, and its Compounds with Oxygen, Chlorine, &c.	363
	Tests for Arsenious Acid	364
Sect. XVIII.	Antimony, its Oxides, Chlorides, and Sulphurets	372
Sect. XIX.	Chromium, and its Compounds with Oxygen	378
	Sesquichloride of Chromium	379
	Compounds of Chromium with Fluorine, &c.	382
	Vanadium, and its Compounds with Oxygen	384
	Compounds of Vanadium with Chlorine, &c.	389
Sect. XX.	Molybdenum and its Compounds with Oxygen	390
	Tungsten and its Compounds with Oxygen	393
	Columbium and its Compounds with Oxygen	395
Sect. XXI.	Uranium and its Oxides	397
	Cerium and its Oxides.—Lantanium	399
Sect. XXII.	Bismuth, and its Compounds with Oxygen, Chlorine, and Sulphur	399
	Titanium and its Compounds with Oxygen	401
	Tellurium and its Oxides	403
Sect. XXIII.	Mercury and its Oxides	406
	Chlorides.—Calomel and Corrosive Sublimate	410
	Iodides, Cyanurets, and Sulphurets	411
Sect. XXIV.	Silver, its Oxide, Chloride, &c.	412
Sect. XXV.	Gold, and its Compounds with Oxygen, Chlorine, and Sulphur	416
Sect. XXVI.	Platinum, and its Compounds with Oxygen, &c.	420
Sect. XXVII.	Palladium, Rhodium, Osmium, and Iridium	424
Sect. XXVIII.	On Metallic Combinations.—Alloys	431

SALTS.

		Page
	GENERAL REMARKS ON SALTS.—CRYSTALLIZATION.	436
	Crystallization	446
Sect. I.	Oxy-salts	458
	Sulphates	460
	Double Sulphates	467
	Sulphites	470
	Hyposulphites and Hyposulphates	471
	Nitrates	471
	Nitrites	475
	Chlorates	476
	Chlorites	477
	Iodates	479
	Phosphates	480
	Pyrophosphates	480
	Metaphosphates	485
	Arseniates	486
	Arsenites	488
	Chromates	489
	Borates	491
	Carbonates	492
Sect. II.	Hydro-salts	498
	Ammoniacal Salts	499
	Phosphuretted Hydrogen Salts	501
Sect. III.	Sulphur-salts	502
	Hydro-sulphurets	502
	Carbo-sulphurets	504
	Arsenio-sulphurets	505
	Molybdo-sulphurets	507
	Antimonio-sulphurets	508
	Tungsto-sulphurets	508
Sect. IV.	Haloid-salts	509
	Hydrargo-chlorides	509
	Auro-chlorides	510
	Platino-chlorides	510
	Palladio-chlorides	511
	Rhodio-chlorides	512
	Iridio-chlorides, and Osmio-chlorides	512
	Oxy-chlorides	512
	Chlorides with Ammonia	514
	Chlorides with Phosphuretted Hydrogen	515
	Double Iodides	515
	Double Bromides and Fluorides	516
	Boro-fluorides	517
	Silico-fluorides	518
	Titano-fluorides	518
	Oxy-fluorides	519

PART III.

ORGANIC CHEMISTRY.

Introductory		521
	General Doctrines concerning Compound Organic Radicals	524
	Theory of Types, and Doctrine of Substitutions	528
Metamorphoses of Organic Compounds		532
	1. By Oxidation:—	
	a. Direct	533

PAGE
Combustion 533
Eremacausis 533
b. Indirect 534
2. By the action of Acids 534
a. Of Nitric Acid 534
b. Of Sulphuric Acid 535
c. Of Phosphoric Acid, &c. 535
3. By the Action of Bases 535
4. By the Action of Heat, or Destructive Distillation . . . 536
5. By the Action of Ferments 537
Theories of Fermentation 538
Fermentation and Putrefaction , ... 539
Putrefaction of the aqueous solution of Cyanogen . . . 540
General views concerning the Organic Acids 541

COMPOUND RADICALS KNOWN OR ADMITTED 542
I. AMIDE, OR AMIDOGEN 543
Its Compounds:
a. With Hydrogen: Ammonia, &c. 544
b. With Metals 545
c. With Platinum: singular bases of Gros and Reiset . . . 545

II. CARBONIC OXIDE (OXALYLE) 548
Its Compounds:
a. With Oxygen: Oxalic Acid 549
Oxalate of Ammonia, &c. 549
b. With Amide: Oxamide 550
Oxamic Acid 551
c. With Chlorine: Phosgene Gas 551
d. With Potassium or Hydrogen 552
Rhodizonic Acid 552
Croconic Acid 552
Mellitic Acid 553
Mellitate of Ammonia 553
Its Metamorphoses 553

III. CYANOGEN 554
Its Compounds:
a. With Hydrogen: Hydrocyanic Acid 555
b. With Oxygen 558
Cyanic Acid 558
Cyanates 559
Urea (Cyanate of Ammonia) 560
Fulminic Acid and Fulminates 561
Cyanuric Acid 562
Cyamelide 563
c. With Nitrogen: Mellone 564
d. With Chlorine 564
e. With Bromine, Iodine, and Sulphur 565
f. With Metals: Cyanides 565
Double Cyanides 567

IV. FERROCYANOGEN 567
Its Compounds:
a. With Hydrogen: Ferrocyanic Acid 567
b. With Metals: Ferrocyanides 568

V. FERRIDCYANOGEN 570
Its Compounds:
a. With Hydrogen: Ferridcyanic Acid 570
b. With Metals: Ferridcynides 570

VI. COBALTOCYANOGEN 570

VII. CHROMOCYANOGEN 571

PAGE

VIII. PLATINOCYANOGEN 571

IX. IRIDIOCYANOGEN, &c. 572
Paracyanogen 573

X. SULPHOCYANOGEN 573
Its Compounds:
a. With Hydrogen: Sulphocyanic Acid 574
b. With Metals: Sulphocyanides 574
Persulphocyanic Acid 574

XI. MELLONE 575
Its Compounds:
a. With Hydrogen: Hydromellonic Acid 575
b. With Metals: Mellonides 576

Products of the distillation of Sulphocyanide of Ammonium 576
Melam 577
Melamine 577
Ammeline 577
Ammelide 577
Tabular Views of these products, and of their relation to Cyanuric Acid, &c. 578

Cyanogen with Carbonic Oxide (oxalyle), or

XII. URYLE 580
Uric Acid 580
Products of its Oxidation:
By Peroxide of Lead 581
Allantoine 581
By Nitric Acid 582
1. Alloxan 582
2. Alloxanic Acid 584
3. Mesoxalic Acid 584
4. Mykomelinic Acid 584
5. Parabanic Acid 585
6. Oxaluric Acid 585
7. Thionuric Acid 585
8. Uramile 586
9. Uramilic Acid 586
10. Alloxantine 586
11. Dialuric Acid 587
12. Murexide 588
13. Murexan 589
Appendix to Uric Acid:
Xanthic or Uric Oxide 59
Cystic Oxide 590

XIII. BENZOYLE 590
Its Compounds:
a. With Oxygen: Benzoic Acid 590
b. With Hydrogen: Hyduret of Benzoyle 591
c. With Chlorine 592
d. With Amide: Benzamide 592
e. Formobenzoilic Acid 592
f. Benzoate of Hyduret of B. 593
g. Hippuric Acid 593
Products derived from Benzoyle:
1. Hyposulphobenzoic Acid 593
2. Bromobenzoic Acid 593
3. Benzoyle (Benzine) 594
4. Sulphobenzide 594
5. Hyposulphobenzidic Acid 594
6. Nitrobenzide 594
7. Azobenzide 594

PAGE
8. Chloride of Benzoyle 594
9. Chlorobenzine 594
10. Benzone 594
11. Hydrobenzamide 595
12. Benzhydramide 595
13. Azobenzoyle 595
14. Azotide of Benzoyle 595
15. Benzamide 595
16. Benzoine 595
17. Hydrobenzoniamide 595
18. Benzile 596
19. Benzilic Acid 596
20. Azobenzoide 596
21. Cyanobenzile 596
21. *b.* Hyduret of Sulphobenzoyle 596
22. Stilbene 596
23. Hyduret of Sulphazobenzoyle 597
24. Nitrobenzoic Acid 597
25. Bromide of Benzoyle 598
26. Hydrocyanate of Benzoine 598
27. Hydrocyanate of Benzile 598
Appendix to Benzoyle :—
1. Amygdaline 598
2. Amygdalinic Acid 598
3. Distilled Water of Bitter Almonds 599
4. Laurel Water 599
Theory of the Formation of the Compounds of Benzoyle . . . 599

XIV. SALICYLE 601
Its Compounds :
a. With Hydrogen : Hyduret of Salicyle 601
b. With Oxygen : Salicylic Acid 602
Products derived from Salicyle :—
c. With Chlorine : Chlorosalicylic Acid 603
d. With Nitric Acid : Nitrosalicylic Acid 603
Appendix to Salicyle :—
Salicine 604
Phloridzine 604

XV. CINNAMYLE 605
Its Compounds :
a. With Hydrogen : Hyduret of Cinnamyle 605
b. With Oxygen : Cinnamic Acid 605
Balsam of Peru 606
Balsam of Tolu 606

XVI. ETHYLE 607
Its Compounds :
a. With Oxygen : Oxide of Ethyle 608
Alcohol 609
Vinous Fermentation 610
b. With Chlorine : Chloride of Ethyle 611
c. With Bromine, Iodine, Sulphur 611
Mercaptan 611
d. Salts of Oxide of Ethyle 612
Acid Sulphate, or Sulphovinic Acid 613
Acid Phosphate, or Phosphovinic Acid 613
Nitrate : Nitric Ether 613
Hyponitrite : Nitrous Ether 614
Carbonate : Carbonic Ether 614
Double Carbonates 614
Oxalate : Oxalic Ether 614
Acid Oxalate : Oxalovinic Acid 615

PAGE

Oxamate: Oxamethan 615
Sulphocarbonate 615
Bicyanurate 615
Benzoate: Benzoic Ether 615
Hippurate: Hippuric Ether 615
Salicylate: Salicylic Ether 615
Compounds connected with Ethyle:
Chlorocarbonic Ether 616
Urethan 616
Transformations of Ethyle:—
Oil of Wine 617
Heavy Oil of Wine 617
Ethionic, Isethionic, Methionic, and Althionic Acids . . 617
Products of the Oxidation of Ethyle and its derivatives . . . 618

XVII. ACETYLE 618
a. Hydrated Oxide of Acetyle, or Aldehyde 618
b. Acetal 619
c. Acetylous or Aldehydic Acid 620
d. Acetic Acid 620
Acetification 620
Acetates 622

Action of Chlorine, &c. on Ethyle, Acetyle, and their derivatives . . 624
1. On Oxide of Ethyle 624
2. On Salts of Ethyle 624
3. On Alcohol 626
Chloral 626
4. On Acetic Acid 626
Chloracetic Acid 626
Bromal 626

Compounds derived from Alcohol, of uncertain constitution . . 627
Olefiant Gas 627
Oil of the Dutch Chemists 627
Chloride of Acetyle 627
Chloretheral 628
Sulphacetylic Acid 628
Action of Bichloride of Platinum on Alcohol 628
Action of Heat on Acetic Acid and the Acetates . . . 629
Acetone 629
Mesitylene 629
Compounds containing Arsenic derived from Acetyle . . . 630

XVIII. KAKODYLE 630
Its Compounds:
a. With Oxygen: Protoxide 630
Kakodylic Acid 631
b. With Chlorine, Iodine, Bromine, Fluorine, Sulphur, Cyanogen . 631
Compounds of Kakodyle containing Platinum 631
Appendix to Ethyle:
Sugar 632
1. Cane Sugar 632
2. Grape Sugar 633
Metacetone 635
Action of Nitric Acid on Sugar 635
Saccharic Acid 635
3. Sugar of Milk or Lactine 636
Mucic Acid 636
Modified Mucic Acid 637
Pyromucic Acid 637
4. Sugar of Mushrooms 637
Vinous or Alcoholic Fermentation 637
Viscous Fermentation 638

PAGE

Mannite 639
Lactic Acid 639

XIX. METHYLE 640
a. Hydrated Oxide: Pyroxilic Spirit 640
b. Oxide of Methyle 640
c. Chloride, Iodide, Sulphuret 640
d. Salts of Oxide of Methyle 641
Neutral Sulphate 641
Acid Sulphate 641
Nitrate 642
Oxalate 642
Benzoate 642
Acetate 642
Other Compounds of Methyle 642

Products of its Oxidation:

XX. FORMYLE 643
Formic Acid 644
Formiates 645
Chloride, Bromide, Sulphuret, &c. of Formyle 645

XXI. CETYLE 646
Hydrated Oxide: Ethal 646

XXII. AMYLE 646
Hydrated Oxide of Amyle, or Oil of Potato Spirit . . . 647
Other Compounds of Amyle 647

Products of its Oxidation:

Valerianic Acid 647
Amilene 648

XXIII. GLYCERYLE 648
Hydrated Oxide of Glyceryle or Glycerine 648

ORGANIC ACIDS 648
1. Citric Acid 648
Citrates 649
Action of Heat on Citric Acid 650
Aconitic Acid 650
Itaconic and Citraconic Acids 651
2. Tartaric Acid 651
Tartrates 652
Tartar Emetic 652
Action of Heat on Tartaric Acid 653
Tartralic Acid 653
Tartrelic Acid 654
Anhydrous Tartaric Acid 554
Pyroracemic Acid 654
3. Racemic Acid 654
Its Salts 655
4. Malic Acid 655
Its Salts 656
Action of Heat on it 656
Maleic Acid 656
Fumaric Acid 656
5. Tannic Acid 657
Its Salts 657
Its conversion into Gallic Acid 657
6. Gallic Acid 658
Its Salts 658
Action of Heat on it 658
Pyrogallic Acid 658
Metagallic Acid 658
Ellagic Acid 659

	Page
Catechu	659
7. Meconic Acid	660
Its Salts	660
Action of Heat on it	660
8. Comenic Acid	661
Its Salts	661
Pyromeconic Acid	661
9. Kinic Acid	661
Its Salts	661
Products of its Decomposition	662
Kinone, Hydrokinone, &c.	662
10. Butyric Acid	663
Its Salts	663
Butyramide	663
Butyrone	664
Caproic Acid	664
Capric Acid	664
Caprylic Acid	664
Hircic Acid	664
Phocenic Acid	664
Cevadic Acid	664
Veratric Acid	664
Crotonic Acid	664
11. Camphoric Acid	664
Anhydrous	664
Camphor	665
Borneo Camphor	665
Camphogen	665
Camphrone	665
12. Valerianic Acid	666
13. Anisic Acid	666
Nitroanisic Acid	666
Anisole	666
14. Œnanthic Acid	666
Œnanthic Ether	667
15. Roccellic Acid	667
16. Cuminic Acid	667
Cumene	667
Cuminole	667
Cumyle	667
17. Eugenic Acid	667
Caryophylline	667
18. Cocinic Acid	668
19. Myristic Acid	668
Myristine	668
20. Palmitic Acid	668
Palmitine	668
21. Cetylic Acid	669
22. Margaric Acid	669
Margarine	669
Margarates	669
23. Stearic Acid	669
Stearates	670
Stearine	671
Action of Nitric Acid on Stearic Acid	671
24. Suberic Acid	671
25. Succinic Acid	671
Its Salts	672
Amber	672
26. Oleic Acid	672
Oleates	672
Oleine	672

PAGE
Action of Heat on Oleic Acid 672
27. Sebacic Acid 673
28. Elaidic Acid 673
Elaidine 673
Action of Nitric Acid on Oleic Acid 673
Pimelic Acid 673
Adipic Acid 673
Lipic Acid 673
Azoleic Acid 673
Acids of Castor Oil 674
Palmine 674
Natural Fats and Fixed Oils 674
Action of Heat on Oils and Fat 674
Acroleine 674
Acryle 675
Acrylic Acid 675
Action of Sulphuric Acid on Fat Oils 675
Sulpholeic, Sulphomargaric, Metamargaric, Hydromargaritic, Metoleic, and Hydroleic Acids 675
Oleéne and Elaéne 676
Action of Nitrous (Hyponitrous) Acid on Fat Oils . . . 676
Action of Nitrate of Mercury on Fat Oils 676
Elaidine 676
Action of Bases on Fat Oils 676
Soaps 676
Plasters 677
Vegetable Fats 677
Spermaceti 677
Cholesterine and Cholesteric Acid 677
Ambreine and Ambreic Acid 677
Wax, Cerine, Myricine 677
Cerosine 678
Athamantine 678
Various Acids 678
Volatile Oils 678
Nonoxygenated Essential Oils 678
Oil of Turpentine 678
Dadyle and Peucyle 679
Oils of Juniper, Lemons, Copaiva, and other Nonoxygenated Oils . 679
Oxygenated Essential Oils 679
Oils of Cinnamon, Anise, Estragon, and other Oxygenated Oils . 679, 680
Draconic Acid and other derivatives from Oil of Estragon . . 680
Coumarine 681
Sulphurated Essential Oils 681
Oil of Mustard and its Derivatives 681
Thiosinnamine, Sinnamine, &c. 681
Sinapoline, Myrosine, Sinapisine, &c. 682
Oils of Garlic, Assafetida, &c. 683
Concrete Volatile Bodies allied to the Volatile Oils . . . 683
Asarone 683
Anemorine, Cantharadine 683
Caoutchouc 684
Action of Heat on Caoutchouc 684
Resins 684
Colophony, Pinic, and Sylvic Acids 684
Resins of Copaiva, Elemi, Benzoin, Balsam of Tolu, &c. . . 685
Benzoéne, Nitrobenzoéne 685
Styrax, Guaiacum, Jalap, Copal, and other Resins . . . 685
Varnishes 685
Action of Heat on Resins 686
Nonazotized Colouring Matters 686
Yellow 686

PAGE
Red 686
Blue 687
Green, Chlorophyle 687
Bitter Vegetable Principles, nonazotized 687
Azotized Colouring Matters and allied Substances 689
Lecanorine, Orcine, Erythrine 690
Pseudoerythrine, Variolarine 690
Archil, Litmus, Phloridzeine 690
Indigo 690
White or reduced Indigo 692
Action of Sulphuric Acid on Indigo 693
Oxidation of Indigo, Isatine 694
Chlorisatine, Bichlorisatine, &c. 694
Isatyde, Sulphesatyde, &c. 696
Indine, Hydrindene, &c. 696
Chlorindopten, &c. 697
Chloranile, Chloranilic Acid, &c. 698
Imasatine, Amasatine, &c. 698
Anilic or Indigotic Acid 699
Picric, Nitropicric, Abazotic Acid 699
Action of Potash on Indigo 700
Anthranilic Acid, Aniline, &c. 700
Tabular view of the Series of Phenyle 701
Chlorinized and Brominized Bases from Aniline . . . 701
Carmine 702
Action of Nitric Acid on Aloes 702
Chrysammic Acid 702
Chrysolepic Acid 703

ORGANIC BASES OR ALKALOIDS 703
1. Liquid Volatile Bases 704
Aniline, Leukol 704
Nicotine, Conine, Quinoline 705
2. Bases from Oil of Mustard 706
3. Bases of Cinchona Bark 706
Quinine, Cinchonine 706
Quinoidine, Aricine, &c. 706
4. Bases of the Papaveracea 707
Morphine 707
Codeine 708
Thebaine, Narceine, &c. 708
Narcotine and its Derivatives 708
Chelidonine 710
Chelerythrine, &c. 710
5. Bases of the Solanaceæ, Strychneæ, &c. 710
Hyoscyamine, Daturine, Stramonine, Atropine . . . 711
Solanine, Veratrine, Sabadilline, Colchicine 711
Aconitine, Delphine, Emetine, Strychnine 712
Brucine, Jervine 713
Other Bases 714
Theobromine, Caffeine 715
Indifferent Nonazotized compounds 715
Starch 715
Dextrine, Leiocoine 716
Inuline, Lichenine, Saponine 717
Gum 718
Arabine, Mucilage, Bassorine 718
Pectine, Pactic Acid 719
Apiine, Glycyrrhizune 720
Woody Fibre 720
Cellulose, Cignine 720
Decay of Wood 720
Brown or Wood Coal 721

PAGE
Mould or Humus 721
Humic Acid, Geine, &c. 721
Crenic and Apocrenic Acids 721
Products of the Distillation of Wood 721
1. Volatile products, soluble in Water 722
Acetate Acid, Pyroxylic Spirit 722
Xylite, Mesite, &c. 722
2. Oily products, insoluble in Water 722
Creosote 722
Picamar, Capnomor, Eupion 725
3. Solid products 725
Paraffine 725
Cedriret, Pittacal, Pyroxanthine 726
Products of the Distillation of Coal 727
Carbolic Acid 727
Table of Substitutions in the series of Phenyle 727
Volatile bases of Coal Tar 728
Kyanol or Aniline 728
Leukol or Quinoline 729
Volatile Carbo-hydrogen in Coal Tar 729
Naphthaline 729
Action of Chlorine and Bromine on Naphthaline, Nomenclature . 730
Chlonaphtase, Bronaphtase, &c. 730
Action of Sulphuric Acid on Naphthaline 735
Action of Nitric Acid on Naphthaline 735
Nitronaphtalase, &c. 735
Action of Sulphuret of Ammonium on Nitronaphtalase, &c. . 737
Naphtalidam 737
Anthracene, Chrysene, and Pyrene 737
Ampeline and Ampelic Acid 738
Fossil Resins, Fossil Wax, Fossil Oil, Naphtha, &c. . . 738
Asphaltum, Petroleum 739
Soot and Lamp Black 740

SULPHURIZED AND AZOTIZED NUTRITIOUS AND ANIMAL AND VEGETABLE COMPOUNDS 740
Vegetable Albumen 740
Vegetable Fibrine 740
Vegetable Caseine 741
Emulsine or Synaptase 741
Fungine, Gliadine 741
Fermentation of Vegetable Juices 741
Diastase, Malt, Must, Beer, or Ale, Wort, Grain, and Potato Spirit 742
Panification 743
Ferment, or Yeast 744
Caseous Oxide, or Aposepidine 744
Animal Albumen 744
Serum, White of Egg 744
Animal Fibrine 745
Animal Caseine 745
Milk 745
Cheese 746
Animal Mucus 747
Horny Matter 747
Composition of the preceding Substances 747
Proteine 748
Products of its decomposition 748
Erythroprotide, Leucine, Oxides of Proteine, &c. . . . 748
Action of Acids on Proteine compounds 749
Relation of Proteine to Sugar and Ammonia 749
Gelatigenous Tissues 750
Gelatine, Chondrine 750
Sugar of Gelatine 750

		Page
	Bone	751
	Ivory Black	751
	Bile	751
	Is Choleate of Soda	752
	Products of decomposition of Bile	753
	Choloidic Acid, Taurine, Cholinic Acid, &c.	753
	Composition of Choleic Acid	754
	Biliary Calculi	754
	Brain and Nervous Matter	755
	Cerebric and Oleophosphoric Acids, Cerebroleine	755
	Gastric Juice	755
	Digestion	756
	Saliva, Pancreatic Juice	756
	Excrements, Urine	757
	Guano	758
	Animal Manure	758
	Urinary Calculi	758
	Lymph, Blood	759
	Globules of the Blood	759
	Colouring Matter of the Blood	760
	Hematosine	761
	Nutrition of Plants and Animals	761
	Equilibrium between the Animal and Vegetable Kingdoms	766

PART IV.

	CHEMICAL ANALYSIS.	769
	Mineral Analysis	769
Sect. I.	Manipulations in Analytical processes	770
Sect. II.	Qualitative Analysis	772
Sect. III.	Quantitative Analysis	775
Sect. IV.	Analysis of Mineral Waters	779
	Classification of Mineral Waters	780
	Organic Analysis	783
	General method of proceeding	785
	Special details of the method	792
	Combustion of Volatile liquids	797
	Combustion of substances rich in Carbon or containing Chlorine	799
	Oxide of Copper, preparation of	800
	Chromate of Lead, preparation of	801
	Combustion tubes	801
	Determination of Carbon	802
	the Hydrogen	804
	Nitrogen	806
	Nitrogen direct	810
	Methods of Control for Organic Analysis	814
	Determination of number of Atoms in Organic Compounds	815
	Examples, Amygdalic Acid, &c.	817
	Determination of the specific gravity of Volatile substances as a means of ascertaining the number of atoms of their Elements	821

APPENDIX.

		Page
I.	Table of Equivalents or Atomic weights of Elements, &c. . .	825
II.	Table of the elastic force of Aqueous vapour . . .	826
III.	Table of the elastic force of the vapour of Alcohol, &c. . .	828
IV.	Table for the conversion of degrees on the Centigrade Thermometer into degrees of Fahrenheit's Scale	829
V.	Table of the strength of Sulphuric Acid	831
VI.	Table of the strength of Nitric Acid	832
VII.	Table of the strength of Alcohol	833
VIII.	Table of Specific Gravities indicated by Baumé's Hydrometer .	834
	Index	835

ERRATA.

Page 47, line 11, for or, read on.
" 78, " 14, for Fig. 4, read Fig. 7.
" 78, " 36, for Fig. 5, read Fig. 8.
" 382, " 16, for ClO, read Cr Cl.
" 551, " 3 from bottom, for Carbonic Acid, read Carbonic Oxide.
" 31, Caption *Specific heat* should precede the paragraph.

INTRODUCTION.

MATERIAL substances are endowed with two kinds of properties, physical and chemical; and the study of the phenomena occasioned by them has given rise to two corresponding branches of knowledge, *Natural Philosophy* and *Chemistry*.

The physical properties are either general or secondary. The general are so called because they are common to all bodies: the secondary, from being observable in some substances only. Among the general may be enumerated extension, impenetrability, mobility, extreme divisibility, gravitation, porosity, and indestructibility.

Extension is the property of occupying a certain portion of space: a substance is said to be *extended* when it possesses length, breadth, and thickness. By *impenetrability* is meant, that no two portions of matter can occupy the same space at the same moment. Every thing that possesses extension and impenetrability is matter.

Matter, though susceptible of *rest* and *motion*, has no inherent power either of beginning to move when at rest, or of arresting its progress when in motion. Its indifference to either state has been expressed by the term *vis inertiæ*, as if it depended on some peculiar force resident in matter, whereas it arises from matter being absolutely passive, and thereby subject to the influence of every force which is capable of acting upon it.*

Matter is *divisible* to an extreme degee of minuteness. A grain of gold may be so extended by hammering that it will cover 50 square inches of surface, and contain two millions of visible points; and the gold which covers the silver wire, used in making gold lace, is spread over a surface twelve times as great. A grain of iron, dissolved in nitro-hydrochloric acid, and mixed with 3137 pints of water, will be diffused through the whole mass: by means of the ferro-cyanide of potassium, which strikes an uniform blue tint, some portion of iron may be detected in every part of the liquid. The grain of iron is hence inferred to have been divided into rather more than 24 millions of parts; and if the dilution were carried still further, the diffusion of iron through the whole liquid

* All the facts of mechanical and chemical science, show that the particles and masses of matter are incessantly acting on one another, and it is to these actions, referred to agents distinct from the matter itself, that the term *Force* is applied. Hence, as in the text, the physical world is usually conceived to be made up of matter and forces; although, according to a juster metaphysics it may be regarded as consisting of *matter in a state of incessant mutual action.* (R.)

might be proved by concentrating any portion of it by evaporation, and detecting the metal by its appropriate tests.

A keen controversy existed at one time concerning the divisibility of matter, some philosophers affirming it to be infinitely divisible, while others maintained an opposite opinion. Owing to the imperfection of our senses the question cannot be determined by direct experiment, because matter certainly continues to be divisible long after it has ceased to be an object of sense. The decision, if effected at all, can only be accomplished indirectly, as an inference from other phenomena. In favour of the former view it was urged, on mathematical grounds, that a surface admits of division without limit: and that to whatever degree matter is divided, it may still be conceived, in possessing extension and surface, to be susceptible of still further division. Plausible, however, as this mode of reasoning may appear, the opposite opinion is daily becoming more general. It is now commonly believed that matter consists of ultimate particles or molecules, which may indeed be conceived to be divisible, but which by hypothesis are assumed to be infinitely hard and impenetrable, and on that account to be incapable of division. These ultimate particles have received the appellation of *atoms*, (from the privative α and τεμνειν to cut,) as expressive of their nature. The arguments adduced in support of this opinion are principally drawn from the phenomena of chemistry, and from the relations which have been observed to exist between the composition and form of crystallized bodies. These subjects will be considered hereafter: it will now suffice to state, in order to show the nature of the argument, that the supposed existence of atoms accounts for numerous facts, which cannot be satisfactorily explained on any other principle.

All bodies descend in straight lines [perpendicular to the curvature of the earth at the place of their descent, and therefore, as the earth is nearly spherical, in directions closely tending towards its centre,] when left at liberty at a distance from its surface. The power which produces this effect is termed *gravity*, *attraction of gravitation*, or *terrestrial attraction*; and the force required to separate a body from the surface of the earth, or prevent it from descending towards it, is called its *weight*. Every particle of matter is equally affected by gravity; and therefore the weight of any body will be proportionate to the number of ponderable particles which it contains.

The minute particles of which bodies consist are disposed in such a manner as to leave certain intervals or spaces between them, and this arrangement is called *porosity*. These interstices may sometimes be seen by the naked eye, and frequently by the aid of glasses; but were they wholly invisible, it would still be certain that they exist. All substances, even the most compact, may be diminished in bulk either by mechanical force or a reduction of temperature. It hence follows that their particles must touch each other at a very few points only, if at all; for if their contact were so perfect as to leave no interstitial spaces, then would it be impossible to diminish the dimensions of a body, because matter is incompressible and cannot yield.—When therefore a body expands, the distance between its particles is increased; and, conversely, when it contracts or diminishes in size, its particles approach each other.*

* Contact is not necessary for the exertion of force between particles or masses,—and probably all actions take place through some distance. Physical contact is nothing more than such a proximity as brings into play powerful corpuscular repulsion. (R.)

By *indestructibility* is meant, that, according to the present laws of nature, matter never ceases to exist. This statement seems at first view contrary to fact. Water and volatile substances are dissipated by heat, and lost; coals and wood are consumed in the fire, and disappear. But in these and all similar phenomena not a particle of matter is annihilated. The apparent destruction is owing merely to a change of form or composition; for the same material particles, after having undergone any number of such changes, may still be proved to possess the characteristic properties of matter.

The *secondary* properties of matter are opacity, transparency, softness, hardness, elasticity, colour, density, solidity, fluidity, and others of a like nature. Several of these properties, especially those last specified, depend on the relative intensity of two opposite forces—cohesion and repulsion. It is inferred, from the divisibility of matter, that the substance of solids and liquids is made up of an infinity of minute particles adhering together so as to constitute larger masses; and that the mutual adhesion of these particles is owing to a power of reciprocal attraction. This force is called *cohesion*, *cohesive attraction*, or the *attraction of aggregation*, in order to distinguish it from terrestrial attraction. Gravity is exerted between different masses of matter, as well as between their particles, and acts at sensible and frequently at very great distances; while cohesion exerts its influence only at insensible and infinitely small distances. It enables similar molecules to cohere, and tends to keep them in that condition. It is best exemplified by the force required to separate a hard body, such as iron or marble, into smaller fragments; or by the weight which twine or metallic wire will support without breaking.

The tendency of cohesion is manifestly to bring the ultimate particles of bodies into immediate contact; and such would be the result of its influence, were it not counteracted by an opposing force, a principle of repulsion, which prevents their approximation. It is a general opinion among philosophers, supported by very strong facts, that this repulsion is owing to the agency of heat, which is somehow attached to the elementary molecules of matter, causing them to repel one another. Material substances are therefore subject to the action of two contrary and antagonizing forces, one tending to separate their particles, the other to bring them into closer proximity. The form of bodies, as to solidity and fluidity, is determined by the relative intensity of these powers. Cohesion predominates in solids, in consequence of which their particles are prevented from moving freely on one another. The particles of a fluid, on the contrary, are far less influenced by cohesion, being free to move on each other with very slight friction. Fluids are of two kinds; elastic fluids or aëriform substances, and inelastic fluids or liquids. Cohesion seems wholly wanting in the former; they yield readily to compression, and expand when the pressure is removed; indeed, the space they occupy is chiefly determined by the force which compresses them. The latter, on the contrary, do not yield perceptibly to ordinary degrees of compression, nor does an appreciable dilatation ensue from the removal of pressure, the tendency of repulsion being in them counterbalanced by cohesion.

[This view of the constitution of bodies is founded on the idea that heat is a distinct substance, capable of penetrating between the particles of ordinary matter, and by its self-repellancy changing the distances of these particles, and thus modifying the properties of the mass. But the progress of investigation seems

by no means favourable to this conception of the nature of heat. It may, we think, be more philosophically maintained that the attractions and repulsions of particles are exclusively dependent on their relation as to distance, as originally suggested by Boscovitch, and that the various states of matter, as solid, liquid, or gaseous, are the direct consequences of the difference in the distance and arrangement of the molecules.]

Matter is subject to another kind of attraction different from those yet mentioned, termed *chemical attraction* or *affinity*. Like cohesion it acts only at insensible distances, and thus differs entirely from gravity. It is distinguished from cohesion by being exerted between dissimilar particles only, while the attraction of cohesion unites similar particles. Thus, a piece of marble is an aggregate of smaller portions attached to each other by cohesion, and the parts so attached are called *integrant* particles; each of which, however minute, being as perfect marble as the mass itself. But the integrant particles consist of two substances, lime and carbonic acid, which are different from one another as well as from marble, and are united by chemical attraction. They are the *component* or *constituent* parts of marble. The integrant particles of a body are therefore aggregated together by cohesion; the component parts are united by affinity.

The chemical properties of bodies are owing to affinity, and every chemical phenomenon is produced by the operation of this principle. Though it extends its influence over all substances, yet it affects them in very different degrees, and is subject to peculiar modifications. Of three bodies, A, B, and C, it is often found that B and C evince no affinity for one another, and therefore do not combine; that A, on the contrary, has an affinity for B and C, and can enter into separate combination with each of them; but that A has a greater attraction for C than for B, so that if we bring C in contact with a compound of A and B, A will quit B and unite by preference with C. The union of two substances is called *combination;* and its result is the formation of a new body endowed with properties peculiar to itself, and different from those of its constituents. The change is frequently attended by the destruction of a previously existing compound, and in that case *decomposition* is said to be effected.

The operation of chemical attraction, as thus explained, lays open a wide and interesting field of inquiry. One may study, for example, the affinity existing between different substances; an attempt may be made to discover the proportions in which they unite; and finally, after collecting and arranging an extensive series of insulated facts, general conclusions may be deduced from them. Hence chemistry may be defined the science, the object of which is to examine the relations that affinity establishes between bodies, ascertain with precision the nature and constitution of the compounds it produces, and determine the laws by which its action is regulated.

Material substances are divided by the chemist into simple and compound. He regards those bodies as compound, which may be resolved into two or more kinds of ponderable matter; those as simple or elementary, which contain but one, [or properly speaking, the elementary bodies of the chemist are those which have as yet resisted all efforts to decompose them.] The number of the latter, which have been clearly ascertained, amounts only to fifty-four; and of these, agreeably to our present knowledge, all the bodies in the earth consist. The list, a few years ago, was somewhat different from what it is at present; for the acquisition of improved methods of analysis has enabled chemists to demon-

strate that some substances, which were once supposed to be simple, are in reality compound; and it is probable that a similar fate awaits some of those which are at present regarded as simple.

The composition of a body may be determined in two ways, analytically or synthetically. By *analysis*, the elements of a compound are separated from one another, as when water is resolved by the agency of galvanism into oxygen and hydrogen; by *synthesis*, they are made to combine, as when oxygen and hydrogen unite by the electric spark, and generate a portion of water. Each of these kinds of proof is satisfactory; but when they are conjoined—when water is resolved into its elements, and then reproduced by their union—the evidence is in the highest degree conclusive.

The first part of this work comprehends an account of the nature and properties of *Heat*, *Light*, and *Electricity*,—agents so diffusive and subtile, that the common attributes of matter cannot be perceived in them. They are altogether destitute of weight; at least, if they possess any, it cannot be discovered by our most delicate balances, and hence they have received the appellation of *Imponderables*. They cannot be confined and exhibited in a mass like ordinary bodies; they can be collected only through the intervention of other substances. Their title to be considered material is therefore questionable, and the effects produced by them have accordingly been attributed by some to certain motions or affections of common matter. It must be admitted, however, that they appear to be subject to the same powers that act on matter in general, and that some of the laws which have been determined concerning them, are exactly such as might have been anticipated on the supposition of their materiality. It hence follows, that we need only regard them as subtile species of matter, in order that the phenomena to which they give rise may be explained in the language, and according to the principles, which are applied to material substances in general; and I shall therefore consider them as such in my subsequent remarks.

The second part comprises *Inorganic Chemistry*. It includes the doctrine of affinity, and the laws of combination, together with the chemical history of all the elementary principles hitherto discovered, and of those compound bodies which are not the product of organization. Elementary bodies are divided into the non-metallic and metallic; and the substances contained in each division are treated in the order which, it is conceived, will be most convenient for the purposes of teaching. From the important part which oxygen plays in the economy of nature, it is necessary to begin with the description of that principle; and from the tendency it has to unite with other bodies, as well as the importance of the compounds it forms with them, it will be useful, in studying the history of each elementary body, to describe the combinations into which it enters with oxygen gas. The remaining compounds which the non-metallic substances form with each other will next be considered. The description of the individual metals will be accompanied by a history of their combinations, first with the simple non-metallic bodies, and afterwards with each other. The last division of this part will comprise a history of the salts.

The third general division of the work is *Organic Chemistry*, a subject which will be conveniently discussed under two heads. In this, derived from the work of Professor Gregory, the several topics are arranged under two heads, the one comprehending the Chemistry of the Compound Radicals, the other treating of the influence of Life on Chemical Products.

The fourth part is a brief outline of *Analytical Chemistry*.

ELEMENTS OF CHEMISTRY.

PART I.

IMPONDERABLE SUBSTANCES.

SECTION I.

HEAT, OR CALORIC.

The term *Heat*, in common language, has two meanings: in the one case, it implies the sensation experienced on touching a hot body; in the other, it expresses the cause of that sensation. When used in the latter sense, it is synonymous with the word *Caloric* (from *Calor*, heat), which is employed exclusively to signify the cause or agent by which all the effects of heat are produced.

Heat, on the supposition of its being material, is a subtile fluid, the particles of which repel each other, and are attracted by all other substances. It is imponderable; that is, it is so exceedingly light, that a body undergoes no appreciable change of weight, either by the addition or abstraction of heat. It is present in all bodies, and cannot be wholly separated from them; for if a substance, however cold, be transferred into an atmosphere which is still colder, a thermometer placed in the body will indicate the escape of heat. That its particles repel one another, is proved by observing that it flies off from a heated body; and that it is attracted by other substances, is inferred from the tendency it has to penetrate their particles, and to be retained by them.

Heat may be transferred from one body to another. Thus, if a cup of mercury at 60° be plunged into hot water, heat passes rapidly from one into the other, until the temperature in both is the same; that is, till a thermometer placed in each stands at the same height. All bodies on the earth are constantly tending to attain an equality, or what is technically called an *equilibrium*, of temperature. If, for example, a number of substances of different temperature be enclosed in an apartment, in which there is no actual source of heat, they will very soon acquire an equilibrium, so that a thermometer will stand at the same point in all. Our varying sensations of heat and cold are owing to a like cause. On touching a hot body, heat passes from it into the hand, and excites the feeling of warmth; when we touch a cold body, heat is communicated to it from the hand, and thus arises the sensation of cold.

Heat is communicated in three ways, by *direct contact*, by *conduction*, and by *radiation*. By *direct contact*, when the hot body touches a cold one, so that the heat may pass directly from one into the other, as when it enters a bar of iron put into a fire, or the hand plunged into hot water. By *conduction*, as when the heat is observed to travel from point to point of the iron bar towards the end remote from the fire. By *radiation*, when the heat leaps as it were from a hot to a cold body through an appreciable interval; as when a red-hot ball, suspended in the vacuum of an air-pump, distributes its heat to surrounding objects, or when we are warmed by standing at some distance before a fire.* In studying these phenomena we must regard both the loss of heat in the hot body, and the gain of heat in the cold one. The mode in which a hot body cools is, firstly, by giving off heat from its surface either by contact or radiation, or both conjointly; and secondly, by the heat in its interior passing from particle to particle through its substance to its surface. The heating of a cold body is effected, firstly, by heat passing into its surface either by contact or radiation, or by both conjointly; and, secondly, by the heat at its surface passing from particle to particle through its interior portions. Hence, in tracing the laws which regulate the distribution of heat, we shall successively consider the communication of heat from one body to another by *contact*, its passage from particle to particle of the same substance or the *conduction* of heat, and its transfer from a sensible distance or *radiation*.

COMMUNICATION OF HEAT BY CONTACT.

The principal conditions which influence the communication of heat from one body to another by contact, are the degree of contiguity, and the conducting power of the substances. The more perfect the approximation, the more rapid, *cæteris paribus*, is the transfer. The contact of two solids, or of a solid with a gas, is in general of a less perfect kind, and at fewer points, than that between a solid and a liquid; and hence, so far as *contact alone* is concerned, the transfer is more rapid in the latter case than in the former. It is still more rapid when liquids are mixed with each other, or gases with gases, owing to the intermixture of their particles. When bodies touch each other at their surfaces only, the question becomes one of conduction, the rapidity of transfer depending on the velocity with which heat passes through the substances in contact. Thus, if a hot mass of iron and another of marble, of equal size, form, and temperature, be plunged into equal quantities of cold water, the iron will cool faster than the marble, because heat passes more rapidly through the substance of the former than through that of the latter. Were two pieces of hot iron similarly plunged, one into mercury, and the other into water, the piece in contact with mercury would cool most rapidly, because that metal is a better conductor than water. Were the experiment made by immersing the iron into mercury, and the marble into water, the rapidity of cooling in the former would very much exceed that in the latter, from two causes;—both from heat passing more rapidly through iron than through marble, and from its being conveyed away more rapidly by mercury than by water. The same principle explains the unequal sensation caused by bodies of equal temperature. Thus the hand receives a more vivid

* Strictly speaking the transfer of heat by direct contact is a case of radiation, in which the surfaces, though still separated by an interval, are at an insensible distance. (R.)

impression of warmth by touching hot iron than from glass of the same temperature; because the quantity of heat which in a given time can be brought from the interior to the surface of the hot body, so as to pass into the skin, is much greater in iron than in glass. In like manner, cold iron feels colder than glass of the same temperature, because the former conveys away from the skin more heat in a given time than the glass.

CONDUCTION OF HEAT.

By this term is expressed the passage of heat from particle to particle through the substance of bodies. Heat is said to be conducted by them or to pass by *conduction*, and the property on which its transmission depends is termed *conducting power*.

Heat obviously passes through bodies with different degrees of velocity. Some substances oppose very little impediment to its passage, while it is transmitted slowly by others. One cannot leave one end of a rod of iron for some time in the fire, and then touch its other extremity, without danger of being burned, though this may be done with perfect safety with a rod of glass or of wood. The observation of these and similar facts, has led to the division of bodies into *conductors* and *non-conductors* of heat. The former division, of course, includes those bodies, such as the metals, which allow heat to pass freely through their substance; and the latter comprises those which do not give an easy passage to it, such as stones, glass, wood, and charcoal.

Some experiments have been made by Despretz, apparently with great care, on the relative conducting power of the metals and some other substances, and the results are contained in the following table. (An. de Ch. et Ph. xxxvi. 422.)

Gold	1000	Tin	303·9
Silver	973	Lead	179·6
Copper	898·2	Marble	23·6
Platinum	381	Porcelain	12·2
Iron	374·3	Fine clay	11·4
Zinc	363		

[The substances used in these experiments were square prisms of equal size, and similarly coated with a black varnish, to render the loss of heat from the surface the same in all. At equal intervals along the bars, small cavities were formed, in which oil or mercury was placed, and in which delicate thermometers were inserted to indicate the progress of temperature from point to point. A lamp applied at one extremity supplied the requisite heat, the constancy of which was ascertained by the temperature of the thermometer, nearest the lamp, becoming stationary and so continuing during the experiment. The heat conducted along the bars gradually raising the temperature of the several thermometers, but to a less and less extent according as they were more distant from the heated end, would thus be distributed along it with more or less equality according to the greater or less conducting power of the material, and the degree in which the different parts of its surface permitted the heat to escape into the surrounding space. When the heat thus escaping from the surface at each point became equal, in virtue of the high temperature, to that received by conduction, no further change of temperature took place. The thermometers now stationary presented, when compared together, in each bar in receding from the heated end,

a progressively diminishing excess of temperature over that of the apartment. From the ratio of this series, as noted for each substance, and which is obviously dependent upon the conducting power, the numbers of the above table were computed. The principle of this mode of experiment and the theory by which the conducting powers may be calculated are due to Fourier.]

An ingenious plan was adopted by Count Rumford (Phil. Trans. 1792,) for ascertaining the relative conducting power of the different materials employed for clothing. He enveloped a thermometer in a glass cylinder blown into a ball at its extremity, and filled the interstices with the substance to be examined. Having heated the apparatus to the same temperature in every instance by immersion in boiling water, he transferred it into melting ice, and observed carefully the number of seconds which elapsed during the passage of the thermometer through 135 degrees.

Air alone required .	576″	Raw Silk . . .	1284″
Lint . . .	1032″	Beaver's Fur . .	1296″
Cotton Wool . .	1046″	Eider Down . .	1305″
Sheep's Wool . .	1118″	Hare's Fur . .	1315″

The general practice of mankind is therefore fully justified by experiment. In winter, clothing of silk or wool is used in order to retain the animal heat; while in summer, cotton or linen stuffs are preferred, that the heat of the body may the more easily escape.

[It should, however, be remembered that although, in Rumford's experiment the cooling is more rapid through air alone than through lint and the other fibrous materials, this effect is due, only, in part, to the conducting power of the air and far more to the mobility of its particles, as explained under the next head. In fact air is a much worse conductor than the solid matter of these fibres, as is proved by the readiness with which they conduct heat, when compacted closely together by pressure, so as to exclude the air from between them. It is thus that a blanket or cloth with a long nap becomes a comparatively good conductor, when flattened down by strong compression; and it is because of the air between its particles that snow preserves the earth beneath it from a very great reduction of temperature.]

The conducting power of solid bodies does not seem to be related to any of the other properties of matter; but it approaches nearer to the ratio of their densities than to that of any other property.

Convection of Heat in Liquids and Airs.—Liquids may be said in one sense to have the power of conveying heat with great rapidity, though in reality they are very imperfect conductors. This peculiarity is referable to the mobility which subsists among the particles of all fluids, and to the change of size which is invariably produced by a change of temperature. When any particles of a liquid are heated they expand, thereby becoming specifically lighter than those which have not received an increase of temperature; and if the former happen to be covered by a stratum of the latter, these from their greater density will descend, while the warmer and lighter particles will be pressed upwards. If, therefore, heat enter at the bottom of a vessel containing a liquid, a double set of currents must be immediately established, the one of hot particles rising towards the surface, and the other of colder particles descending to the bottom. These currents take place with such rapidity, that if a thermometer be placed at the bottom, and another at the top of a long jar, the fire being applied below, the upper one

will begin to rise almost as soon as the lower. [Similar currents are still more rapidly produced when heat is applied to the lower part of a mass of atmospheric air, or other gaseous matter.] The transport of hot particles by this process has been termed the *convection* of heat.

But if, instead of heating the bottom of the jar of liquid, the heat enter by the upper surface, very different phenomena will be observed. The intestine movements cannot then be formed, because the heated particles, from being lighter than those below them, remain constantly at the top: the heat can descend through the fluid only by transmission from particle to particle, a process which takes place so very tardily, as to have induced Count Rumford to deny that water can conduct at all. In this, however, he was mistaken; for the opposite opinion has been successfully supported by Hope, Thomson, and the late Dr. Murray, though they all admit that water, and liquids in general, mercury excepted, possess the power of conducting heat in a very slight degree.

[In the more recent experiments of Despretz, the conduction of heat in water was proved by applying a constant source of temperature to the upper surface of a prismatic column of the liquid, contained in a vessel made of bad conducting materials. The progress of the heat downwards, as in his experiments with solids, was marked by thermometers placed at intervals along the axis of the column, their stems being suffered to project horizontally through one of the upright sides of the vessel. When they had attained a stationary condition he found their excesses of temperature, over the temperature of the ambient air, to follow the same law as in the case of conduction along solid bars.]

It is extremely difficult to estimate the conducting power of aëriform fluids. Their particles move so freely on each other, that the moment a particle is dilated by heat, it is pressed upwards with great velocity by the descent of colder and heavier particles, so that an ascending and descending current is instantly established. Besides, gaseous bodies allow a passage through them by radiation. Now the quantity of heat which passes by these two channels is so much greater than that which is conducted from particle to particle, that we possess no means of determining their proportion. It is certain, however, that the conducting power of gaseous fluids is exceedingly imperfect, probably even more so than that of liquids.

RADIATION.

When the hand is placed beneath a hot body suspended in the air, a distinct sensation of warmth is perceived, though from a considerable distance. This effect does not arise from the heat being conveyed by means of a hot current; since all the heated particles have an uniform tendency to rise. Neither, for reasons above assigned, can it depend upon the conducting power of the air; because aërial substances possess that power in a very low degree, while the sensation in the present case is excited almost on the instant. There is yet another mode by which heat passes from one body to another; and as it takes place in all gases, and even *in vacuo*, it is inferred that the presence of a medium is not necessary to its passage. This mode of distribution is called *Radiation* of Heat, and the heat so distributed is called *Radiant* or *Radiated Heat.* It appears, therefore, that a heated body suspended in the air cools, or is reduced to an equilibrium with surrounding bodies, in three ways; first, by the conduct-

ing power of the air, the influence of which is very trifling; secondly, by the mobility of the air in contact with it; and thirdly, by radiation.

Laws of Distribution.—Heat is emitted from the surface of a hot body equally in all directions, and in right lines, like radii drawn from the centre to the surface of a sphere; so that a thermometer placed at the same distance on any side would stand at the same point, if the effect of the ascending current of hot air could be averted. The calorific rays, thus distributed, pass freely through a vacuum and the air, without, in a sensible degree, being arrested by the latter or affecting its temperature. When they fall upon the surface of a solid or liquid substance they may be disposed of in three different ways:—1, they may rebound from its surface, or be *reflected;* 2, they may be received into its substance, or be *absorbed;* and, 3, they may pass directly through it, or be *transmitted.* In the first and third cases, the temperature of the body on which the rays fall is altogether unaffected; whereas, in the second, it is increased. The heating influence varies with the distance from the radiating body. The rate or law of decrease, as ascertained by careful experiment, and as may be inferred from mathematical considerations, is, that the intensity of heat, like that of light, diminishes in the same ratio as the squares of the distances from the radiating point increase. Thus the thermometer will indicate four times less heat at two inches, nine times less at three inches, and sixteen times less at four inches, than it did when it was only one inch from the heated substance.

The radiation of heat by hot bodies is singularly influenced by the nature and condition of their surfaces, a circumstance which was first examined by Leslie, to whose Essay on Heat, published in 1804, we must still refer for [much] of our knowledge on this subject. It follows from these researches that velocity of radiation depends more on the *surface* than the *substance* of a radiating body: that the most imperfect radiators are to be sought among those bodies which are highly smooth and bright, such as polished gold, silver, tin, and brass; but that these same metals radiate freely when their smoothness and polish are destroyed, as by scratching their surfaces with a file, or covering them with whiting or lamp black. A metallic surface seems adverse to radiation independently of its smoothness, since a highly polished piece of glass radiates far better than an equally polished metallic surface. Scratching a surface probably favours radiation by multiplying the number of radiating points.

[The results of Leslie's experiments are included in the following table:

RADIATING POWERS.

Lamp Black	100	Tarnished Lead	45
Writing Paper	98	Clean Lead	19
Sealing Wax	95	Polished Iron	15
Crown Glass	90	Tin, Gold, Silver, Copper, polished	12
China Ink	88		
Red Lead	80		
Plumbago	75		

[The recent researches of Melloni have disclosed new facts, and suggested other views respecting the conditions of surface which influence radiation. He found that where in polishing the surface of a metal, the outer layers are rendered *denser* by the pressure used, the radiating power is impaired, and he ascribes the effect of roughening a metallic surface, in Leslie's experiments, to the partial removal or breaking up of this denser coating. Cast silver which

is less dense than hammered silver, he found, with the same polish of surface to have one third more of radiating power. By scratching the surface of the hammered metal its power of radiation was augmented in the ratio of 10 to 18. Roughening the surface of the cast silver produced the contrary effect, lowering the radiating power in the ratio of 13.7 to 13.4, and a like result was caused by scratching a surface of polished marble. It would seem, therefore, that the radiating power is closely connected with the molecular structure of the outer layer of the mass, and has no definite relation to the roughness or smoothness of its surface. Taylor's Scientif. Mem.]

[Until recently it has been very generally maintained, that the radiation of heat was influenced by the colour of the radiant surface, dark colours being supposed to possess this property in the highest degree. This seems to have been hastily inferred from Leslie's experiments, which placed lamp black at the head of the list of the bodies used; although in the same table writing paper and glass have precedence of China ink and plumbago. The same inference has been more lately deduced from the observations of Dr. Starke, as referred to in the London edition of this work. These, however, were not so conducted as to isolate the effect of radiation from other cooling influences, and could not lead to any certain conclusion. The latest experiments on the subject, those of Dr. A. D. Bache, executed with the greatest care, furnished conclusive proof that *colour alone has no influence upon the radiating power of a surface.*]

Reflection of Heat.—The existence of a reflecting power may be shown by standing at the side of a fire in such a position that the heat cannot reach the face directly, and then placing a plate of tinned iron opposite the grate, and at such an inclination as permits the observer to see in it the reflection of the fire: as soon as it is brought to this inclination, a distinct impression of heat will be perceived upon the face. If a line be drawn from a radiating substance to the point of a plane surface by which its rays are reflected, and a second line from that point to the spot where its heating power is exerted, the angles which these lines form with a line perpendicular to the reflecting plane are called the angles of *incidence* and *reflection*, and are invariably equal to each other. It follows from this law, that when a heated body is placed in the focus of a concave parabolic reflector, the diverging rays which strike upon it assume a parallel direction with respect to each other; and that when these parallel rays impinge upon a second concave reflector standing opposite to the former, they are made to converge, so as to meet together in its focus. Their united influence is thus brought to bear upon a single point.

It has been known for ages that the heat contained in the solar rays admits of being reflected by mirrors, and a like property has long since been recognized in the rays emitted by red-hot bodies; but that heat emanates in invisible rays, which are subject to the same laws of reflection as those that are accompanied by light, is a modern discovery, noticed indeed by Lambert, but first decisively established by Saussure and Pictet, of Geneva. They first proved it of an iron ball heated so as not to be luminous even in the dark, and then of a vessel of boiling water (Pictet's Essai sur le Feu, p. 65, 1790); but for most of our knowledge of this subject we must again refer to the labours of Leslie. He demonstrated that the reflecting power depends on the nature and condition of surfaces, and that those qualities which are adverse to radiation, are precisely such as promote reflection. Bright smooth metallic surfaces, as polished silver, brass, or tin, which are retentive of their own heat, are little prone to receive

heat from other sources, but cause such rays to fly off from them; while those qualities of a surface which facilitate radiation from a hot body, likewise unfit it for reflecting the rays which fall upon it from surrounding objects. His experiments, indeed, justify the conclusion that the faculty of radiation is inversely as that of reflection.

[By a reference to Melloni's results, before mentioned, it will be apparent that this inverse relation of radiation and reflection is far from being a general law. Thus the polished surface of cast silver, used in his experiments, is not only a better reflector, but a better radiator than the roughened one.]

[The following table, derived from the experiments of Buff, exhibits the comparative reflecting power of various surfaces. Of 100 rays, incident at an angle of 60° from the perpendicular, there are reflected by

Polished Gold . . .	76	Polished Brass, varnished .	41
" Silver . . .	62	Looking Glass . . .	20
" Brass . . .	62	Glass Plate, blackened on back	12
Brass, without polish . .	52	Metal Plate, blackened .	6]

Absorption of Heat.—Every increase of temperature arising from radiant heat is due to its absorption or reception into the body on which it falls. If a pencil of heat impinge on the surface of a body, through which no portion of it is directly transmitted, it must either be absorbed or reflected: those rays which are reflected cannot be absorbed; and those which are not reflected must be absorbed. The number of absorbed rays is supplemental to that of the reflected rays. It hence follows that as the reflecting power is materially influenced by the nature of surfaces, the absorptive power must be so likewise. Those qualities of a surface which increase reflection are to the same extent adverse to absorption; and those which favour absorption are proportionally injurious to reflection.

[Conceiving reflection and radiation to be inversely related, as was erroneously inferred from Leslie's experiments, and seeing that reflection and absorption are also thus related, it has been usually maintained, as the general law, that the conditions favourable to radiation and absorption are the same. Accordingly the experiments of Leslie, on this point, show that a surface coated with lamp black has great power to absorb the heat incident upon it, while one of polished metal has but little, and that the latter is improved in this respect by being roughened. Yet it cannot be inferred, as a general fact, that absorption and radiation follow the same law. A roughened surface of marble, or of cast silver, though, no doubt, possessed of higher powers of absorption than when smooth, is, as we have seen, inferior in radiating power.]

[The colour of surfaces, though, as hereafter to be shown, highly influential in the absorption of heat associated with light, as in the rays of the sun, appears to be without effect upon uncombined or dark heat. It is true that the experiment of Dr. Starke, (see London edition of this work,) have been adduced to prove the reality of such an influence; but they are open to serious objections, some of which have been already hinted at under the head of radiation.]

An interesting connection has been traced by Nobili and Melloni between the absorbing and conducting power of surfaces. (An. de Ch. et Ph. xlviii. 198.) In their experiments variations of temperature were estimated by the *thermo-multiplier*, and these researches, if free from fallacy, justify the inference that the

radiating and absorbing powers of surfaces for simple heat are in the inverse order of their conducting power.

Transmission of Heat.—Radiant heat passes with perfect freedom through a vacuum. The air and gaseous substances present but a feeble barrier to its progress; so feeble, indeed, that the degree of impediment which they occasion has not yet been appreciated. Most transparent media of a denser kind, on the contrary, such as the diamond, rock-crystal, glass, and water, even in thin strata, interfere greatly with its passage. This last remark, however, is only applicable to *simple radiant heat*, that is, to heat unassociated with light. The solar rays pass readily through glass, both heat and light being refracted in their passage, as is shown by the action of a burning glass or lens; and though much of the heat emitted by the flame of a lamp or a red-hot ball of iron is arrested by glass, many calorific rays are directly transmitted along with the light. But the result is different when the heated body is not luminous. A thin screen of glass interposed between such an object and a thermometer certainly intercepts most of the rays that fall upon it; and the sole question which can be raised is, whether the small effect on the thermometer is caused by direct transmission, or by the screen first becoming warm by absorbing the rays, and then acting by its radiation on the thermometer. On this point the philosophic world was long much divided; but the question has been at length finally set at rest by the masterly researches of Melloni, made with the thermo-multiplier (An. Ch. et Ph. xlviii. 198, liii. 5, lv. 337, lx. 402). He has proved that solids and liquids differ in transmissibility to the rays of heat, just as they differ in their action on light. This may be expressed by the terms *transcalent* and *intranscalent* (*trans* through, *caleo* I heat), or *diathermanous* and *adiathermanous* (δια through, θερμαινω I heat), corresponding to the adjectives transparent and opaque as applied to light. The principal conclusions flowing from his researches are the following:—

1. Though transcalent bodies are also in general more or less transparent, the only known exceptions being opaque black glass and black mica, yet the transcalency and transparency of a substance are not in the same proportion.

2. Radiant heat falling perpendicularly on laminæ of transcalent bodies having parallel surfaces suffers in all the same degree of reflection, which amounts to 39-1000ths of the incident rays on entering, and 37-1000ths on leaving the lamina.

3. Transcalent bodies differ in the degree of their transcalency. Rock-salt is the only known substance which is perfectly diathermanous: heat from any source falling on a lamina of pure rock-salt with parallel faces, is not at all absorbed, all the rays which are not reflected being directly transmitted; and this is true whether the laminæ be thick or thin. The result is different with other transcalent bodies, which always absorb a portion of the incident rays.

[Of 100 rays of heat from the same source, successively incident on laminæ of a number of substances of equal thickness, there were transmitted through

Rock-salt . . .	92	Gypsum	20
Calc Spar . . .	62	Black Glass (opaque) .	16
Plate Glass . . .	40	Alum	12

Of 100 rays similarly incident on strata of liquids, there were transmitted through

Chloride of Sulphur .	63	Alcohol	15
Bi Sulphuret of Carbon .	63	Water	11
Ether	21		

Of 100 rays incident on similar laminæ of differently coloured glasses, there were transmitted through

Violet Glass . . .	53	Blue	33
Red	47	Green	26
Yellow	34		

It thus appears that while rock-salt is the most transcalent substance known, clear glass arrests more than one half of the incident heat; and what is still more remarkable, transparent alum and limpid water intercept more of the rays than the deepest coloured and even opaque glasses.]

4. In glass and liquids those are most transcalent which have the greatest refractive power in regard to light. This is shown in No. 3, where only 11 per cent. of the incident heat passed through water, and 63 through a similar stratum of bisulphuret of carbon. But the law is not applicable to chrystalline bodies; thus, as above, 92 per cent. of the incident rays find their way through rock-salt, and 12 per cent. through a similar stratum of alum; while their refractive powers for light are nearly the same.

5. The quantity of radiant heat transmissible through glass varies with the temperature of the source from which the rays emanate.

[Thus using as sources of heat the lamp of Locatelli; a red-hot spiral of platinum wire; a blackened copper plate at 734°; and the same at 212°, Melloni found the heat incident from these various sources to be transmitted in the following proportion, assuming 100 as the measure of the incident rays:

Substance.	*Lamp.*	*Hot Platinum.*	*Copper* 734°.	*Copper* 212°.
Rock-salt . . .	92	92	92	92
Calc Spar . . .	39	28	6	0
Plate Glass . . .	39	24	6	0
Gypsum . . .	14	5	0	0
Alum . . .	9	2	0	0

It thus appears that rock-salt is not only the most transcalent of bodies, but is equally so to heat of all temperatures.

But the action of media upon radiant heat consists not merely in stopping a certain portion of it, but in separating it into two portions, hence a second plate of the same kind of substance intercepts but little of the heat which has passed through the first. Thus if 1000 rays be incident upon a plate of alum, only 90 will pass through, but if these 90 be allowed to fall on a second plate of the same substance, 81, or 9-10ths of the whole will be transmitted.]

Hence it should follow, as Melloni has proved, that comparatively little heat is absorbed by multiplying screens of the same material, or increasing the thickness of one screen: it is the first screen, or the side of one screen, next the radiating substance, by which the principal absorption of heat is effected. The quantity of heat arrested by increasing the thickness of a screen decreases in a very rapid ratio. These facts establish between heat and light new and deeply interesting relations, which will be referred to in the next section.

[It further appears from these experiments that the kind of heat thus transmitted differs for different media, and hence that there are various kinds or states of radiant heat, just as there are various kinds or states of light as manifested by its different colours. Calc Spar, for example, transmits 91 per cent. of the heat which has passed through alum and 81 of that which has passed through

gypsum, while the green tourmaline transmits only 1 in the 100 coming from the alum, and no less than 30 which have passed through black glass.]

6. Melloni has established the refrangibility of heat by diathermanous media. Prior observers failed of obtaining decisive evidence of this property, in consequence of using prisms or lenses of glass, the feeble transcalency of which unfits it for such an inquiry; but with a prism of rock-salt Melloni easily demonstrated the general principle, and proved that heat from different sources, like light of different colours, has different degrees of refrangibility.

Polarization and double Refraction of Heat.—These properties of radiant heat, which Melloni with all his skill vainly attempted to demonstrate, have lately been established in regard to heat, both from luminous and non-luminous sources, by Forbes,—a discovery of great interest, as drawing still closer the relations of heat and light, and for which he has received the well-merited honour of the Keith medal, awarded by the Royal Society of Edinburgh. Forbes has polarized heat by all the methods which polarize light,—by reflection, refraction, and double refraction. He also depolarized heat; and as this occurs only as a consequence of double refraction, he thereby proved the double refraction of heat. The instrument used by Forbes was the thermo-multiplier, brought to such extreme delicacy that it is supposed sensible to 1-1500ths of a degree of Fahrenheit's thermometer. (Phil. Trans. Ed. 1835.)

Theory of Radiation.—The tendency which all bodies evince to attain an equality of temperature by means of radiation, has given rise to two ingenious theories, suggested respectively by Pictet and Prevost. According to the former, bodies of equal temperature do not radiate at all; and when the temperature is unequal, the hotter give calorific rays to the colder bodies till an equilibrium is established, at which moment the radiation ceases. Prevost, on the contrary, conceived radiation to go on at all times, and from all substances, whether their temperature were the same or different from that of surrounding objects (Recherches sur la Chaleur). Consistently with this view, the temperature of a body falls whenever it radiates more heat than it absorbs; its temperature is stationary when the quantities emitted and received are equal; and it grows warm when the absorption exceeds the radiation. Of these theories the preference is very generally accorded to the latter.

Adopting, then, the theory of Prevost, it will be useful to examine a few instances of its application;—and, first, in regard to the experiments with conjugate mirrors. If a metallic ball in the focus of one mirror, and a thermometer in that of the other, be of the same temperature as the surrounding objects (say at 60°), the thermometer will remain stationary. It will indeed receive rays from the ball; but as it emits an equal number in return, its temperature will be unchanged. If the ball is above 60° the thermometer will rise, because it then receives a greater number of rays than it emits. If, on the contrary, the ball is below 60°, the thermometer, being the warmer of the two bodies, emits more rays than it receives, and its temperature will fall.

The same mode of reasoning explains an interesting experiment originally performed by the Florentine Academicians, and since carefully repeated by Pictet. He placed a piece of ice instead of the metallic ball in the focus of his mirror, and observed that the thermometer in the opposite focus immediately descended, but rose again as soon as the ice was removed. On replacing the ice in the focus, the thermometer again fell, and reascended when it was with-

drawn. It was supposed by some philosophers that this experiment proved the existence of frigorific rays, endowed with the property of communicating coldness; whereas, all the preceding remarks were made on the supposition that cold is merely a negative quality arising from the diminution of heat. Nor is the foregoing experiment inconsistent with such an opinion: on the contrary, it is readily accounted for by the theory of Prevost, and might have been anticipated by its application. The thermometer, in fact, has its temperature lowered, because it emits more rays than it receives; and it rises when the ice is removed, because it then receives a number of calorific rays radiated by the warmer surrounding objects, which were intercepted by the ice while it was in the focus.

An elegant application of this theory was made by Dr. Wells, to account for the formation of *Dew*. The most copious deposit of dew takes place when the weather is clear and serene; and the substances that are covered with it are always colder than the contiguous strata of air, or than those bodies on which dew is not deposited. In fact, dew is a deposition of water previously existing in the air as vapour, and which loses its gaseous form only in consequence of being chilled by contact with colder bodies. In speculating, therefore about the cause of this phenomenon, the chief object is to discover the cause of the reduction of temperature. The explanation proposed by Wells, in his excellent Treatise on Dew, and now universally adopted, is founded on the theory of Prevost. If it be admitted that bodies radiate at all times, their temperature can remain stationary only by their receiving from surrounding objects as many rays as they emit; and should a substance be so situated that its own radiation may continue uninterruptedly without an equivalent being returned to it, its temperature must necessarily fall. Such is believed to be the condition of the ground in a calm starlight evening. The calorific rays which are then emitted by substances on the surface of the earth, are dispersed through free space and lost; nothing is present in the atmosphere to exchange rays with them, and their temperature consequently diminishes. If, on the contrary, the weather be cloudy, the radiant heat proceeding from the earth is intercepted by the clouds, an interchange is established, and the ground retains nearly, if not quite, the same temperature as the adjacent portions of air.

All the facts hitherto observed concerning the formation of dew, tend to confirm this explanation. Dew is deposited sparingly or not at all in cloudy weather; all circumstances which promote free radiation are favourable to its deposition; good radiators of heat, such as grass, wood, the leaves of plants, and filamentous substances in general, fall in temperature, in favourable states of the weather, to an extent of 10, 12, or even 15 degrees below that of the circumambient air; and while these are drenched with dew, pieces of polished metal, smooth stones, and other imperfect radiators, are barely moistened, and are nearly as warm as the air in their vicinity.

Cooling of Bodies.—Heated bodies cool by two very different methods. When a hot body is enveloped in solid substances, its heat is withdrawn solely by communication, and the velocity of cooling depends on the conducting power. Cooling is effected in a similar manner when the heated body is immersed in a liquid; but the velocity of cooling then depends partly on the conducting power of the liquid, and partly on the mobility of its particles. In elastic fluids the cooling takes place both by communication and radiation; and in a vacuum it is produced solely by radiation.

The term *velocity of cooling* above employed, signifies the number of degrees lost by a hot body during equal intervals of time, as one minute or one second; and by the *law of cooling* is meant the relation which the velocities of cooling bear to each other. The first attempt to fix the law of cooling was by Newton. Observing that the velocity of cooling in a hot body diminishes continually as the excess of its temperature declines, he conceived that the heat lost during each interval of time was a constant fraction of its excess of heat at the beginning of that interval, and he inferred as a general law of cooling that while the times of cooling form an arithmetical series, the velocities of cooling are in a geometric progression. [But, from the admirable researches of Dulong and Petit, it appears that this law is only approximately true when the excess of temperature of the hot body is small, and quite inapplicable in other cases. The following is the law of cooling in vacuo deduced from their experiments. When a body cools in vacuo, the surrounding temperature being constant, the velocity of cooling for excess of temperature, in arithmetical progression, increases as the terms of a geometrical progression diminished by a certain quantity.]

EFFECTS OF HEAT.

The phenomena that may be ascribed to this agent, and which may therefore be enumerated as its effects, are numerous. With respect to animals, it is the cause of the feelings of cold, agreeable warmth, and burning, according to its intensity. It excites the system powerfully, and without a certain degree of it the vital actions entirely cease. Over the vegetable world its influence is obvious to every eye. By its stimulus co-operating with air and moisture, the seed bursts its envelope and yields a new plant, the buds open, the leaves expand, and the fruit arrives at maturity. With the declining temperature of the seasons the circulation of the sap ceases, and the plant remains torbid till it is again excited by the stimulus of heat.

The dimensions of every kind of matter are regulated by this principle. Its increase, with few exceptions, separates the particles of bodies to a greater distance from each other, producing expansion, so that the same quantity of matter is thus made to occupy a larger space; and the diminution of heat has an opposite effect.

The form of bodies is dependent on heat. By its increase solids are converted into liquids, and liquids are dissipated in vapour; by its decrease vapours are condensed into liquids, and these become solid. If matter ceased to be under the influence of heat, all liquids, vapours, and doubtless even gases, would become permanently solid; and all motion on the surface of the earth would be arrested.

When heat is accumulated to a certain extent in bodies, they shine or become *incandescent*. On this important property depend all our methods of artificial illumination.

Heat exerts a powerful influence over chemical phenomena. There is, indeed, scarcely any chemical action which is not in some degree modified by this principle; and hence a knowledge of its laws is indispensable to the chemist. By its means bodies previously separate are made to combine, and the elements of

compounds are disunited. An undue proportion of it is destructive to all organic and many mineral compounds; and it is essentially concerned in combustion, a process so necessary to the wants and comforts of man.

Of the various effects of heat above enumerated, several will be discussed in other parts of the work. In this place it is proposed to treat only of its influence over the dimensions and form of bodies, a subject which will be conveniently studied under the three heads of expansion, liquefaction, and vaporization.

EXPANSION.

[Assuming with the generality of chemists that heat is a peculiar species of matter, whose particles are strongly repulsive of one another, and attractive in various degrees of the particles of ponderable bodies, we may readily conceive that the entrance of heat into a mass will have the effect of removing the integrant molecules to greater distances from each other, and that thus the body will be made to occupy a greater space, or to expand.]

This effect of heat is opposed to cohesion—that force which tends to make the particles of matter approximate, and which must be overcome before any expansion can ensue. Heat, therefore, should produce the greatest expansion in those bodies which are least influenced by cohesion, an inference fully justified by observation. Thus the force of cohesion is greatest in solids, less in liquids, and least of all in aëriform substances; while the expansion of solids is trifling, that of liquids much more considerable, and that of elastic fluids far greater.

It may be laid down as a rule, the reason of which will now be obvious, that all bodies are expanded by heat, and that the expansions of the same body increases with the quantity of heat which enters it. But this law does not apply, unless the form and chemical constitution of the body is preserved. For if a change in either be occasioned, then the reverse of expansion may ensue; not, however, as the direct consequence of an augmented temperature, but as the result of a change in form or composition.

To prove the expansion of solids, we need only take the exact dimensions in length, breadth, and thickness, of any substance when cold, and measure it again while strongly heated, when it will be found to have increased in every direction. This dilatation from heat and consequent contraction in cooling take place with a force which appears to be irresistible.

Expansion of Solids.—The expansion of solids has engaged the attention of several experimenters, who have endeavoured to determine the exact quantity by which different substances are lengthened by a given increase of heat, and whether or not their elongation is equable at different temperatures. Their expansion, for example, from the freezing point of water to 122°, is equal to what takes place betwixt 122° and 212°. The researches of Dulong and Petit (An. de C. et P. vii.) prove that solids do not dilate uniformly at high temperatures, but expand in an increasing ratio; that is, the higher the temperature beyond 212°, the greater the expansion for equal additions of heat. It is manifest, indeed, from their experiments, that the rate of expansion is an increasing one even between 32 and 212; but the differences which exist within this small range are so inconsiderable as to escape observation, and for most practical purposes may be disregarded.

The subjoined table includes the most interesting results of Lavoisier and

Laplace, who have carefully investigated the linear expansion of solids. (Biot, i. 158.)

Names of Substances.	Elongation when heated from 32° to 212°.
Glass tube without lead, a mean of three specimens	$\frac{1}{1115}$ of its length.
English flint glass	$\frac{1}{1248}$
Copper	$\frac{1}{581}$
Brass—mean of two specimens	$\frac{1}{532}$
Soft iron forged	$\frac{1}{819}$
Iron wire	$\frac{1}{812}$
Untempered steel	$\frac{1}{927}$
Tempered steel	$\frac{1}{807}$
Lead	$\frac{1}{351}$
Tin of India	$\frac{1}{516}$
Tin of Falmouth	$\frac{1}{462}$
Silver	$\frac{1}{524}$
Gold—mean of three specimens	$\frac{1}{602}$
Platinum, determined by Borda	$\frac{1}{1167}$

Knowing the elongation of any substance for a given number of degrees of the thermometer, its total increase in bulk may in general be calculated by trebling the number which expresses its increase in length.

[According to the curious observations of Mitscherlich, crystalline bodies, of certain forms, are differently affected by heat in different directions. Thus a rhomb of calcareous spar, while expanded in the direction of its axis of double refraction, or the line joining its two obtuse summits, is contracted in all directions at right angles to this. Hence the angles of the crystal are changed by heat, the obtuse ones diminishing and the acute ones enlarging, so as to approach the figure more nearly to the form of a cube. M. Fresnel found the effect on a crystal of sulphate of lime to be just the reverse of this, the expansion occurring chiefly at right angles to the axis. It is doubtless owing to a similar cause that glass and other solids, which are liable to various degrees of crystalline arrangement of their parts, have been found, when examined under these different conditions, to possess different expansibilities.]

Expansion of Liquids.—The expansion of liquids is proved by putting a common thermometer, made with mercury or alcohol, into warm water, when the dilatation of the liquid will be shown by its ascent in the stem. The experiment is indeed illustrative of two other facts. It proves, first, that the dilatation increases with the temperature; for if the thermometer be plunged into several portions of water heated to different degrees, the ascent will be greatest in the hottest water, and least in the coolest portions. It demonstrates, secondly, that liquids expand more than solids. The glass bulb of the thermometer is itself expanded by the hot water, and therefore is enabled to contain more mercury than before; but the mercury being dilated to a much greater extent, not only occupies the additional space in the bulb, but likewise rises in the stem. Its ascent marks the difference between its own dilatation and that of the glass, and is only the apparent, not the actual, expansion of the liquid.

Different liquids do not expand to the same degree from an equal increase of temperature. Alcohol expands much more than water, and water than mercury. In being heated from 32° to 212°

Alcohol is increased in volume, by	$\frac{1}{9^{th}}$
Fixed Oils	$\frac{1}{11}$
Water	$\frac{1}{2276}$
Mercury	$\frac{1}{55.5}$

From the frequency with which mercury is employed in philosophical experiments, it is important to know the exact amount of its expansion. This subject has been investigated by several philosophers, but the experiments of Lavoisier and Laplace, and especially of Dulong and Petit, from the extreme care with which they were made, are entitled to the greatest confidence. According to the former the actual dilatation of mercury, in passing from the freezing to the boiling point of water, amounts to $\frac{100}{5412}$ of its volume; but the result obtained by Dulong and Petit, who found it $\frac{100}{5550}$, is probably still nearer the truth. Adopting the last estimate, this metal dilates, for every degree of Fahrenheit's thermometer, $\frac{1}{9990}$ of the bulk which is occupied at the temperature of 32°. The apparent expansion of mercury contained in glass is of course less than the absolute expansion. Between the limits of 32° and 212°, Lavoisier and Laplace estimate the apparent expansion at $\frac{1}{63}$, and Dulong and Petit at $\frac{1}{64.8}$ of its volume, being $\frac{1}{11664}$ for each degree of Fahrenheit's thermometer.

[The most expansible of liquids are those which have been produced by the condensation of certain gases, and those discovered by Sir D. Brewster in the minute cavities of crystals of topaz and quartz. Liquified carbonic acid expands according to Thilorier, at the rate $1\frac{1}{120th}$ of its volume, for each degree of the thermometer; which is four times the expansion of air and other gases. According to Dr. Mitchell its dilatation is three times that of air. The liquids are believed to be even more expansible, and are probably in part composed of liquified gases.]

All experimenters agree that liquids expand in an *increasing ratio*, or that equal increments of heat cause a greater dilatation at high than at low temperatures. Thus, if a fluid is heated from 32° to 122° it will not expand so much as it would do in being heated from 122° to 212°, though an equal number of degrees is added in both cases. In mercury the first expansion, according to Deluc, is to the second as 14 to 15; in olive oil as 13·4 to 15; in alcohol as 10·9 to 15; and in pure water as 4·7 to 15.

[The augmenting expansion of mercury, as measured by Dulong and Petit at successive intervals of 180°, is seen in the following table:

From 32° to 212°	$\frac{1}{9990}$
" 212° to 392°	$\frac{1}{9685}$
" 392° to 572°	$\frac{1}{9540}$

An interesting exception to this law of an increased rate of expansion, has been found by Desprets in the dilatation of *fused sulphur*, which he observed to expand in a diminishing ratio with equal successive additions of temperature.]

There is a peculiarity in the effect of heat upon the bulk of some fluids; namely, that at a certain temperature increase of heat causes them to contract, and its diminution makes them expand. This singular exception to the general effect of heat is only observable in those liquids which increase in bulk in passing from the liquid to the solid state, and is remarked only within a few degrees of temperature above their point of congelation. Water is a noted example of it. Ice swims upon the surface of water, and therefore must be lighter than it;

a convincing proof that water in the act of freezing must expand. The specific gravity of ice is nearly 0·92, which gives the volume of ice to that of water as 1 to 0·92; that is, water expands by about 1-11th of its volume in passing into ice.

But it is not only during the act of congelation that water expands; since it begins to dilate some time before it actually freezes. Dr. Croune noticed this phenomenon so early as the year 1683, and it has since been observed by various philosophers. To render this obvious, fill a flask, capable of holding three or four ounces, with water at the temperature of 60°, and adapt to it a cork, through which passes a glass tube open at both ends, about the eighth of an inch wide, and ten inches long. After having filled the flask, insert the cork and tube, and pour a little water into the latter till the liquid rises to the middle of it. On immersing the flask into a mixture of pounded ice and salt, the water at first contracts, and therefore descends in the tube; but soon after an opposite movement ensues, indicating dilatation, though the water within the flask is at the same time yielding heat to the freezing mixture in which it is immersed.

To the inference deduced from this experiment it was objected, that the ascent of the water in the tube is not referable to expansion in the liquid, but to contraction of the flask, diminishing its capacity. In fact, this cause does operate, though not to a degree sufficient to account for the whole effect; and, accordingly, it has been proved by an elegant and decisive experiment of Dr. Hope, that water does really expand previous to congelation. He believes the greatest density of water to be between 39·5° 40°; that is, boiling water obeys the usual law till it has cooled to the temperature of about 40°, after which the abstraction of heat produces increase instead of decrease of volume (Phil. Trans. Ed. v. 379). Hallström, who has examined this point with much care, estimates it at 39°.

The expansion of water at the moment of freezing is attributed to a new and peculiar arrangement of its particles. Ice is in reality crystallized water, and during its formation the particles arrange themselves in ranks and lines, which cross each other at angles of 60° and 120°, and consequently occupy more space than when liquid. This may be seen by examining the surface of water while freezing in a saucer.

Water is not the only liquid which expands under reduction of temperature, as the same effect has been observed in a few others which assume a highly crystalline structure on becoming solid;—fused iron, antimony, zinc, and bismuth, are examples of it. Mercury is a remarkable instance of the reverse; for when it freezes, it suffers a very great contraction.

Expansion of Gases.—As the particles of air and aëriform substances are not held together by cohesion, it follows that increase of temperature must occasion a considerable dilatation of them; and, accordingly, they are found to dilate from equal additions of heat much more than solids or (most) liquids.

This subject had been unsuccessfully investigated by several philosophers, who failed in their object chiefly because they neglected the precaution of drying the gases upon which they operated.

[The general laws of their dilatation were detected by Dalton and Gay Lussac nearly at the same time, and afterwards still more fully investigated by Dulong and Petit.

The laws thus deduced are as follows:

1st. All gases dilate equally between the same limits of temperature.

2d. Each gas dilates uniformly by equal successive additions of temperature.

3d. The dilatation of any one gas between the same limits of temperature is the same, whatever be the degree of its condensation, provided the pressure be maintained uniform during the expansion. From similar experiments, the same philosophers were led to infer that steam and other vapours, apart from the liquids that produce them, expand in a ratio sensibly the same with the so called permanent gases.

According to the experiments above referred to, 100 parts of air or other gaseous matter, in being heated from 32° to 212°, expand to 137·5 parts. The increase from 180° is therefore 37·5 for the 100 parts, or 0·375 for 1 part. This divided by 180 ($\frac{0{\cdot}375}{180}$), gives for the expansion of dry air for each degree of Fahrenheit's thermometer $\frac{1}{480}$th of the volume of the air at 32°. Thus if a cubic foot of air at 32° be raised one degree, its volume will become $1\frac{1}{480}$th cubic feet.

The more recent and elaborate investigations of Rudberg, Magnus and Regnault, have proved the expansibility of atmospheric air to be somewhat less than that above stated. According to Rudberg the mean expansion of dry air at the common pressure for each degree from 32° to 212° is $\frac{1}{493}$rd of its volume at 32°; according to Magnus it is very nearly $\frac{1}{491}$st; and according to Regnault a little more than $\frac{1}{491}$st.]

This point being established, it is easy to ascertain what volume any given quantity of air should occupy at any given temperature. Suppose a certain portion of air to occupy 20 measures of a graduated tube at 32°, it may be desirable to determine what would be its bulk at 42°. For every degree of heat it has increased by $\frac{1}{480}$th of its original volume, (assuming for simplicity the old co-efficient of expansion,) and therefore, since the increase amounts to ten degrees, the 20 measures will have dilated by $\frac{10}{480}$ths. The expression will therefore be $20 + 20 \times \frac{10}{480} = 20{\cdot}416$. The volume which the air occupies at 32° is a necessary element in all such calculations. Thus, having 20·416 measures of air at 42°, the corresponding bulk for 52° cannot be calculated by the formula $20{\cdot}416 + 20{\cdot}416\frac{10}{480}$; the real expression is $20{\cdot}416 + 20\frac{10}{480}$, because the increase is only $\frac{10}{480}$ths of the space occupied at 32°, which is 20 measures. A similar remark applies to the formula for estimating the effect of heat on the height of the barometer.

[Hitherto the same co-efficient of expansion $\frac{1}{480}$ has been considered applicable to all gases, and even to steam and other vapours, and this would obviously be the case were they all equally expansible, as affirmed in the first of the above laws. But Magnus and Regnault have shown that there are slight but sensible differences in the expansibility of these bodies. The following table from Regnault's memoir, shows the increase of volume of the different gases when heated from 32° to 212° under ordinary atmospheric pressure.

Air	0.36650	Nitrous Oxide	0.37195
Hydrogen	0.36706	Cyanogen	0.38767
Carbonic Oxide	0.36688	Sulphurous Acid	0.39028]
Carbonic Acid	0.37099		

[The second law, though generally assumed as true for all parts of the scale, was only tested by Gay Lussac, between 32° and 212°. This was done by comparing the march of a mercurial with that of an air thermometer, exposed together to the same successive temperatures in the apparatus before described.

The correspondence between the instruments was found to be very exact. Dulong extended the comparison to lower, and to higher temperatures, and inferred that the two instruments agree in their indications from 64·8 to 212°,—but that above the latter point the expansions of the air diminish for successively equal increments of temperature, measured by the mercurial thermometer. Nearly the same results have been deduced by Regnault, excepting that he found the point at which the air thermometer fell behind the mercurial to vary in different instruments, owing to the difference of expansion of different kinds of glass. In atmospheric air and carbonic acid, he found the expansion, for a given increase of temperature, to be greater as the gas is more condensed. This increase of expansibility, by augmented pressure, was observed in a still more marked degree with cyanogen and sulphurous acid gases. With the latter the dilatation under 1 atmosphere of pressure was 0.3902, and under $1\frac{29}{100}$ atmosphere, was 0.3980.

These experiments would seem to prove that the increase of expansibility as the pressure is augmented, is most rapid in the cases of those gases which require the least compression for their liquefaction, such as the two last mentioned. Hence Regnault inferred the probability that the vapours, which are even more condensible than these gases, would be found to possess expansibilities exceeding by a still greater amount that of atmospheric air. Hitherto, however, they have been regarded as having exactly the same expansibility, and hence been included in the first of the laws above announced.

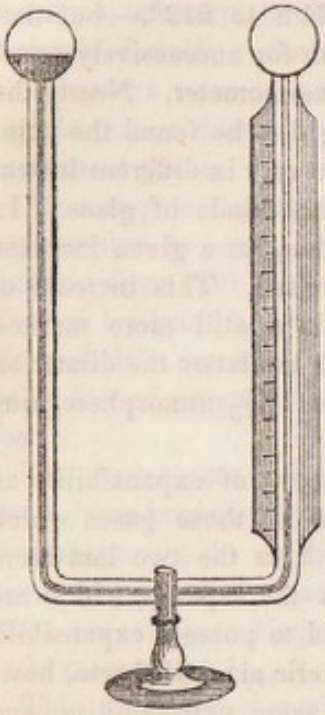
It is an interesting fact, ascertained in these experiments, that hydrogen gas preserves its expansibility 0.34706, unaltered as high as $3\frac{1}{2}$ atmospheres, the limit to which he carried his experiments on this substance.]

ON THE THERMOMETER.

The influence of heat over the bulk of bodies is better fitted for estimating a change in the quantity of that agent than any other of its properties; for substances not only expand more and more as the temperature increases, but in general return exactly to their original volume when the heat is withdrawn. The first attempt to measure the intensity of heat on this principle was made early in the seventeenth century, and the honour of the invention is by some bestowed on Sanctorius, by others on Cornelius Drebel, and by others on the celebrated Galileo. The material used by Sanctorius was atmospheric air. There are, however, two forcible objections to the general employment of this thermometer. In the first place, its dilatations and contractions are so great, that it is inconvenient to measure them when the change of temperature is considerable; and, secondly, its movements are influenced by pressure as well as by heat, so that the instrument would be affected by variations of the barometer, though the temperature should be quite stationary.

For the reasons just stated, the common air thermometer is rarely employed; but a modification of it, described in 1804 by Leslie in his Essay on Heat under the name of *Differential Thermometer*, is entirely free from the last objection, and is admirably fitted for some special purposes. This instrument was invented a century and a half ago by Sturmius, Professor of Mathematics at Altdorff, who has left a description and sketch of it in his *Collegium Curiosum*, p. 54, published in the year 1676; but like other air thermometers it had fallen

into disuse, till it was again brought into notice by Leslie. As now made it consists of two thin glass balls joined together by a tube, bent twice at a right angle, as represented in the annexed figure. Both balls contain air, but the greater part of the tube is filled with sulphuric acid coloured with carmine. It is obvious that this instrument cannot be affected by any change of temperature acting equally on both balls; for as long as the air within them expands or contracts to the same extent, the pressure on the opposite surfaces of the liquid, and consequently its position, will continue unchanged. Hence the differential thermometer stands at the same point, however different may be the temperature of the medium. But the slightest difference between the temperature of the two balls will instantly be detected; for the elasticity of the air on one side being then greater than that on the other, the liquid will retreat towards the ball whose temperature is lowest.



Solid substances are not better suited to the construction of a thermometer than gases; for while the expansion of the latter is too great, that of the former is so small that it cannot be measured except by the adaptation of complicated machinery. Liquids which expand more than the one and less than the other, are exempt from both extremes; and, consequently, we must search among them for a material with which to construct a thermometer. The principle of selection is plain. A material is required whose expansions are uniform, and whose boiling and freezing points are very remote from one another. Mercury fulfils these conditions better than any other liquid. No fluid can support a greater degree of heat without boiling than mercury; and none, except alcohol and ether, can endure a more intense cold without freezing. It has, besides, the additional advantage of being more sensible to the action of heat than other liquids, while its dilatations between 32° and 212° are almost perfectly uniform. Strictly speaking, the same quantity of heat does occasion a greater dilatation at high than at low temperatures, so that, like other fluids, it expands in an increasing ratio. But it is remarkable that this ratio, within the limits assigned, is exactly the same as that of glass; and therefore, if contained in a glass tube, the increasing expansion of the vessel compensates for that of the mercury.

We cannot here describe in detail the method of constructing a mercurial thermometer. This well known instrument consists of a tube of a uniform small bore, having a ball blown at one end. The ball and part of the tube are filled with mercury, the air is expelled by boiling the mercury, and the tube is hermetically sealed.

In order to graduate the thermometer, two fixed points are required: these are obtained by immersing it first in melting ice, marking the point at which it stands; and secondly in boiling water, at the level of the sea, and under the usual atmospheric pressure, the point at which it stands being also marked.

The distance between these two points may be divided into any number of equal parts or degrees. Fahrenheit, whose scale is used in this country, divided it into 180 degrees, beginning his scale at a point 32 of these degrees below the freezing point of water, which is the zero of his scale. Celsius, the author

of the centigrade scale, most frequently employed on the Continent, placed his zero at the freezing point, and divided the distance between that and the boiling point into 100 degrees. Reaumur adopted the same starting point or zero, but divided the same distance into 80 degrees only. Hence, the boiling point of water, on Fahrenheit's scale, is 212°, on the centigrade scale 100°, and on that of Reaumur 80°.

It is easy to reduce the temperature expressed by one thermometer to that of another, by knowing the relation which exists between their degrees. Thus, 180 is to 100 as 9 to 5, and to 80 as 9 to 4; so that nine degrees of Fahrenheit are equal to five of the centigrade, and four of Reaumur's thermometer. Fahrenheit's is therefore reduced to the centigrade scale by multiplying by five, and dividing by nine; or to that of Reaumur, by multiplying by four instead of five, previously subtracting 32°, because the zero of Fahrenheit is 32° lower than that of the others. The same process, reversed, enables us to reduce degrees of the other scales to those of Fahrenheit.

But, to save the trouble of such reductions, I have subjoined a table which shows the degrees on the centigrade scale and that of Reaumur, corresponding to the degrees of Fahrenheit's thermometer.

Fahr.	Cent.	Reaum.	Fahr.	Cent.	Reaum.	Fahr.	Cent.	Reaum.
212	100	80	113	45	36	14	−10	− 8
203	95	76	104	40	32	5	−15	−12
194	90	72	95	35	28	4	−20	−16
185	85	68	86	30	24	−13	−25	−20
176	80	64	77	25	20	−22	−30	−24
167	75	60	68	20	16	−31	−35	−28
158	70	56	59	15	12	−40	−40	−32
149	65	52	50	10	8			
140	60	48	41	5	4			
131	55	44	32	0	0			
122	50	40	23	-5	-4			

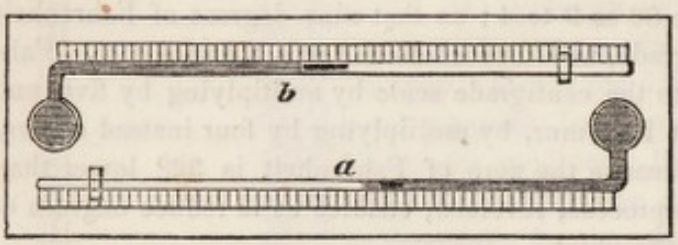
The mercurial thermometer may be made to indicate temperatures which exceed 212°, or fall below zero, by continuing the degrees above and below those points. But as mercury freezes at 39 degrees below zero, it cannot indicate temperatures below that point; and indeed the only liquid which has been used for such purposes is alcohol.

[It has been observed that mercurial thermometers slowly change their zero, which uniformly becomes higher than at the time of graduation. This phenomenon due to a diminished capacity of the ball, has been ascribed to the atmosphere continually pressing on its exterior, while a vacuum exists in the interior of the tube. As the principal contraction ensues after the tube is sealed, it is proper to allow some time to elapse between the sealing and graduation of the instrument.

M. Person has found that the elevation of the zero is very great when the instrument has been exposed to a high temperature for *some hours*. Former observers have tried the effect of a temperature as high as 300°, allowing the instrument to commence cooling immediately after reaching that point; in this case the rise of the zero was only about 1°; but M. P. operating at 440°, and maintaining that temperature for several hours, obtained an elevation of 12°, 15°

and even 17°. After such a prolonged heating he thinks that farther change is probably prevented, especially if sudden fluctuations be avoided. It is obvious from these facts that no mercurial thermometer, however accurate when first constructed, can be relied upon after long use, and especially if exposed to extremes of temperature, unless its scale be rectified from time to time by experiment.]

Register Thermometer.—For some purposes, especially in making meteorological observations, it is a very desirable object to ascertain the highest and lowest temperature which has occurred in a given interval of time, during the absence of the observer. The instrument employed with this intention is called a *Register Thermometer*, and the most convenient kind with which I am acquainted, is that described in the Philosophical Transactions of Edinburgh, iii. 245, by Dr. John Rutherford. The thermometer for ascertaining the most intense cold is made with alcohol, and the bulb is bent at a right angle to the stem, so that the latter may conveniently be placed in a horizontal position. In the spirit is immersed a cylindrical piece of black enamel, *a*, of such size as to move freely within the tube. In order to make an observation, the enamel should be brought down to the surface of the spirit, an object easily effected by slight percussion while the bulb is inclined upwards. When the thermometer sinks by exposure to cold, the enamel likewise retreats towards the bulb, owing to its adhesion to the spirit; but, on expanding, the spirit passes directly beyond the enamel, leaving it at the extreme point to which it had been conveyed by the previous contraction.



For registering the highest temperature, a common mercurial thermometer of the same form as the preceding is employed, having a small cylindrical piece of black enamel *b*, at the surface of the mercury. When the mercury expands, the enamel is pushed forward; and as the stem of the thermometer is placed horizontally, it does not recede when the mercury contracts, but remains at the spot to which it had been conveyed by the previous dilatation. The enamel is easily restored to the surface of the mercury by slight percussion while the bulb is inclined downwards; but this should be performed with care, lest the enamel, in falling abruptly, should interrupt the continuity of the mercurial column, and interfere with the indications of the instrument.

Pyrometers.—The instruments for measuring intense degrees of heat are called *pyrometers*, and must be formed either of solid or gaseous substances. The former alone have been hitherto employed, though the latter, from the greater uniformity with which they expand, are better calculated for the purpose. The action of most pyrometers depends on the elongation of a metallic bar by heat; and the difficulty in their construction consists in finding an infusible metal of uniform expansibility, and in measuring the degree of expansion with exactness. The best of these is Daniell's pyrometer, which, with a little practice, may be used with facility, and appears susceptible of very great precision.

[" It consists of two parts, which may be distinguished as the register and the scale. The register is a solid bar of black-lead earthenware, highly baked.

In this a hole is drilled, into which a bar of any metal, six inches long, may be dropped, and which will then rest upon its solid end. A cylindrical piece of porcelain, called the index, is then placed upon the top of the bar, and confined in its place by a ring or strap of platinum passing round the top of the register, which is partly cut away at the top, and tightened by a wedge of porcelain. When such an arrangement is exposed to a high temperature, it is obvious that the expansion of the metallic bar will force the index forward to the amount of the excess of its expansion over that of the black-lead, and that, when again cooled, it will be left at the point of greatest elongation. What is now required, is the measurement of the distance which the index has been thrust forward from its first position; and this, though in any case but small, may be effected with great precision by means of the scale.]

[" This is independent of the register, and consists of two rules of brass, accurately joined together at a right angle by their edges, and fitting square upon two sides of the black-lead bar. At one end of this double rule a small plate of brass projects at a right angle, which may be brought down upon the shoulder of the register, formed by the notch cut away for the reception of the index. A moveable arm is attached upon this frame, turning at its fixed extremity upon a centre, and at its other, carrying an arc of a circle, whose radius is exactly five inches, accurately divided into degrees and thirds of a degree. Upon this arm, at the centre of the circle, another lighter arm is made to turn, one end of which carries a nonius with it, which moves upon the face of the arc, and subdivides the former graduation into minutes of a degree; the other end crosses the centre, and terminates in an obtuse steel point, turned inwards at a right angle.]

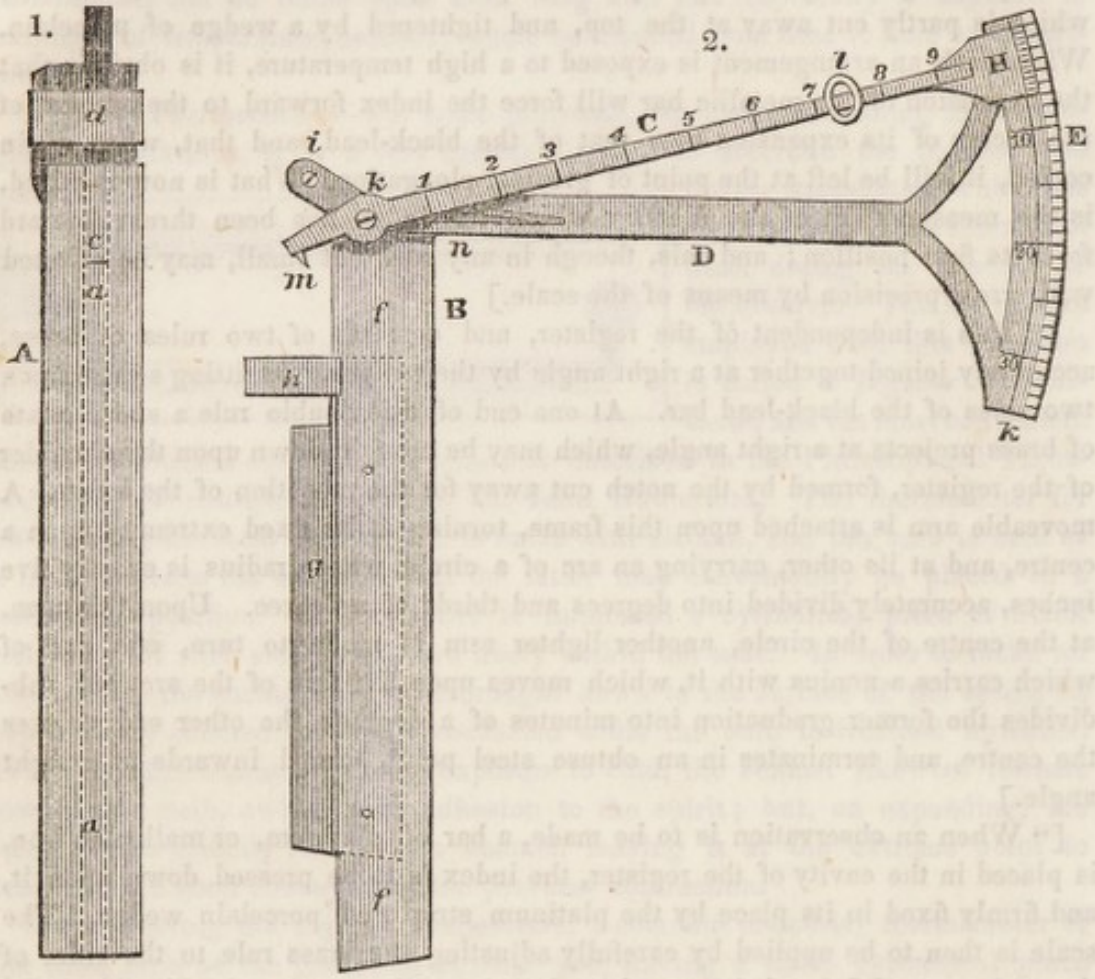
[" When an observation is to be made, a bar of platinum, or malleable iron, is placed in the cavity of the register, the index is to be pressed down upon it, and firmly fixed in its place by the platinum strap and porcelain wedge. The scale is then to be applied by carefully adjusting the brass rule to the sides of the register, and fixing it by pressing the cross piece upon the shoulder, and placing the moveable arm, so that the steel point of the radius may drop into a small cavity made for its reception, and coinciding with the axis of the metallic bar. The minute of the degree must then be noted, which the nonius indicates upon the arc. A similar observation must be made after the register has been exposed to the increased temperature which it is designed to measure, and again cooled, and it will be found that the nonius has been moved forward a certain number of degrees or minutes. The scale of this pyrometer is readily connected with that of the thermometer by immersing the register in boiling mercury, whose temperature is as constant as that of boiling water, and has been accurately determined by the thermometer. The amount of expansion for a known number of degrees is thus determined, and the value of all other expansions may be considered as proportional.]

[" The melting point of cast iron has been thus ascertained to be 2786°, and the highest temperature of a good wind furnace about 3300°; points which were estimated by Mr. Wedgwood at 20577° and 32277° respectively.]

[" In the accompanying figures, 1, represents the register; A is the bar of black-lead; $a\ a'$ the cavity for the reception of the metal bar; $c\ c'$ is the index, or cylindrical piece of porcelain; d the platinum band, with its wedge, e.

2, is the scale by which the expansion is measured; $f\ f'$ is the greater rule

upon which the smaller, *g*, is fixed square. The projecting arm, *h*, is also fitted square to the ledge, under the platinum band, *d*. D is the arm which carries the graduated arc of the circle fixed to the rule, *f f'*, and moveable upon the centre,



i. C is the lighter bar, fixed to the first, and moving upon the centre, *k*. H is the nonius at one of its extremities, and *m* the steel point at the other."] (Daniell's Introd. to Chem. Phil.)

The pyrometer of Wedgewood acts on a different principle, being founded on the property which clay, a compound of alumnous earth and water, possesses of gradually losing its water when exposed to an increasing temperature, and of contracting as the water is dissipated. This instrument, however, is no longer employed by scientific men, because its indications cannot be relied on. Every observation requires a separate piece of clay, and the observer is never sure that the contraction of the second piece, from the same heat, will be exactly similar to that of the first; especially as it is difficult to procure specimens of the earth, the composition of which is in every respect the same.

The subjoined table includes some of the most interesting points in the scale of temperature which have been determined. (Bridges' Graham.)

—148°	Fahr.	Greatest artificial cold. Thilorier.*
—135	"	Solid compound of alcohol and carbonic acid melts.
—91	"	Greatest artificial cold measured by Walker.

* [—146 Mitchell, at which temperature alcohol of .789, "assumed the appearance of melted wax—and sulphuric ether is not in the slightest degree altered." R. B.]

—58°	Fahr.	Temperature of planetary space. Fourier.
—60	"	Greatest natural cold observed by Ross.
—55	"	Greatest natural cold observed by Parry.
—47	"	Sulphuric ether congeals.
—39	"	Melting point of solid mercury.
—7	"	A mixture of equal parts of alcohol and water freezes.
+7	"	A mixture of one part of alcohol and three parts of water freezes.
+20	"	Strong wine freezes.
+32	"	Ice melts.
+50	"	Medium temperature of the surface of the globe.
+52	"	Mean temperature of England.
+98	"	Heat of the human blood.
+150	"	Wood-spirit boils.
+173	"	Alcohol boils.
+212	"	Water boils.
+442	"	Tin melts.
+612	"	Lead melts.
+662	"	Mercury boils.
+980	"	Red heat. Daniell.
+1141	"	Heat of a common fire. Do.
+1869	"	Brass melts. Do.
+1873	"	Silver melts. Do.
+2786	"	Cast iron melts. Do.

Though the thermometer is one of the most valuable instruments of philosophical research, it must be confessed that the sum of information which it conveys is very small. It does indeed point out a difference in the temperature of two or more substances with great nicety; but it does not indicate how much heat any body contains. The thermometer gives the same kind of information which may be discovered, though less accurately, by the feelings; it recognizes in bodies that state alone which affects the senses with an impression of heat or cold,—the condition expressed by the word *temperature*. All we learn by this instrument is, whether the temperature of one body is greater or less than that of another; and if there is a difference, it is expressed numerically, namely, by the degrees of the thermometer. But it must be remembered that these degrees are parts of an arbitrary scale, selected for convenience, without any reference whatever to the actual quantity of heat present in bodies.

SPECIFIC HEAT.

A little reflection will evince the propriety of these remarks. If two glasses of unequal size be filled with water just taken from the same spring, the thermometer will stand in both at the same height, though their *quantities* of heat are certainly unequal. This observation naturally suggests the inquiry, whether different kinds of substances, whose temperatures as estimated by the thermometer are the same, contain equal quantities of heat,—if, for example, a pound of iron contains as much heat as a pound of water or mercury. The foregoing remark shows that equality in temperature is not necessarily connected with equality in quantity of heat; and the inference has been amply confirmed by experiment. If equal quantities of water are mixed together, one portion being at 100° and the other at 50°, the temperature of the mixture will be the arith-

metical mean or 75°; that is, the 25 degrees lost by the warm water will exactly suffice to heat the cold water by the same number of degrees. It is hence inferred, that equal weights or measures of water of the same temperature contain equal quantities of heat; and the same is found to be true of other bodies. But if equal weights or equal bulks of *different* substances are employed, the result will be different. Thus, if a pint of mercury at 100° be mixed with a a pint of water at 40°, the mixture will have a temperature of 60°, so that the 40 degrees lost by the former, heated the latter by 20 degrees only; and when, reversing the experiment, the water is at 100° and the mercury at 40°, the mixture will be at 80°, the 20 degrees lost by the former causing a rise of 40 in the latter. The fact is still more strikingly displayed by substituting equal weights for measures.

[For instance, on mixing a pound of mercury at 162°, with a pound of water at 100, the temperature of the mixture will be 102°. In this case

The mercury by losing	60°
raises the water	2°

Again if the water be at 162° and the mercury at 100°, the temperature of the mixture will be 160°.

Here the water by losing	2°
raises the mercury	60°

So likewise if water at 100° be mixed with an equal weight of spermaceti oil at 40°, the mixture will be found at 80°. In this case

The water by losing	20°
raises the oil	40°

Again, if the oil be 100° and the water at 40°, the temperature of the mixture will be only 60°.

Here the oil by losing	40°
raises the water	20°]

It appears from these facts, that the same quantity of heat imparts twice as high a temperature to mercury as to an equal volume of water; that a similar proportion is observed with respect to equal weights of spermaceti oil and water; and that the heat which gives 2 degrees to water will raise an equal weight of mercury by 60 degrees, being the ratio of 1 to 30. Hence, if equal quantities of heat be added to equal weights of water, spermaceti oil, and mercury, their temperatures in relation to each other will be expressed by the numbers 1, 2, and 30; or, what amounts to the same, in order to increase the temperature of equal weights of those substances to the same extent, the water will require 30 times more heat than the mercury, and twice as much as the oil. The peculiarity exemplified by these substances, and which it would be easy to illustrate by other examples, was first noticed by Black. It is a law admitted to be universal, and may be thus expressed: that *equal* quantities of different bodies require *unequal* quantities of heat to heat them equally. This difference in bodies was expressed by Black by the term *capacity* for heat, but the term *specific heat* is now generally preferred.

The singular fact of substances of equal temperature containing unequal quantities of heat naturally excites speculation about its cause, and various attempts

have been made to account for it. The explanation deduced from the views of Black is the following. He conceived that heat exists in bodies in two opposite states: in one it is supposed to be in chemical combination, exhibiting none of its ordinary characters, and remaining as it were concealed, without evincing any signs of its presence; in the other, it is free and uncombined, passing readily from one substance to another, affecting the senses in its passage, determining the height of the thermometer, and, in a word, giving rise to all the phenomena which are attributed to this active principle.

Though it would be easy to start objections to this ingenious conjecture, it has the merit of explaining phenomena more satisfactorily than any view that has been proposed in its place. It is entirely consistent with analogy. But in admitting the plausibility of this explanation, it is proper to remember that it is at present entirely hypothetical; and that the language suggested by an hypothesis should not be unnecessarily associated with the phenomena to which it owes its origin. Accordingly, the word *sensible* is better than *free* heat, and *insensible* preferable to *combined* or *latent* heat; for by such terms the fact is equally well expressed, and philosophical propriety strictly preserved.

It is of importance to know the specific heat of bodies. The most convenient method of discovering it, is by mixing different substances together in the way just described, and observing the relative quantities of heat requisite for heating them by the same number of degrees.

This method was first suggested by Black, and was afterwards practised to a great extent by Crawford and Irvine.* But the same knowledge may be obtained by reversing the process,—by noting the relative quantities of heat which bodies give out in cooling; for if water requires 30 times more heat than mercury to raise its temperature by one or more degrees, it must also lose 30 times as much in cooling. The calorimeter of Lavoisier and Laplace is founded on this principle. In this instrument the heat given out by a hot body in cooling is measured by the quantity of ice liquefied by it. But although the principle is unexceptionable, there are difficulties in the application of it which render the calorimeter an incorrect instrument. It is, therefore, unnecessary here to describe it in detail.

[In the experiments of Dulong and Petit, which were conducted with great exactness, the different substances were inclosed in a polished silver vessel, in the centre of which was the bulb of a thermometer to indicate the progress of cooling. The silver vessel was placed in a large reservoir, exhausted of its air. The time required by equal weights of the different substances to cool, through the same number of degrees in circumstances exactly similar being proportioned to the quantity of heat which they gave out, indicated the comparative specific heats.]

[In applying the method of mixtures it is not necessary that both the bodies should be liquid. Thus, if a pound of pure copper at 300° be immersed in a pound of water at 50°, it will yield its excess of heat to the water, and in time both will arrive at a common temperature, 72°. The 228° lost by the copper having raised the water 22°, the specific heat of the former will be to that of the latter as 22 to 228; that is, assuming the specific heat of water as 1·000, that of copper will be $\frac{22}{228}=0{\cdot}096$. By a skilful use of this method Regnault has lately ascertained the specific heats of a large number of bodies, elementary

* Crawford on Animal Heat, and Irvine's Chemical Essays.

and compound. The following table includes some of the more important results, obtained by him and other experimenters :]

SPECIFIC HEATS.

[Water	=1·000	Iron	=0·114
Ether	=0·520	Copper	=0·095
Alcohol	=0·660	Lead	=0·031
Sulphuric Acid	=0·333	Gold	=0·032
Nitric Acid	=0·442	Antimony	=0·051
Sulphur	=0·202	Tin	=0·056
Carbon	=0·241	Iodine	=0·054
Mercury	=0·033	Phosphorus	=0·188
Arsenic	=0·081	Glass	=0·177
Platinum	=0·032	Calomel	=0·041
Silver	=0·057	Common Salt	=0·225
Zinc	=0·095	Nitrate of Soda	=0·240
Tellurium	=0·051	Lime	=0·205
Nickel	=0·109	Magnesia	=0·276]
Cobalt	=0·107		

The determination of the specific heat of gaseous substances is a problem of importance, and has occupied the attention of several experimenters of great science and practical skill; but the inquiry is beset with so many difficulties that, in spite of the talent which has been devoted to it, our best results can be viewed as approximations only, requiring to be corrected by future research. Crawford first investigated this subject, but his results are admitted to have been erroneous, and need not here be cited. Lavoisier and Laplace, by means of the calorimeter, obtained more accurate results; but those most to be depended on were obtained by Delaroche and Bérard by means of a modification of the calorimeter, in which they observed, not how much ice was melted, but how far water was heated by the hot body during its cooling. Their experiments were made with such skill as to inspire great confidence. They are contained in the following table; the specific heat of the gases being referred to air as unity in the two first columns, and to water in the third.

Names of Substances.	Under equal Volumes and constant Pressure.	Under equal Weights.	
Atmospheric air	1·0000	1·0000	0·2669
Hydrogen gas	0·9033	12·3400	3·2936
Oxygen gas	0·9765	0·8848	0·2361
Nitrogen gas	1·0000	1·0318	0·2754
Nitrous oxide gas	1·3503	0·8878	0·2369
Olefiant gas	1·5530	1·5763	0·4207
Carbonic oxide gas	1·0340	1·0805	0·2884
Carbonic Acid gas	1·2583	0·8280	0·2210
Water			1·0000
Aqueous vapour			0·8470

Although objections have been started to these experiments, and other methods of ascertaining the specific heats of gases proposed by Haycraft, Delarive and Marcet, and others; yet on the whole we may conclude that, although the spe-

cific heats of the gases are not accurately known, the numbers of Delaroche and Bérard are probably the best approximations hitherto published.

[Dulong had recourse to a different and highly ingenious method. This consisted in ascertaining the velocity of sound in each gas, as measured by the note the same organ pipe gave in each. By peculiar mathematical relations connecting the specific heat with the vibratory motion of gases he calculated the former.]

The circumstances which merit particular notice, concerning the specific heats of bodies, may be arranged under the eight following heads:—

1. Every substance has a specific heat peculiar to itself; whence it follows, that a change of composition will be attended by a change of specific heat.

2. The specific heat of a body varies with its form. A solid has a smaller specific heat than the same substance when in the state of a liquid; the specific heat of water, for instance, being 9 in the solid state, and 10 in the liquid. Whether the same weight of a body has a greater specific heat in the solid or liquid form than in that of vapour, is a circumstance not yet decided.

[The specific heat of bodies in the state of vapour has only been determined in a few instances. That of aqueous vapour is 0·847, water being 1·000. Thus the specific heats of water, in its three states of solid, liquid and vapour, are ·900, 1·000, 0·847.]

3. When a given weight of any gas is made to vary in density and volume while its elasticity is unchanged, as when air confined in a tube over mercury is heated and suffered to expand without variation of pressure, the specific heat is believed to remain constant.

4. Of the specific heat of equal volumes of the same gas at a varying density and elasticity, as when air is forced into a bottle with different degrees of force, nothing certain has been established.

[By an ingenious contrivance Dalton ascertained that about 50° of heat are evolved when air is compressed to one half of its original bulk, and that on the other hand 50° are absorbed by a corresponding rarefaction.] (Manchester Mem., vol. v.)

5. The specific heats of equal weights of the same gas vary as the density and elasticity vary. Thus, when 100 measures of air expand by diminished pressure to 200 measures, its specific heat is increased; and when the same quantity of air is compressed into the space of 50 measures, its specific heat is diminished. The exact rate of increase is unknown; but, according to Delaroche and Bérard, the ratio is less rapid than the diminution in density; that is, the specific heat of any gas being 1, it is not two, but between one and two, when its volume is doubled.

6. The specific heats of solids and liquids were formerly thought, especially by Crawford and Irvine, to be constant at all temperatures, so long as they suffer no change of form or composition. Dalton, however, (Chemical Philosophy, part i., p. 50,) endeavours to show that the specific heats of such bodies are greater in high than at low temperatures; and Petit and Dulong, in the essay already quoted, have proved it experimentally with respect to several of them.

It is difficult to determine whether the increased specific heat observed in solids and liquids at high temperatures is owing to the accumulation of heat within them, or to their dilatation. It is ascribed in general to the latter, and I believe correctly; because the expansion and contraction of gases by change of

pressure, without the aid of heat, is attended with corresponding changes of specific heat.

7. Change of specific heat always occasions a change of temperature. Increase in the former is attended by diminution of the latter; and decrease in the former, by increase of the latter. The explanation of these facts is obvious. In the first case, a quantity of heat becomes insensible, which was previously in a sensible state; in the second, heat is evolved, which was previously latent.

8. An important relation between the specific heats of some elementary substances and their equivalents was discovered by Dulong and Petit, namely, that the product of the specific heat of each element by the weight of its atom is a constant quantity. This relation, if general, would be of great interest, as leading directly to the inference that the atoms of elementary substances are associated with equal quantities of heat, and enabling chemists to calculate either the specific heats of elements from their equivalents, or conversely their equivalents from their specific heats. (An. de Ch. et Ph. x. 403.) The relation above alluded to was exemplified by Dulong and Petit by a table similar to the subjoined.

	Specific Heat.		Relative Weights of Atoms.		Product of the Sp. Heat of each element by the weight of its atom.
Lead . . .	0·0293	×	103· 6	=	3·0353
Tin . . .	0·0514	×	57· 9	=	2·9760
Zinc . . .	0·0927	×	32· 3	=	2·9942
Tellurium . .	0·0912	×	32· 3	=	2·9457
Copper . . .	0·0949	×	31· 6	=	2·9988
Nickel . . .	0·1035	×	29· 5	=	3·0532
Iron . . .	0·1100	×	28	=	3·0800
Sulphur . . .	0·1880	×	16· 1	=	3·0268
Platinum . . .	0·0355	×	98· 8	=	3·3098
Bismuth . . .	0·8288	×	71	=	2·0448
Cobalt . . .	0·1498	×	29· 5	=	4·4191
Arsenic . . .	0·081	×	37· 7	=	3·0537
Carbon . . .	0·25	×	6·12	=	1·5300
Iodine . . .	0·089	×	126· 3	=	11·2407
Phosphorus . .	0·385	×	15· 7	=	6·0445
Mercury . . .	0·0330	×	202	=	6·6660
Silver . . .	0·0557	×	108	=	6·0156
Gold . . .	0·0298	×	199· 2	=	5·9361

It will be observed, on inspecting the last column of the table, that the product of the specific heat into the equivalent is very nearly 3 for the first nine substances. Platinum deviates visibly from the law; and bismuth, cobalt, and iodine, strikingly. The four last elements would nearly coincide with the law, were their respective equivalents estimated at half the numbers given in the tables, as would carbon were its equivalent doubled. These coincidences are too close and numerous to arise from chance, and justify a belief in the law having a real foundation dependent on the connection between heat and the elementary particles of matter. The researches of Avogadro and Neumann give additional weight to this opinion by tracing the same law in many compound bodies, those compounds alone being compared together whose atomic

constitution is similar. (An. de Ch. et Ph. LV. 80, and LVII. 113; and Pog. An. XXIII. 1.)

ON LIQUEFACTION.

All bodies are solid, liquid, or gaseous; and the form they assume depends on the relative intensity of cohesion and repulsion. Should the repulsive force be comparatively feeble, the particles will adhere so firmly together, that they cannot move freely upon one another, thus constituting a solid. If cohesion is so far counteracted by repulsion, that the particles move on each other freely, a liquid is formed.* And should the cohesive attraction be entirely overcome, so that the particles not only move freely on each other, but would, unless restrained by external pressure, separate from one another to an almost indefinite extent, an aëriform substance will be produced.

Now the property of repulsion is manifestly owing to heat; and as it is easy within certain limits to increase or diminish the quantity of this principle in any substance, it follows that the form of bodies may be made to vary at pleasure: that is, by heat sufficiently intense every solid may be converted into a fluid, and every fluid into vapour. This inference is so far justified by experience, that it may safely be considered as a law. The converse ought also to be true; and, accordingly, several of the gases have already been condensed into liquids by means of pressure, and liquids have been solidified by cold. The temperature at which liquefaction takes place is called the melting point, or point of fusion; and that at which liquids solidify, their point of congelation. Both these points are different for different substances, but uniformly the same, under similar circumstances, in the same body.

The most important circumstance relative to liquefaction is Black's discovery that a large quantity of heat disappears, or becomes insensible to the thermometer, during the process. If a pound of water at 32° be mixed with a pound of water at 172°, the temperature of the mixture will be intermediate between them, or 102°. But if a pound of water at 172° be added to a pound of ice at 32°, the ice will quickly dissolve, and on placing a thermometer in the mixture, it will be found to stand, not at 102°, but at 32°. In this experiment, the pound of hot water, which was originally at 172°, actually loses 140 degrees of heat, all of which enters into the ice, and causes its liquefaction, but without affecting its temperature; whence it follows that a quantity of heat becomes insensible during the melting of ice, sufficient to raise the temperature of an equal weight of water by 140 degrees. This explains the well-known fact, on which the graduation of the thermometer depends,—that the temperature of melting ice or snow never exceeds 32°. All the heat which is added becomes insensible, till the liquefaction is complete.

[Recent experiments, made with great care by both Provostayé and Regnault, have proved that the number of degrees of heat which becomes insensible during the liquefaction of ice is greater than as above stated, being according to the

* It is an obvious objection to this view that the excess of either force above its antagonist would cause a motion of the particles. Where the cohesion is the superior force the particles would be drawn nearer, where repulsion is in excess they would be separated to greater distances. In the quiescent state of the particles the two forces must evidently be *in equilibrium*, and this whether the mass be a solid or a liquid. (R.)

independent researches of both observers 143.05. (Ann. de Chem. et de Phys. 1843.)]

The loss of sensible heat which attends liquefaction seems essentially necessary to the change, and for that reason is frequently called the *heat of fluidity*. The actual quantity of heat required for this purpose varies with the substance, as is proved by the following results obtained by Irvine. The degrees indicate the extent to which an equal weight of each material may be heated by the heat of fluidity which is proper to it.

	Heat of Fluidity.		Heat of Fluidity.
Sulphur . . .	143°68F.	Zinc	493°
Spermaceti . .	145°	Tin	500°
Lead	162°	Bismuth	550°
Bees-wax . . .	175°		

As so much heat disappears during liquefaction, it follows that heat must be evolved when a liquid passes into a solid. This may easily be proved. The temperature of water in the act of freezing remains at 32°, though exposed to an atmosphere in which the thermometer is at zero. That the water under such circumstances may preserve its temperature, heat must be supplied as fast as it is abstracted; and it is obvious that the only source of supply is the heat of fluidity. Further, if pure recently boiled water be cooled very slowly, and kept very tranquil, its temperature may be lowered to 21° without any ice being formed; but the least motion causes it to congeal suddenly, and in doing so its temperature rises to 32°. (Blagden in Phil. Trans. 1788.)

The explanation which Black gave of these phenomena constitutes what is called his *doctrine* of *latent heat*, which was partially explained on a former occasion (page 33). He conceived that heat in causing fluidity loses its property of acting on the thermometer, in consequence of combining chemically with the solid substance, and that liquefaction results, because the compound so formed does not possess that degree of cohesive attraction on which solidity depends. When a liquid is cooled to a certain point, it parts with its heat of fluidity, which is set free or becomes sensible, and the cohesion natural to the solid is restored. The same mode of reasoning was applied by Black to the conversion of liquids into vapours, a change during which a large quantity of heat disappears.

A different explanation of the phenomena was proposed by Irvine. Observing that a solid has a smaller specific heat than the same substance while liquid, he argued that this circumstance alone accounts for heat becoming insensible during liquefaction. For since the specific heat of ice and water, or in other words, the quantity of heat required to raise their temperature by the same number of degrees, was found to be as 9 to 10, Irvine inferred that ice must contain one-tenth less heat than water of the same temperature, and that as this difference must be supplied to the ice when it is converted into water, the change must necessarily be accompanied with the disappearance of heat. Irvine applied the same argument to the liquefaction of all solids, and likewise to account for the heat which is rendered insensible during the formation of vapour.

Two objections may properly be urged against the opinion of Irvine. In the first place, no adequate reason is assigned for the liquefaction. It accounts for the disappearance of heat which accompanies liquefaction, but does not explain

why the body becomes liquid; whereas the hypothesis of Black affords an explanation both of the change itself, and of the phenomena that attend it. But the second objection is still more conclusive. Irvine argued on the belief that a liquid has in every case a greater specific heat than when solid; and though this point has not been demonstrated in a manner entirely decisive, yet from the experiments hitherto made, it appears that liquids in general have greater specific heats than solids, and that therefore Irvine's assumption is probably correct in regard to them. In like manner he believed vapours to have greater specific heats than the liquids that yield them; but from the fact of most gases having smaller specific heats than liquids, it is probable that the specific heats of elastic fluids in general are inferior to those of the liquids from which they are derived. The disappearance of heat during vaporization is not explicable on the views of Irvine; it is necessary to employ the theory of Black to account for that change, and therefore the same doctrine should be applied to the analogous phenomenon of liquefaction.

The loss of sensible heat in liquefaction is the basis of many artificial processes for producing cold, all of which are founded on the principle of liquefying solid substances without supplying heat. The heat of fluidity being then derived from that which had previously existed within the solid itself in a sensible state, the temperature necessarily falls. The degree of cold thus produced depends upon the quantity of heat which disappears; and this again is dependent on the quantity of solid matter liquefied, and on the rapidity of liquefaction.

[This depression of temperature is exhibited not only when the solid becomes liquid, apart from other bodies as in the case of melting ice, but likewise in many instances when it is liquefied by being dissolved in water, or some other menstruum. Thus crystallized glauber salts, sal ammoniac and nitre, while dissolving in water, cause a considerable reduction of temperature. It is a curious fact that a further addition of water to certain saline solutions renders them colder, thus seeming to indicate an increased degree of liquidity. Consistently with this Person has recently found that while by dissolving 1 part of common salt in 4 parts of water, 10 units of heat become insensible: by dissolving the same quantity of salt in 50 parts of water, 22 such units disappear. Comptes Rendus, 1844.]

The most common method of producing cold is by mixing together equal parts of snow and salt. The salt causes the snow to melt by reason of its affinity for water, and the water dissolves the salt; so that both of them become liquid. The cold thus generated is 32 degrees below the temperature of freezing water; that is, a thermometer placed in the mixture would stand at zero. This is the way originally proposed by Fahrenheit for determining the commencement of his scale.

Any other substances which have a strong affinity for water may be substituted for the salt; and those have the greatest effect in producing cold whose affinity for that liquid is greatest, and which consequently produce the most rapid liquefaction. Crystallized chloride of calcium, proposed by Löwitz, is by far the most convenient in practice. It may be made by dissolving marble in hydrochloric acid, and concentrating the solution by evaporation, till, upon letting a drop of it fall upon a cold saucer, it becomes a solid mass. It should then be withdrawn from the fire, and when cold be speedily reduced to a fine powder. From its extreme deliquescence it must be preserved in well-stopped vessels.

The following table by Mr. Walker, contains the best proportions for producing intense cold. (Phil. Trans. 1801.)

FRIGORIFIC MIXTURES WITH SNOW.*

MIXTURES. Parts by Weight.	Thermometer sinks.	Degree of cold produced.
Sea-salt . . . 1 Snow 2	From any Temperature to −5°	
Sea-salt . . . 2 Hydrochlorate of Ammonia 1 Snow 5	From any Temperature to −12°	
Sea-salt . . . 10 Hydrochlorate of Ammonia 5 Nitrate of Potassa . 5 Snow 24	From any Temperature to −18°	
Sea-salt . . . 5 Nitrate of Ammonia . 5 Snow 12	From any Temperature to −25°	
Diluted Sulphuric Acid† 2 Snow 3	from +32° to −23°	55 degrees.
Concentrated Hydrochloric Acid . . . 5 Snow 8	from +32° to −27°	59
Concentrated Nitrous Acid 4 Snow 7	from +32° to −30°	62
Chloride of Calcium . 5 Snow 4	from +32° to −40°	72
Crystallized Chloride of Calcium . . . 3 Snow 2	from +32° to −50°	82
Fused Potassa . . 4 Snow 3	from +32° to −51°	83

Freezing mixtures are also made by the rapid solution of salts, without the use of snow or ice; the following table, by Walker, includes the most important of them. The salts must be finely powdered and dry. (Phil. Trans. 1795.)

MIXTURES. Parts by Weight.	Temperature falls.	Degree of Cold produced.
Hydrochlorate of Ammonia 5 Nitrate of Potassa . 5 Water 16	from +50° to +10°	40 degrees.
Hydrochlorate of Ammonia 5 Nitrate of Potassa . 5 Sulphate of Soda . . 8 Water 16	from +50° to +4°	46
Nitrate of Ammonia . 1 Water 1	from +50° to +4°	46
Nitrate of Ammonia . 1 Carbonate of Soda . 1 Water 1	from +50° to −7°	57
Sulphate of Soda . . 3 Diluted Nitrous Acid‡ . 2	from +50° to −3°	53
Sulphate of Soda . . 6 Hydrochlorate of Ammonia 4 Nitrate of Potassa . 2 Diluted Nitrous Acid . 4	from +50° to −10°	60

* The snow should be freshly fallen, dry, and uncompressed. If snow cannot be had, finely pounded ice may be substituted for it.

† Made of strong acid, diluted with half its weight of snow or distilled water.

‡ Composed of fuming nitrous acid 2 parts in weight, and one of water; the mixture being allowed to cool before being used.

MIXTURES. Parts by Weight.	Thermometer falls.	Degree of cold produced.
Sulphate of Soda . . 6 Nitrate of Ammonia . 5 Diluted Nitrous Acid . 4	from +50° to −14°	64
Phosphate of Soda . 9 Diluted Nitrous Acid . 4	from +50° to −12°	62
Phosphate of Soda . 9 Nitrate of Ammonia . 6 Diluted Nitrous Acid . 4	from +50° to −21°	71
Sulphate of Soda . . 8 Hydrochloric Acid . 5	from +50° to 0°	50
Sulphate of Soda . . 5 Diluted Sulphuric Acid* 4	from +50° to +3°	47

These artificial processes for generating cold are much more effectual when the materials are previously cooled by immersion in other frigorific mixtures. One would at first suppose that an unlimited degree of cold might be thus produced; but it is found that when the difference between the mixture and the air becomes very great, the communication of heat from one to the other becomes so rapid, as to put a limit to the reduction. The greatest cold produced by Walker did not exceed 100 degrees below the zero of Fahrenheit.

Though we shall probably never succeed in depriving any substance of all its heat, bodies doubtless contain a certain definite quantity of this principle, and various attempts have been made to calculate its amount.

To be satisfied that such calculations cannot be trusted, it is sufficient to know that the estimates made by different chemists respecting the absolute quantity of heat in water vary from 900 to nearly 8000.†

VAPORIZATION.

Aëriform substances are commonly divided into vapours and gases. The former are characterised by their ready conversion into liquids or solids, either by a moderate increase of pressure, the temperature at which they were formed remaining the same, or by a moderate diminution of that temperature, without change of pressure. Gases, on the contrary, retain their elastic state more obstinately: they are always gaseous at common temperatures; and, with one or two exceptions, cannot be made to change their form, unless by being subjected to much greater pressure than they are naturally exposed to. Several of them, indeed, have hitherto resisted every effort to compress them into liquids. The only difference between gases and vapours is in the relative forces with which they resist condensation.

Heat is the cause of vaporization as well as of liquefaction. A sufficiently intense heat would doubtless convert every liquid and solid into vapour. Some bodies, however, resist the strongest heat of our furnaces without vaporizing. These are said to be *fixed* in the fire; those which, under the same circumstances, are converted into vapour, are called *volatile*.

The disposition of various substances to yield vapour is very different; and the difference depends doubtless on the relative power of cohesion with which they are endowed. Fluids, in general, are more easily vaporized than solids, as

* Composed of equal weights of strong acid and water, being allowed to cool before use.

† Dalton's New System of Chemical Philosophy.

would be expected from the weaker cohesion of the former. Some solids, such as arsenic and sal-ammoniac, pass at once into vapour without being liquefied; but most of them become liquid before assuming the elastic condition.

Vapours occupy more space than the substances from which they were produced. Gay Lussac found that water, in passing from its point of greatest density into vapour, expands to 1696 times its volume, alcohol to 659 times, and ether to 443 times, each vapour being at 212° and under a pressure of 29·92 inches of mercury. This shows that vapours differ in density. Watery vapour is lighter than air at the same temperature and pressure in the ratio of 1000 to 1604; or the sp. gr. of air being 1000, that of watery vapour is 625. The vapour of alcohol, on the contrary, is half as heavy again as air; and that of ether is more than twice and a half as heavy.

The dilatation of vapours by heat was found by Gay Lussac to follow the same law as gases; that is, for every degree of Fahrenheit, they increase by $\frac{1}{480}$th of the volume they occupied at 32°.* But this law only holds of vapours when separated from the liquids that yield them. If liquid be present heat not only expands the vapour but increases its volume by the addition of a new quantity of vapour. In like manner, the contraction of a vapour by cold will deviate from the above law, as soon as the cold condenses any part of it into liquid.

Vapours vary in volume under varying pressure according to the same law as gases, provided always that the gaseous state is preserved. This law, which was discovered by Boyle and Mariotte, and is more fully explained in the section on atmospheric air, merely expresses the fact that the volume of gaseous substances at a constant temperature is inversely as the pressure to which they are subject.

Vaporization is conveniently studied under two heads,—*Ebullition* and *Evaporation*. In the first, the production of vapour is so rapid that its escape gives rise to a visible commotion in the liquid; in the second, it passes off quietly and insensibly.

EBULLITION.

The temperature at which vapour rises with sufficient freedom for causing the phenomena of ebullition, is called the *boiling point*. The heat requisite for this effect varies with the nature of the fluid.

[The following table exhibits the boiling point of a number of liquids:

	Boiling point.		Boiling Point.
Hydrochloric Ether	52°	Crys. Chloride of Calcium	302°
Sulphuric Ether	96°	Oil Turpentine	314°
Bi Sulphuret of Carbon	116°	Phosphorus	554°
Ammonia (sp. gr. 0.945)	140°	Sulphuric Acid (sp. gr. 1.843)	620°
Alcohol (sp. gr. 0.798)	172°	Whale Oil	630°
Water	212°	Mercury	662°]
Nitric Acid (sp. gr. 1.42)	248°		

The boiling point of the same liquid is constant, so long as the necessary conditions are preserved; but it is liable to be affected by several circumstances. The nature of the vessel has some influence upon the boiling point. Thus Gay Lussac observed that pure water boils precisely at 212° in a metallic vessel, and

* See remarks on this subject, page 24.

at 214° in one of glass, owing apparently to its adhering to glass more powerfully than to a metal. It is likewise affected by the presence of foreign particles: when a few iron filings are thrown into water boiling in a glass vessel, its temperature quickly falls from 214° to 212°, and remains stationary at the latter point.

[More recent observations, by Marcet, have shown that when the surface of the vessel, whether of glass or metal, is coated with sulphur, shellac, or other substances of the same kind, boiling takes place at 212°. In this case the temperature of the water is the same as that of the steam. Without such a coating the boiling point varies

In glass vessels	from 212°.54 to 215°. 6
In metallic vessels	from 212°.27 to 212°.36 (Ann. de Chem.)

In this case the temperature of the steam is, of course, less than that of the liquid.

M. Magnus in his late able investigations of the same subject, maintains that the various degrees of adhesion of the liquid to the surface of the vessel causes these differences. When this adhesion is equal to or exceeds the cohesion of the particles of the liquid, the particles more remote from the surface being held together only by their cohesion will be converted into steam. The temperature at which this takes place is the true boiling point; but when there is no adhesion of the liquid to the surface, or when this force is less than the cohesion of the liquid, then the boiling will take place in contact with the surface, because there the restraining force is less, and the boiling temperature will be lower than if the adhesion were equal to or greater than the cohesion. Hence glass, well washed with sulphuric acid so as to promote contact and adhesion, raises the boiling point to 221°. (Ann. de Chem. 1844.)]

But the circumstance which has the greatest influence over the boiling point of liquids is variation of pressure. All bodies upon the earth are constantly exposed to considerable pressure; for the atmosphere itself presses with a force equivalent to a weight of 15 pounds on every square inch of surface. Liquids are exposed to this pressure as well as solids, and their tendency to take the form of vapour is very much counteracted by it. In fact, they cannot enter into ebullition at all, till their particles have acquired such elastic force as enables them to overcome the pressure upon their surfaces: that is, till they press against the atmosphere with the same force as the atmosphere against them. Now the atmospheric pressure is variable, and hence it follows that the boiling point of liquids must also vary.

The pressure of the atmosphere is equal to a weight of 15 pounds on every square inch of surface, when the barometer stands at 30 inches, and then only does water boil at 212°. If the pressure be less, that is, if the barometer fall below 30 inches, then the boiling point of water and every other liquid will be lower than usual; or if the barometer rise above 30 inches, the temperature of ebullition will be proportionally increased. On this account water boils at a lower temperature on the top of a hill than in the valley beneath it; for as the column of air diminishes in length as we ascend, its pressure must likewise suffer a proportional diminution. The ratio between the depression of the boiling point and the diminution of the atmospheric pressure is so exact, that it has been proposed as a method for determining the heights of mountains. Accord-

ing to Wollaston an elevation of 530 feet makes a diminution of one degree.* (Phil. Trans. for 1817.)

The influence of the atmosphere over the point of ebullition is best shown by removing its pressure altogether. Robison found that fluids boil *in vacuo* at a temperature 140° lower than in the open air. (Black's Lectures, i. 151.)

Water cannot be heated under common circumstances beyond 212°, because it then acquires such expansive force as enables it to overcome the atmospheric pressure, and fly off in the form of vapour. But if subjected to sufficient pressure, it may be heated to any extent without boiling. This is best done by heating water while confined in a strong copper vessel, called Papin's Digester. In this apparatus, on the application of heat, a large quantity of vapour collects above the water, and checks ebullition by the pressure which it exerts upon the surface of the liquid. There is no limit to the degree to which water may thus be heated, provided the vessel is strong enough to confine the vapour; but the expansive force of steam under these circumstances is so enormous as to overcome the greatest resistance.

Robison (Brewster's edition of his works, p. 25) found that the tension of steam is equal to two atmospheres at 244°, and to three at 270°. The results of Southern's experiments, given in the same volume, fix upon 250·3° as the temperature of which steam has the force of two atmospheres, on 293·4° for four, and 343·6° for eight atmospheres.

This subject has been examined by a commission appointed by the Parisian Academy of Sciences, and Dulong and Arago took a leading part in the inquiry. The results, which are given in the following table, were obtained by experiment up to a pressure of 25 atmospheres, and at higher pressures by calculation. (Brande's Journal, N. S. viii. 191.)†

Elasticity of the vapour, taking atmospheric press. as unity.	Temperature according to Fahrenheit.	Elasticity of the vapour, taking atmospheric press. as unity.	Temperature according to Fahrenheit.
1	212	4	293·72
1½	233·96	4½	300·28
2	250·52	5	307·5
2½	263·84	5½	314·24
3	275·18	6	320·36
3½	285·08	6½	326·26

* An instrument constructed for accurately noting the boiling temperature of water at different heights, invented by Wollaston, has with some modifications been employed successfully for measuring the height of mountains in Virginia and Pennsylvania. Prof. W. and H. Rogers, and recently Prof. Forbes, of Edinburgh, had made numerous accurate observations with a somewhat similar instrument. By comparison with barometric and trigonometric measurements, it has been found that in Virginia and Pennsylvania one degree of depression of the boiling point corresponds to an elevation of 548·5 feet. The estimate of Prof. Forbes for Edinburgh, is almost precisely the same. Col. Wright found that in the Andes one degree corresponded to about 600 feet.

Prof. Forbes has inferred from his observations that the depressions of the boiling point are accurately proportional to the heights above the earth's surface, a law which gives great simplicity to the calculation of altitudes from these data. (R.)

† For an account of Regnault's elaborate researches on the same subject, see Ann. de Chim., 1844. (R.)

Elasticity of the vapour, taking atmospheric press. as unity.	Temperature according to Fahrenheit.	Elasticity of the vapour, taking atmospheric press. as unity.	Temperature according to Fahrenheit.
7	331·70	19	413·78
7½	336·86	20	418·46
8	341·78	21	422·96
9	350·78	22	427·28
10	358·88	23	431·42
11	366·85	24	435·56
12	374·00	25	439·34
13	380·66	30	457·16
14	386·94	35	472.73
15	392·86	40	486·59
16	398·48	45	491·14
17	403·82	50	510·60
18	408·92		

The elasticity of steam is employed as a moving power in the steam-engine. The construction of this machine depends on two properties of steam, namely, the expansive force communicated to it by heat, and its ready conversion into water by cold.

The formation of vapour is attended, like liquefaction, with loss of sensible heat. This is proved by the well-known fact that the temperature of steam is precisely the same as that of the boiling water from which it rises; so that all the heat which enters into the liquid is solely employed in converting a portion of it into vapour, without affecting the temperature of either, provided the latter is permitted to escape with freedom. The heat, which then becomes latent, to use the language of Black, is again set free when the vapour is condensed into water. The exact quantity of heat rendered insensible by vaporization may therefore be ascertained by condensing the vapour in cold water, and observing the rise of temperature which ensues. From the experiments of Black and Watt, conducted on this principle, steam of 212°, in being condensed into water of 212°, gives out as much heat as would raise the temperature of an equal weight of water by 950 degrees, all of which had previously existed in the vapour without being sensible to a thermometer.

The latent heat of steam and several other vapours has been examined by Dr. Ure, whose results are contained in the following table. (Phil. Trans. for 1818.)

[Equal weights.	Latent heat.
Vapour of water at boiling point, ...	1000°
Alcohol, sp. gr. 825, ...	457°
Ether, boiling point, 112°, ...	312·9
Petroleum, ...	183·8
Oil of Turpentine, ...	183·8
Nitric acid, sp. gr. 1.494, boiling point, 165°	550
Liquid ammonia, sp. gr. 0·978, . .	865·9
Vinegar, sp. gr. 1.007	903]

[When evaporated at temperatures below the boiling point, a liquid renders latent a greater quantity of heat than when it is converted into vapour at that point. By accurate experiments, on the vaporization of water, it has been proved that the latent heat of the vapour when added to the sensible heat, or

temperature at which it is formed, always amounts to a constant quantity. Thus with water evaporating at

32°	the latent heat is	1180,	the sum being	1212
100°	"	1112	"	1212
212°	"	1000	"	1212
300	"	900	"	1212

The same law is believed to hold with liquids in general.]

The disappearance of heat that accompanies vaporization was explained by Black and Irvine, in the way already mentioned under the head of liquefaction; and as the objections to the views of Irvine were then stated, it is unnecessary to mention them on the present occasion.

The variation of volume and elasticity in vapours is attended, as in gases, with a change of sp. heat and a consequent variation of temperature (page 35). Thus when steam, highly heated and compressed in a strong boiler, is permitted to escape by a large aperture, the sudden expansion is attended with a great loss of sensible heat: its temperature instantly sinks so much, that the hand may be held in the current of vapour without inconvenience. The same principle accounts for the fact, first ascertained by Watt, that distillation at a low temperature is not attended with any saving of fuel. For when water boils at a low temperature in a vacuum, the vapour is in a highly expanded state, and contains more insensible heat than steam of greater density.

EVAPORATION.

Evaporation as well as ebullition consists in the formation of vapour, and the only assignable difference between them is, that the one takes place quietly, the other with the appearance of boiling. Evaporation occurs at common temperatures. This fact may be proved by exposing water in a shallow vessel to the air for a few days, when it will gradually diminish, and at last disappear entirely. Most fluids, if not all of them, are susceptible of this gradual dissipation; and it may also be observed in some solids, as for example in camphor. Evaporation is much more rapid in some fluids than in others, and it is always found that those liquids the boiling point of which is lowest evaporate with the greatest rapidity. Thus alcohol, which boils at a lower temperature than water, evaporates also more freely; and ether, whose point of ebullition is yet lower than that of alcohol, evaporates with still greater rapidity.

The chief circumstances that influence the process of evaporation are extent of surface, and the state of the air as to temperature, dryness, stillness, and density.

1. Extent of surface. Evaporation proceeds only from the surface of fluids, and therefore, *cæteris paribus*, must depend upon the extent of surface exposed.

2. Temperature. The effect of heat in promoting evaporation may easily be shown by putting an equal quantity of water into two saucers, one of which is placed in a warm, the other in a cold situation. The former will be quite dry before the latter has suffered appreciable diminution.

3. State of the air as to dryness or moisture. When water is covered by a stratum of dry air, the evaporation is rapid even when its temperature is low. Thus in dry cold days in winter, the evaporation is exceedingly rapid; whereas it goes on very tardily, if the atmosphere contain much vapour, even though the air be very warm.

4. Evaporation is far slower in still air than in a current, and for an obvious reason. The air immediately in contact with the water soon becomes moist, and thus a check is put to evaporation. But if the air be removed from the surface of the water as soon as it has become charged with vapour, and its place supplied with fresh dry air, then the evaporation continues without interruption.

5. Pressure on the surface of liquids has a remarkable influence over evaporation. This is easily proved by placing ether in the vacuum of an air-pump, when vapour rises so abundantly as to produce ebullition.

[It was long ago observed by Saussure, and others, that water evaporates very slowly when placed on red hot metal, but that as the surface is allowed to cool, or reaching a certain temperature, much below redness, the liquid bursts almost explosively into steam. In the former condition it is easy to observe that the liquid is not in contact with the heated surface. But when the temperature falls to a certain point the contact takes place, and at the same moment steam is rapidly formed. Water and other liquids placed in this condition of repulsion, seem to have new and peculiar relations to heat. According to Boutigny's late admirable researches, the liquid, thus brought to what he calls the *spheroidal state*, is endowed with the property of *perfectly reflecting* the heat falling upon its surface from the red hot metal. In proof of this he found that a thermometer plunged in water, in the spheroidal state, became stationary at the temperature 205°·7, although the surrounding metal was at a strong red heat. The vapour escaping from the water, in this state, is of very low tension, but has the temperature of the surrounding vessel, thus differing, strikingly, from the vapour produced by ordinary boiling. The passage from the spheroidal to the common condition, he very plausibly regards as the cause of the fulminating explosions of steam boilers. Among the important results of his observations the following are especially deserving notice.

1. The lowest temperature at which water can pass to the spheroidal state in notable quantity is 287°·6.

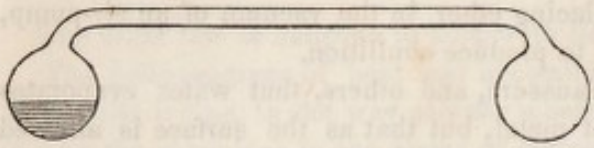
2. Water in this state evaporates more rapidly, as the temperature of the containing vessel is more elevated, but the formation of vapour is greatly slower than in the ordinary condition. At 382° the spheroidal liquid loses by evaporation in a given time (*only one fiftieth* of what would evaporate by boiling.)

3. Whatever be the temperature of the containing vessel, that of the spheroidal liquid is *invariable* and *always below its boiling point*, though in a fixed ratio to that point, being for water 205°·7 F. (Ann. de Chim. 1844).]

As a large quantity of heat passes from a sensible to an insensible state during the formation of vapour, it follows that cold should be generated by evaporation. The fact may readily be proved by letting a few drops of ether evaporate from the hand, when a strong sensation of cold will be excited; or if the bulb of a thermometer, covered with lint, be moistened with ether, the production of cold will be marked by the descent of the mercury. But to appreciate the degree of cold which may be produced by evaporation, it is necessary to render it very rapid and abundant by artificial processes; and the best means of doing so is by removing pressure from the surface of volatile liquids. Water placed under the exhausted receiver of an air-pump evaporates with great rapidity, and so much cold is generated as would freeze the water, did the vapour continue to rise for some time with the same velocity. But the vapour itself soon fills the vacuum, and retards the evaporation by pressing upon the surface of the water. This difficulty may be avoided by putting under the receiver a substance, such

as sulphuric acid, which has the property of absorbing watery vapour, and consequently of removing it as quickly as it is formed. Such is the principle of Leslie's method for freezing water by its own evaporation.*

The action of the cryophorus, an ingenious contrivance of the late Dr. Wollaston, depends on the same principle. It consists of two glass balls, perfectly free from air, and joined together by a tube, as here represented.—One of the balls contains a portion of distilled water, while the other parts of the instrument, which appear empty, are full of aqueous vapour, which checks the evaporation from the water by the pressure it exerts upon its surface. But when the empty ball is plunged into a freezing mixture, all the vapour within it is condensed; evaporation commences from the surface of the water in the other ball, and it is frozen in two or three minutes by the cold thus produced.



Liquids which evaporate more rapidly than water, cause a still greater reduction of temperature. The cold produced by the evaporation of ether in the vacuum of the air-pump is so intense as, under favourable circumstances, to freeze mercury.†

[According to Thilorier, a mixture of solid carbonic acid and ether, by its evaporation depresses the temperature to —148; but the most striking example of the cooling effect of evaporation is that furnished in the recent experiment of Boutigny, who by the rapid evaporation of liquid sulphurous acid in a red hot crucible, actually froze a portion of water in the midst of the heated mass.—Ann. de Chim. 1843.]

Scientific men have differed concerning the cause of evaporation. It was once supposed to be owing to chemical attraction between the air and water, and the idea is at first view plausible, since a certain degree of affinity does to all appearance exist between them. But it is nevertheless impossible to attribute the effect to this cause. For evaporation takes place equally *in vacuo* as in the air; nay, it is an established fact, that the atmosphere positively retards the process, and that one of the best means of accelerating it is by removing the air altogether. The experiments of Dalton prove that heat is the true and only cause of the formation of vapour. He finds that the actual quantity of vapour which can exist in any given space is dependent solely upon the temperature.

Dalton also found that the tension or elasticity of vapour is always the same, however much the pressure may vary, so long as the temperature remains constant, and there is liquid enough present to preserve the state of saturation proper to the temperature. This law holds good, whether the vapour be pure, or mixed with air or any other gas.

The elasticity of watery vapour at temperatures below 212° was carefully examined by Dalton (Manchester Memoirs, vol. v.); and his results, together with those since published by Ure (Phil. Trans. 1818), are presented in a tabular form at the end of the volume. They were obtained by introducing a portion of water into the vacuum of a common barometer, and estimating the tension of its vapour by the extent to which it depressed the column of mercury at different temperatures.

A knowledge of the influence of heat and pressure over the volume of gaseous

* See art. Cold, in the Supplement to the Encyclopædia Britannica.

† See a paper by the late Dr. Marcet, in Nicholson's Journal, vol. xxxiv.

matter is elegantly employed in calculating the sp. gr. of vapour; but before giving the mode of making the calculation, it will be useful to explain what is meant by *specific gravity* or *density*. These terms are generally used to denote the compactness of a substance, or the quantity of ponderable matter contained in a body compared with the space which it occupies. The sp. gr. of a substance is found by dividing its weight by its volume. Thus, if d, w, v, represent the sp. gr. weight and volume of aqueous vapour, and d', w', v', the sp. gr. weight and volume of air, then $d=\frac{w}{v}$, and $d'=\frac{w'}{v'}$. Hence, comparing these sp. gravities, $d : d' :: \frac{w}{v} : \frac{w'}{v'}$; if the volumes are equal, then $d : d' :: w : w'$; and if the weights are equal, $d : d' :: \frac{1}{v} : \frac{1}{v'}$. Consequently, the sp. gravities of substances which have an equal volume are directly as their weights; and when the weights are equal, the sp. gravities are inversely as the volumes. Accordingly, if we weigh an equal volume of any number of substances, temperature and pressure being the same in all, the sp. gr. of each respectively will be represented by its weight. Thus, Gay Lussac ascertained that if a certain volume of air at 212° and 30 Bar. weigh 1000 grains, an equal volume of aqueous vapour, at the same temperature and pressure, will weigh 625 grains; and, therefore, the sp. gr. of steam is 625 compared to that of air as 1000. Atmospheric air is universally taken as a term of comparison for the sp. gr. of gaseous substances, and pure water for that of liquids and solids.

It admits of inquiry whether liquids of weak volatility, such as mercury and oil of vitriol, give off any vapour at common temperatures. An opinion has prevailed, that evaporation not only takes place from the surface of these and similar liquids at all times, but that vapour of exceedingly weak tension is emitted at common temperatures from all substances however fixed in the fire, even from the earths and metals, when they are either in a vacuum, or surrounded by gaseous matter. It has accordingly been supposed, that the atmosphere contains diffused through it minute quantities of the vapours of all the bodies with which it is in contact; and this idea has been made the basis of a theory of the origin of meteorites. But this doctrine has been successfully combated by Faraday, in his essay On the Existence of a Limit to Vaporization, (Phil. Trans. 1826). He has there shown that in many substances the forces of gravity and cohesion are sufficient to overpower elasticity, and that at ordinary temperatures they give off no vapour whatever.

The presence of vapour has a considerable influence over the bulk of gases; and as chemists often determine the quantity of gaseous substances by measure, it is important to estimate the increase of volume due to the presence of moisture. The mode by which a vapour acts is obvious. When two gases, which do not act chemically on each other, are intermingled, each retains the elasticity suited to its volume, exactly as if the other gas were absent; so that the elasticity of the mixture is the sum of the elastic forces of its ingredients. The same remark applies to the mixture of gases and vapours. If a few drops of water are added to a portion of dry air, confined in a glass tube over mercury, the air will speedily become saturated with vapour, and must in consequence be increased in bulk. For the elastic power of the vapour being added to that previously exerted by the gas alone, the mixture will necessarily exert a stronger

pressure upon the mercury that confines it, and will therefore occupy a greater space. It is equally clear that the degree of augmentation will depend on the temperature; for it is the temperature alone which determines the elasticity of the vapour.

As the elasticity of vapour is not at all affected by mere admixture with gases, it is easy to correct the fallacy to which its presence give rise, by means of the data furnished by the experiments of Dalton. The formula for the correction is thus deduced. Let n be the bulk of dry air or other gas expressed in the degrees of a graduated tube; p the elasticity of the dry air, equal to the atmospheric pressure as measured by a barometer; n' the bulk of the air when saturated with watery vapour, and f the elasticity of that vapour (Biot's Traité de Phys. i. 303). Now, as the elasticity of a gas for equal temperatures is inversely as its volume, it follows that when the dry air increases in bulk from n to n', its elasticity will diminish in the ratio of n' to n. Hence its elasticity ceases to be $=p$, and is expressed by $\frac{pn}{n'}$; p is then $=\frac{pn}{n'}+f$; that is, the elasticity of the moist air, added to the elasticity of the vapour present, is equal to the pressure of the atmosphere. From this last equation are deduced the following values: $pn+fn'=pn'$; $pn=pn'-fn'$; and $n=\frac{n'(p-f)}{p}$. One example will suffice for showing the use of this formula. Having 100 measures of air saturated with watery vapour at 60°, the barometer standing at 30 inches, how many measures would the air occupy if quite dry? $n'=100$; $p=30$; $f=0{\cdot}524$, the tension of watery vapour at 60°, according to Dalton's table.* Hence $n=\frac{100\times(30-0{\cdot}524)}{30}=\frac{100\times 29{\cdot}746}{30}=98{\cdot}25$, which is the answer required.

The quantity of vapour present in the atmosphere is very variable, in consequence of the continual change of temperature to which the air is subject. But even when the temperature is the same, the quantity of vapour is still found to vary; for the air is not always in a state of saturation. At one time it is excessively dry, at another it is fully saturated; and at other times it varies between these extremes. This variable condition of the atmosphere as to saturation is ascertained by the hygrometer.

Hygrometers.—A great many hygrometers have been invented; but they may all be referred to three principles. The construction of the *first kind of hygrometer* is founded on the property possessed by some substances of expanding in a humid atmosphere, owing to a deposition of moisture within them; and of parting with it again to a dry air, and in consequence contracting. Of these, none is better than the human hair, which not only elongates freely from imbibing moisture, but, by reason of its elasticity, recovers its original length on drying. The hygrometer of Saussure is made with this material.

[*The second kind of hygrometer* depends upon the cooling effect of evaporation. The bulb of a thermometer, covered with a piece of silk or linen, is exposed to a current of air, or is rapidly swung round until its temperature ceases to be any further depressed. The reduction of its temperature below that of the surrounding medium, as marked by an adjoining instrument, furnishes the means of computing the quantity of moisture in the atmosphere. When the air is

* Manchester Memoirs, vol. v.

saturated with moisture the wet bulb will undergo no change of temperature, because in that state there is no evaporation. But where the air is dry, or contains less than a saturating amount of moisture, a greater or less evaporation will take place, which, by robbing the thermometer of heat will continue to reduce its temperature until the loss from this cause becomes counterbalanced by the heat that flows in from the warmer surrounding medium. When this takes place the temperature of the wet bulb becomes stationary.

This simple form of the hygrometer first used by Sir John Leslie, is called the *Wet-bulb Hygrometer.* With the aid of proper formulæ of computation it is capable of furnishing the most exact results.]

The third kind of hygrometer is on a principle entirely different from the foregoing. When the air is saturated with vapour, and any colder body is brought into contact with it, deposition of moisture immediately takes place on its surface. The degree indicated by the thermometer when dew begins to be deposited, is called the *dew-point.* If the saturation be complete, the least diminution of temperature is attended with the formation of dew; but if the air is dry, a body must be several degrees colder before moisture is deposited on its surface; and indeed the drier the atmosphere, the greater will be the difference between its temperature and the dew-point. Attempts were made to estimate the hygrometric state of the air on this principle by the Florentine Academicians, but the first accurate method was introduced by Le Roi, and since adopted by Dalton. It consists simply in putting cold water into a glass vessel, the outside of which is carefully dried, and marking the temperature of the liquid at which dew begins to be deposited on the glass. The water when necessary is cooled either by means of ice or a freezing mixture. A convenient form of apparatus is a small cup made of thin silver, nicely gilt on the outside, capable of holding about half an ounce of water, and fitted into a case of turned wood lined with cloth, which serves as a stand for the cup during an observation. The water is cooled by successively adding a few grains of a powder made of equal parts of nitre and sal-ammoniac intimately mixed, stirring with the bulb of a small thermometer. As soon as dew is deposited, the temperature is noted; and the first observation is corrected by waiting until the cup and its contents grow warmer, and observing the temperature at which the dew begins to disappear. The last observation is the most trustworthy. This method, when deliberately performed, so that the cup, the solution, and the thermometer should have time to acquire the same temperature, is susceptible of great precision.

The hygrometer of Daniell, described in his Meteorological Essays, acts on the same principle. It consists of a cryophorus, as described at page 49, but modified somewhat in form, and containing ether instead of water. Within one of its balls is fixed a delicate thermometer, the bulb of which is partially immersed in the ether so as to indicate its temperature, and the other ball is covered with muslin. When the instrument is used the muslin is moistened with ether, and the cold produced by its evaporation condenses the vapour within the cryophorus, and causes the ether to evaporate rapidly in the other ball. The cold thus generated chills the ether itself and the ball containing it; and in a short time its temperature descends so low, that dew is deposited on the surface of the glass. As soon as this takes place, the temperature is observed by the thermometer.

The same object is attained in a still easier way by means of a contrivance described by Jones, of London, (Phil. Trans. 1826,) and soon after by Cold-

stream, of Leith, (Phil. Journ. ix. 155.) It consists of a delicate mercurial thermometer, the bulb of which is made of thin black glass, and, excepting about a fourth of its surface, is covered with muslin. On moistening the muslin with ether, the temperature of the bulb and mercury falls, and the uncovered portion of the bulb is soon rendered dim by the deposition of moisture. The temperature indicated at that instant by the thermometer is the dew-point.

It is desirable on some occasions, not merely to know the hygrometric condition of air or gases, but also to deprive them entirely of their vapour. This may be done to a great extent by exposing them to intense cold; but the method now generally preferred is by bringing the moist gas in contact with some substance which has a powerful chemical attraction for water. Of these none is preferable to chloride of calcium.

CONSTITUTION OF GASES WITH RESPECT TO HEAT.

From the experiments of Faraday on the liquefaction of gaseous substances, gases may be viewed as the vapours of extremely volatile liquids. Most of these liquids, however, are so volatile, that their boiling point, under the atmospheric pressure, is lower than any natural temperature; and hence they are always found in the gaseous state. By subjecting them to great pressure, their elasticity is so far counteracted that they become liquid. But even when thus compressed, a very moderate heat is sufficient to make them boil; and on the removal of pressure they resume the elastic form, most of them with such violence as to cause a report like an explosion, and others with the appearance of brisk ebullition. Intense cold is produced at the same time, in consequence of their heat passing from a sensible to an insensible state.

The process for liquefying gases, as first employed by Faraday, consists in exposing them, as they are evolved, to the pressure of their own atmosphere. The materials for producing the gas are put into a strong glass tube, which is afterwards sealed hermetically, and bent in the middle, as represented by the figure. The gas is generated, if necessary, by the application of heat; and when the pressure becomes sufficiently great, the liquid is formed and collects in the free end of the tube, which is kept cool to facilitate the condensation. Most of these experiments are attended with danger from the bursting of the tubes, against which the operator must protect himself by the use of a mask.



The pressure required to liquefy gases is very variable, as will appear from the following table of the results obtained by Faraday:

Sulphurous acid gas	2	atmospheres at	45°
Sulphuretted hydrogen gas	17	"	50°
Carbonic acid gas	36	"	32°
Chlorine gas	4	"	60°
Nitrous oxide gas	50	"	45°
Cyanogen gas	3·6	"	45°
Ammoniacal gas	6·5	"	50°
Muriatic acid gas	40	"	50°

Additional light has been thrown on the nature of gases by M. Thilorier, who has succeeded in obtaining carbonic acid gas in a solid state (Ann. de Ch. et Ph. lx. 431). It is procured by directing a jet of the liquid carbonic acid into

a small glass phial, which is rapidly filled with solid carbonic acid in the form of a white flocculent powder. The solidification is evidently produced by the cold occasioned by the sudden transition of a liquid into a gas, in which state it occupies a space 400 times greater than its original volume. The degree of cold thus produced is estimated by Thilorier at—148°, at which temperature carbonic acid appears to be almost deprived of its elastic force; for the solid exposed to the ordinary atmospheric pressure and temperature evaporates slowly and quietly, and is gradually converted into carbonic acid gas.

[Recently M. Natterer has succeeded in liquefying nitrous oxide gas by compressing it with a small iron pump in a tube of wrought iron, at a pressure of 50 atmospheres. In this way he obtained about half a pint of a clear liquid of a sweet taste occupying about $\frac{1}{400}$th of the volume of the original gas, and which could be kept several hours exposed to the air. By uniting mechanical pressure with the intense cold produced by Thilorier's bath of solid carbonic acid and ether, under the exhausted receiver, Faraday has very lately obtained many new and striking results. Among these the following may be mentioned:

Olefiant gas became a colourless transparent liquid but did not solidify.

Hydriodic acid was obtained, both in the solid and liquid states, the former greatly resembling ice.

Hydrobromic acid gave like results.

Sulphuretted Hydrogen became a white transparent crystalline mass, resembling solid nitrate of ammonia or camphor.

Carbonic acid, in passing from the liquid to the solid state, without being dispersed as in Thilorier's experiment in the form of snow, concretes into a solid, transparent as crystal. In this condition its vapour exerts a pressure of only six atmospheres.

Nitrous Oxide, solidified by exposing its liquid to the cold bath, was a beautiful transparent crystalline body, so little volatile that in this state the pressure of its vapour did not amount to one atmosphere. The cold produced by the evaporation of the liquefied gas is far greater even than that of the baths of solid carbonic acid and ether. This bath, which instantly freezes mercury, immediately caused the liquid nitrous oxide to boil violently.

Cyanogen readily became solid, as previously shown by Bussy.

Ammonia, perfectly pure and dry, was converted into a transparent, crystalline, white substance, heavier than liquid ammonia, and owing to its volatility, at this temperature, diffusing very little vapour. (Ann. de Chim. Jan. 1845.)]

SOURCES OF HEAT.

[The sources of heat may be reduced to six: 1. The sun. 2. The interior of the earth. 3. Electricity. 4. Vital action. 5. Mechanical action. 6. Chemical action. These, with the exception of the second and two last, will be more conveniently considered in other parts of the work.

Internal Heat of the Globe.—The impressions of temperature due to the sun's rays, upon the earth's surface, are felt less and less as we descend to greater depths, and at a moderate distance, varying with the nature of the superficial strata, entirely disappear. The depth of the layer thus beyond the reach of the influences from above, and which is called the invariable stratum, ranges from 50 to 100 feet. Beneath this the temperature is seen to be progressively higher as we descend, the rate of its increase being 1° for from 40 to 50 feet. Sup-

posing the law continued, at the depth of two miles, water would be converted into steam; at four miles, tin and bismuth would be melted; at five, lead; and at thirty miles the temperature would be high enough to melt iron and almost all kinds of rocky material. We may hence infer that the great mass of our globe is in a state of fluidity from heat, and that its solid portion forms but a thin covering or crust around the molten matter of the interior.

The chemical and mechanical actions concerned in earthquakes and volcanoes, have, with strong reason, been traced to this cause, and form an interesting branch of chemical and physical inquiry, which, however, cannot properly find a place in this work.]

The mechanical method of exciting heat is by friction and percussion. When parts of heavy machinery rub against one another, the heat excited, if the parts of contact are not well greased, is sufficient for kindling wood. The axle-trees of carriages have been burned from this cause, and the sides of ships are said to have taken fire by the rapid descent of the cable. Count Romford has given an interesting account of the heat excited in boring cannon, which was so abundant as to heat a considerable quantity of water to its boiling point. It appeared from his experiments that a body never ceases to give out heat by friction, however long the operation may be continued; and he inferred from this observation that heat cannot be a material substance, but is merely a property of matter. Pictet observed that solids alone produce heat by friction, no elevation of temperature taking place from the mere agitation of fluids with one another. He found that the heat excited by friction is not in proportion to the hardness and elasticity of the bodies employed. On the contrary, a piece of brass rubbed with a piece of cedar wood produced more heat than when rubbed with another piece of metal; and the heat was still greater when two pieces of wood were employed.

[*Chemical action.*—Referring to a future section for an account of the agency of combustion, as a source of heat, we will here restrict ourselves to the effects of ordinary chemical combination in developing heat.

It has long been known that in nearly every case of active chemical union, between two or more substances, a rise of temperature is produced. But, until recently, no satisfactory attempt has been made to discover the relation between the amount of heat evolved and the proportion in which the bodies combine. The late researches of Hess, Graham, Abrea and others, on this subject, have disclosed many interesting facts, which, although as yet but partially reducible to simple laws, promise, when further extended, to disclose definite relations in the heat of combination.

Thus Abrea has found that in combining anhydrous sulphuric acid with successive chemical equivalents of water, the quantities of heat successively evolved are related nearly in the proportion of the following series of numbers:

Equivalents of water	1st	2d	3d	4th	5th	6th
Heat evolved	1	$\frac{1}{3}$rd	$\frac{1}{6}$th	$\frac{1}{12}$th	$\frac{1}{16}$th	$\frac{1}{24}$th

From numerous experiments on the heat evolved in the combination of acids with bases, Hess has inferred the following law: When a diluted acid combines with a base the amount of heat set free by the union, when added to that liberated during the dilution of the acid in the first instance, is exactly equal to that evolved by the combination of the anhydrous acid with the base; in other words

the aggregate of heat evolved in such cases is a constant quantity. With sulphuric acid and ammonia the following were his results:

	With Ammonia.	With Water.	Sum.
Sulphuric Acid . .	595·8		595·8
First dilution . .	518·9	77·8	596·7
Second dilution . .	480·5	116·7	597·2]

SECTION II.

LIGHT.

Optics, from *οπτομαι I see*, is the science which treats of light and vision. On the nature of light two rival theories exist, the *undulatory* and *corpuscular*. Prior to and about the time of Newton's celebrated analysis of solar light in 1672, Descartes, Hooke, Huygens, and others, had entertained the former; but Newton, in adopting the latter, led to its almost general reception. He considered light to consist of inconceivably minute particles, too subtile to exhibit the common properties of matter, though really material, which emanate from luminous bodies, such as the sun, the fixed stars, and incandescent substances, travel with immense velocity, and excite the sensation of light by passing bodily through the substance of the eye, and striking against the expanded nerve of vision, the retina. This theory, with which the language of optics has become identified, prevailed with almost no opposition from the time of Newton till 1801, when the undulatory theory was revived and supported with great ability by Young (Phil. Trans.). By the researches of others, the testimony in favour of this doctrine gradually gained ground, and at present it is all but generally adopted. While some phenomena, as the absorption and refraction of light, are even yet obscurely explained by either theory, others, especially the phenomena of interference and polarized light, are wholly inexplicable by the corpuscular, and receive a most lucid explanation by the undulatory theory. On this ground the former is considered untenable, and the latter alone suitable to the present condition of science. But to enter at length into this argument would be so foreign to the design of this treatise, that the reader is referred to Pouillet's *Elémens de Physique*, Young's Essays, Airy's Tracts, 2nd edition, and Herschel's article on Light in the Encyclopedia Metropolitana.

I shall now, however, state the laws of light in the ordinary language, which is founded on the corpuscular theory, and analogous to that which has been employed in treating of heat.

Diffusion of Light.—Light emanates from every visible point of a luminous object, and is equally distributed on all sides if not intercepted, diverging like radii drawn from the centre to the circumference of a circle. Thus, if a single luminous point were placed in the centre of a hollow sphere, every point of its concavity would be illuminated, and equal areas would receive equal quantities of light. The smallest portion of light which can be separated from contiguous portion is called *a ray of light*. Each ray, when not interrupted in its course,

and while it remains in the same medium, moves in a straight line; as is obvious by the appearance of shadows cast by the side of a house, or of a sunbeam admitted through a small aperture into a dark room. Owing to these modes of distribution, it follows that the quantity of light which falls upon a given surface decreases as the square of its distance from the luminous object increases, the same law which regulates the heating power of a hot body. (Page 12.)

The passage of light is progressive, time being required for its motion from one place to another. By astronomical observations it is found that light travels at the rate of nearly 195,000 miles in a second of time, and would require about eight minutes to pass from the sun to the earth. Owing to this prodigious velocity, the light caused by the firing of a cannon or a sky-rocket is seen by different spectators at the same instant, whatever may be their respective distances from the rocket, the time required for light to travel 100 or 1000 miles being inappreciable to our senses.

When light falls upon any body, it may, like radiant heat (page 12), dispose of itself in three different ways, being *reflected*, *refracted* or *absorbed*. The phenomena connected with the two former modes of distribution I shall proceed to consider in succession; while those of absorbed light will be included under the head of *Decomposition of Light*.

REFLECTION OF LIGHT.

Light may be reflected by all media, whether solid, liquid, or gaseous, when it passes from one medium into another of a different nature or density; but there is great difference in the power of reflection. Bright metallic surfaces, such as polished brass and silver, or clean mercury, reflect nearly all the rays which fall upon them; while those which are dull and rough reflect but few. The reflection of light, like that of heat, takes place at the surface of bodies, and appears influenced rather by the condition of the surface than by the nature of the reflecting body. The direction of the reflected ray, whatever may be the nature or figure of the reflecting surface, is regulated by these two laws.

I. The incident and reflected rays always lie in the same plane, which plane is perpendicular to the reflecting surface.

II. The incident and reflected rays always form equal angles with the reflecting surface; or, what amounts to the same, the angle of incidence is always equal to the angle of reflection.

Hence, if the reflecting surface be a plane mirror, the direction of the reflected ray, being known, gives us that of the incident ray; and *vice versâ*.

These laws apply equally to curved reflecting surfaces, whether convex or concave. As a curve may be viewed as a polygon with very short sides, it follows, from obvious mathematical considerations, that parallel rays, falling on a convex mirror, are scattered or made to diverge; while if they fall on a concave mirror they are concentrated, or made to converge into its focus. On the same principle it is plain that divergent rays, falling on a convex surface, are rendered parallel by reflection; and that rays, diverging from the focus of a concave mirror on its surface, are also reflected in parallel lines.

When the concave mirror is spherical, the parallel rays falling on it are not strictly collected into one point or focus; this only happens when the mirror is accurately parabolic. Hence, if a luminous body be placed in the focus of one

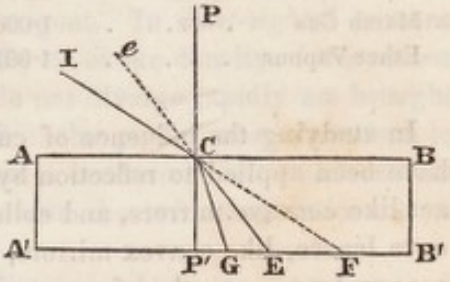
parabolic reflector, the rays which it gives off are all collected in the focus of a second parabolic reflector placed opposite to the first.

On these principles are constructed the reflecting telescope and the reflecting microscope; but this treatise is not the place for a description of these useful instruments.

REFRACTION OF LIGHT.

Light traverses the same transparent medium, such as air, water, or glass, in a straight line, provided no reflection occurs, and there is no change of density; but when it passes from one medium into another, or from one part of the same medium into another of a different density, a change of direction always ensues at the plane of junction of the media, except when the ray is perpendicular to that plane. For instance, let AB A′B′, fig. 1, represent a vertical section of a vessel full of water, and PP′ the perpendicular to the surface of the water at the point C. Should a ray of light enter the water perpendicularly to its surface, as in the line of PC, it will continue on its course to P′ without deviation; but if it descend obliquely, as in the direction of IC, it will suffer a bend at C, and proceed to E, instead of advancing along the dotted line to F. Conversely, were a ray of light to emanate from E and emerge at C, it would not advance to *e*, but take the direction of CI. By comparing the direction of the refracted ray in these two cases in relation to the vertical PP′, it will be seen that the ray approaches the perpendicular in entering from air into water, and recedes from it in passing out of water into air. The same remark applies to the passage of light from or into air into or out of solid or liquid media in general.

Fig. 1.



Bodies differ in their power of refracting light. In general, the denser a substance is, the greater is the deviation which it produces. If in fig. 1 sulphuric acid were mixed with the water, the ray IC would be refracted to some point between E and G; and if a solid cake of glass were substituted for that liquid, the refracted ray would be bent down to CG. But this is far from universal:—alcohol, ether, and olive oil, which are lighter than water, have a higher refractive power. Observation has shown it to be a law, to which no exception is yet known, that oils and other highly inflammable bodies, such as hydrogen, diamond, phosphorus, sulphur, amber, olive oil, and camphor, have a refractive power which is from two to seven times greater than that of incombustible substances of equal density. But whatever may be the refractive power of bodies in relation to each other, refraction is always governed by the two following laws, discovered in 1618 by Snell, though usually ascribed to Descartes.

1. The direction of the incident and refracted ray is always in a plane perpendicular to the surface common to the media.

2. The sine of the angle of incidence and the sine of the angle of refraction are in a constant relation for the same media.

The sine of the angle of refraction being taken = 1, the sines of the angles of incidence in different substances may thus be referred to a common measure or unit of comparison. In common flint glass the ratio is nearly as 1·6 to 1;

in water, as 1·336 to 1. The numbers representing the sines of the angles of incidence are called the *indices of refraction*, and indicate the degree of refractive power. Thus, the index of refraction of flint glass is 1·6; that of water, 1·336; that of the diamond, 2·755.

Subjoined is a table of the refractive indices of gases, that of a vacuum being unity.

Name of Gas.	Ref. Index.	Name of Gas.	Ref. Index.
Oxygen	1·000272	Carbonic Oxide . . .	1·000340
Hydrogen	1·000138	Carbonic Acid . . .	1·000449
Nitrogen	1.000300	Hydrochloric Acid . .	1·000449
Chlorine	1·000772	Ammonia	1·000385
Protoxide of Nitrogen .	1·000503	Cyanogen	1·000834
Binoxide of Nitrogen .	1·000303	Hydrocyanic Acid . .	1·000451
Olefiant Gas . . .	1·000678	Sulphurous Acid . .	1·000665
Marsh Gas . . .	1·000443	Hydrosulphuric Acid .	1·000644
Ether Vapour . . .	1·001530	Bisulphuret of Carbon Vapour	1·001500

In studying the influence of curved media on light on the same principles as have been applied to reflection by curved mirrors, it is found that convex lenses act like concave mirrors, and collect the refracted rays into a focus; while concave lenses, like convex mirrors, cause the rays to diverge. The properties of convex lenses are, therefore, extensively applied in the construction of the refracting telescope, which is the kind most commonly employed, and of the refracting microscope.

A convex lens fitted into the wall of a darkened chamber constitutes the arrangement of a *camera obscura*, the inverted images of external objects being received on a disk of paper or a white board. In the simple telescope the lens is placed at the extremity of a tube of such length that the image may be formed within the tube, and the observer looks from the other end at the image formed in the air. The eye acts on the same principle. Luminous rays entering the transparent parts of the eye are refracted by the cornea and crystalline lens, and are brought into a focus at the bottom of the eye, an inverted image of external objects being formed upon the retina as on the table of a camera obscura. For distinct vision it is necessary that this image should be formed exactly on the retina. Hence, were the eye an ordinary lens, having an invariable focus, our range of vision would be very narrow; an eye fitted for seeing at a distance would be useless for near objects; and persons who could see near objects would be blind to remote ones. Two rays emanating from a distant point cannot *both* fall upon so small an object as the eye, unless they are nearly parallel; for if they diverged by even a very small angle, they would before reaching the eye separate by an interval exceeding the diameter of the cornea. On the contrary, rays in rapid divergence may enter the eye provided the point from which they emanate be close to it; and the nearer the object, the more divergent the rays which enter. When, therefore, we observe a distant landscape, then successively notice nearer and nearer objects, and lastly cast the eyes upon the page of a book only six inches distant, we receive rays coming from a multitude of different objects, each set of rays having its own peculiar divergence, and requiring a separate focus; and yet, so wonderful is the adjusting power of the eye, a single minute suffices for distinctly seeing all the objects so beheld, without the consciousness of an effort.

The adjustment of the eye for different distances appears to depend on a power of increasing or decreasing the distance between the posterior part of the eye and the lens; though the mechanism by which this is accomplished is unknown. Some ascribe it to a change in the figure of the whole eye-ball, produced by the muscles which move the eye; but Brewster, I think with better reason, considers the position of the lens to be varied by the same contractile tissue which determines the movements of the iris and the size of the pupil. To this adjusting power, however, there is a limit.* The distance at which most persons see small objects distinctly is about six inches: at shorter distances the rays are so divergent, that their focal point falls behind the retina, and indistinct vision is the consequence. Persons called *long-sighted* are unable to see near objects distinctly, owing to a weak refracting power of the eye, due to deficient convexity or density in the humours of the eye. This is the infirmity of advancing life, and is remedied by convex glasses, which cause diverging rays to be parallel or slightly convergent. In *short-sighted* persons the refractive power, either from undue convexity or undue density of the cornea and lens, is so powerful, that all rays which do not diverge rapidly are brought to a focus before they reach the retina. Youth is the period most obnoxious to this imperfection, and assistance is derived from a concave glass, which causes parallel rays to diverge, and thereby counteracts the refracting influence of the eye.

Since the rays which fall on a convex lens from any object are divergent, and are collected into a focus behind the lens, it follows that the image there formed must be inverted, the rays from the top of the object forming the lower part, in point of position of the image. Yet the eye sees objects erect. This remarkable fact has not yet been satisfactorily explained. It has been supposed by some that in infancy we actually see objects inverted, and only discover that they are not so by the correction derived from experience; but this fallacy has been fully corrected by observation on persons born blind, who first obtained the power of vision when of an age to describe what they saw.

Double Refraction.—If on a piece of paper with a black line on its surface we place a rhombohedron of Iceland-spar, and then look at the line through the crystal, it will be found that in a certain position the line appears single as when seen through water or glass; but in other positions of the crystal two lines are visible parallel to each other, and separated by a distinct interval. The light in passing through the crystal is divided into two portions, one of which obeys the laws of refraction already explained (page 52); whereas the other portion proceeds in a wholly different direction, and hence gives the appearance of two objects instead of one. The former is termed the *ordinary*, the latter the *extraordinary* ray. This phenomenon is known by the name of *double refraction*, and has been witnessed in many crystallized substances, as in minerals and artificial salts.

Light transmitted through Iceland-spar or other doubly refracting substances, is found to have suffered a remarkable change. In this state it is distinguished

* A different explanation has been very lately suggested by Prof. Forbes. The lens being composed of a central nucleus of comparatively solid matter, and of soft gelatinous substance towards the margin, he conceives that by the combined action of the muscles of the eye pressing on the outside, and communicating tension to the contents of the globe, the borders of the lens are pressed in towards the axis and its whole form is rendered more nearly globular. This would of course diminish the focal distance. (Comp. Rend., 1844.) R.

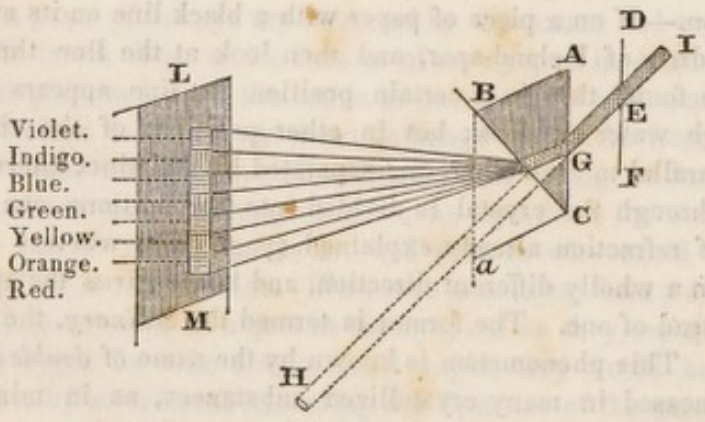
from common light by the circumstance, that when it falls upon a plate of glass at an angle of 56° 11′, it is almost completely reflected in one position of the glass, and is hardly reflected at all in another: if reflected when the plane of reflection is vertical, no reflection ensues when the reflecting plane is horizontal, the incident angle being maintained at 56° 11′. This curious property, so different from common light, has been theoretically ascribed to a kind of *polarity* of such sort, that each side of a ray of light is thought to have a character different from the two adjacent sides at right angles to it; and hence the origin of the term *polarized light*, by which this property is distinguished. Light is polarized by reflection from many substances, such as glass, water, air, ebony, mother-of-pearl, and many crystallized substances, provided the light is incident at a certain angle peculiar to each surface, and which is called the *polarizing angle*. Thus, the polarizing angle for glass is 56° 11′, and for water 53° 14′; that is common light reflected by glass and water at the angles stated will be polarized.

The phenomena of double refraction and polarized light constitute a department of optics of great and increasing interest; but it is too remote from the pursuits of a chemical student to be treated of at length in this work. Those interested in such studies will find an excellent guide in Brewster's Treatise on Optics in the Cabinet Cyclopedia.

DECOMPOSITION OF LIGHT.

The analysis of light may be effected either by refraction or absorption. Newton, who discovered the compound nature of solar light effected its decomposition by refraction, employing a solid piece of glass bounded by three plane surfaces, well known under the name of the *prism*. His mode of operating consisted in admitting a ray of light IG, fig. 2, into a dark chamber through a window-shutter DEF, and interposing the prism ACB, so that the ray should pass

Fig. 2.



obliquely through two surfaces, and be refracted by both. On receiving the refracted ray upon a piece of white paper LM, there appeared, instead of a spot of white light, an oblong coloured surface composed of seven different tints, called the *prismatic* or *solar spectrum*. On subjecting each of these colours to refraction no further separation was accomplished; but on causing the rays separated by one prism to pass through a second of the same power and in an inverted position CB*a*, the seven colours disappeared, and a spot of white light appeared at H, in the very position which it would have occupied had both

prisms been absent. From such and similar experiments Newton inferred that white light is a mixture of seven *colorific* rays—red, orange, yellow, green, blue, indigo, and violet; and that the separation of these primary or simple rays depended on an original difference of refrangibility, violet being the most refrangible and red the least so.

[The recent experiments of Herschel have disclosed the existence, beyond the limit of the violet space, of other rays still more refrangible, which from their colour, he proposes to call Lavender rays. That these are distinct from the violet light, is proved by their retaining their tint unaltered after being concentrated by a lens.]

Though a prism is the most convenient instrument for decomposing light, the separation of the coloured rays is more or less effected by refracting media in general. Lenses, accordingly, disperse the colorific rays at the same time that they refract them; and this effect constitutes one of the greatest difficulties in the construction of telescopes, in so much as the separation or *dispersion*, as it is termed, of these rays diminishes the distinctness of the image. The combinations by which the defect is remedied are called *achromatic*.

Newton's analysis of light led him to explain the origin of the colours of natural objects. Of opaque bodies those are black which absorb all the light that falls upon them, and those white which reflect it unchanged: the various combinations of tints are the consequence of certain rays being absorbed, while those alone whose intermixture produces the observed colour are reflected. The same applies to transparent media, which are colourless like pure water when the light passes through unchanged, but are coloured when some rays are transmitted and others absorbed. This absorption of certain rays by coloured media, such as glass of different tints, affords another mode of decomposing light; and Brewster has ingeniously applied it to analyse the seven colours which compose the prismatic spectrum. He has proved by such experiments, what has been maintained before, that the seven colours of the spectrum are occasioned not by seven, but by three simple or primary rays; namely, the red, yellow, and blue. These rays are concentrated in those parts of the spectrum where each primary colour respectively appears; but each spreads more or less over the whole spectrum, the mixture of red and yellow giving orange, of yellow and blue green, and red with blue and a little yellow causing the violet.

The prismatic colours, according to the experiments of Sir W. Herschel, differ in their illuminating power: the orange illuminates in a higher degree than the red, the yellow than the orange. The maximum of illumination lies in the brightest yellow or palest green. The green itself is almost equally bright with the yellow; but beyond the full deep green the illuminating power sensibly decreases. The blue is nearly equal to the red, the indigo is inferior to the blue, and the violet is the lowest on the scale. (Phil. Trans. 1800.)

Calorific rays in Light.—The solar rays, both direct and diffused, are capable of exciting heat. When reflected or transmitted, no such effect results: the concave reflector and burning glass remain cool, though intense heat is developed at their foci; and the atmosphere is not heated by the solar rays to which it gives a passage. But opaque bodies which absorb light are invariably heated by it, and the temperature is proportional to the absorbent power. Hence, dark-coloured substances, which are more absorbent than light ones, become hotter when exposed to sunshine. This is attested by the general preference given to light-coloured clothing during summer. Hooke, and subsequently Franklin,

proved the fact by exposing pieces of cloth of the same texture and size, but different colours, upon snow to sunshine; when the snow under the dark specimens was found to melt more freely than under the light ones, the effect being nearly proportional to the depth of shade. Davy arrived at similar results. The coloured rays of the spectrum differ in heating power. This is shown generally by looking at the sun through glass of different colours, when it will be found that red and yellow glasses heat and oppress the eye much more than blue or green ones; but the fact was first rigidly demonstrated by Sir W. Herschel, by placing the bulb of a delicate thermometer in the coloured spaces of the solar spectrum. He found that it stood highest in the red space, fell lower and lower when successively removed towards the violet, and was lowest in the violet space. (Phil. Trans. 1800.)

The foregoing facts are explicable on the suppositions either that light is convertible into heat by absorption, or that heat is merely associated with light, and is absorbed along with it. Herschel maintained the latter view, and founded it on his observation that, though the red space of the spectrum is hotter than the other coloured spaces, there is a spot a little beyond the red, where little or no light appears, where the thermometer is higher than in the red itself. He hence inferred that there exists in the solar beam a distinct kind of ray, which causes heat but not light; and that these rays, from being less refrangible than the luminous ones, deviate in a smaller degree from their original direction in passing through the prism.

All succeeding experimenters confirm the statement of Herschel, that the prismatic colours differ in heating power; but they do not agree as to the spot where the heat is greatest. Englefield, Davy, and others affirmed with Herschel that it is beyond the red ray; while others, and in particular Leslie, contended that it is in the red itself. The observations of Seebeck (Edin. Journal of Science, i. 358) explained these contradictory statements, by showing that the point of greatest heat varies with the kind of prism which is employed for forming the spectrum. When he used a prism of fine flint-glass, the greatest heat was uniformly beyond the red; with a prism of crown-glass, the red itself was the hottest part; and with a prism externally of glass, but containing water within, the maximum heat was neither in the red itself, nor beyond it, but in the yellow. These experiments have been confirmed by Melloni, who has succeeded with a prism of rock-salt in separating the spot of maximum heat from the coloured part of the spectrum by a much greater interval than had been done previously, and dissipating all remaining doubt as to the existence in solar light of calorific rays distinct from those rays which produce colour. As in simple radiant heat (page 15), there exist in solar light calorific rays of different characters, some being more, some less, refrangible. The former are proportionally less absorbed by feebly diathermanous media than the latter; whereas good diathermanous media absorb the less refrangible more freely than the more refrangible rays. For instance, the heat of the violet passes through water more readily than that of the yellow space, that of the yellow than the red; but in employing media always rising in transcalency, as crown-glass, flint-glass, and rock-salt, the obstruction to the least refrangible calorific rays continually decreases. Hence, in successively taking prisms of rock-salt, flint-glass, crown-glass, and water, the spot of greatest heat will be found first far beyond the red, then nearer the red, then in the red itself, and lastly in the yellow space of the spectrum. On using a prism still less transcalent than water,

the maximum heat would be found on the violet side of the yellow space. By causing light, terrestrial as well as solar, to pass first through water, and then through glass coloured green by oxide of copper, Melloni so effectually absorbed all the calorific rays, that the issuing light did not affect the most delicate thermoscope. It would hence follow, not merely that light is associated with calorific rays quite distinct from the luminous rays, but that the latter contributes nothing to the heat evolved during its absorption.

Chemical rays.—Solar light is capable of producing powerful chemical changes. One of the most striking instances of it is its power of darkening the white chloride of silver; an effect which takes place slowly in the diffused light of day, but in the course of two or three minutes by exposure to sunshine. This effect was once attributed to the influence of the luminous rays; but Ritter and Wollaston traced it to the presence of certain rays that excite neither heat nor light, and which, from their peculiar agency, are termed *chemical* rays. The greatest chemical action is exerted just beyond or at the verge of the violet part of the prismatic spectrum; the spot next in energy is the violet itself; and the property gradually diminishes in advancing to the green, beyond which it seems wholly wanting. It hence follows that the chemical rays are still more refrangible than the luminous, in consequence of which they are dispersed in part over the blue, indigo, and violet, but in the greatest quantity at the extreme border of the latter.

The Daguerréotype, as well as Mr. Talbot's method of Photography, is founded on the action of the chemical rays on certain substances. The iodide of silver, formed by exposing a plate of silver to the vapour of iodine, is the substance used in the Daguerréotype. The chloride, iodide, and bromide of silver, formed on the surface of paper in a thin and uniform layer, are the bases of Talbot's method. The delicacy and beauty of the images produced in the Daguerréotype, however, far surpasses anything that has hitherto been produced on paper. For details on this subject, the student is referred to a little treatise by M. Arago, which has been translated into English.

Magnetizing rays.—The more refrangible rays of light were once thought to possess the property of rendering steel and iron magnetic; but since the experiments of Riess and Moser, this notion has been abandoned. (Brewster's Journal, ii. 225.)

TERRESTRIAL LIGHT.

Under this head is included all kinds of artificial light. The common method of obtaining such light is by the combustion of inflammable matter, which gives out so much heat that the burning substance is rendered luminous in the act of being burned. All bodies begin to emit light when heat is accumulated within them in great quantity; and the appearance of glowing or shining, which they then assume, is called *incandescence*. The temperature at which solids in general begin to shine in the dark is between 600° and 700°; but they do not appear luminous in broad daylight till they are heated to about 1000°. The colour of incandescent bodies varies with the intensity of the heat. The first degree of luminousness is an obscure red. As the heat augments, the redness becomes more and more vivid, till at last it acquires a full red glow. If the temperature still increase, the character of the glow changes, and by degrees it becomes white, shining with increasing brilliancy as the heat augments. Liquids and

gases likewise become incandescent when strongly heated: but a very high temperature is required to render a gas luminous, more than is sufficient for heating a solid body even to whiteness. The different kinds of flame, as of the fire, candles, and gas light, are instances of incandescent gaseous matter.

Artificial lights differ in colour, and accordingly exhibit different appearances when transmitted through a prism. The white light of incandescent charcoal, which is the principal source of the light from candles, oils, and the illuminating gases, contains the three primary calorific rays, the red, yellow, and blue. The dazzling light emitted by lime intensely heated, first proposed by Lieut. Drummond for the trigonometrical survey (Phil. Trans. 1830), and of late so successfully applied by Messrs. Cooper and Carey for their gas microscope, gives the prismatic colours almost as bright as in the solar spectrum. The light emitted by iron feebly incandescent consists principally of the red rays, as does the red light obtained by means of strontia and lithia; that from ignited boracic acid is such a mixture of the blue and yellow rays as constitute green; and incandescent soda emits a yellow light almost wholly free from the rays which cause the red and blue colours.

Artificial light differs from solar light in containing heat in two states. It contains simple radiant heat like that radiated from a body not luminous, and which may be separated by transmission through a plate of moderately thick glass; but the light so purified still heats any body which absorbs it, possessing calorific rays associated with its luminous rays like those in solar light (page 61), and like them susceptible of refraction by transparent media. Thus, Daniell found that the rays from incandescent lime were concentrated by convex lenses, and set fire to phosphorus placed in the focus (Phil. Mag. N. S. ii. 59). Agreeably to the researches of Melloni (page 8), artificial light contains different modifications of radiant heat, which not only differ in refrangibility, but in transmissibility through diathermanous media.

The chemical agency of artificial light is analogous to that from the sun. In general the former is too feeble for producing any visible effect; but light of considerable intensity, such as that from ignited lime, darkens chloride of silver, and seems capable of exerting the same chemical agencies as solar light, though in a degree proportionate to its inferior brilliancy. (An. of Phil. xxvii. 451.)

Light emanates from some substances either at common temperatures or at a degree of heat disproportioned to the effect, giving rise to an appearance which is called *phosphorescence*. This is exemplified by a composition termed *Canton's phosphorus*, made by mixing three parts of calcined oyster-shells with one of the flowers of sulphur, and exposing the mixture for an hour to a strong heat in a covered crucible. The same property is possessed by chloride of calcium (Homberg's phosphorus), anhydrous nitrate of lime (Baldwin's phosphorus), some carbonates and sulphates of baryta, strontia, and lime, the diamond, some varieties of fluor-spar called *chlorophane*, apatite, boracic acid, borax, sulphate of potassa, sea-salt, and by many other substances. Scarcely any of these phosphori act unless they have been previously exposed to light, though they do not always shine with light of the same colour as that which excites the phosphorescence: for some, diffused daylight or even lamp-light will suffice; while others require the direct solar light, or the light of an electric discharge. Exposure for a few seconds to sunshine enables Canton's phosphorus to shine in a dark room for several hours afterwards. Warmth increases the intensity of light, or will renew it after it has ceased;—but it diminishes the duration.

When the phosphorescence has ceased it may be restored, and in general for any number of times, by renewed exposure to sunshine; and the same effect may be produced by passing electric discharges through the phosphorus. Some phosphori, as apatite and chlorophane, do not shine until they are gently heated; and yet if exposed to a red heat, they lose the property so entirely that exposure to solar light does not restore it. Pearsall has remarked that in these minerals the phosphorescence, destroyed by heat, is restored by electric discharges; that specimens of fluor-spar, not naturally phosphorescent, may be rendered so by electricity; and that this agent exalts the energy of natural phosphori in a very remarkable degree. (R. Inst. Journal, N. S. i.) The theory of these phenomena is obscure. Chemical action is not the cause, for these phosphori shine *in vacuo* or in gases which do not act chemically on them, and some even under water. It may be presumed that light causes in them a certain vibratory state analogous to that, though in a far lower degree, which exists in incandescent matter.

[From the recent experiments of Becquerel and others, it appears that the rays of the violet extremity of the spectrum are the real agents in producing these phenomena of phosphorescence, while the red rays have the effect of extinguishing the light. Conceiving the rays which are active in producing phosphorescence, to be distinct from the so called chemical rays, although associated with them in the spectrum, they have been distinguished by Draper and others by the name of phosphorogenic rays.]

Another kind of phosphorescence is observable in some bodies when strongly heated. A piece of lime, for example, heated to a degree which would only make other bodies red, emits a brilliant white light of such intensity that the eye cannot support its impression.

A third species of phosphorescence is observed in the bodies of some animals, either in the dead or living state. Some marine animals, and particularly fish, possess it in a remarkable degree. It may be witnessed in the body of the herring, which begins to phosphoresce a day or two after death, and before any visible sign of putrefaction has set in. Sea-water is capable of dissolving the luminous matter; and it is probably from this cause that the waters of the ocean sometimes appear luminous at night when agitated. This appearance is also ascribed to the presence of certain animalcules, which, like the glow-worm of this country, or the fire-fly of the West Indies, are naturally phosphorescent.

[It has lately been inferred by Matteuci, from numerous experiments, that the phosphorescence of the glow-worm is due to a slow combustion: carbonic acid being evolved in oxygen, while the animal continues luminous. This effect he found to be increased by heat. The phosphorescence of the fire-fly and various other animals, as well as of decaying animal and vegetable matter, is probably owing to the same cause.]

Light sometimes appears during the process of crystallization. This is exemplified by a tepid solution of sulphate of potassa in the act of crystallizing; and it has been likewise witnessed under similar circumstances in a solution of fluoride of sodium and nitrate of strontia. Another instance of the kind is afforded by the sublimation of benzoic acid. Allied to this phenomenon is the phosphorescence which attends the sudden contraction of porous substances. Thus, on decomposing by heat the hydrates of zirconia, peroxide of iron, and green oxide of chromium, the dissipation of the water is followed by a sudden increase of density suited to the changed state of the oxide, and a vivid glow

appears at the same instant. The essential conditions are, that a substance should be naturally denser after decomposition than it was previously, and that the transition from one mechanical state to the other should be abrupt.

Instruments designed for measuring intensities of light are termed *photometers*. That of Leslie is the only one used to estimate the strength of the sun's light. It consists of his differential thermometer, with one ball made of black glass. The clear ball transmits all the light that falls upon it, and therefore its temperature is not affected; it is all absorbed, on the contrary, by the black ball, and by heating and expanding the air within, causes the liquid to ascend in the opposite stem. The whole instrument is covered with a case of thin glass, the object of which is to prevent the balls from being affected by currents of cold air. The action of this photometer depends on the absorption of the heat by which light is accompanied.

Leslie recommended his photometer also for determining the relative intensities of artificial light, such as that of candles, oil, or gas. This application of it differs from the foregoing, because light from terrestrial sources contains calorific rays of different properties; some being largely absorbed by glass, and others freely transmissible. The former, being for the most part arrested by the outer glass case, will not cause any great error; but the latter must give rise to serious fallacies whenever the calorific and luminous rays of the two lights are not in the same ratio. This is rarely, if ever, the case with lights which differ in colour. Thus, the light emitted by burning cinders or red-hot iron, even after passing through glass, contains a quantity of calorific rays, which is out of all proportion to the luminous ones; and, consequently, they may and do produce a greater effect on the photometer than some lights whose illuminating powers are far stronger.

A photometer on a different principle has been described by Rumford in his Essays. It determines the relative strength of lights by a comparison of their shadows, and is susceptible of great accuracy when employed with the required care; but,* like the foregoing, its indications cannot be trusted when there is much difference in the colour of the lights. In this case, the best procedure is, to observe the distance from each light at which any given object, as a printed page, ceases to be distinctly visible. The illuminating power of the lights so compared is as the squares of their distances.

[An ingenious attempt has recently been made by MM. Fizeau and Foucault, to compare the intensity of solar radiation with that of the charcoal points in the voltaic circuit, and that of lime ignited by the oxyhydrogen blow-pipe. The intensities were measured by the time of exposure to the light, necessary to render the Daguerre plate sensible to mercurial vapour. The effects are therefore proportional, rather to the chemical than the luminous rays. Assuming the lime light as unity, the voltaic light was found to be 34.3, and the solar 146. (Ann. de Chim. July, 1844.)]

ON THE RELATIONS OF HEAT AND LIGHT.

Radiant heat and light have the most intimate resemblance. They are distributed, reflected, refracted, absorbed, transmitted, polarized, according to laws so exactly parallel, as to force on the mind the conviction that their causes are

* See an Essay on the Construction of Coal Gas Burners, &c., in the Edinburgh Philosophical Journal, for 1825.

likewise similar. If light be due to ethereal vibrations, it is difficult not to assign a similar cause to radiant heat. The obstacle to adopting this view arises from the peculiar relations of heat to matter as connected with change of form, with specific heat, and with heat of temperature. The outline of such an undulatory theory might be thus stated :—Heat may be considered identical with the universal ether, so that the terms ether and matter of heat would apply to the same substance. Diffused within the pores of bodies this ether causes the condition of temperature, and in a state of more intimate union it determines their form. Conduction may be due to a peculiar vibration of ether, advancing slowly among the molecules of matter, and modified by their presence,—a radiation from particle to particle. Common radiation of heat may be ascribed, not to the ether itself being ejected from a hot body, but to ethereal impulses originating in the same manner as those of light, but having waves of different grades both of length and intensity. It would not be prudent, however, at present, to embody such a theory with the ordinary doctrines of heat, though as a scientific speculation it is a subject of great and increasing interest.

SECTION III.

ELECTRICITY.

Elementary Facts.—When certain substances, such as amber, glass, sealing-wax, sulphur, are rubbed with dry silk or cloth, they are found to have acquired a property, not observable in their ordinary state, of causing contiguous light bodies to move towards them; or if the substances so rubbed be light and freely suspended, they will move towards contiguous bodies. After a while this curious phenomenon ceases; but it may be renewed an indefinite number of times by friction. The principle thus called into action is known by the name of *electricity*, from the Greek word ἤλεκτρον, amber, because the electric property was first noticed in it. The same term is applied to the science which treats of the phenomena of electricity.

When a substance by friction or any other means acquires the property just stated, it is said to be *electrified*, or to be *electrically excited*; and its motion towards other bodies, or of other bodies towards it, is ascribed to a force called *electric attraction*. But its influence, on examination, will be found to be not merely attractive; on the contrary, light substances, after touching the electrified body, will be disposed to *recede* from it just as actively as they approached it before contact. This is termed *electric repulsion*. By aid of the electrical machine, electric attraction and repulsion may be displayed by a great variety of amusing and instructive experiments, showing how readily an invisible power is called into operation, and how wonderfully inert matter is subject to its control. But the student may witness these effects quite satisfactorily by very simple apparatus. Let him suspend a thread of white sewing silk from the back of a chair so that one end may hang freely, taking the precaution to moisten that end slightly by holding it between the fingers, while the rest of the thread

is carefully dried by the fire; and let him then place near the free end a piece of sealing-wax previously rubbed on the sleeve of his coat. The silk will move towards it; but after touching the excited wax two or three times, it will recede from it.

When an electrified body touches another which is not electrified, the electric property is imparted by the former to the latter. Thus, on touching the free end of the suspended silk thread with the excited wax, the silk will itself be excited, as shown by its moving towards a book, a knife, or other unexcited object placed near it. But although electricity is always imparted by an excited to an unexcited body by contact, the latter does not always exhibit electric excitement. If, for example, the suspended silk be wetted along its whole length, it will be strongly attracted by the excited wax, but after contact it will not evince the least sign of being itself electrified. Nevertheless, electricity is communicated to the silk in both cases; only it is retained by silk when dry, and is lost as soon as received by wet silk. Such observations led to the discovery that electricity passes with great ease over the surface of some substances, and with difficulty over that of others, and hence to the division of bodies into *conductors* and *non-conductors* of electricity. If electricity be imparted to one end of a conductor, such as a copper wire, the other extremity of which touches the ground, or is held by a person standing on the ground, the electricity will pass along its whole length and escape in an instant, though the wire were several miles long; whereas excited glass and resin, which are non-conductors, may be freely handled without losing any electricity except at the parts actually touched. To the class of conductors belong the metals, charcoal, plumbago, water, and aqueous solutions, and substances generally which are moist or contain water in its liquid state, such as animals and plants, and the surface of the earth. These, however, differ in their conducting power: of the metals, Harris found silver and copper to be the best conductors; and after these follow gold, zinc, platinum, iron, tin, lead, antimony, and bismuth (Phil. Trans. 1827). This order, as Forbes has remarked, is nearly that of their conducting powers for heat. Aqueous solutions of acids and salts conduct much better than pure water. To the list of non-conductors belong glass, resins, sulphur, diamond, dried wood, precious stones, earth and most rocks when quite dry, silk, hair, and wool. Air and gases in general are non-conductors if dry, but act as conductors when saturated with moisture.

This knowledge is of continual application in electrical experiments. When it is wished to collect electricity on a metallic surface, the metal must be *insulated*, that is, cut off from contact with the earth, and with conductors touching the ground, by means of some non-conductor; an object commonly effected either by supporting it on a handle of glass, or by placing it on a stool made with glass feet. Another mode of insulating is to suspend a substance by silk threads. But such insulators must be dry; since they begin to conduct as soon as they grow damp, and conduct well, as in the experiment above described, when wet. Again, electrical experiments are very apt to fail in damp weather, because the moisture both carries off electricity directly, and by being deposited on the glass supports destroys the insulation.

To diminish this inconvenience it is usual to keep the insulators warm, and to coat them with a varnish made by dissolving the resin called shell-lac in alcohol, this resinous matter being much less prone to attract moisture from the air than glass. The same principles account for an error once prevalent that a

metal cannot be excited by friction: if held in the hand, indeed, it exhibits no sign of excitement when rubbed, because the electricity is carried off as soon as excited; but if, while carefully insulated, it is rubbed with a dry cat's fur, excitement readily ensues.

On comparing the electric properties manifested by glass and sealing-wax when both are rubbed by a woollen or silk cloth, they will be found essentially different; hence it is inferred that there are two kinds or states of electricity, one termed *vitreous*, because developed on glass, and the other *resinous* electricity, from being first noticed on resinous substances. These two kinds of electricity, one or other of which is possessed by every electrified substance, are also termed *positive* and *negative*, the terms *vitreous* and *positive* being used synonymously, as are *resinous* and *negative*: they are also denoted by the signs + and —. If two electrified substances are both positive or +, or both negative or —, they are invariably disposed to recede from each other, that is, to exhibit electric repulsion; but if one be +, and the other —, their mutual action is as constantly attractive. The end of a silk thread, after contact with an electrified stick of sealing-wax, is repelled by the wax, because both are —; but a dry warm wine-glass, if rubbed with cloth or silk, will be +, and if then presented to the thread, attraction will ensue. A silk thread in a *known* electric state, thus indicates the kind of electricity possessed by other substances: a convenient mode of doing this, is to draw a thread of white silk rapidly through a fold of coarse brown paper previously warmed, by which means its whole length will be rendered +.

When two substances are rubbed together so as to electrify one of them, the other, if in a state to retain electricity, will be excited also, one being always —, and the other +. It is easy to be satisfied of this by very simple experiments. Rub a stick of sealing-wax on warm coarse brown paper, and the paper will be found to repel a positively excited thread of silk, while the wax will attract it; if a warm wine-glass be rubbed on the brown paper, the glass will be +, as shown by its repelling the + thread, while the same thread will be attracted by the — paper; friction of sealing-wax on a silk riband renders the wax — and the riband +, but with glass the riband is —. If two silk ribands, one white and the other black, be made quite warm, placed in contact, and then drawn quickly through the closed fingers, they will be found on separation to be highly attractive to each other, the white being +, and the black —. The back of a cat is + to all substances with which it has been tried, and smooth glass is + to all except the back of a cat. Sealing-wax is — to all the substances just enumerated, but becomes + by friction with most of the metals. The reader will perceive from these facts that the same substance may acquire both kinds of electricity, becoming + by friction with one body, and — with another.

THEORIES OF ELECTRICITY.

The nature of electricity, like that of heat, is at present involved in obscurity. Both these principles, if really material, are so light, subtile, and diffusive, that it has hitherto been found impossible to recognise in them the ordinary characteristics of matter; and therefore electric phenomena may be referred, not to the agency of a specific substance, but to some property or state of common matter, just as sound and light are produced by a vibrating medium. But the effects of electricity are so similar to those of a mechanical agent—it appears so distinctly

to emanate from substances which contain it in excess, and rends asunder all obstacles in its course so exactly like a body in rapid motion, that the impression of its existence as a distinct material substance *sui generis* forces itself irresistibly on the mind. All nations, accordingly, have spontaneously concurred in regarding electricity as a material principle; and scientific men give a preference to the same view, because it offers an easy explanation of phenomena, and suggests a natural language easily intelligible to all.

Theory of two Electric Fluids.—This theory, the fundamental facts of which were supplied partly by Dufay, and partly by Symmer, is founded on the assumed existence of two electric fluids, which Dufay distinguished by the terms *vitreous* and *resinous* electricity. In order to account for electric phenomena by this supposition, the two fluids are assumed to possess the following properties:—They are both equally subtile and elastic, universally diffused and therefore present in all bodies, possessed of the most perfect fluidity, each highly repulsive to its own particles, and as highly attractive to those of the opposite kind, these attractive and repulsive forces being exactly equal at the same distance, and both varying inversely as the square of the distance varies. Electric quiescence is ascribed to these fluids being combined and neutralized with each other; and electric excitation is the consequence of either fluid being in excess. Their combination is destroyed by several causes, of which friction is one.

This theory, as commonly stated, takes little or no cognizance of any attraction between the electric fluids and other material substances. But it would be against all analogy to suppose no such influence to exist; and indeed the supposition of an attractive force acting at insensible distances seems necessary to account for the impediment caused by non-conductors to the free movement of the electric fluids.

Theory of a single Fluid.—The celebrated American philosopher, Franklin, proposed a different theory, founded on the supposition of a single electric fluid, the particles of which are conceived to repel each other with a force diminishing as the squares of the distance, and to be attracted by matter in general according to the same law. Material substance in its unelectric state is regarded as a compound of electricity and matter, saturated and neutralized with each other. It is also an assumption, shown to be necessary by Æpinus and Cavendish, that ponderable bodies repel each other with the same force and according to the same law as the particles of electricity. From the nature of these postulates it will be easy to anticipate their application. Unelectric bodies are such as have their natural quantity of electricity, which precisely suffices to saturate and neutralize the matter of which they consist. They are then electrically indifferent; because the repulsion exerted between the electricity and matter of contiguous bodies is exactly counteracted by the attraction of the electric fluid in each for the matter of the other. Electrical excitement is occasioned either by increase or diminution of the natural quantity of electricity. These opposite states are denoted by the algebraic terms *positive* and *negative*; the former corresponding to the vitreous, the latter to the resinous electricity of Dufay.

To the theory of Franklin it is usually objected that it involves an assumption at variance with the laws of gravitation, namely, that of matter being repulsive to itself; but this objection is unfounded, as the laws of gravitation have been investigated for matter only when in its ordinary state, and probably do not apply in cases of electric excitement. The researches of Mossotti on the forces which regulate the internal constitution of bodies amply justify this conclusion.

Adopting with Franklin a single electric fluid, he has shown that gravitation is perfectly consistent with the supposition that the molecules of matter are repulsive to each other. He has supported this opinion by a mathematical investigation of the conditions of equilibrium both for the molecules of matter and for the electric fluid. The results at which he arrived show that two molecules of matter surrounded by their electric atmospheres, are mutually attractive when separated by a sensible distance;—that the attraction increases on the approach of the atoms up to a certain point, where the attractive force attains its maximum, and beyond which the molecules are mutually repulsive. In this manner, gravitation, cohesion, and the resistance of matter to compression, are attributed to the same forces. These views certainly afford a happy explanation of the molecular mechanism; but as they have not yet been sufficiently tested, I shall retain the theory of the two electricities, which was adopted in former editions, substituting however, agreeably to present usages, the terms positive and negative, for vitreous and resinous electricity.

CAUSES OF ELECTRIC EXCITEMENT.

Friction.—This cause of electric excitement having been already mentioned, it here only remains to state the usual modes of developing electricity by friction. A supply of negative electricity is easily obtained by rubbing a stick of sealing-wax, or a glass tube covered with sealing-wax, with silk or woollen cloth; and positive electricity is freely developed when a dry glass tube is rubbed with silk, brown paper, or flannel, the surface of which is covered with a little amalgam. But for obtaining an abundant supply of electricity it is necessary to employ an electrical machine, which is a mechanical contrivance for exposing a large surface of glass to continuous fraction. As now constructed, it is formed either with a cylinder or plate of glass which is made to revolve upon an axis, and pressed during rotation by cushions or rubbers made of leather stuffed with flannel, and covered usually with silk. On the rubber is spread an amalgam of tin and zinc, rendered adhesive by admixture with a small quantity of lard or tallow. To prepare the amalgam, melt in a Hessian crucible one ounce of tin and three of zinc, then add two ounces of mercury heated to near its boiling point, stir briskly with a stick for a few minutes, and pour the mixture on a clean dry stone: when cold, pulverize and sift, and preserve the fine powder in a well-corked dry phial. Another essential part of the machine is the *prime conductor*, which is an insulated conductor, commonly made of brass, placed in such immediate proximity to the revolving glass, that the electric state of the one is instantly imparted to the other.

The electricity developed by the electrical machine is due partly to friction, which disunites the combined electric fluids of the glass and rubber, but principally to the oxidation of the amalgam. The positive fluid accumulates in the glass and passes from it to the prime conductor, while the negative fluid accumulates in the rubber, and its conductor. But to keep up the supply of electricity, the rubber must be connected with the ground, so that its — fluid may escape; or if we wish to obtain — electricity from the rubber, the prime conductor should communicate with the ground, that its + fluid may escape.

Change of temperature.—The operation of this cause of electric excitement was first noticed in certain minerals, such as tourmalin and boracite, not possessed of that symmetric arrangement of parts commonly observed in crystals,

and which are electrified by the application of heat. But a far more general principle was detected by Seebeck, who found that the electric equilibrium is disturbed in certain metallic rods or wires when one extremity has a different temperature from that of the other, whether the difference be effected by the application of heat or cold. This observation has been since shown by Cumming to be true of all metals (An. of Phil. N. S. v. 427); and the same object has been examined by Prideaux (Phil. Mag. and An. iii.). The experiment is usually made by heating or cooling the point of junction of two metallic wires, which are soldered together; but Becquerel has proved that the contact of different metals is not essential. (An. de Ch. et Ph. xli. 353.)

Chemical action.—Another, and perhaps by far the most fertile, source of electricity is chemical action. This was strongly denied by Davy, in his Bakerian lecture for 1826; but the experiments of Becquerel, De la Rive, and Pouillet, afford decisive proof that chemical union and decomposition are both attended with electrical excitement. (An. de Ch. et Ph. vol. 35, 36, 37, 38, and 39).

Contact.—Another reputed source of electricity is contact of different substances, especially of metals; a source originally suggested by Volta, who founded on it a theory of galvanism. Volta stated that clean plates of zinc and copper, insulated by glass handles, became electric by being made to touch each other, and then separated. When the zinc alone was insulated, it became +, and when the copper alone was insulated, it became —. But the quantity of electricity thus developed is confessedly so small as to require the most delicate instruments to detect it; and the experiments of De la Rive (An. de Ch. et Ph. xxxix. 297; lxii. 147,) and those of Parrot (ibid. xlvi. 361), have shown, in a manner apparently decisive, that the electricity developed in such experiments is derived either from a slight degree of chemical action, or from friction; and that contact alone, if unattended by chemical action or by friction, produces not the least excitement of electricity. I apprehend, therefore, that the facts adduced by Volta must be rejected.

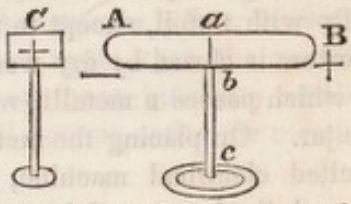
Changes of form.—The changes of form caused in a substance by variations of temperature, such as liquefaction and solidification, the formation and condensation of vapour, constitute another reputed source of electricity. Pouillet, however, questions this opinion; and maintains, that in every case where change of form produces electric excitement, there is also chemical action. Thus, when water evaporates, the electricity is due to the separation of the water from its saline impregnations, or to its action on the containing vessel; and pure water, evaporated in platinum vessels, produces no excitement. He ascribes to the separation of water from saline matter, constantly going on at the surface of the earth, and to the chemical changes produced in the growth of vegetables, the developement of a great part of the atmospheric electricity. My own experiments have given similar results; but Harris, with an apparatus of great delicacy, has detected electricity during the evaporation of pure water in plantinum vessels, although in very small quantity.

[Recent observations have shown that currents of steam, under certain conditions, may be successfully employed for the generation of large quantities of electricity. The accidental discovery by a workman in New Castle of the electricity of a steam boiler, led to a series of experiments, by Armstrong and others, and subsequently by Faraday; showing that when the steam boiler is insulated and the steam allowed to escape by apertures, properly constructed, the boiler

and its appendages become strongly charged with electricity. Faraday found that while the boiler was thus rendered negative, the issuing steam was in the opposite, or positive state, and he inferred that the whole phenomena arose from the rubbing of the condensed water against the sides of the tube from which the steam was issuing, and was thus due to a species of friction, rather than to the passage of the water from the liquid to the aëriform state. This discovery has given rise to a new and very powerful apparatus for accumulating electricity, called the *hydro-electric* machine. It consists of a boiler supported on glass pillars, and furnished with a long range of jets, mounted at the end with wood. Steam of high pressure is used, and the electricity of the steam is conducted into the ground by a row of metallic points placed in front of the jets. From a machine of this kind sparks have been obtained twenty inches long, and the electric supply is so abundant as to charge a battery more rapidly than the most powerful machine of the ordinary construction.]

Proximity to an electrified body.—It is a direct consequence of the attractive and repulsive powers ascribed to the electric fluids, that an unelectrified conductor must be excited by the vicinity of an electrified body. Let AB, fig. 1, be an unexcited conductor, supported on an insulating glass rod *bc;* and let C, containing free positive electricity, and similarly insulated, be placed near it on the side A. The free positive electricity on C will both repel the positive fluid of AB, and attract its negative fluid, and the result of these concurring forces is instantly to decompose a portion of the combined electricities of AB, the free negative fluid approaching as close as possible to C, and the positive fluid receding from it. The relative position of these fluids is indicated in the figure by the signs + and —, the former denoting positive and the latter negative electricity. The opposite ends of the conductor AB are thus oppositely electrified, and in an equal degree: the excitement is found, as would be anticipated, to be greatest at the extremities, and to diminish gradually towards the middle line *ab*, which is neutral. The quantity of electricity thus set free depends on the extent to which C is excited, and on its distance from AB. If now C be suddenly withdrawn, the opposite fluids at A and B coalesce, and the equilibrium of AB is restored. But so long as C retains its position, A will be negative, even were it uninsulated. The only effect of communication with the ground is to neutralize the positive fluid at B by supplying to it negative electricity from the earth: if after having effected this by touching the cylinder for an instant with the finger, C be withdrawn, AB is left with an excess of the negative fluid.—The electricity thus developed by the contiguity of an electrified body is said to be *induced*, or to be excited by *induction.*

Fig. 1.



The student should reflect carefully on these inferences from the theory of electricity, since the applications of such knowledge are numerous. A few of these may now be enumerated:—

1. An electrified body attracts light objects near it, because it induces in them a state opposite to itself. The attraction is most lively when the light object is a conductor, and in contact with the ground, since it then more completely assumes an electric state opposed to that of the inducing body. A non-conductor is very imperfectly electrified by induction, because the electric fluids cannot quit each other from inability to move through the non-conductor.

2. If a stick of sealing-wax, strongly — be presented to a thread or pith ball

which is also negatively, but feebly, excited, repulsion will ensue at a considerable distance, followed by attraction when the distance is small. This attraction is due to the strongly excited wax acting by induction on the feebly — thread, thereby causing it to have an excess of + electricity.

3. The + electricity collected on the prime conductor of an electrical machine is by some ascribed, not to a transfer of that fluid from the glass to the prime conductor, but to a part of the combined electricities of the prime conductor being separated by induction, and the — fluid being imparted to the + glass. The same view is applicable to any system of conductors in contact with the prime conductor, as also to conductors connected with the rubber. It is difficult to say which explanation is the more correct, or whether both may not be true.

4. On moving the hand towards the prime conductor of an excited electrical machine, the hand becomes — by induction, and the spark ultimately obtained restores the equilibrium. In like manner a negatively electrified cloud renders + a contiguous tree or tower, and then a stroke of lightning follows as a consequence of attraction between the two accumulated fluids.

5. The action of the *Leyden jar* depends on the principle of induced electricity. A glass jar or bottle with a wide mouth is coated externally and internally with tinfoil, except to within three or four inches of its summit; and its aperture is closed by dry wood or some imperfect conductor, through the centre of which passes a metallic rod communicating with the tinfoil on the inside of the jar. On placing the metallic rod in contact with the prime conductor of an excited electrical machine, while the outer coating communicates with the ground, the interior of the jar acquires a charge of + electricity, and the exterior becomes as strongly —. The exterior may be handled without destroying the charge, provided no communication be at the same time made with the interior. But when a conductor communicates with both surfaces at the same instant, the two fluids rush together with violence, and the equilibrium is restored. Whether in this and similar cases the two fluids coalesce entirely on the intermediate conductor, or whether each from its velocity may not in part pass the other, and be projected to the opposite surface, is a question on which electricians are not agreed.

The Leyden jar affords the means of passing through bodies a large quantity of electricity. For not only may jars of any required size be employed, but it is easy so to arrange any number of such jars, that they shall all be charged and discharged at the same time, constituting what is termed an *electrical battery*. The arrangement is made by placing a number of Leyden jars in a box lined with tinfoil, by which means their outer surfaces have free metallic communication with each other, and connecting their inner surfaces by wires.

6. The principle of induced electricity was ingeniously applied by Volta in the construction of the *Condenser*. This apparatus, fig. 2, consists of two brass plates, A and B, supported on a common stand D. One of the plates B is attached to the stand by means of a hinge C, so that, though represented upright, it may be placed horizontally, and be thus withdrawn from the vicinity of the plate A, the support of which is made of glass. On electrifying the insulated plate positively, the plate B, expressly placed close to A, is rendered — by induction; and, as happens in the Leyden jar, the excitement of B will be proportional to that of A. The — charge of B tends to preserve the + charge of A, which may

Fig. 2.



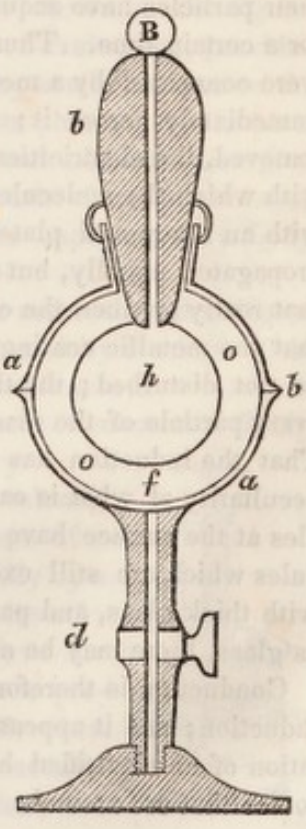
consequently receive still more electricity by contact with any + surface, without losing what it had previously acquired. Thus is electricity accumulated or *condensed* on A; so that a substance too feebly excited to produce any appreciable effects of itself, may by repeated contact with the insulated plate of a condenser communicate a charge of considerable intensity. The effect of the accumulation is made apparent by withdrawing B, and bringing A in contact with a delicate electrometer. The condenser is much employed in experiments of delicacy, and the plate A is often permanently fixed on the gold leaf electrometer.

7. The *Electrophorus* is another contrivance of Volta's, which acts by induced electricity. It consists essentially of two parts; one being a flat cake of resin, made by pouring melted resin into a shallow plate or circular dish of tinned iron, and the other a disk of brass, of rather smaller diameter than the resin, supplied with a glass handle. The surface of the resin is negatively excited by friction or flapping with silk or flannel, and the brass disk is laid upon it. The resin being a non-conductor retains its own electricity in spite of the super-imposed brass, and decomposes the combined electricities of the latter, causing its under surface to be +, and its upper —. On touching the brass with the finger, its upper surface is neutralized; and on then withdrawing the brass plate, it is found to have an excess of + electricity. On replacing the brass as before, the resin, having lost none of its electricity in the process, acts again upon the metallic disk as on the first occasion, and will continue so to act for an indefinite number of times. Kept in a dry place, the electrophorus will keep in action for months.

INDUCTION BY CONTIGUOUS PARTICLES.

That the excitation by induction of a body at a distance is effected from particle to particle of the interposed substance, is beautifully shown in the results obtained by Faraday, concerning the influence of the nature of the medium on the amount of inductive charge transmitted. The instrument, Fig. 3, which he has termed an *inductometer*, consists of a hollow sphere of brass *a a b*, and a sphere of smaller size, *h*, also of brass, which is placed exactly concentric with it. The interval between these, *o o*, may be occupied by any substance, as air, or glass, or sulphur, and then the central sphere being insulated from the outer by the shell-lac column *b*, and having been excited from the machine, through the ball and wire B, the outer one is uninsulated, and the whole becomes a Leyden jar, in which the material may be varied at the will of the experimenter. By means of the tube and stopcock *f d*, the air in *o o*, may be removed and any other gas substituted for it. The outer sphere opens at *b* in two, so that melted sulphur or shell-lac, may be poured in to form the inductive medium.

Fig. 3.

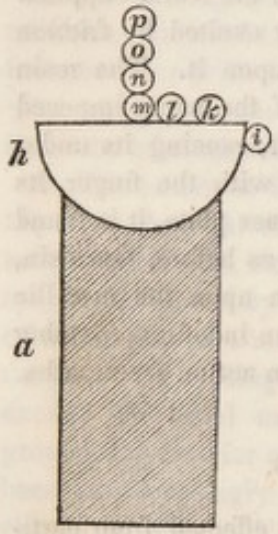


When the internal sphere is excited always to the same degree, the charge of the external coating should be the same, no matter what might be the nature of the intervening substance, if the action took place simply at a distance after the manner of gravitation. But this is not the case. With the same internal charge, the excitation of the external sphere was found to be, that

with air being 100, with shell-lac, 150, with flint-glass, 176, and with sulphur, 224. In these cases, therefore, the molecular excitation was transmitted in proportion to these numbers, which express, therefore, the degree of excitation, that a common amount of inductive influence is able to produce in masses of these bodies. All gases, no matter how different in chemical properties and constitution, even though the temperature and pressure do not remain the same, possessed the same specific inductive capacity as air.

This principle is further shown in an interesting manner by the fact, that the induction is not exercised only in the straight line connecting the solid inducing and induced bodies, but that at every intervening point there is a lateral action exercised by the interposed molecules of air which may be themselves considered centres of inductive force. Thus, Fig. 4, if a cylinder *a* of shell-lac be excited by friction and a brass hemisphere *h*, placed on top of it, the intensity of the induced electricity will be found to depend not merely on the distance from the excited source and the nature of the interposed material, but to be more energetic in certain positions in the air, as when the carrier ball of Coulomb's torsion electrometer was placed at *o*, than when it was lower or higher at *n* or *p*.

Fig. 4.



Faraday has been led by his experiments to conclude, that the difference between conducting and non-conducting bodies is, that the former assume with exceeding rapidity, under an inductive influence, this condition of molecular excitation, and hence appear to allow the electricity to pass, actually and instantly, through their substance, whereas in reality it is only that the separation and recomposition of the electricities of the chain of molecules has been so accomplished. They lose also this condition as soon as the exciting cause has been removed, whereas, non-conductors, when their particles have acquired electrical excitation, remain in that state of tension for a certain time. Thus, if the internal and external coatings of a Leyden jar were connected by a metallic wire, the inductive action should be propagated immediately across it; but the instant that the source of the excitation was removed, the electricities of the two coatings should recombine, from the facility with which the molecules of the wire could assume the inverse condition. But with an interposed plate of glass the result is different, the inductive action is propagated equally, but more slowly; and that it is the particles of the glass that really produce the charge by their excitation, is demonstrated by the fact, that the metallic coatings may be removed, and yet the accumulated electricities be not disturbed; the tin-foil serving, only, to discharge at the same moment every particle of the glass, as if a wire had been individually applied to each. That the induction has acted on the substance of the glass, explains also the peculiarity of what is called the secondary or residual charge. When the particles at the surface have been discharged, they are acted on by the deeper molecules which are still excited, and hence acquire a second inductive charge, and with thick glass, and particularly with bodies which do not insulate quite so well as glass, there may be even a third or a fourth charge of this kind.

Conduction is therefore only the highest, most intense, and most rapid form of induction; and it appears from Faraday's investigations, that the permanent excitation of an electrified body has its origin also in the inductive influence of the bodies that are around. (Elements of Chem. by R. Kane.)

ELECTROSCOPES AND ELECTROMETERS.

It is very important, in experiments on electricity, to possess easy methods of discovering when a substance is electrified, of ascertaining its *intensity* or the degree to which it is excited, and distinguishing the kind of excitement. The means for effecting these objects are founded on electrical attraction and repulsion, and the instruments employed for the purpose are called *Electroscopes* and *Electrometers;* the latter denoting the intensity of electricity,—the former merely indicating excitement, and the electrical state by which it is produced. The term electrometer, however, is often indiscriminately applied to all such instruments, since the methods of ascertaining the kind of excitement give at the same time some idea of its intensity.

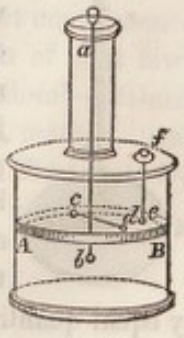
Gold Leaf Electrometer.—Several simple electroscopic methods have already been indicated (page 69). Small balls made of the pith of elder are used for the same purpose. A single pith ball, suspended by a cotton thread, is attracted by a feebly electrified substance. Also, when two pith balls are suspended from the same point by cotton threads of equal length, and an electrified body is placed near them, the two balls are thrown by induction into the same electric state, and diverge. The gold leaf electrometer, figure 5, invented by Bennett, acts upon the same principle, but is far more delicate. It consists of a glass cylinder cemented below upon a brass plate CD, and covered above by a brass plate AB, pierced in its centre for the insertion of a glass tube *bc*, the top of which is closed by a brass plate *a*: into this plate is screwed a thick brass wire, which passes through the glass tube, and from the lower end *d* of which two slips of gold leaf are suspended. These different parts are put together while quite dry, all the joinings are secured by wax cement, and the glass is covered by lac varnish. The effect of these arrangements is to insulate the plate *a* with its wire and gold leaves, while the latter are secure against being moved by currents of air. The approach of any electrified body, even though feebly excited, to the plate *a*, is immediately detected by the divergence of the leaves, as shown in the figure. The instrument is equally useful in indicating the kind of excitement, provided the plate and leaves be permanently electrified, which may easily be done on the same principle as in charging the metallic disk of an electrophorus. If the plate be thus charged with + electricity, the leaves diverge, and continue divergent for some time if the air be dry. In this state, the approach of a body charged with + electricity increases the divergence; while the approach of a body charged with — electricity has a contrary effect.

Fig. 5.



Quadrant Electrometer.—An instrument much used for estimating the degree or intensity of electricity is the *quadrant electrometer*, invented by Henley. This instrument, though convenient for experiments of illustration, is not suited to those of research, wherein the object is to examine the effects of substances feebly electrified, and ascertain their relative forces with accuracy.

Fig. 6.



Torsion Electrometer.—This instrument, invented by Coulomb, is peculiarly fitted for scientific investigation. It consists of a small needle of gum-lac *c d*, fig. 6, suspended horizontally by a silk thread as spun by the silkworm, or by a fine silver wire *a b;* on the point of the needle is fixed a small gilt ball made of the pith of elder; and the whole is covered with a glass case to protect it from moisture and currents of air. The pith ball, when the apparatus is at rest, is in contact with the knob *e* of a metallic conductor *fe*, which passes through a hole in the glass case, and

is secured in its place by cement; but when an excited body is made to touch the conductor, the pith ball in contact with it is similarly excited, and recedes from it to an extent proportional to the degree of excitement. The needle consequently describes the arc of a circle, which is measured on the graduated arc A B, and in its revolution twists the supporting thread more or less according to the length of the arc described. The torsion thus occasioned calls into play the elasticity of the thread,—a feeble but constant force, which opposes the movement of the needle, measures by the extent to which it is overcome by the repulsive force exerted, and brings back the needle to its original position as soon as the electric equilibrium is restored. It has been proved that the force which causes the torsion is exactly proportional to the arc described by the needle.

Balance Electrometer.—Harris has made a happy application of the common balance and weights to estimate the mutual attraction of oppositely electrified surfaces. The apparatus, figure 4, consists of a brass beam B B′, supported by a conductor C D standing on a wooden frame A A′; *d* is a scale for holding weights, and E its support; *a*, *b*, are gilt cones made of light wood, *a* being suspended by a silver wire from B′, and *b* insulated by the glass support A′ *d*′. The instrument is prepared for use by placing *a* and *d* in exact equipoise; the cone *a* is suspended so that its base shall be opposite and parallel to the base of the cone *b*, as may be done by means of three adjusting screws in the frame A A′; and *b* is raised by help of a graduated brass slide *c*, until the bases of the cones are just in contact. The cone *b* is then depressed to any desired distance, which may be varied at will during an experiment, and it is connected with the inner coating of a Leyden jar, the outer coating of which communicates with the frame A A′, and along C D B′ with the cone *a*: these cones may thus be made parts of a charged Leyden jar, and be oppositely excited, as indicated by the signs + and —. The attractive forces exerted between their bases tend to draw down the cone *a* into contact with *b*, discharging the jar; but before it can do so, it has to overcome the weight which may be in the scale *d*. By this ingenious contrivance any number of attractive forces are estimated by a common standard, namely, the number of grains which each is able to raise.

Fig. 7.

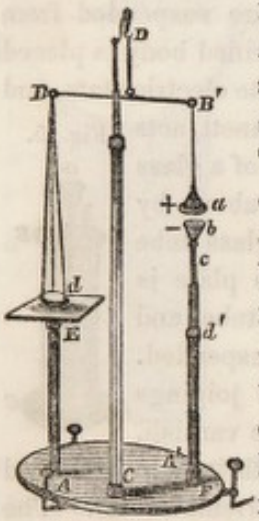
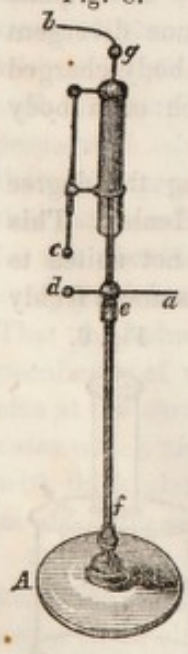


Fig. 8.



Unit Jar.—This is another contrivance by Harris, and is a most important addition to our stock of electrical apparatus. It is formed of a small inverted Leyden jar, figure 5, supported and insulated by a slender glass rod *ef*, which is covered with lac varnish, and fixed into a wooden frame A. The inner coating of this jar is in metallic contact with a brass ball *d* and a wire *a*, which wire communicates with the prime conductor of an active electrical machine; whereas the brass ball *c* and wire *b* are connected with its outer coating. If the wire *b* be held in the hand, or otherwise communicate with the ground, the electrical machine being in action, the jar is charged in the usual manner, and is discharged by a spark passing between the two brass balls *c* and *d*. The interval may be increased or diminished by causing one of the balls to be moveable by means of a slide or screw. It will be readily conceived that successive sparks through the same interval must be caused by equal quantities of electricity; and experiment shows this to be the case, pro-

vided the apparatus is clean and dry, and the charges are taken nearly at the same time, that is, while the air in relation to temperature, pressure, and moisture, may be considered constant. On taking six successive sparks we employ six times as much electricity as for one charge, and three times as much as for two charges, the quantity of electricity being proportional to the number of charges. It is on this account Harris introduced the term unit jar. It is used for charging Leyden jars or batteries with known proportions of electricity.

Electric Intensity.—Before concluding this account of electrometers, it will be useful to refer to the kind of information which they supply. From their mode of action, it is plain that they indicate the *degree* of electric excitement, the remoteness from the unexcited state, a condition expressed by the terms *tension* and *intensity*. If two insulated brass disks of equal size be supplied with equal quantities of free electricity, they will affect an electrometer equally, and therefore their intensity or tension is equal; but if one of the disks be larger than the other, the smaller will have the highest tension. In fact, one square inch of the smaller disk will possess more free electricity than the larger, and that is precisely the condition which constitutes differences of intensity. Of any number of electrified substances, that will have the highest intensity which has the most free electric fluid on unity of surface.

LAWS OF ELECTRICAL ACCUMULATION.

1. The quantity of free electricity which an insulated conductor is capable of receiving is independent of its quantity of matter. Thus, two brass spheres of the same size, one solid and the other hollow, will take equal quantities of electricity, and possess equal intensities. The cause of this is referable to the second law.

2. The free electricity of an insulated conductor is always accumulated on its surface, where it forms a layer or stratum enveloping the substance on every side, and therefore possessed of the same figure. The cause of free electricity being disposed upon the surface of conductors is ascribed to the mutual repulsion of its particles, which gives them a tendency to recede as far as possible from each other, and to be arrested at the surface solely by some counteracting force, such as the interposition of an imperfect conductor.

3. The mode in which electricity is distributed over the surface of a conductor is dependent on its figure. On a sphere it forms an uniform stratum of equal thickness all around, that is, each part of the surface has the same quantity of electricity as any other part of equal size. But on an ellipsoid the stratum is thickest at the extremities of the longer axis, and the accumulation at those parts is greater and greater as the length of that axis becomes more and more predominant. In all conductors which are much longer than broad, as in a narrow metallic bar, as also in those which have elongated pointed terminations, the principal accumulation is at the ends and projecting points.*

The unequal accumulation of electricity on conductors is a direct consequence of the law of electric repulsion; and Poisson, assuming the truth of that law, has arrived by calculation at the very same conclusions which Coulomb obtained by experiment. Those who are prepared to follow such very high mathematical inquiries are referred to Poisson's original Essay, to the article on Electricity by Whewell, in the Encyclopedia Metropolitana, and to a late work on Electricity by Murphy.

* This has been established experimentally by Coulomb.

4. The electric fluid accumulated at the surface of conductors tends to escape by the repulsion of its particles. Its pressure against the air, or its effort to escape, at any part, is considered proportional to the square of the quantity; so that if the electric accumulations at four different parts of an excited conductor are as 1, 2, 3, and 4, the pressure against the air at those parts will be as 1, 4, 9, and 16. Hence electricity passes off with great rapidity from the ends or projecting points of conductors, a result quite conformable to experience. But the equilibrium of an excited conductor is perhaps never entirely restored by the direct diffusion of its excess due to its own repulsion; for the conductor necessarily tends to induce a state opposite to itself in contiguous conductors and in the circumambient air, and then the attraction of oppositely electrified surfaces is called into play.

5. Coulomb proved experimentally, by aid of his torsion electrometer, that the repulsion of two similarly electrified bodies varies inversely as the square of their distances.

6. The attraction of two oppositely electrified bodies varies inversely as the square of the distance between them. Coulomb, who verified this law by experiment, also showed that the attractive force, the distance being constant, varies by the same law as that for repulsion just stated.

Harris has given a beautiful demonstration of these laws by means of his balance electrometer and unit jar (page 78), the cones *a b*, of figure 4, being connected respectively with the outer and inner coatings of a large Leyden jar. On giving to it a constant charge by means of the unit jar, and varying the distance, the weights raised, or the attractive force, were found to vary inversely as the square of the distance between the cones. On preserving the distance constant, giving a charge capable of raising one grain, and then successively doubling, trebling, and quadrupling the quantity first given to the inner coating, the weights raised were 4, 9, and 16 grains.

7. It may be inferred from the law No. 6, that when, in two oppositely excited bodies, the whole quantity of electricity and the distance vary together and at the same rate, the attractive force will be unchanged. This has been fully proved by Harris. In fact, doubling the electricity on both cones, is to quadruple the attractive force between them; and doubling the distance diminishes the force by four times: the force is thus diminished by one cause as much as it is increased by the other, and therefore continues unchanged.

8. Having ascertained the nature of the influence exerted by the atmosphere over the striking distance of a charged Leyden jar, that is, the interval through which the electricity will pass, so as to discharge it, by including the balls connected with its outer and inner coating within glass vessels susceptible of exhaustion. He then found that the resistance to the passage of a charge varies as the square of the density of the air. Agreeably to the same law, the striking distance, when the charge is constant, varies inversely as the density of the air: a charge which strikes through one inch of air when the barometer is at 30 inches, will pass through two inches in air so rarefied as to support only 15 inches of mercury, and through four inches when the mercurial column is 7·5 inches. Hence in a perfect vacuum a Leyden jar ought to discharge itself through any interval; and in the higher parts of the atmosphere, where the air is much rarefied, two oppositely-excited clouds will neutralize each other, though separated by very great distances.

It is not apparent from the preceding remarks, whether the striking distance is

influenced by change of the density or the elasticity of the confined air, since in rarefying air by the air-pump, the rarefaction increases, and the elasticity decreases at the same rate. Harris has shown, contrary to what one might anticipate, that the influential condition is density, and not elasticity. For on rarefying air by heat so as to preserve its original elasticity, the striking distance was exactly the same as in cold air rarefied to the same degree by the air-pump; and in air first rarefied by the air-pump, and then heated until it had recovered its original elasticity, its volume and density being kept the same, the varied elasticity had no influence on the charge required to pass through a constant distance. From these and similar experiments Harris infers that the remarkable conducting power known to be possessed by hot air is due to its rarity alone.—Though I have not had occasion to repeat these experiments on hot air, I have entire confidence in their accuracy; inasmuch as, not to mention the known skill and exactness of Harris, I find that the striking distance for the same charge is greater in air than in carbonic acid gas, and greater in hydrogen gas than in air, the elasticities being equal.

9. The continuance of an excited charge on an insulated conductor is commonly ascribed to the pressure of the air. An opposite opinion, however, has been maintained. Morgan (Phil. Trans. 1785), published some experiments to prove that a space entirely free from air, such as a Torricellian vacuum, is a non-conductor of electricity; and Cavallo (Treatise on Electricity), showed that exhaustion may be carried very far within the bell-jar of an air-pump without an electrified body placed under it losing its charge. On repeating these experiments, at the request of Harris, I obtained similar results. These phenomena appear to indicate the existence of an adhesive force between the particles of electricity and the surface of bodies, which causes an obstacle to their escape.

10. Some elegant and most ingenious experiments have been made by Wheatstone to determine the velocity of electricity (Phil. Trans. 1834). His principal conclusions are the following:—

1. The velocity of electricity along a copper wire exceeds that of light through the planetary space.

2. The disturbance of the electric equilibrium in a wire communicating at its extremities with the two coatings of a charged jar, travels with equal velocity from the two ends of the wire, and occurs latest in the middle of the circuit.

3. The light of electricity of high tension has a less duration in passing as a spark than the millionth part of a second.

HISTORICAL NOTICE.

The science of electricity is of modern origin. The knowledge of the ancients was confined to the fact that amber and the *lyncurium* (supposed to be tormalin) acquired the property of attracting light bodies by friction. It was not known that other bodies may be similarly excited until the commencement of the 17th century, when Gilbert of Colchester detected the same property in a variety of other substances, and thereby laid the foundation of the science of electricity. A few additional facts were noticed during the same century by Boyle, Otto de Guericke, and Wall, and in 1709 Hawkesbee published an account of many curious electrical experiments; but no material progress was made until Stephen Grey (Phil. Trans. 1729 to 1733) drew the distinction between conductors and

non-conductors of electricity, and illustrated it by new and striking experiments. Soon after, Dufay in France distinguished between the two kinds of electricity; and in 1759 (Phil. Trans. li. 340) Symmer added the important fact that friction developes both kinds of electricity at the same time, an observation which led to the theory of two electric fluids as now understood. These discoveries, added to the confirmation of Franklin's opinion as to the identity of the cause of lightning and electricity, fixed the attention of scientific men upon the new study, and soon acquired for it a high rank among the sciences.

For further details respecting its origin and early progress the reader may consult the history of electricity by Priestley.

SECTION IV.

GALVANISM.

The science of Galvanism owes its name and origin to the experiments on animal irritability made by Galvani, Professor of Anatomy at Bologna, in the year 1790. In the course of the investigation he discovered the fact, that muscular contractions are excited in the leg of a frog recently killed, when two metals, such as zinc and silver, one of which touches the crural nerve, and the other the muscles to which it is distributed, are brought into contact with one another. Galvani imagined that the phenomena are owing to electricity present in the muscles, and that the metals only serve the purpose of a conductor. He conceived that the animal electricity originates in the brain, is distributed to every part of the system, and resides particularly in the muscles. He was of opinion that the different parts of each muscular fibril are in opposite states of electrical excitement, like the two surfaces of a charged Leyden phial, and that contractions take place whenever the electric equilibrium is restored. This he supposed to be effected during life through the medium of the nerves, and to have been produced in his experiments by the intervention of metallic conductors.

The views of Galvani had several opponents, one of whom, the celebrated Volta, Professor of Natural Philosophy at Pavia, succeeded in pointing out their fallacy. Volta maintained that electric excitement is due solely to the metals, and that the muscular contractions are occasioned by the electricity thus developed passing along the nerves and muscles of the animal. To the experiments instituted by Volta we are indebted for the first voltaic apparatus, which has properly received the name of the *voltaic pile*; and to the same distinguished philosopher belongs the real merit of laying the foundation of the science of Galvanism (Phil. Trans. 1800).

The identity of the agent concerned in the phenomena of galvanism and of the common electrical machine, is now a matter of demonstration. Voltaic and common electricity are due to the same force, excited by different conditions, operating in general in a different manner and under different circumstances. The effects of the latter are caused by a comparatively small quantity of electri-

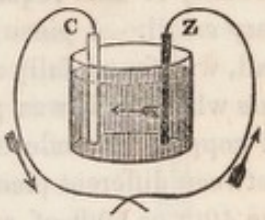
city brought into a state of insulation, in which state it exerts a high intensity, as evinced by its remarkable attractive and repulsive energies, and by its power to force a passage through obstructing media. In galvanism the electric agent is more intimately associated with other substances, is developed in large quantity, but never attains a high tension, and produces its peculiar effects while flowing along conductors in a continuous current.

VOLTAIC ARRANGEMENTS OR CIRCLES.

Arrangements for exciting galvanism are divided into simple and compound; the former being voltaic circles in their most elementary form, and the latter a collection of simple circles acting together; it will hence be proper to commence the description of them with the most simple.

Simple Voltaic Circles.—When a plate of zinc and a plate of copper are placed in a vessel of water, and the two metals are made to touch each other, either directly or by the intervention of a metallic wire, galvanism is excited. The action is, indeed, very feeble, and not to be detected by ordinary methods; but if a little sulphuric acid be added to the water, numerous globules of hydrogen gas will be evolved at the surface of the copper. This phenomenon continues uninterruptedly while metallic contact between the plates continues, in which state the circuit is said to be *closed;* but it ceases when the circuit is broken, that is, when metallic contact is interrupted. The hydrogen gas which arises from the copper plate results from water decomposed by the electric current, and its ceasing to appear indicates the moment when the current ceases. In this case the voltaic circle consists of zinc, copper, and interposed dilute acid; and the circle gives rise to a current only when the two metals are in contact. This arrangement is shown in figure 1, where metallic contact is readily made or broken by means of copper wires soldered to the plates. By employing a galvanometer (p. 94), it is found that a current of + electricity continually circulates in the closed circuit from the zinc through the liquid to the copper, and from the copper along the conducting wires to the zinc, as indicated by the arrows in the figure. A current of — electricity, agreeably to the theory of two electric fluids, ought to traverse the apparatus in a direction precisely reversed; but for the sake of simplicity I shall hereafter indicate the course of the + current only.

Fig. 1.



Two metals are not absolutely essential to the formation of a simple circle. A current is obtained from one metal and two liquids, provided the liquids are such that a stronger chemical action takes place on one side of the metal than on the other. Nay, a plate of metal, with two portions of the same liquid, but of different strengths, forms a simple circle; and even the same liquid, of but one strength, if one side of the metal be more rapidly acted on by it than the other, will produce a current. This may be effected, for example, by having one side rough, the other polished.

An interesting kind of simple voltaic circle is afforded by commercial zinc. This metal, as sold in the shops, contains traces of tin and lead, with rather more than one per cent. of iron, which is mechanically diffused through its substance: on immersion in dilute sulphuric acid, these small particles of iron and the adjacent zinc form numerous voltaic circles, transmitting their currents

through the acid which moistens them, and disengaging a large quantity of hydrogen gas. Pure distilled zinc is very slowly acted on by dilute sulphuric acid of sp. gr. ranging from 1·068 to 1·215; but if fused with about two per cent. or rather less, of iron filings, it is as readily dissolved as commercial zinc. Sturgeon has remarked that commercial zinc, with its surface amalgamated, which may be done by dipping a zinc plate into nitric acid diluted with two or three parts of water, and then rubbing it with mercury, resists the action of dilute acid fully as well as the purest zinc. This fact, of which Faraday in his late researches has made excellent use, appears due to the mercury bringing the surface of the zinc to a state of perfect uniformity, preventing those differences between one spot and another, which are essential to the production of minute currents; one part has the same tendency to combine with electricity as another, and cannot act as a discharger to it (Faraday).

While the current formed by the contact of two metals gives increased effect to the affinity of one of them for some element of the solution, the ability of the other metal to undergo the same change is proportionally diminished. Thus, when plates of zinc and copper touch each other in dilute acid, the zinc oxidizes more, and the copper less, rapidly than without contact. This principle was beautifully exemplified by the attempt of Davy to preserve the copper sheathing of ships. A sheet of copper immersed in sea-water, or a solution of chloride of sodium, in an open vessel, undergoes rapid corrosion; and a green powder commonly termed submuriate of copper, but which is really an oxy-chloride, is generated: atmospheric oxygen dissolved in sea-water unites both with copper and sodium, the latter yields its chlorine to another portion of copper, and the oxide and chloride of copper unite. But if the copper be in contact with zinc or some metal more electro-positive than itself, the zinc undergoes the same change as the copper did, and the latter is preserved. Davy found that the quantity of zinc required thus to form an efficient voltaic circle with copper was very small. A piece of zinc as large as a pea, or the head of a small round nail, was found fully adequate to preserve 40 or 50 square inches of copper; and this wherever it was placed, whether at the top, bottom, or middle of the sheet of copper, or under whatever form it was used. And when the connection between different pieces of copper was completed by wires, or thin filaments of the 40th or 50th of an inch in diameter, the effect was the same; every side, every surface, every particle of the copper remained bright, whilst the iron or the zinc was slowly corroded. Sheets of copper defended by 1-40th to 1-1000th part of their surface of zinc, malleable and cast iron, were exposed during many weeks to the flow of the tide in Portsmouth harbour, and their weight ascertained before and after the experiment. When the metallic protector was from 1-40th to 1-150th, there was no corrosion nor decay of the copper; with smaller quantities, such as 1-200th to 1-460th, the copper underwent a loss of weight which was greater in proportion as the protector was smaller; and as a proof of the universality of the principle, it was found that even 1·1000th part of cast iron saved a certain proportion of the copper (Phil. Trans. 1824).

Unhappily for the application of this principle in practice, it is found that unless a certain degree of corrosion takes place in the copper, its surface becomes foul from the adhesion of sea-weeds and shell-fish. The oxy-chloride of copper, formed when the sheathing is unprotected, is probably injurious to these plants and animals, and thus preserves the copper free from foreign bodies.

Simple voltaic circles may be formed of very various materials: but the com-

binations usually employed consist either of two perfect and one imperfect conductor of electricity, or of one perfect and two imperfect conductors. The substances included under the title of perfect conductors are metals and charcoal, and the imperfect conductors are water and aqueous solutions. It is essential to the operation of the first kind of circle, that the imperfect conductor act chemically on one of the metals; and in case of its attacking both, the action must be greater on one metal than on the other. It is also found generally, if not universally, that the metal most oxidized is positive with respect to the other, or bears to it the same relation as zinc to copper in figure 1. Davy, in his Bakerian lecture for 1826 (Phil. Trans.), to which the reader is referred, has given lists of different arrangements of both the kinds just mentioned.

Faraday has shown that the presence of water is not essential. A battery may be composed of other liquid compounds, such as a fused metallic chloride, iodide, or fluoride, provided it is decomposable by galvanism, and acts chemically on one metal of the circle more powerfully than on the other.

Metallic bodies are not essential to the production of galvanic phenomena. Combinations have been made with layers of charcoal and plumbago, of slices of muscle and brain, and beet-root and wood; but the force of these circles, though accumulated by the union of numerous pairs, is extremely feeble, and they are very rarely employed in practice.

Of the simple voltaic circles described by Davy, the only one used for ordinary purposes is that composed of a pair of zinc and copper plates excited by an acid solution arranged as in figure 1. The form and size of the apparatus are exceedingly various. Instead of actually immersing the plates in the solution, a piece of moistened cloth may be placed between them. Sometimes the copper plate is made into a cup for containing the liquid, and the zinc is fixed between its two sides, as shown by the accompanying transverse vertical section, figure 2; care being taken to avoid actual contact between the plates, by interposing pieces of wood, cork, or other imperfect conductor of electricity. Another contrivance, which is much more convenient, because the zinc may be removed at will and have its surface cleaned, is that represented by the annexed woodcut (fig. 3). C is a cup made with two cylinders of sheet copper, of unequal size, placed one with the other, and soldered together at bottom, so as to leave an intermediate space *a a a*, for containing the zinc cylinder z and the acid solution. The small copper cups *b b* are useful appendages; for by filling them with mercury, and inserting the ends of a wire, the voltaic circuit may be closed or broken with ease and expedition. This apparatus is very serviceable in experiments on electro-magnetism.

Fig. 2.

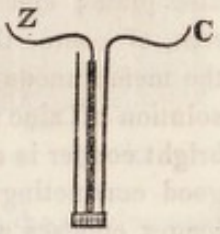
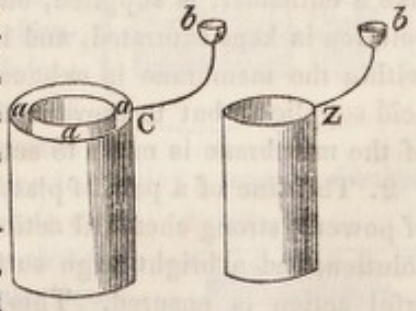


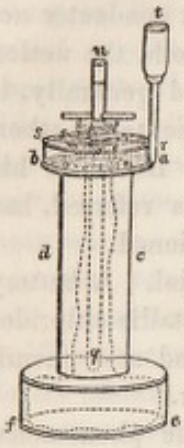
Fig. 3.



Another kind of circle may be formed by coiling a sheet of zinc and copper round each other, so that each surface of the zinc may be opposed to one of copper, and separated from it by a small interval. The London Institution possesses a very large apparatus of this sort, made under the direction of Pepys, each plate of which is 60 feet long and two wide. The plates are prevented from coming into actual contact by interposed ropes of horsehair; and the coil, when used, is lifted by ropes and pulleys, and let down into a tub

containing dilute acid. The contrivance of opposing one large connected surface of zinc to a similar surface of copper originated with Hare of Philadelphia, who, from its surprising power of igniting metals, gave it the name of *calorimotor*.

Fig. 4.



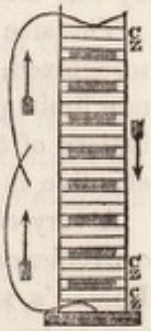
An excellent arrangement has been described by Daniell, of which fig. 4 represents a modification more simple and perhaps equally effective. It consists of a cylinder of copper, *a b c d e f*, 3 inches wide from *a* to *b*, $1\frac{1}{2}$ inches from *c* to *d*, and four inches from *e* to *f*, the corresponding heights being half an inch, 5 inches, and 2 inches; *l m n o*, is a collar of copper, which by the arms *r r*, *s s*, rests on the top of the cylinder, and to which a membranous tube formed of the gullet of an ox is tied, the membrane being longer than the copper cylinder, so as to be baggy below and nearly fill the space *e f*; *u p q*, is a rod of amalgamated zinc resting on the collar *l m n o*, by means of a piece of wood *r s*, which perforates it; *u*, *t*, are cups to hold mercury for making contact. Between the membrane and copper cylinder is poured a saturated solution of blue vitriol, and within the membrane dilute sulphuric acid of about sp. gr. 1·136, which is made with 1 measure of strong acid and 8 of water. The exciting acid is thus in contact with the zinc, but not with the copper. When this circle is in action, the electric current passes from the zinc through the acid, membrane, and solution of blue vitriol to the copper. The arrangement is founded on two important principles, established by Daniell:—

1. However active a circle, as made heretofore, may be when first excited, its energy is known rapidly to diminish, and in a few minutes to fall much below its original power. Daniell has traced the cause to reduction of oxide of zinc by nascent hydrogen at the surface of the copper plate, whereby this metal becomes coated with zinc, and is thus more or less converted at its surface into a zinc plate; and as two zinc plates under like conditions do not produce a current, of course the action declines. In the new circle this defect is avoided by the membranous septum which protects the copper plate from contact with the solution of zinc: the nascent hydrogen reduces oxide of copper, and a film of bright copper is deposited on the copper plate, thus constantly presenting a clean good conducting surface; while the hydrogen itself, not escaping as gas, no longer opposes an obstacle, as it does when allowed to assume the gaseous form, to the passage of electricity, from the solution to the copper plate. To supply the loss of oxide of copper, a copper disc, *a*, *v*, *x*, *b*, studded with holes like a cullender, is supplied, on which rest crystals of blue vitriol, whereby the solution is kept saturated, and its conducting power preserved. When the acid within the membrane is exhausted, the membrane itself is removed, and fresh acid supplied: but to prevent the necessity of frequent renewal, the lower part of the membrane is made to act as a reservoir of acid.

2. The zinc of a pair of plates may be much reduced in size without any loss of power: strong chemical action on a small surface of zinc, a good conducting solution, and a bright large surface of copper, are conditions by which a powerful action is ensured. This is indicated by Davy's protectors for copper sheathing (page 84); but it was not previously known that the principle was applicable to the construction of voltaic apparatus. The great merit of this circle is its *constancy*: by keeping up the supply of blue vitriol and acid, its energy will continue invariable for hours, or for an indefinite period. A similar apparatus has been described by Mullins (Phil. Mag. & An. ix. 122).

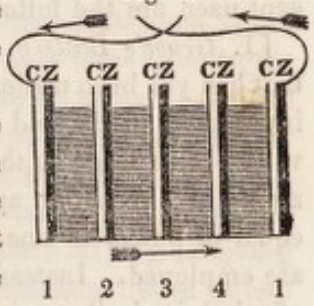
Compound voltaic circles.—This expression is applied to voltaic arrangements which consist of a series of simple circles. The first combinations of the kind were described by Volta, and are now well known under the names of *voltaic pile* and *crown of cups*. The voltaic pile is made by placing pairs of zinc and copper, or zinc and silver plates, one above the other, as in figure 5, each pair being separated from those adjoining by pieces of cloth, rather smaller than the plates, and moistened with a saturated solution of salt. The relative position of the metals in each pair must be the same in the whole series; that is, if the zinc be placed below the copper in the first pair, the same order should be observed in all the others. Without such precaution the apparatus would give rise to opposite currents, which would neutralize each other more or less according to their relative forces. The pile, which may consist of any convenient number of combinations, should be contained in a frame formed of glass pillars, fixed into a piece of thick dry wood, by which it is both supported and insulated. Any number of these piles may be made to act in concert by establishing metallic communication between the + extremity of each pile and the — extremity of the pile immediately following.

Fig. 5.



The voltaic pile is now rarely employed, because we possess other modes of forming galvanic combinations which are far more powerful and convenient. The galvanic battery proposed by Cruickshank consists of a trough of baked wood, about 30 inches long, in which are placed at equal distances 50 pairs of zinc and copper plates previously soldered together, and so arranged that the same metal shall always be on the same side. Each pair is fixed in a groove cut in the sides and bottom of the box, the points of junction being made water-tight by cement. The apparatus thus constructed is always ready for use, and is brought into action by filling the cells left between the pairs of plates with some convenient solution, which serves the same purpose as the moistened cloth in the pile of Volta. By means of the accompanying woodcut the mode in which the plates are arranged will easily be understood.

Fig. 4.



Other modes of combination are now in use, which facilitate the employment of the voltaic apparatus and increase its energy. Most of these may be regarded as modifications of the crown of cups. In this apparatus the exciting solution is contained in separate cups or glasses, disposed circularly or in a line; each glass contains a pair of plates; and each zinc plate is attached to the copper of the next pair by a metallic wire, as represented in figure 7. Instead of glasses, it is more convenient in practice to employ a trough of baked wood or glazed earthenware, divided into separate cells by partitions of the same material; and in order that the plates may be immersed into and taken out of the liquid conveniently and at the same moment, they are all attached to a bar of dry wood, the necessary connection between the zinc of one cell, and the copper of the adjoining one being accomplished, as in figure 8, by a slip or wire of copper.

Fig. 7.

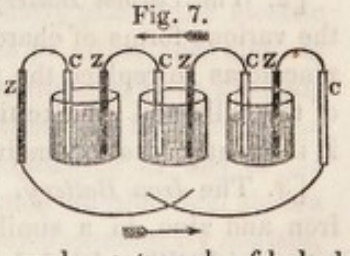
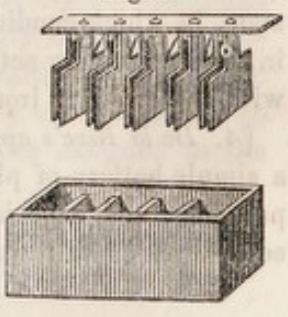


Fig. 8.



A material improvement in the foregoing apparatus was

suggested by Wollaston (Children's Essay in Phil. Trans. 1815), who recommended that each cell should contain one zinc and two copper plates, so that both surfaces of the former metal might be opposed to one of the latter. The plates communicate with each other, and the zinc between them with the copper of the adjoining cell. An increase of one half the power is said to be obtained by this method.

The size and number of the plates may be varied at pleasure. It is now recognized, however, that increasing the number of plates beyond a very moderate limit gives for most purposes no proportionate increase of power; so that a battery of 50 or 100 pair of plates, thrown into vigorous action, will be just as effective as one of far greater extent.

A very effective battery, which, I apprehend, from its constancy of action, convenience, cheapness, and power, will supersede all others, is made with Daniell's simple circles (page 86). Twenty of these, arranged on a wooden tray in two rows, has an energy sufficient for the performance of most experiments of demonstration or research.

[An improvement lately introduced in the construction of the battery cells, consists in substituting for the membrane, used by Daniell and Mullins, a diaphragm, or hollow cylinder of porous earthenware. To obtain great power in a small compass, these arrangements are constructed of solid elements differing as much as possible in their chemical relations. The plates are brought as near each other as conveniently practicable, and the fluids used are such as with great exciting energy combine the highest conducting power. Such arrangements are called *sustaining batteries*. The most useful of these forms of apparatus at present used are the following:

[1. *Grove's Battery*. In this, probably the most powerful voltaic combination that has yet been made, the metals used are zinc and platinum, the latter dipping into strong nitric acid contained in the porous cell, while the zinc in the outer vessel is exposed to the action of dilute sulphuric acid. According to the experiments of Jacobi, an apparatus of this kind having 6 square feet of platinum is equal in power to one of the ordinary form in which 100 square feet of copper are employed. Instead of sheets of platinum, a cheaper arrangement with plates of platinized silver or iron may be employed. This very efficient arrangement, first suggested by Mr. Smee, is known under his name.]

[2. The *Carbon Battery*, of Cooper, Bunson, and others. In this, carbon in the various forms of charcoal, coke, anthracite, and plumbago, is associated with zinc so as to replace the platinum of the preceding arrangement. The material of the cells and the exciting liquids are the same. While little inferior in energy, it is greatly less expensive than the battery of Grove.]

[3. The *Iron Battery*. A very active combination is formed by connecting iron and zinc, in a similar manner; the former in contact with the nitric, the latter with diluted sulphuric acid. This is particularly powerful, according to Schoenbein, when the iron is previously brought into what he calls the passive state, in which condition it is not acted upon by nitric acid alone. He succeeded in forming a very active arrangement by the combination of iron in this state with the ordinary iron.]

[4. *De la Rive's apparatus*. This excellent electrician has recently shown that a simple battery of platinum and zinc, in which the nitric acid is replaced by a peroxide, and especially by *peroxide of lead*, is capable, when charged with acidulated or salt water, of producing very energetic effects. The peroxide,

reduced to a fine dry powder, is heated with care in a porous porcelain vessel, and the platinum placed in the middle of it so as to be completely surrounded by the peroxide. The external vessel containing the zinc plate is charged with acidulated or salt water. A single pair of this arrangement was found to have much greater activity in producing chemical effects than the same pair when excited by nitric and sulphuric acid as in Grove's arrangement.]

It must be remembered that in a compound circle, the extreme plates at either end, not being in contact with the exciting fluid, are in reality superfluous, and serve only as conductors. Hence the current, instead of flowing from the zinc to the copper, seems to flow from the copper to the zinc. But if we abstract the extreme plates, which serve only as conductors, it is then seen that the direction of the current corresponds to that of the simple circle (see fig. 5.)

During the action of a simple circle, as of zinc and copper, excited by dilute sulphuric acid, all the hydrogen developed in the voltaic process is evolved at the surface of the copper. This fact is not apparent when common zinc plates are used, owing to the numerous currents which form on the surface of the zinc (page 85); but when a plate of amalgamated zinc and another of platinum are introduced into dilute sulphuric acid of sp. gr. 1.068, no gas whatever appears until contact between the plates is made, and then hydrogen gas rises solely from the platinum, while zinc is tranquilly dissolved. On weighing the amalgamated plate before and after the action has continued for half an hour or an hour, and collecting the hydrogen gas evolved during that interval, the weight of the hydrogen set free and of zinc dissolved will be as 1 to 32.3, being the ratio of their chemical equivalents. Faraday, who has proved this, has also shown that in a compound voltaic circle, say of 10 amalgamated zinc plates and 10 of platinum, each of the former during a given period of action loses exactly the same weight, and from each of the latter an equivalent quantity of hydrogen gas is evolved. This separation of one ingredient of the exciting solution at one plate, while the element previously combined with it unites with the other plate, seems essential to voltaic action. It is in some way connected with the passage of the current across the exciting liquid. Oxygen in a free state may by oxidizing zinc cause electric excitement; but the voltaic current is not established unless the oxygen formed part of a previous liquid compound in contact or communication with both the plates.

Among the different kinds of voltaic apparatus is usually placed the electric column of De Luc, which is formed of successive pairs of silver and zinc, or silver and Dutch metal leaf, separated by pieces of paper, arranged as in a voltaic pile. It is remarkable for its power of exhibiting attractions and repulsions like common electricity, but cannot produce chemical decomposition or any of the effects most characteristic of a voltaic current, and is rather an electrical than a voltaic instrument. It is quoted as a proof of electric developement by contact, since it will continue in action for years without being cleaned or taken to pieces. True it is that the more oxidable metal of the column is slowly corroded, and that no electricity is excited when the paper is quite or nearly free from hygrometric moisture, the presence of which is necessary to the oxidation of the zinc and copper; but at the same time the quantity of electricity excited seems so disproportioned to the corrosion, that the one can scarcely be assigned as the cause of the other.

LAWS OF THE ACTION OF VOLTAIC CIRCLES.

Electricians distinguish between *quantity* and *intensity* in galvanism, as in ordinary electricity (page 79); and by most persons, as also in this work, the same meaning is attached to them. The electric intensity of a voltaic circle is most correctly estimated by the divergence which in the broken circuit it causes in a gold leaf or other electrometer; and as the intensity is never considerable, it is often necessary to employ a condenser. The charges accumulated on the extreme plates of a voltaic circle cannot acquire a high tension, because the liquid which separates them is a good conductor for all charges except such as are of a very feeble intensity. Accordingly, a simple circle has necessarily a very feeble tension. The circle which gives the highest tension is one which excites electricity sufficient for duly charging the apparatus, while it opposes an obstacle to spontaneous discharge. A battery of numerous small plates excited by water, or a weak saline or acid solution, fulfils these conditions.

The quantity of electricity circulating in a voltaic battery is exactly the same in all its parts. It is found to be exactly proportional to the magnetic and chemical effects which it is capable of producing; and hence the quantity of electricity moving through any closed circuit is readily estimated either by the deflection which it causes on a magnetic needle, or by its power of chemical decomposition. When quantity of electricity is alone desired, a single pair of plates is just as useful as a compound circle.

The following numerical results were obtained by Ritchie by means of a magnetic galvanometer:—

1. The power of a single pair of plates in deflecting the magnetic needle is directly proportional to the surface of the plates which is covered with dilute acid.

2. A plate of zinc introduced into a rectangular cup of copper, as in figure 2, page 85, deflects the needle twice as much as when one side of the zinc and the adjacent surface of copper are protected by a coating of cement from the action of the acid solution.

3. The deflection produced by a pair of plates, in an acid solution of uniform strength, varies inversely as the square root of the distance between them,—a law previously established by Cumming.

4. The same law, as previously deduced by Cumming and Barlow, applies to variations in the length of the wire by which the zinc and copper plates are connected. If, all other circumstances being uniform, the conducting wire varies from 4 feet to 1 foot in length, the deflecting power will vary in the ratio of 1 to 2. Ritchie has stated that with short metallic wires the deflection varies inversely as the square root of the length of the whole circuit, that is, of the solid and liquid conductors taken together.

Ritchie has also shown, agreeably to general observation, that the deflecting power of a compound circle is not increased by increasing the number of its plates. This is another proof that the direct influence of a number of plates is to increase the intensity and not the quantity of electricity; for the prevailing opinion that the magnetic needle takes no cognizance of intensity is fully borne out by the experiments of Faraday.

Though the quantity of a compound decomposed by a battery is proportional to the actual quantity of electricity which passes, yet, as a compound exposed

to voltaic action is almost always an imperfect conductor, the quantity of electricity capable of passing through it varies with its intensity. Hence chemical decomposition depends on the quantity and intensity together, and affords a criterion of the increased tension of a compound circle due to the number of its plates.

[The most extensive combinations for exhibiting the effects of *tension* are those which have been constructed by Mr. Crosse, and more recently Mr. Gassiot. The arrangements used by the latter consist of 3520 pairs of copper and zinc cylinders placed in separate glass vessels, which are coated with black varnish and well insulated. The phenomena presented by this apparatus before and after the completion of the circuit, serve to illustrate the difference between the electricity when accumulated at the extremities of the battery and at rest, and electricity in current; in other words, between what are called the *static* and *dynamic* conditions. The following are the conclusions he derived from his experiments.

1. The elements constituting the voltaic battery assume polar tension *before* the circuit is completed, even in a single cell; this polar state being shown to exist by the opposite actions on the electroscope of the two extremities of the battery.

2. The tension thus produced, when heightened by a repetition of series, is such that a succession of sparks passes between the polar extremities of the battery *before their actual contact.*

3. These static effects precede and are independent of the completion of the circuit, as well as of any perceptible chemical or dynamic action.

4. To produce these static effects in the voltaic battery it is indispensable that the elements be such that they are capable of combining by their chemical affinities; and the more those affinities are exalted the smaller is the number of parts composing the series requisite to exhibit the effects of tension. These effects, therefore, furnish direct evidence of the first step towards chemical combination, or dynamic action.

5. When the current is established, either by actual contact of the extremities, or merely by their approximation so as to admit of a succession of sparks, its dynamic effects on the magnetic needle are the same in both cases; each spark producing a constant deflection of the needle. It is hence inferred that the current, even when the circuit is closed, may be regarded as a series of discharges succeeding each other with infinite rapidity.

6. When the circuit is closed the dynamic effects of a *chemical* kind, though feeble, are precisely the same in character as those of the more powerful voltaic combinations. (Gassiot, Phil. Trans.)]

CONDUCTION OF GALVANIC CURRENTS.

[Great differences exist amongst bodies in their power of conducting galvanic electricity. The following table exhibits, according to Pouillet's experiments, the relative conducting powers of the various metals.

Palladium	5791	Bismuth	384
Silver	5152	Brass	from 900 to 200
Gold	3975	Caststeel	" 800 " 500
Copper	3838	Iron	600
Platinum	855	Mercury	100]

EFFECTS OF GALVANISM.

The effects producible by voltaic combinations are conveniently divisible into the electrical, magnetic, and chemical phenomena.

I. *Electrical Effects.*—These are so called, as being analogous to the effects of ordinary electricity. An active broken circuit produces the phenomena of electric repulsion, as already stated (p. 89 & 91). A Leyden phial may also be charged by contact of its inner coating with one wire of the circle, while the outer communicates either with the other wire or with the ground: a full charge, though of feeble intensity, is almost instantly given. On approximating the wires of an active circle, a brilliant spark passes between them just before contact, as well as in the act of breaking contact. When the electric current is made to pass through the body of an animal, as on holding the conducting wires in the hands, previously moistened to facilitate conduction, a distinct shock is felt, which is powerful when a battery of high tension is employed. On sending the current through fine metallic wires or pieces of plumbago or compact charcoal, these conductors become intensely heated, the wires even of the most refractory metals are fused, and a vivid white light appears at the charcoal points, equal, if not superior, in splendour to that of phosphorus burning in oxygen gas; a phenomenon in no wise referable to combustion, as it takes place in a vacuum or under water. If the electric current pass through thin metallic leaves, the metals burn with vivid scintillations:—gold leaf emits a white light tinged with blue, silver a beautiful emerald green light, copper a bluish white light with red sparks, lead a rich purple, and zinc a brilliant white light fringed with red. In burning leaves, fusing wire, and igniting charcoal, a large quantity of electricity is the only requisite: the large battery of Children, though capable of fusing several feet of platinum wire, had an electric tension so feeble, that it did not affect the gold leaves of the electrometer, gave a shock scarcely perceptible even when the hands were moist, communicated no sensible charge to a Leyden jar, and could not produce chemical decomposition. If the quantity and intensity of the current are both great an arc of light appears between the charcoal points after contact, even through an interval of an inch or more.

The electrical effects of galvanism are so similar to those of the electrical machine, that it is impossible to witness and compare both series of phenomena without referring them to the same agent. The question of identity early occupied the attention of Wollaston, who made some very beautiful and conclusive experiments to prove that not only are the electrical effects of the machine producible by galvanism, but that the chemical effects of galvanism may be characteristically produced by a current from an electrical machine (Phil. Trans. 1801). The subject has been examined anew by Faraday, who has subjected the effects of electricity and galvanism to a minute and critical comparison: he has obtained ample proof of the decomposing power of an electric current from an electrical machine, both by repeating the experiments of Wollaston and devising new ones of his own. He has also completed the chain of evidence by deflecting a magnetic needle with an electric current from the machine; an observation, indeed, which had been previously made by Colladon. These researches have led to a remarkable contrast between the quantity of electricity concerned in the production of voltaic and ordinary electrical phenomena. Faraday states that the quantity of electric fluid employed in decomposing a single grain of water is equal to that of a very powerful flash of lightning; and this statement, surprising as it is, is supported by such strong evidence, that it is difficult to withhold assent to the assertion.

II. *Magnetic Effects of Galvanism.*—The power of lightning in destroying and reversing the poles of a magnet, and in communicating magnetic properties to pieces of iron which did not previously possess them, was noticed at an early period of the science of electricity, and led to the supposition that similar effects may be produced by the common electrical and voltaic apparatus. Attempts were accordingly made to communicate the magnetic virtue by means of electricity and galvanism; but no results of importance were obtained till the winter of 1819, when Oersted of Copenhagen made his famous discovery, which forms the basis of a new branch of science. (An. Phil. xvi. 273.)

The fact observed by Oersted was, that the metallic wire of a closed voltaic circle,—and the same is true of charcoal, saline fluids, and any conducting medium which forms part of a closed circle,—causes a magnetic needle placed near it to deviate from its natural position, and assume a new one, the direction of which depends upon the relative position of the needle and the wire. On placing the wire above the magnet and parallel to it, the pole next the negative end of the battery always moves westward; and when the wire is placed under the needle, the same pole goes towards the east. If the wire is on the same horizontal plane with the needle, no declination whatever takes place; but the magnet shows a disposition to move in a vertical direction, the pole next the negative side of the battery being depressed when the wire is to the west of it, and elevated when it is placed on the east side.

When the influence of the earth's magnetism on the needle which impedes its free motion, is counteracted by another magnet placed near it, the needle places itself directly across the connecting wire; so that the real tendency of a magnet is to stand at right angles to an electric current.

The communicating wire is also capable of attracting and repelling the poles of a magnet. When the connecting wire is held vertically near a horizontally suspended magnet, on the west side of it, and approached to the north pole, attraction ensues, till they come very close, when repulsion follows. When the wire is approached to the south pole, similar effects ensue, in an inverted order. If the wire be held on the east side, the effects are reversed; the current in both cases being supposed to flow upwards through the wire.

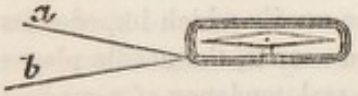
The discovery of Oersted was no sooner announced, than the experiments were repeated and varied by philosophers in all parts of Europe, and, as was to be expected, new facts were speedily brought to light. Among the most successful of those who early distinguished themselves were Ampère, Biot, and Arago, of Paris, and Davy and Faraday in this country. A host of other able men have since added their contributions; and their joint labours have established an altogether new science, *Electro-Dynamics*, which has already become one of the most important branches of physical knowledge, and still offers a rich harvest of discovery to its cultivators. Those who wish to enter deeply into the study of this subject should consult the *Recueil d'Observations Electro-Dynamiques* by Ampère, Cumming's Manual of Electro-Dynamics, Murphy's Treatise on Electricity, and the second edition of Barlow's Essay on Magnetic Attractions. A less mathematical, and therefore more generally intelligible, treatise has been drawn up with great ability by Roget, and published as part of the Library of Useful Knowledge; and a Popular Sketch of Electro-Magnetism has been given by Watkins of Charing-cross. To these works I refer as supplying that detail of the facts and theories of electro-dynamics, which, as belonging more to the province of physics than chemistry, is unsuited to the design of this volume.

The phenomena of electro-dynamics are solely produced by electricity in

motion. The passage of electricity through solid or liquid conductors is essential; in fact, a magnetic needle is a *galvanoscope*, by which means the existence and direction of an electric current may be detected. In this way, Ampère demonstrated the fact, that electricity passes uninterruptedly through the battery when the circuit is closed, and not at all in the broken circuit.

But a magnetic needle will not only indicate the existence and direction of an electric current: it may even serve, by the degree of deflection, as an exact measure of its force. When used for this purpose, under the name of *galvanometer*, some peculiar arrangements are required in order to ensure the requisite delicacy and precision. Experiment proves that a magnet is equally affected by every point of a conductor along which an electric current is passing; so that a wire transmitting the same current will act with more or less energy, according as the number of its parts contiguous to the needle is made to vary. On this principle is constructed the *Galvanometer* or *Multiplier* of Schweigger. A copper wire is bent into a rectangular form consisting of several coils, and in the centre of the rectangle is placed a delicately suspended needle, as shown in figure 9. Each coil adds its influence to that of the others; and as the current, in its progress along the wire, passes repeatedly above and below the needle in opposite directions, their joint action is the same. In order to prevent the electricity from passing laterally from one coil to another in contact with it, the wire should be covered with silk. The ends of the wire, *a* and *b*, are left free for the purpose of communication with the opposite ends of the voltaic circle. The needle ought to be rendered *astatic*, that is the influence of the earth's magnetism ought to be destroyed by placing another magnet above the rectangle, having its north pole adjacent to the south pole of the first. The instrument is thus rendered extremely delicate.

Fig. 9.

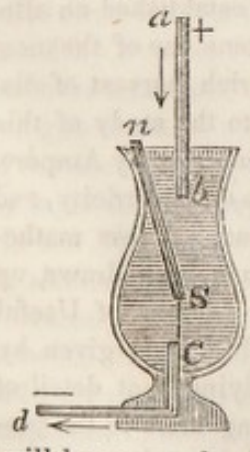


The mutual influence of a magnetic pole and a conducting wire changes with the distance between them; and experiment leads to the conclusion that the attraction of a magnetic pole on a *single* point of a conductor varies as the square of the distance; the same well known law which regulates the distribution of heat and light, as well as electricity.

On examination, all the phenomena described by Oersted are found to be referable to a force acting tangentially on the poles of a magnet, and in a plane perpendicular to the direction of the current.

The same principle accounts for the rotation of a magnetic pole round a current, discovered by Faraday. Into the centre of the bottom of a cup, as in the vertical section, figure 10, a copper wire c *d* was inserted, a cylindrical magnet *n* s was attached by a thread to the copper wire c, and the cup was nearly filled with mercury, so that pole *n* only of the magnet projected. A conductor *a b* was then fixed in the mercury perpendicularly over the wire c. On connecting the conducting wires with the opposite ends of a battery, a current was transmitted from one wire through the mercury to the other. If the + current descend, the north pole of the magnet, if uppermost, will rotate round the wire *a b*, passing from east through the south to west like the movements in the hands of a watch; and if the current ascend, the line of rotation will be reversed. Under similar circumstances the south pole would in each case rotate in the opposite direction.

Fig. 10.



If a magnetic pole rotate round a conductor, a conductor will be equally disposed to rotate round a magnetic pole, just as a magnet moves towards iron or iron towards a magnet, according as one or other is free to move. Accordingly, on fixing a magnet vertically in the middle of a cup of mercury, fig. 11, and transmitting a current by the movable conductor *a b* through the mercury, and along a second conductor *d*, fixed as before in the bottom of the cup, Faraday found that the free extremity *b* of the wire moved round the pole of the magnet in a direction similar to the last.

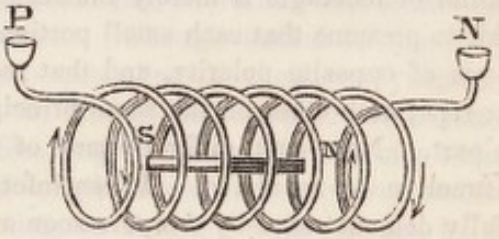
Fig. 11.



It is obvious that the direction of rotation imparted by a fixed current to the movable pole, will be identical with that which the same pole tends to impart to the same current.

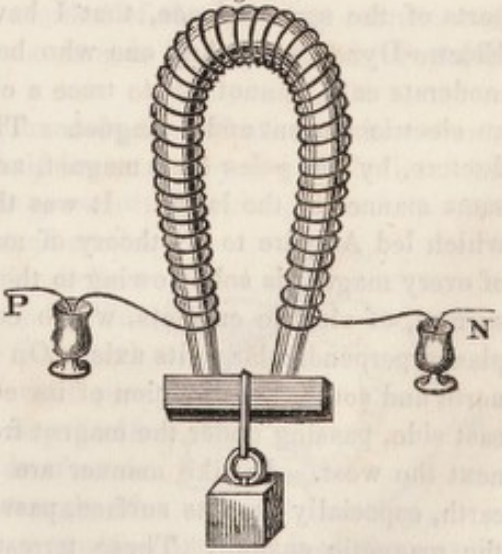
A current of voltaic electricity not only determines the position of a magnet, but renders steel permanently magnetic. This was observed nearly at the same time by Arago and Davy, who found that when needles are placed at right angles to the conducting wire, permanent magnetism is communicated; and Davy also succeeded in producing this effect even with a shock of electricity from a Leyden phial. Arago, at the suggestion of Ampère, made a voltaic conductor into the form of a helix, into the axis of which he placed a needle, as in figure 12. As in this arrangement the current nearly in every part of its course is at right angles to the needle, and as each coil adds its effect to that of the others, the united action of the helix is extremely powerful. The needle was thus fully magnetized in an instant.

Fig. 12.



Though soft iron does not retain magnetism, its magnetic properties, while under the influence of an electric current, are very surprising. A piece of soft iron, about a foot long and an inch in diameter, is bent into the form of a horse-shoe, a copper wire is twisted round the bar at right angles to its axis, and an armature of soft iron, to which a weight may be attached, is fitted to its extremities, as in fig. 13. On connecting the ends of the wire with a simple voltaic circle, even of small size, the soft iron instantly becomes a powerful magnet, and will support considerable weights. Increasing the number of coils gives a great increase of power; but as the length of wire required for that purpose diminishes the influence of the current (page 90), the following arrangement has been successfully adopted. The total length of copper wire intended to be used is cut into several portions, each of which, covered with silk or cotton thread to prevent lateral communication, is coiled separately on the iron. The ends of all the wires are then collected into two separate parcels, and are made to commu-

Fig. 13.



nicate with the same voltaic battery, taking care that the + current shall pass along each wire in the same direction. The current is thus divided into a number of branches, and has only a short passage from one end of the battery to the other, though it gives energy to a multitude of coils. A combination of this kind, connected with a battery of five feet square, supported 2063 pounds, or nearly a ton weight.

In witnessing the influence of voltaic conductors over the directive property of magnets, and in inducing magnetism, it is difficult to divest one's self of the conviction that these conductors, while transmitting a current, are themselves magnetic. This belief was early entertained by those who repeated the experiments of Oersted, and experimental evidence of its truth was speedily adduced. Arago and Davy found that a copper wire connecting the end of a voltaic combination attracted iron filings, but that they instantly fell off as soon as the circuit was broken; and a conductor, when its movements were not impeded by friction or gravity, was proved by Ampère to be obedient, like an ordinary magnet, to the magnetic agency of the earth.

Since, therefore, the conductors just described may be regarded as magnets, such magnetized conductors ought mutually to repel or attract each other, when poles of the same or a different nature are adjacent; and as the action of a whole spiral or rectangle is merely the accumulated effect of its individual parts, it is fair to presume that each small portion of a conductor has its opposite sides in a state of opposite polarity, and that two such contiguous portions should attract or repel each other on the same principle as the spirals of which they constitute a part. Nay, even different parts of the same conductor ought to be mutually attractive or repulsive. These inferences from the facts already detailed were fully demonstrated by Ampère soon after the discovery of Oersted. He proved that two voltaic conductors, or two portions of the same conductor, attract each other when the currents have the same direction, and are mutually repulsive when they are traversed by opposite currents; which is exactly what would be anticipated from the magnetic influence of conductors.

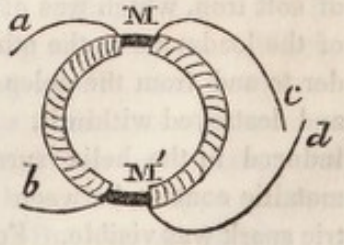
These are a few examples of the numerous facts experimentally proved by Ampère concerning the action of voltaic conductors on each other. It is to this branch of the subject the term of *Electro-Dynamics*, or the science of electricity in motion, is sometimes restricted, while the mutual action of conductors and magnets is called *Electro-Magnetism*; but these two branches are so entirely parts of the same science, that I have included both under Ampère's term of Electro-Dynamics. Any one who has studied the few preceding pages with moderate care, cannot fail to trace a close analogy between a helix traversed by an electric current and a magnet. The former is effected by other voltaic conductors, by the poles of a magnet, and by the magnetism of the earth, in the same manner as the latter. It was this similarity, or rather identity, of action which led Ampère to his theory of magnetism. He supposes that the polarity of every magnet is solely owing to the circulation, within its substance and at its surface, of electric currents, which continually pass around all its particles in planes perpendicular to its axis. On placing a magnet in its natural position of north and south, the direction of its currents is as follows: they descend on the east side, passing under the magnet from east to west, and ascending on the side next the west. In like manner are currents supposed to circulate within the earth, especially near its surface, passing from east to west in planes parallel to the magnetic equator. These terrestrial currents cause all bodies, which are freely suspended, and are possessed of electric currents, to place themselves in

such a position that the current on their under side should flow in parallelism, and in the same direction, with that in the earth immediately beneath. That the existence of such currents will account for the directive property of the earth, follows from the mutual action of conductors; and Barlow, to render the analogy still more complete, constructed a hollow sphere of wood in which electric currents were made to circulate in the same direction as they are thought to do in the earth; and by placing an astatic needle on different parts of its surface, he found that all the phenomena of terrestrial magnetism might be imitated. Observation has even supplied a cause for the existence of currents in the earth, moving in the direction which theory requires. The diurnal rotation of our planet on its axis exposes its surface to be heated in a direction passing from east to west; and the discoveries which have been made in thermo-electricity (page 72) sufficiently prove the probability of electric currents being established in the conducting matter of the earth by the successive heating of its parts. In short, the theory of Ampère connects the facts of electro-dynamics with the phenomena of terrestrial magnetism, and affords a splendid instance of the application of mathematical analysis to physical research.

Volta-electric Induction.—The developement of electricity by the vicinity of an excited body, already described under the name of induced electricity (page 73), led Faraday to inquire whether electricity in motion, as well as that of tension and at rest, may not be excited by induction. Though baffled in his early attempts, he at last succeeded in laying open a new branch of electro-dynamics, which vies in interest and importance with the fundamental discovery of Oersted (Phil. Trans. 1831). A copper wire 203 feet long was passed in form of a helix round a large block of wood, and an equal length of a similar wire was wound on the same block and in the same direction, so that the coils of each helix should be interposed, but without contact, between the coils of the other. The ends of one of the helices were connected with a galvanometer, and the other with a strong galvanic battery, with the view of ascertaining whether the passage of an electric current through one helix would induce a current in the adjoining helix. It was found that the galvanometer needle indicated a current at the moment both of completing and breaking the circuit, but that in the interval no deflection took place; and similarly the induced currents readily magnetized a sewing needle, while the electric current along the inducing helix was in the act of beginning or ceasing to flow, but at no other period. In the former case the direction of the induced current is opposite to that of the inducing current, and in the latter case it is the same. This phenomenon is distinguished by Faraday under the name of *volta-electric induction.*

The inducing power of a magnet greatly exceeds that of an electric current. A ring of soft iron was covered to nearly half its extent by several helices, the ends of which were brought together so as to constitute a compound helix terminating in the conductors *a b*, figure 14; and on the other half of the ring were arranged similar helices which communicated by *c d* with a galvanometer. The two sets of helices were thus separated from each other by portions of the ring M M′, and were protected by cloth from direct contact with the ring itself. At the moment the wires *a b* touched the ends of a voltaic combination, the galvanometer was strongly affected: the needle then returned to its former position and remained there until

Fig. 14.



the voltaic circuit was broken, when the needle was again deflected as strongly as before, but in the opposite direction. The action was still greater when both compound helices were on the same part of the ring, the induction being increased apparently by the closer contiguity of the helices. Other arrangements have been devised by Faraday, for producing similar results; and to the action in all these cases he has given the name of Magneto-electric induction.

The phenomena arising from magneto-electric and volta-electric induction are manifestly owing to the same condition of the induced wire: the action on the needle, though different in force, is identical in kind. It is equally clear that the agent brought into operation in the induced wire is an electric current, or, to dismiss the language of theory, that the induced wire is in the same electric state as the conducting wire in a closed voltaic circle. Its power in magnetizing steel and deflecting a magnet is sufficient evidence of this; but Faraday, by magneto-electric induction, succeeded in throwing a frog's leg into spasms by connecting it with the induced wire, and by arming the ends of that wire with points of charcoal, and separating them at the instant the galvanic circuit of the inducing wire was broken or restored, sparks of electricity were obtained. The mode in which soft iron contributes to the effect is likewise obvious. An electric current circulating round a bar of soft iron has been shown to convert it into a temporary magnet possessed of surprising power (page 95); and it is doubtless to this magnet, called into temporary existence by the electric current, most of the induced electricity is to be ascribed. Faraday reduced this to certainty by surrounding a cylinder of soft iron with one helix connected with the galvanometer, and converting the soft iron into a temporary magnet, not by a voltaic battery, but by placing at each end of the cylinder the opposite pole of a magnet. During the act of applying the magnetic poles to the iron, the galvanometer needle was deflected; and the deflection was reproduced, but in the opposite direction, when the magnetism of the iron was ceasing by the removal of the magnet. Similarly, when a helix was wound on a hollow cylinder of pasteboard, and a real magnet was introduced, the galvanometer was deflected: the needle then remained quiescent so long as the magnet was left in the cylinder; but in the act of its removal, the needle was again deflected, though, as usual, in the opposite direction.

These singular phenomena, which establish such new and intimate relations between voltaic and magnetic action, and supply additional evidence in favour of Ampère's beautiful theory of magnetism, have led to an experiment by which, at first view, an electric spark appeared to be derived from the magnet itself. After Faraday had announced his experiment, above mentioned, of obtaining a spark from the induced wire, other attempts were made to effect the same object with a magnet, without the aid of galvanism. The first person who succeeded in this country was Forbes, who operated with a powerful loadstone (Phil. Trans. Ed. 1832). A helix of copper wire was formed round the middle of a cylinder of soft iron, which was of such length that its extremities reached from one pole of the loadstone to the other. On applying and withdrawing the soft iron cylinder to and from the poles of the loadstone, magnetism was alternately created and destroyed within it. At these periods of transition, electric currents were induced in the helix surrounding the soft iron; and when, at these instants, metallic contact between the conducting wires of the helix was broken, an electric spark was visible. Forbes succeeded best by connecting one wire with a cup of mercury, and removing the other wire from contact with its surface at the

instant when an assistant withdrew the armature of soft iron from the loadstone. In this experiment, therefore, the electricity was obtained from the helix, and was induced in it by the soft iron while in the act of acquiring or losing magnetism. The same experiment was performed by Faraday with a loadstone belonging to Daniell; and shortly before the experiment of Forbes, Nobili and Antinori succeeded with an ordinary steel magnet. Pixii in Paris afterwards performed this experiment with great effect by causing a strong horse-shoe magnet to revolve upon an axis, its poles passing in rapid succession in front of a soft iron armature of the same form; and a still better arrangement is to cause the armature to revolve in front of the poles of a powerful magnet, as in the instrument fitted up by Saxton, and exhibited at the Adelaide-rooms, London. It produces brilliant sparks, renders platinum wire red hot, and gives a strong shock. It explodes gunpowder, and also a mixture of oxygen and hydrogen gases, and decomposes water rapidly.

Intimately associated with magneto-electric induction, if not referable to the very same origin, is the induction of electric currents by movement. On introducing a magnet into a hollow helix of copper wire, or other solid conductor, as also on withdrawing the magnet after its introduction, an electric current was momentarily induced in the wire; and if, the magnet being stationary, the helix were moved in its vicinity, an electric current is likewise induced. The direction of the movement is not immaterial: it is essential that the plane in which the conductor moves should form an angle with the axis of the magnet; and the most powerful currents were induced, when the plane of motion was at right angles to that axis, and hence parallel to the electric currents which Ampère supposes to exist in the magnet. With regard to the direction of an induced current, Faraday's researches establish this law, deduced by Ritchie: if a wire conducting voltaic electricity produce on magnets or conductors certain motions, whether repulsive, attractive, or rotatory, and if the battery be removed, the ends of the wires brought into metallic contact, and the same motions be produced by mechanical means, the conductor will have the same electric state induced in it as it had when connected with the battery. (Phil. Mag. 3rd series, iv. 12.)

Faraday has applied this principle in a most happy manner to explain the phenomena of rotation discovered by Arago. If a plate of copper be revolved close to a magnetic needle suspended so that it may rotate in a plane parallel to the plate, the needle will rotate in the same direction; and, reciprocally, a rotating magnet tends to give rotation to a contiguous copper-plate. The same effects are produced by the rotation not only of all metals, but, according to Arago, of all bodies whether solid, liquid, or gaseous. These effects, which Faraday has principally examined in reference to the rotation of metals, are entirely owing to electric currents induced by the rotation, and flowing at right angles to the direction of motion.

If motion in the vicinity of a magnet induce an electric current, the same effect would be anticipated from the magnetic influence of the earth; and this fact has been proved by Faraday by most decisive and interesting experiments. When a bar of soft iron is held in the position of the dipping needle, the direction of which, in regard to terrestrial magnetism, is analogous to the axis of a common magnet, it acquires magnetic properties; and accordingly, on introducing a soft cylinder into a hollow helix of copper placed in the line of the dip, a galvanometer connected with the helix was instantly affected. But the use of iron may be dispensed with altogether; for when a helix of copper wire was simply moved

at right angles to the dipping needle, electric currents were induced by the magnetism of the earth. The form of a helix is not even necessary: the movement of a piece of copper wire across the line of dip developed currents in the wire. The same effect was produced by the rotation of a copper plate placed horizontally so as to be nearly at right angles to the line of dip; and the revolution of a copper globe acted in the same manner. Faraday concludes that the rotation of the earth on its axis ought similarly to influence the conducting matters of its surface; and that electric currents should be thereby induced from the equatorial regions to either pole. He throws out the suggestion whether the aurora borealis and australis may not be produced by the returning currents passing from the poles of the earth into the atmosphere.

III. *Chemical Effects of Galvanism.*—The chemical agency of the voltaic apparatus, to which chemists are indebted for a most powerful instrument of analysis, was discovered by Carlisle and Nicholson, soon after the invention was made known in this country. The substance first decomposed by it was water. When two gold or platinum wires are connected with the opposite ends of a battery, and their free extremities are plunged into the same cup of water, but without touching each other, hydrogen gas is disengaged at the — and oxygen at the + wire. By collecting the gases in separate tubes as they escape, they are found to be quite pure, and in the exact ratio of two measures of hydrogen to one of oxygen. When wires of a more oxidable metal are employed, the result is somewhat different. The hydrogen gas appears as usual at the — wire; but the oxygen, instead of escaping, combines with the metal, and converts it into an oxide.

This important discovery led many able experimenters to make similar trials. Other compound bodies, such as acids and salts, were exposed to the action of galvanism, and all of them were decomposed without exception, one of their elements appearing at one side of the battery, and the other at its opposite extremity. An exact uniformity in the circumstances attending the decomposition was also remarked. Thus, in decomposing water or other compounds, the same kind of body was always disengaged at the same side of the battery. The metals, inflammable substances in general, the alkalies, earth, and the oxides of the common metals, were found at the — wire; while oxygen, chlorine, and the acids, went over to the + surface.

In performing some of these experiments, Davy observed, that if the conducting wires were plunged into separate vessels of water, made to communicate by some moist fibres of cotton or amianthus, the two gases were still disengaged in their usual order, the hydrogen in one vessel, and the oxygen in the other, just as if the wires had been immersed into the same portion of that liquid. This singular fact, and another of the like kind observed by Hisinger and Berzelius, induced him to operate in the same way with other compounds, and thus gave rise to his celebrated researches on the transfer of chemical substances from one vessel to another (Phil. Trans. 1807). In these experiments two agate cups, N and P, were employed, the first communicating with the —, the second with the + wire of the battery, and connected together by moistened amianthus. On putting a solution of sulphate of potassa or soda into N, and distilled water into P, the acid very soon passed over to the latter, while the liquid in the former, which was at first neutral, became distinctly alkaline. The process was reversed by placing the saline solution in P, and the distilled water in N, when the alkali went over to the — cup, leaving free acid in the other. That the acid

in the first experiment, and the alkaline base in the second, actually passed along the amianthus, was obvious; for on one occasion, when nitrate of oxide of silver was substituted for the sulphate of potassa, the amianthus leading to N was coated with a film of metal. A similar transfer was effected by putting distilled water into N and P, and a saline solution in a third cup placed between the two others, and connected with each by moistened amianthus. In a short time the acid of the salt appeared in P, and the alkali in N. It was in pursuing these researches that Davy made his great discovery of the decomposition of the alkalies and earths, which till then had been regarded as elementary. (Phil. Trans. 1808.)

Such is a statement of the principal phenomena of electro-chemical decomposition according to the earlier experiments. The facts then observed were received as established truths of science, and passed current without suspicion or scrutiny till the present time. But Faraday, in his revision of this part of the science, has not only added much new matter, but proved that several points, which were considered as fundamental maxims, are erroneous. Before describing his results, however, I will define the new terms which he has had occasion to introduce.—In order to decompose a compound, it is necessary that it should be liquid, and that an electric current should pass through it; an object easily effected by dipping into the liquid the ends of the metallic wires which communicate with the voltaic circle. These extremities of the wires are commonly termed *poles*, from a notion of their exerting attractive and repulsive energies towards the elements of the decomposing liquid, just as the poles of a magnet act towards iron; and each is further distinguished by the term *positive* or *negative*, according as it affects an electrometer with + or — electricity. Now Faraday contends that these poles have not any attractive or repulsive energy, and act simply as a path or door to the current: he hence calls them *electrodes*, from ηλεκτρον, and ὁδος, a way. The electrodes are the surfaces, whether of air, water, metal, or any other substance, which serve to convey an electric current into and from the liquid to be decomposed. The surfaces of this liquid which are in immediate contact with the electrodes, and where the elements make their appearance, are termed *anode* and *cathode*, from ανα, *upwards*, and ὁδος, the way in which the sun rises, and κατα, *downwards*, the way in which the sun sets. The anode is where the + current is supposed to enter, and the cathode where it quits, the decomposing liquid, its direction, when the electrodes are placed east and west, corresponding with that of the + current which is thought to circulate on the surface of the earth (page 96). To *electrolyze* a compound, is to decompose it by the direct action of galvanism, its name being formed from ηλεκτρον and λυω, *to unloose or set free*; and an electrolyte is a compound which may be electrolyzed. The elements of an electrolyte are called ions, from ιον, going, neuter participle of the verb to go. *Anions* are the ions which appear at the anode, and are usually termed the electro-negative ingredients of a compound, such as oxygen, chlorine, and acids; and the electro-positive substances, hydrogen, metals, alkalies, which appear at the cathode, are *cations*. Whatever may be thought of the necessity for some of these terms, the words electrode, electrolyze, and electrolyte, are peculiarly appropriate, and are already in use.

The principal facts determined by Faraday may be arranged under the following propositions:—

1. All compounds, contrary to what has been hitherto supposed, are not electrolytes, that is, are not directly decomposable by an electric current. But in

making this assertion, it is necessary to distinguish between primary and secondary decomposition. Water is an electrolyte, its hydrogen being delivered up at the — and its oxygen at the + electrode. A solution of hydrochloric acid is likewise an electrolyte, being resolved into chlorine and hydrogen. But nitric and sulphuric acids and ammonia are not electrolytes, though the first and last are decomposed by secondary action. Thus, on subjecting nitric acid to voltaic action, the water of the solution is electrolyzed, and its hydrogen arriving at the + electrode, decomposes the nitric acid, water being there reproduced and nitrous acid formed. So, in a solution of ammonia, the oxygen of decomposed water unites at the + electrode with the hydrogen of the ammonia, and nitrogen gas is evolved. Very numerous secondary actions are occasioned in this way, because the disunited elements are presented in a nascent form, which is peculiarly favourable to chemical action; and in many instances the electrode itself, which is commonly metallic, is chemically attacked. Thus, when chlorine is evolved against an electrode of gold, oxygen at one of some easily oxidable metal, as copper or iron, or sulphur against a silver electrode, chloride of gold, oxide of copper or iron, and sulphuret of silver, are generated. If these changes are caused by very feeble currents acting slowly, as for weeks, months, or years, the new products have opportunity to assume regularly crystalline forms. It is by such means that Becquerel has succeeded in procuring artificial minerals exactly resembling those which are found in mines (Traité d'Electricité); and Crosse has since obtained similar results (Phil. Mag. and An. ix. 229). Taking these facts in conjunction with the researches of Fox on the electrical state of mineral veins, there can be no longer a doubt that feeble electric currents within fissures of rocks, induced by terrestrial magnetism, by variations of temperature at different parts of the rock, or by the different nature of the walls of the fissures, or of the solutions with which they are filled, may have been one principal source of metalliferous deposits; nor is it at all unreasonable or unphilosophical to suppose that the enormous mineral masses which now constitute our metalliferous veins may have been the work of such feeble currents acting during hundreds or thousands of centuries. Feeble agencies operative for a long period are often just as efficacious in effecting great changes as powerful agents at work during a short period; and Becquerel, in opening this new line of inquiry, has supplied a principle by which the scientific geologist may explain many of those obscure phenomenon which fall within his observation.

2. Most of the salts which have been examined are resolvable into acid and oxide, apparently without reference to their proportions. But in compounds of two elements, the ratio of combination has an influence which has hitherto been wholly overlooked. No two elements appear capable of forming more than one electrolyte. Hydrochloric acid and fused metallic protochlorides, such as the chlorides of lead and silver, and protochloride of tin, are readily decomposed; while bichloride of tin and other perchlorides resist decomposition. Substances which consist of a single equivalent of one element and two or more equivalents of some other element, are not electrolytes: this is the reason why sulphuric and nitric acid and ammonia do not yield primarily to voltaic action. This principle bids fair to become very important in determining which of several compounds of two elements contains single equivalents. Water, which is remarkable for its easy decomposition, may hence be inferred to be a true binary compound.

3. It has been ascertained that most of the elements are *ions*, and it is probable that all of them are so; but there are several important elements, such as nitrogen, carbon, phosphorus, boron, silicon, and aluminium, which have not yet

been proved to be *ions*. This arises from the difficulty of obtaining these elements in compounds fitted for electrolytic action.

4. A single *ion*, that is, one ion not in combination with another, has no tendency to pass to either of the electrodes, and is quite indifferent to the passing current, unless it be itself a compound ion, and therefore electrolyzable. The character of true electrolytic action consists in the separation of *ions*, one passing to one electrode and another to the opposite electrode, and appearing there at the same instant, unless the appearance of one or both be prevented by some secondary action.

5. There is no such thing as a transfer of *ions* in the sense usually understood. In order that the elements of decomposed water should appear at the opposite electrodes, there must be water between the electrodes; and for the similar separation of sulphuric acid and soda, there must be a line of particles of sulphate of soda extending from one electrode to the other. Thus, if a solution of sulphate of magnesia be covered with pure water, care being taken to avoid all admixture of particles, and the + metallic termination or pole touch the magnesian solution only, while the — pole is in contact with the water only, a deposit of magnesia occurs just where the pure water and the magnesian solution meet, and none reaches the — pole. In Davy's experiment, where sulphuric acid and soda appeared to quit each other, and pass over separately into a vessel of pure water, there was certainly by capillary attraction an actual transfer of the salt before decomposition occurred.

6. In the foregoing experiment a surface of water acts as the — electrode, clearly showing the contact of a metallic conductor with the decomposing liquid not to be essential. Faraday has proved that even air may serve as an electrode. A current from the prime conductor of an electrical machine was made to pass from a needle's point through air to a pointed piece of litmus paper moistened with sulphate of soda, and then to issue from a similarly moistened point of turmeric paper. True electrolytic action took place, the litmus becoming red and the turmeric paper brown, though both extremities of the decomposing solution communicated solely with a stratum of air.

7. Electro-chemical decomposition cannot occur unless an electric current is actually transmitted through the electrolyte; or, in other terms, an electrolyte is always a conductor of electricity. Water, which conducts an electric current, ceases to do so when it passes into ice, and then also resists decomposition—an observation equally true of all electrolytes on becoming solid. Moreover, liquids which resist electro-chemical decomposition do not permit the current of a voltaic circle to pass. The alliance between conduction and decomposition is so constant, that the latter may be regarded as a means by which voltaic currents are transmitted through liquid compounds. Agreeably to this notion, solidity may interfere with conduction by chaining down the elements of a compound, and thereby preventing their transfer to the electrodes. Improving the conduction of a liquid, as by adding sulphuric acid to pure water, increases the decomposing power of a voltaic circle, the exciting fluid within the apparatus remaining the same; and Faraday has proved that the quantity of a compound decomposed is exactly proportional to the quantity of electricity which passes, however much other circumstances, such as the size of electrodes and conducting wires, number and size of plates, and nature of exciting fluid, may vary. Changes in these conditions do, indeed, influence the quantity of electricity transmitted; but then the degree of chemical decomposition varies in the same proportion. The fore-

going facts at first led to the opinion that the current of a voltaic circle cannot pass through liquids, except those of a metallic nature, unless decomposition ensues at the same time; but Faraday has noticed that when the intensity is too feeble to effect decomposition, a small quantity of electricity may be transmitted, sufficient to be discovered by a galvanometer. This does not, however, essentially interfere with the law just announced.

8. Chemical compounds differ in the electrical force required for decomposition. A current of very feeble tension suffices to decompose iodide of potassium, while a much higher intensity is required for disuniting the elements of water. The order of easy decomposition in the annexed substances is as follows:— Solution of iodide of potassium; fused chloride of silver; fused protochloride of tin; fused chloride of lead; fused iodide of lead; solution of hydrochloric acid; and water acidulated with sulphuric acid. By extending tables of this kind, a ready method will be known for comparing the tension of voltaic circles.

9. The conduction of the electric currents within the cells of a voltaic circle depends on chemical decomposition equally with that between platinum electrodes. No substance not an electrolyte can serve to excite a voltaic apparatus; and for the passage of electricity from plate to plate through the intervening solution, the separation of substances previously combined in the required ratio is essential. Neither free oxygen nor a solution of chlorine can excite a current, though they attack the zinc and develope electricity; and in a voltaic circle excited by dilute sulphuric acid, the electricity set in motion is due to decomposed water and oxidized zinc, and not at all to the union of the oxide of zinc with sulphuric acid. The platinum electrodes and intervening liquids may be viewed as one of the cells of the circle, except that the plates act merely as conductors, without any oxidation, the current passing in virtue of the decomposed solution. In the zinc and copper cells the current is urged on by the appetency of the zinc and oxygen to unite; whereas, in passing between the electrodes, the electricity has to surmount the mutual attraction of oxygen and hydrogen, or some similar force, without the assistance of any opposing affinity. Hence, in experiments on decomposition, the course of the electricity should be facilitated by employing large electrodes and wires, and placing them at a short distance from each other in a good conducting solution.

The principles above established show the importance of exciting all the cells of a voltaic circle with a liquid of the same strength. The electricity circulating in a voltaic apparatus with the conducting wires in contact, is equal to that which the feeblest cell is able to transmit, any chemical action in other cells more than sufficient for exciting that quantity being wasted.

[The important law of definite electro-chemical decomposition, first demonstrated by Faraday, has lately been confirmed and extended by Edmond Becquerel, in a series of researches applied to a great number of binary and ternary compounds. The following is a summary of conclusions to which he has been led.

Using the term *equivalent of electricity*, for the amount of electricity necessary to decompose one equivalent of water, he finds,

1. That one equivalent of a compound formed by the union of an equivalent of acid, and an equivalent of a base, always requires one equivalent of electricity for its electro-chemical decomposition.

2. When an electrical current is transmitted through two or more binary compounds, the decomposition takes place in such a way, that for one equivalent of electricity employed, one equivalent of the body which acts the part of an acid,

or electro-negative element in each compound, is disengaged at the positive pole.

As, from the fact that an equivalent of electricity is required to decompose an equivalent of any compound, we may conclude that the electro-positive and electro-negative elements of that compound, in uniting, would *disengage* the same amount of electricity, he infers the following laws:—

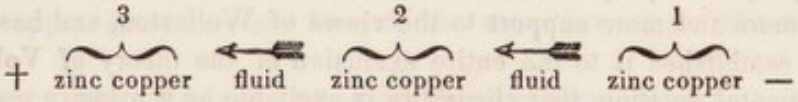
1. When one equivalent of a body, either simple or compound, unites with one or more equivalents of another, the first playing the part of an electro-negative element or acid, one equivalent of electricity is set free.

2. If an equivalent of an electro-negative body, such as oxygen, has already entered into combination with another body, which acts as a base, and if a *second equivalent* of the former unites with the compound thus produced to form a deuto salt or compound; at the time of this second action another equivalent of electricity is disengaged.

Thus the quantity of electricity set free depends solely on the body which acts the part of acid in the compound. (Comp. Rendus, Mar. 1844.)]

THEORIES OF GALVANISM AND ELECTRO-CHEMICAL THEORY.

Of the theories proposed to account for the developement of electricity in voltaic combinations, three in particular have excited the notice of philosophers. The first originated with Volta, who conceived that electricity is set in motion, and the supply kept up, solely by contact or communication between the metals (page 82). He regarded the interposed solutions merely as conductors, by means of which the electricity developed by each pair of plates is conveyed from one part of the apparatus to the other. Thus, in the pile or ordinary battery, represented by the following series:—



Volta considered that contact between the metals occasions the zinc in each pair to be +, and the corresponding copper plate to be —; that the + zinc in each pair except the last, being separated by an intervening stratum of liquid from the — copper of the following pair, yields to it its excess of electricity; and that in this way each zinc plate communicates, not only the electricity developed by its own contact with copper, but also that which it had received from the pair of plates immediately before it. Thus, in the three pairs of plates contained in brackets, the second pair was thought to receive electricity from the first only, and the third pair from the first and second. In batteries constructed on the principle of the crown of cups (fig. 6), the *electro-motion*, as Volta called it, is ascribed to metallic communication between the zinc of one glass and the copper of the adjoining one.

The second is the *chemical theory*, proposed by Wollaston. Volta attached little importance to the chemical changes which never fail to occur in every voltaic circle, whether simple or compound, considering them as casual or unessential phenomena, and therefore neglected them in the construction of his theory. The constancy of their occurrence, however, soon attracted notice. In the earlier discussions on the cause of spasmodic movements in the frog (page 82), Fabroni contended, in opposition to Volta, that the effect was not owing to electricity at

all, but to the stimulus of the metallic oxide formed, or of the heat evolved during its production. More extended researches soon proved the fallacy of this doctrine: but Fabroni made a most ingenious use of the facts within his knowledge, and paved the way to the chemical theory of Wollaston.

Wollaston, fully admitting electricity as the voltaic agent, assigned chemical action as the cause by which it is excited. The repetition and extension of Volta's experiments by the English chemists speedily detected the error he had committed in overlooking the chemical phenomena which occur within the pile. It was observed that no sensible effects are produced by a combination of conductors which do not act chemically on each other; that the action of the pile is always accompanied by the oxidation of the zinc; and that the energy of the pile in general is proportional to the activity with which its plates are corroded. Observations of this nature induced Wollaston to conclude that the process begins with the oxidation of the zinc,—that oxidation, or, in other terms, chemical action, was the primary cause of the developement of electricity,—that the fluid of the circle served both to oxidize the zinc and to conduct the electricity which was excited,—and that contact between the plates served only to conduct electricity, and thereby complete the circuit.

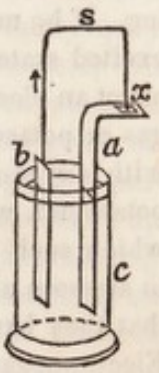
The third theory of the pile was proposed by Davy, and is intermediate between the two former. He adduced many experiments in support of Volta's statement, that the electric equilibrium is disturbed by the contact of different substances, without any chemical action taking place between them. He acknowledged, however, with Wollaston, that the chemical changes contribute to the general result; and he maintained that, though not the primary movers of the electric current, they are essential to the continued and energetic action of every voltaic circle. The electric excitement was begun, he thought, by metallic contact, and maintained by chemical action.

The progress of inquiry since these theories first came into notice, has gradually given more and more support to the views of Wollaston, and has at last, I apprehend, established it to the entire exclusion of the theory of Volta. The very fundamental position, that electricity is excitable as a primary result by the contact of different substances, is warmly contested, and, as some think with strong reason, has been disproved (page 72); but admitting, for the sake of argument, that a *small* effect, which is all that can now be contended for, may thus be produced, it is altogether insignificant when contrasted with the astonishing phenomena exhibited by a voltaic circle. The experiments of De la Rive, in reference to this question, appear irreconcilable with the theory of Volta (An. de Ch. et Ph. xxxviii. 225; lxi. 38; lxii. 147). This ingenious philosopher contends that the direction of a voltaic current is not determined by metallic contact, nor even by the nature of the metals relatively to each other, but by their chemical relation to the exciting liquid. As the result of his inquiries, he states, that of two metals composing a voltaic circle, that one which is most energetically oxidized will be + with respect to the other. Thus, when tin and copper are placed in acid solutions, the former, which is most rapidly corroded, gives a + current through the liquid to the copper, as the zinc does in the circle in fig. 1; but, if they are put into a solution of ammonia, which acts most on the copper, the direction of the current will be reversed. Copper is + in relation to lead in strong nitric acid, which oxidizes the former most freely; whereas in dilute nitric acid, by which the lead is most rapidly dissolved, the lead is +. Even two plates of copper immersed in solutions of the same acid, but of different strength,

will form a voltaic circle, the plate on which chemical action is most free causing a current of + electricity to the other: nay, it is possible to construct a compound circle solely with zinc plates and one acid solution (page 83,) provided the same side of each plate be more rapidly oxidized than the other.

The admirable researches of Faraday (Phil. Trans. 1833 & 34), supply conclusive evidence against the theory of Volta, proving metallic contact not to be essential to voltaic action, inasmuch as it is procured characteristically without contact. A plate of zinc, *a*, fig. 15, about 8 inches long by $\frac{1}{2}$ an inch wide, was cleaned and bent at a right angle; and a plate of platinum, of the same width and 3 inches long, was soldered to a platinum wire, *b s x*, the point of which, *x*, rested on a piece of bibulous paper lying upon the zinc, and moistened with a solution of iodide of potassium. On introducing the plates into a vessel, *c*, filled with dilute sulphuric and nitric acid, a + current instantly ensued in the direction of the arrow, as testified by the hydrogen evolved at the plate *a*, by the decomposed iodide of potassium, and by a galvanometer. We have thus a simple circle of the same construction and action as in figure 1, except in the absence of metallic contact.

Fig. 15.



The arrangement of figure 15, however, though good for establishing a principle, is not adapted for ordinary practice. The moist paper at *x* is a much less perfect conductor than a metal, and thus obstructs the passage of the current; nay, it does more, for it tends to establish an opposite current. In fact, on removing the dilute acid from *c*, and putting the zinc plate, *a*, in contact with the plate of platinum, an ordinary simple circle would be formed, in which a positive current would flow from the zinc at *x* through the solution to and along the wire *x s b*. This current, in Faraday's experiment, was so feeble compared with the one excited by the acid solution, that its influence was scarcely appreciable; but if the opposed currents had been of the same force, no action would have ensued.

To explain how chemical action excites electricity, recourse is had to the electro-chemical theory, first started by Davy in his essay on *Some Chemical Agencies of Electricity* (Phil. Trans. 1807). The views of Davy, which in some form or other have been adopted by most persons who have speculated on this subject, are founded on the assumption, now rendered so much more plausible than in his day, that electrical and chemical attractions are owing to one and the same agent. He considered chemical substances to be endowed with *natural electric energies;* meaning thereby that a certain electric condition, either + or —, is natural to the atoms or combining molecules of bodies; that chemical union is the result of electrical attraction taking place between oppositely excited atoms, just as masses of matter when oppositely excited are mutually attracted; and that ordinary chemical decomposition arises from two combined atoms being drawn asunder by the electric energies of other atoms more potent than those by which they were united. Electro-chemical decomposition was at once explained by Davy on the same principles. He regarded the metallic terminations or *poles* of a voltaic circle (page 101) as two centres of electrical power, each acting repulsively to particles in the same electric state as itself, and by attraction on those which were oppositely excited. The necessary result was, that if the electric energy of the battery exceeded that by which the elements of any compound subject to its action were held together, decomposition followed, and each ele-

ment was transferred bodily to the pole by which it was attracted, passing through solutions not containing the original compound, and refusing to unite with substances for which under other circumstances it would have combined. Substances which appeared at the + pole, such as oxygen, chlorine, and acids, were termed *electro-negative* substances; and those *electro-positive* bodies, which were separated at the — pole.

The views of Davy, both in his original essay and his subsequent explanations (Phil. Trans. 1826), were so generally and obscurely expressed, that chemists have never fully agreed, as to some points of the doctrine, about his real meaning. If he meant that a particle of free oxygen or free chlorine is in a negatively excited state, then his opinion is contrary to the fact, that neither of those gases affect an electrometer with — or any kind of electricity, any more than hydrogen gas or potassium alone exhibit any evidence of + excitement. If sulphur unites with oxygen because it has a + electric energy, why should it unite with potassium, which confessedly is far more + than itself? The only mode in which such facts as these seem reconcilable with the electro-chemical theory, is to suppose all bodies in their uncombined state to be electrically indifferent, but that they have a natural appetency to assume one state in preference to another. Electro-negative bodies are such as assume negative excitement under a certain approximation to others which at the same time become positively excited, chemical union being the consequence. On this supposition it is intelligible that sulphur may be in + relation to oxygen, and — to potassium, just as black silk is positively electrified by friction with sealing-wax, and negatively by white silk. Accordingly, Berzelius, and others who have since speculated on this subject, have been obliged to modify the theory as first given by Davy; and it is viewed at present in different ways by different persons. The following is what appears to me most correctly to harmonize with the laws of electricity and the phenomena to be explained:—A particle of zinc and a particle of oxygen, each possessed of + and — electricity, assume in combining opposite electric conditions, and combine, in consequence of such assumption, the particles adhering together by virtue of their opposite states, just as two oppositely excited pith balls are mutually attractive. The zinc particle in becoming + gives off — electricity to the mass of zinc or other body to which it had belonged; and, in like manner, the particle of oxygen, in becoming —, supplies + electricity to adjacent particles of oxygen or other adjacent substances. Thus electro-positive bodies in the act of combining give off — electricity, and electro-negatives set free + electricity. In general, these opposite electricities instantly neutralize each other; but under favourable circumstances, as in Pouillet's experiments, such effect is prevented. So, in an experiment by De la Rive, of transmitting dry chlorine gas mixed with air through an insulated copper tube, chloride of copper is generated: if the gases pass onward in a continuous current, the + electricity set free by the chlorine is carried off by the air, while the tube is rendered negative by the — electricity lost by those particlss of copper which combine with the chlorine.

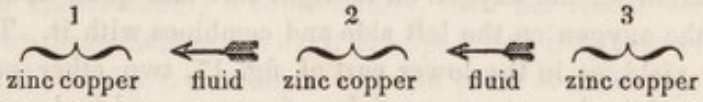
Chemical decomposition also excites electricity; and by this theory it ought to do so. For a particle of zinc in quitting oxygen is +, must recover — electricity before it can resume its natural state, and in doing so leaves contiguous substances +; and, similarly the — oxygen renders objects — by robbing them of their + electricity. Hence, a body in combining excites in others an electric

state opposite to that which it assumes; while in the act of decomposition it produces an effect exactly the reverse.

Again, it follows from the theory, that unless the zinc can assume the + state by getting rid of — electricity, it cannot unite with oxygen; and that chemical union will more readily ensue, the more freely a connecting medium for carrying off such — electricity is supplied. This is applicable to Davy's method of preserving copper in sea-water (page 84). A piece of zinc in contact with copper corrodes rapidly by carrying off its — electricity; while the copper thus constantly rendered —, is prevented from assuming the + state, and hence loses its power of uniting either with oxygen or chlorine. These principles readily apply to a simple voltaic arrangement, composed of zinc, copper, and dilute acid. In the broken circuit, the oxidation of the zinc causes the liquid, which supplies the oxygen to be +; while the zinc plate is made — by the electricity given off by the oxidizing particle of zinc. This happens whether the copper plate is present or not. The + electricity diffused in the acid solution is in part taken up by the copper plate which thereby becomes +, and is in part lost by neutralizing the — electricity on the zinc plate. In the closed circuit, the — electricity on the zinc escapes along the conducting wire to the copper plate; the effect of which is to promote the oxidation of the zinc on the principle above stated, and by rendering the copper —, to facilitate the extraction of + electricity from the liquid. A current of + electricity thus circulates from the zinc through the liquid to the copper, and of — electricity in the opposite direction (page 83). The plate which by chemical action with the liquid excites electricity, is called the *generating plate;* while the other is the *conducting plate*, because it performs the office of a conductor merely: in the common circle, zinc is the generating, and copper the conducting plate.

In a compound circle, represented by three pairs of plates, as in fig. 16, each pair of plates, indicated by the brackets, sends a current of + electricity from

Fig. 16.



the zinc through the liquid to the copper, rendering each copper plate +, while each zinc plate is —. The first copper and second zinc plates, being oppositely electrified, neutralize each other; and the same occurs with the second copper and third zinc, as with any number of plates similarly situated. The extreme plates alone can evince an electric state, the zinc in the broken circuit being —, and the copper +; and if these plates are connected by a wire, they, like the other zinc and copper plates of the series, neutralize each other, and a continuous current is established through the whole battery, of + electricity in one direction, as shown by the arrows, and of — in the other. Thus, the quantity of electricity which circulates in one part of the closed battery, which is aptly called a *circle*, is, contrary to the notion of Volta (page 105), the same in every part (page 90). The influence of a number of plates is to augment the intensity only (page 87). This subject has been ably discussed by De la Rive. (An. de Ch. et Ph. lxii. 180.)

Chemists are not agreed as to the order of electric energy in which the elements should be arranged. The following is that given by Berzelius, and may be viewed as approximative rather than rigidly exact:—Sulphur, nitrogen, and hydrogen scarcely occupy their true position in the series. The two former are less electro-negative than chlorine and fluorine, and hydrogen, I conceive, should

occupy a prominent station among the electro-positive elements. All the bodies in the first series are — with regard to those in the second. In the first series each element is —, and in the second +, to all those which follow it.

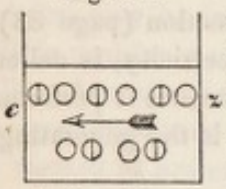
1. *Negative Electrics.*—Oxygen, sulphur, nitrogen, chlorine, iodine, fluorine, phosphorus, silenium, arsenic, chromium, molybdenum, tungsten, boron, carbon, antimony, tellurium, columbium, titanium, silicon, osmium, hydrogen.

2. *Positive Electrics.*—Potassium, sodium, lithium, barium, strontium, calcium, magnesium, glucinium, yttrium, aluminium, zirconium, manganese, zinc, cadmium, iron, nickel, cobalt, cerium, lead, tin, bismuth, uranium, copper, silver, mercury, palladium, platinum, rhodium, iridium, gold.

Theory of Chemical Decomposition.—Compounds are decomposed by galvanism, so far as is known, only when they are more or less fluid, that state being apparently necessary for giving mobility to the elements, which are otherwise chained down to one spot and prevented from separating. Davy's opinion, that an element is actually transferred beyond the place in which the decomposing compound exists, is untenable after the experiments of Faraday (page 103).

The facts adduced by the latter philosopher are inconsistent with the hypothesis of Davy, by which he accounted for chemical decomposition and transfer, namely, that attraction is exerted for the elements of compounds by the metallic conductors *a b*. The most feasible theory is that of Grotthus, of there being successive decompositions and recompositions in the line of particles lying between the electrodes. Let the upper part of fig. 17 represent a row of three particles of water lying between the electrodes *c z*, oxygen being represented by ◯, and hydrogen by ◑. A + current, in passing through them, is assumed to impart a kind of polar or magnetic virtue to the particles of oxygen and hydrogen, whereby affinity is weakened or destroyed on one side, and exalted on the other: each particle of hydrogen, for example, loses its attraction for the oxygen on its right side and quits it, but acquires an attraction for the oxygen on the left side and combines with it. Three particles of water thus yield, as in the lower part of fig. 17, two other particles which are generated; while the extreme particles of oxygen and hydrogen are set free. There is thus no transfer from one spot to another; the oxygen and hydrogen are set free at the place where they pre-existed; and they are evolved as gases, unless, by some secondary action, they should unite with the matter of the electrodes or with some element of the solution.

Fig. 17.



The preceding theoretical questions have been discussed on the assumption of electricity, as explained in the last section, being an independent principle susceptible of rapid motion from one body to another; and that the condition of a voltaic conducting wire is similar to that of a wire leading from the ground to the prime conductor of an electrical machine, or which connects the inner and outer surface of a charged Leyden phial, except that the voltaic current moves slowly, owing to its lower tension and the interposed imperfect conductor. Some conceive that what is called an electric current is not an actual transfer of any thing, but a process of induction among the molecules of a conductor passing progressively along it. Others, denying independent materiality to electricity, may ascribe it to a wave of vibrating matter, just as the phenomena of optics are explained by the undulatory theory. But whatever theory of the nature of electricity may be adopted, it seems necessary, after the experiments of Faraday on the identity of voltaic and common electricity, that the nature of an electric and voltaic current is essentially the same.

PART II.

INORGANIC CHEMISTRY.

PRELIMINARY REMARKS.

In teaching a science such as chemistry, the details of which are numerous and complicated, it would be injudicious to follow the order of discovery, and proceed from individual facts to the conclusions which have been deduced from them. An opposite course is indispensable. It is necessary to discuss general principles in the first instance, in order to aid the beginner in remembering insulated facts, and in comprehending the explanations connected with them. The second part of this work will therefore commence with an explanation of the leading doctrines of the science. One inconvenience, indeed, arises from this method. It is often necessary, by way of illustration, to refer to facts of which the beginner is ignorant; and hence on some occasions more knowledge will be required for understanding a subject fully, than the reader may have at his command. But these instances will, it is hoped, be rarely met with; and when they do occur, the reader is advised to quit the point of difficulty, and return to the study of it when he shall have acquired more extensive knowledge of the details.

To the chemical history of each substance its chief physical characters will be added. A knowledge of these properties is not only advantageous in assisting the chemist to distinguish one body from another, but in many instances it is applied to uses still more important. The character called *specific gravity*, the meaning of which was explained at page 49, is of so much importance that the mode of determining it will be mentioned in this place. The process consists in weighing a body carefully, and then determining the weight of an equal bulk of water, the latter being regarded as unity. If, for example, a portion of water weigh nine grains, and the same bulk of another body 20 grains, its sp. gr. is determined by this formula;—as 9 : 20 : : 1 (assumed as the sp. gr. of water) to the fourth proportional 2·2222; so that the sp. gr. of any substance is found by dividing its weight by the weight of an equal volume of water. It is easy to discover the weight of equal bulks of water and any other liquid by filling a small bottle of known weight with each successively, and weighing them.* The method of obtaining the necessary data in case of a solid is some-

* Bottles are prepared for this purpose by the philosophical instrument makers.

what different. The body is first weighed in air, is next suspended in water by means of a hair attached to the scale of the balance, and is then weighed again. The difference between the two weights gives the weight of a quantity of water equal to the bulk of the solid. This rule is founded on the hydrostatic law, that a solid body, immersed in any liquid, not only weighs less than it does in air, but the difference corresponds exactly to the weight of liquid which it displaces; and it is obvious that the liquid so displaced is exactly of the same dimensions as the solid. Another method is by the use of the bottle recommended for taking the sp. gr. of liquids. After weighing the bottle filled with water, a known weight of the solid is put into it, which of course displaces a quantity of water precisely equal to its own volume. The exact weight of the displaced water is found by weighing the bottle again, after its outer surface is made perfectly dry.

The determination of the sp. gr. of gaseous substances is an operation of much greater delicacy. From the extreme lightness of gases, it would be inconvenient to compare them with an equal bulk of water, and therefore atmospheric air is taken as the standard of comparison. The first step of the process is to ascertain the weight of a given volume of air. This is done by weighing a very light glass flask, furnished with a good stopcock, while full of air; and then weighing it a second time, after the air has been withdrawn by means of the air-pump. The difference between the two weights gives the information required. According to the observation of Prout, 100 cubic inches of pure and dry atmospheric air, at the temperature of 60° and when the barometer stands at 30 inches, weigh 31·0117 grains. By a similar method the weight of any other gas may be determined, and its sp. gr. be inferred accordingly. For instance, suppose 100 cubic inches of oxygen gas are found to weigh 34·109 grains, its sp. gr. will be thus deduced; as 31·0117 : 34·109 : : 1 (the sp. gr. of air) : 1·1025, the sp. gr. of oxygen.

There are four circumstances to which particular attention must be paid in taking the specific gravity of gases :—

1. The gas should be perfectly pure, otherwise the result cannot be accurate.

2. Due regard must be had to its hygrometic condition. If it is saturated with moisture, the necessary correction may be made by the formula of page 50; or it may be dried by the use of substances which have a powerful attraction for moisture, such as chloride of calcium, quicklime, or fused potassa.

3. As the bulk of gaseous substances, owing to their elasticity and compressibility, is dependent on the pressure to which they are exposed, no two observations admit of comparison, unless made under the same elevation of the barometer. It is always understood, in taking the sp. gr. of a gas, that the barometer must stand at 30 inches, by which means the operator is certain that each gas is subject to equal degrees of compression. An elevation of thirty inches is called the standard height; and if the mercurial column be not of that length at the time of performing the experiment, the error arising from this cause must be corrected by calculation. It has been established by experiment that the bulk of gases is inversely as the pressure to which they are subject. Thus, 100 measures of air, under the pressure of 30 inches of mercury, will dilate to 200 measures, if the pressure be diminished by one half; and will be compressed to 50 measures, when the pressure is double, or equal to a mercurial column of 60 inches. The correction for the effect of pressure may therefore be made by the rule of three, as will appear by an example. If a certain por-

tion of gas occupy the space of 100 measures at 29 inches of the barometer, its bulk at 30 inches may be obtained by the following proportion; as 30: 29:: 100: 96·66.

It is understood that the temperature of the mercurial column is constant: if not so, correction must be made for the change in the volume of the mercury produced by change of temperature, on the principle laid down at page 22.

4. For a similar reason the temperature should always be the same. The standard or mean temperature is 60°; and if the gas be admitted into the weighing-flask when the thermometer is above or below that point, the formula of page 24 should be employed for making the necessary correction.

Chemical Nomenclature.—The first attempt to form a systematic chemical nomenclature was by Lavoisier, Berthollet, Guyton de Morveau, and Fourcroy, soon after the discovery of oxygen gas. To avoid an undue use of new terms, the known elements and the more familiar compound bodies were allowed to retain the names which usage had assigned to them. The newly-discovered elements were named from some striking property. Thus, oxygen, from οξυς acid, and γενναειν to generate, was so called from a belief that it is the universal cause of acidity; and the term hydrogen, from ὑδωρ water, and γενναειν, was applied to the inflammable element of water. The compounds into which oxygen enters were termed *acids* or *oxides*, according as they do or do not possess acidity. The name of an acid was derived from the substance acidified by the oxygen, to which was added the termination in *ic*. Thus sulphur*ic* and carbon*ic* acids signified compounds of sulphur and carbon with oxygen. Should sulphur or any other body form two acids, the name of that containing least oxygen was made to terminate in *ous*, as sulphur*ous* acid. The termination in *uret* was applied to compounds of the simple non-metallic substances with each other, with a metal, or with a metallic oxide: thus, sulph*uret* and carb*uret* of iron signify compounds of sulphur and carbon with iron. The general term *salt* comprehended compounds of acids with alkaline bases, and the names of the salts were so contrived as to indicate the substances contained in them. If the acid contain a maximum of oxygen, the name of the salt terminated in *ate*; if a minimum, the termination in *ite* was used: thus, sulph*ate* and phosph*ate* of potassa are salts of sulphur*ic* and phosphor*ic* acids; while the terms sulph*ite* and phosph*ite* of potassa denote salts of that alkaly with sulphur*ous* and phosphor*ous* acids.

These instances suffice to exhibit the principles by which the framers of the nomenclature were guided. Their object was to apply similar names to similar things, and so to construct those names as to indicate the nature or composition of the bodies to which they were attached. The same views have been acted on by succeeding chemists, who, with this intention, have availed themselves of the laws of definite combination. The more essential parts of this method, as adopted in these elements, are the following:—The names of newly-discovered elements are selected from some obvious property: thus, chlorine and iodine were so called from their colour. The termination of a name is rendered similar to those of nearly allied substances: thus, iod*ine*, and flour*ine* received that termination from their analogy to chlorine; the compounds of chlorine, iodine, bromine, and flourine, from their relations to oxygen, are termed chlor*ides*, iod*ides*, &c.; and the compounds of selenium, and other similar inflammables, are called seleni*urets*, from their analogy to sulph*urets* and phosph*urets*. The names of metals, except some, as iron and tin, whose names have been sanctioned by

usage, terminate in *um*, as potassium and titanium. The names of alkaline bases, when expressed by one word, terminate in *a*, as potassa and morphia. When one substance forms with oxygen three or more acids, a Greek preposition is usually prefixed to indicate the relative quantity of oxygen: thus, *hypo*nitrous acid contains less oxygen than the nitrous: *hyper*nitrous would apply to an acid with more oxygen than the nitrous; and *hypo*sulphur*ic* acid indicates an acid with less oxygen than the sulphuric, and more than the sulphurous. *Per* is sometimes prefixed with the same intention as *hyper*: thus, *per*chloric acid contains more oxygen than the chloric. Different oxides of the same metal are distinguished by derivates from the Greek or Latin. An oxide consisting of an equivalent of each element is denoted either by the term oxide without any affix, or by *proto*xide (πρωτος, first); the highest grade is the *per*oxide; and the intermediate grades are distinguished by Latin numerals expressing the number of equivalents of oxygen combined with one equivalent of the metal, such as *bin*oxide, *ter*oxide, &c. Sesqui, one and a half, is used to indicate the relation of 1 to $1_{\frac{1}{2}}$, or 2 to 3, as in the Sesquioxide of iron or cobalt. The Greek numerals *dis*, *tris*, *tetrahis*, are prefixed in like manner to denote oxides formed with one equivalent of oxygen, and two, three, or more equivalents of a metal. More complex ratios, such as 3 eq. of a metal to 4 eq. of oxygen, are denoted by a fraction, $\frac{3}{4}$, placed before the name of the oxide.

The same system is extended not merely to the union of elements generally with each other, but to compounds of a more complex nature, such as the salts. To a salt formed of an equivalent of the acid and alkali, its generic name without other addition is applied; but if two or more equivalents of the acid are attached to one eq. of the base, or two or more equivalents of the base to one eq. of the acid, a numeral is prefixed so as to indicate its composition. The two salts of sulphuric acid and potassa are called sulphate and *bi*sulphate; the first containing an eq. of the acid and alkali, and the latter one eq. of the alkali to two of the acid. The three salts of oxalic acid and potassa are termed the oxalate, *bin*oxalate, and *quadr*oxalate of potassa; because one eq. of the alkali is united with one eq. of acid in the first salt, with two in the second, and with three in the third. In the chromate and *di*chromate of oxide of lead, one eq. of the acid is united with 1 eq. of oxide in the former, and with two in the latter. The term salt has of late received considerable extension, being now applied to compounds analogous to common salts in constitution, though not formed of an acid and alkali. The grounds on which this has been done, and the nomenclature introduced in consequence, are explained in the section of the salts.—In speaking of salts of metallic oxides, many chemists are in the practice, for the sake of brevity, of mentioning the name of the metals only. Thus, in the expressions *sulphates of silver and lead*, the *oxide* of silver, and *oxide* of lead, are to be understood. The present comprehensive sense in which the word *salt* is used begins to render this practice objectionable.

The generic part of the name of a compound is usually formed from that ingredient which is considered the most highly electro-negative. Thus, to compounds of oxygen and chlorine, chlorine and iodine, iodine and sulphur, sulphur and potassium, in which the first of each pair is the electro-negative element, the correct appellations are oxides of chlorine, chloride of iodine, iodide of sulphur, sulphuret of potassium; and not chloride of oxygen, iodide of chlorine, sulphuret of iodine, and potassiuret of sulphur. This practice is invariably observed in this treatise.

Convenient and philosophical as this nomenclature may at first appear, its principles are now felt to be far from coextensive with the science. It much needs extension and modification. To many of the complex compounds known to chemists it is impracticable to apply convenient names correctly expressive of their constitution; and this has led to the use of those symbolic characters which have become general among chemists, and which are essential to the present state of chemistry. The mode of employing such notation will be explained in the second section of this part.

SECTION I.

AFFINITY.

All chemical phenomena are owing to Affinity or Chemical Attraction. It is the basis on which the science of chemistry is founded. It is, as it were, the instrument which the chemist employs in all his operations, and hence it forms the first and leading object of his study.

Affinity is exerted between the minutest particles of different kinds of matter, causing them to combine so as to form new bodies endowed with new properties. It acts only at insensible distances; in other words, apparent contact, or the closest proximity, is necessary to its action. Everything which prevents such contiguity is an obstacle to combination; and any force which increases the distance between particles already combined, tends to separate them permanently from each other. In the former case, they do not come within the sphere of their mutual attraction; in the latter, they are removed out of it. It follows, therefore, that though affinity is regarded as a specific power distinct from the other forces which act on matter, its action may be promoted, modified, or counteracted by them; and consequently, in studying the phenomena produced by affinity, it is necessary to inquire into the conditions that influence its operation.

The most simple instance of the exercise of chemical attraction is afforded by the admixture of two substances. Water and sulphuric acid, or water and alcohol, combine readily. On the contrary, water shows little disposition to unite with ether, and still less with oil; for, however intimately their particles may be mixed together, they are no sooner left at rest than the ether separates almost entirely from the water, and a total separation takes place between that fluid and the oil. Sugar dissolves very sparingly in alcohol, but to any extent in water; while camphor is dissolved in a very small degree by water, and abundantly by alcohol. It appears, from these examples, that chemical attraction is exerted between different bodies with different degrees of force. There is sometimes no proof of its existence at all; between some substances it acts very feebly, and between others with great energy.

Simple combination of two substances is a common occurrence; of which the solution of salts in water, the combustion of phosphorus in oxygen gas, and the neutralization of a pure alkali by an acid, are instances. But the phenomena are often more complex. The formation of a new compound is often attended by the destruction of a pre-existing one; as when some third body acts on a

compound, for one element of which it has a greater affinity than they have for one another. Thus, oil has an affinity for the volatile alkali, ammonia, and will unite with it, forming a soapy substance called a liniment. But the ammonia has a still greater attraction for sulphuric acid; and hence, if the acid be added to the liniment, the alkali will quit the oil, and unite by preference with the acid. If a solution of camphor in alcohol be poured into water, the camphor will be set free because the alcohol combines with the water. Sulphuric acid, in like manner, separates baryta from nitric acid. Combination and decomposition occur in each of these cases;—combination of sulphuric acid with ammonia, of water with alcohol, of baryta with sulphuric acid;—decomposition of the compounds formed of oil and ammonia, of alcohol and camphor, of nitric acid and baryta. These are examples of what Bergmann called *single elective affinity*;—elective, because a substance manifests, as it were, a choice for one of two others, uniting with it by preference, and to the exclusion of the other. Many of the decompositions that occur in chemistry are instances of single elective affinity.

The order in which these decompositions take place has been expressed in tables; of which the following, drawn up by Geoffroy, is an example:—

Sulphuric acid.

Baryta,
Strontia,
Potassa,
Soda,
Lime,
Ammonia,
Magnesia.

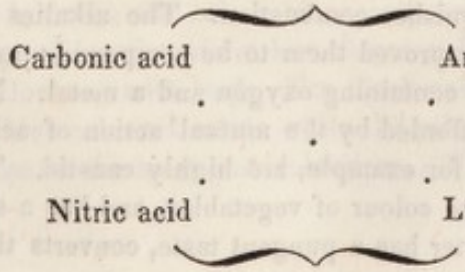
This table signifies, first, that sulphuric acid has an affinity for the substances placed below the horizontal line, and may unite separately with each; and, secondly, that the bases of the salts so formed will be separated from the acid by adding any of the alkalies or earths which stand above it in the column. Thus, ammonia will separate magnesia, lime ammonia, and potassa lime; but none can withdraw baryta from sulphuric acid, nor can ammonia or magnesia decompose sulphate of lime, though strontia or baryta will do so. Bergmann conceived that these decompositions are solely determined by chemical attraction, and that consequently the order of decomposition represents the comparative forces of affinity; and this view, from the simple and natural explanation it affords of the phenomenon, was for a time very generally adopted. But Bergmann was in error. It does not necessarily follow, because lime separates ammonia from sulphuric acid, that the lime has a greater attraction for the acid than the volatile alkali. Other causes are in operation which modify the action of affinity to such a degree, that it is impossible to discover how much of the effect is owing to that power. It is conceivable that ammonia may in reality have a stronger affection for sulphuric acid than lime, and yet that the latter, from the great influence of disturbing causes, may succeed in decomposing sulphate of ammonia.

The propriety of the foregoing remark will appear from the following example:—When a stream of hydrogen gas is passed over oxide of iron heated to redness, the oxide is reduced to the metallic state, and water is generated. On the contrary, when watery vapour is brought into contact with red-hot metallic iron, the oxygen of the water quits the hydrogen and combines with the iron. It follows from the result of the first experiment, according to Bergmann, that

hydrogen has a stronger attraction than iron for oxygen; and from that of the second, that iron has a greater affinity for oxygen than hydrogen. But these inferences are incompatible with each other. The affinity of oxygen for the two elements, hydrogen and iron, must either be equal or unequal. If equal, the result of both experiments was determined by modifying circumstances; since neither of these substances ought on this supposition to take oxygen from the other. But if the forces are unequal, the decomposition in one of the experiments must have been determined by extraneous causes, in direct opposition to the tendency of affinity.

The fallacy of Bergmann's opinion was detected by Berthollet. He first showed that the relative forces of chemical attraction cannot always be determined by observing the order in which substances separate each other when in combination, and that the tables of Geoffroy are merely tables of decomposition, not of affinity. He likewise traced all the various circumstances that modify the action of affinity, and gave a consistent explanation of the mode in which they operate. Berthollet went even a step further. He denied the existence of elective affinity as an invariable force, capable of effecting the perfect separation of one body from another, and maintained that all the instances of complete decomposition attributed to elective affinity are in reality determined by one or more of the collateral circumstances that influence its operation. But here this acute philosopher went too far. Bergmann erred in supposing the result of chemical action to be in every case owing to elective affinity; but Berthollet ran into the opposite extreme in declaring that the effects formerly ascribed to that power are never produced by it. That chemical attraction is exerted between bodies with different degrees of energy, is, I apprehend, indisputable. Water has a much greater affinity for hydrochloric acid and ammoniacal gases than carbonic and hydrosulphuric acids, and for these than for oxygen and hydrogen. The attraction of lead for oxygen is greater than that of silver for the same substance. The disposition of gold and silver to combine with mercury is greater than the attraction of platinum and iron for that fluid. As these differences cannot be accounted for by the operation of any modifying causes, we must admit a difference in the force of affinity in producing combination. It is equally clear that in some instances the separation of bodies from one another can only be explained on the same principle. No one, I conceive, will contend that the decomposition of hydriodic acid by chlorine, or of hydrosulphuric acid by iodine, is determined by the concurrence of any modifying circumstances.

Affinity is the cause of changes still more complicated than those which have just been considered. In a case of single elective affinity, three substances only are present, and two affinities are in play. But it frequently happens that two compounds are mixed together, and four different affinities brought into action. The changes that may or do occur under these circumstances may be studied by aid of a diagram. Thus, in mixing together a solution of carbonate of ammonia and nitrate of lime, their mutual action may be represented in the following manner:—



Each of the acids has an attraction for both bases, and hence it is possible either that the two salts should continue as they were, or that an interchange of principles should ensue, giving rise to two new compounds,—carbonate of lime and nitrate of ammonia. According to the views of Bergmann, the result is solely dependent on the comparative strength of affinities. If the affinity of carbonic acid for ammonia, and of nitric acid for lime, exceed that of carbonic acid for lime, added to that of nitric acid for ammonia, then will the two salts experience no change whatever; but if the latter affinities preponderate, then, as does actually happen in the present example, both the original salts will be decomposed, and two new ones generated. Two decompositions and two combinations take place, being an instance of what is called *double elective affinity*. Kirwan applied the terms *quiescent* and *divellent* to denote the tendency of the opposing affinities,—the action of the former being to prevent a change, the latter to produce it.

The doctrine of double elective affinity was assailed by Berthollet on the same ground and with the same success as in the case of single elective attraction. He succeeded in proving that the effect cannot always be ascribed to the sole influence of affinity. For, to take the example already adduced, if carbonate of ammonia decompose nitrate of lime by the mere force of a superior attraction, it is manifest that carbonate of lime ought never to decompose nitrate of ammonia. But if these two salts are mixed in a dry state and exposed to heat, double decomposition does take place, carbonate of ammonia and nitrate of lime being formed; and therefore, if the change in the first example was produced by chemical attraction alone, that in the second must have occurred in direct opposition to that power. It does not follow, however, because the result is sometimes determined by modifying conditions, that it must always be so. I apprehend that the decomposition of the solid cyanuret of mercury by hydrosulphuric acid gas, which takes place even at a low temperature, cannot be ascribed to any other cause than a preponderance of the divellent over the quiescent affinities.

ON THE CHANGES THAT ACCOMPANY CHEMICAL ACTION.

The leading circumstance that characterises chemical action is the loss of properties experienced by the combining substances, and the acquisition of new ones by the product of their combination. The change of property is sometimes inconsiderable. In a solution of sugar or salt in water, and in mixtures of water with alcohol or sulphuric acid, the compound retains so much of the character of its constituents, that there is no difficulty in recognising their presence. But more generally the properties of one or both of the combining bodies disappear entirely. One would not suppose from its appearance, that water is a compound body; much less that it is composed of two gases, oxygen and hydrogen, neither of which, when uncombined, has ever been compressed into a liquid. Hydrogen is one of the most inflammable substances in nature, and yet water cannot be set on fire: oxygen, on the contrary, enables bodies to burn with great brilliancy, and yet water extinguishes combustion. The alkalies and earths were regarded as simple till Davy proved them to be compound; and certainly they evince no sign whatever of containing oxygen and a metal. Numerous examples of a similar kind are afforded by the mutual action of acids and alkalies. Sulphuric acid and potassa, for example, are highly caustic. The former is intensely sour, reddens the blue colour of vegetables, and has a strong affinity for alkaline substances; the latter has a pungent taste, converts the blue colour of

vegetables to green, and combines readily with acids. On adding these principles cautiously to each other, a compound results called a *neutral salt*, which does not in any way affect the colouring matter of plants, and in which the other distinguishing features of the acid and alkali can no longer be perceived. They appear to have destroyed the properties of each other, and are hence said to *neutralize* one another.

The other phenomena that accompany chemical action are changes of *density*, *temperature*, *form*, and *colour*.

1. *Change of density*. It is observed that two bodies rarely occupy, after combination, the same space which they possessed separately. In general their bulk is diminished, so that the sp. gr. of the new body is greater than the mean of its components. Thus a mixture of 100 measures of water and an equal quantity of sulphuric acid does not occupy the space of 200 measures, but considerably less. A similar contraction frequently attends the combination of solids. Gases often experience a remarkable condensation when they unite. The elements of olefiant gas, for instance, would expand to four times the bulk of that compound, if they were suddenly to become free, and assume the gaseous form. But the rule is not without exception. The reverse happens in some metallic compounds; and there are examples of combination between gases without any change of bulk.

2. *A change of temperature* generally accompanies chemical action. Heat is evolved either when there is a diminution in the bulk of the combining substances without change of form, or when a gas is condensed into a liquid, or a liquid becomes solid. The heat caused by mixing sulphuric acid with water is an instance of the former; and the common process of slaking lime, during which water loses its liquid form in combining with that earth, is an example of the latter. The rise of temperature in these cases is obviously referable to diminished sp. heat in the new compound; but intense heat sometimes accompanies chemical action under circumstances in which an explanation founded on a change of sp. heat is inadmissible. At present it is enough to have stated the fact; its theory will be discussed under the subject of combustion. The production of cold seldom or never takes place during combination, except when heat is rendered insensible by the conversion of a solid into a liquid, or a liquid into a gas. All the frigorific mixtures act in this way.

3. *The changes of form* that attend chemical action are exceedingly various. The combination of gases may give rise to a liquid or a solid; solids sometimes become liquid, and liquids solid. Several familiar chemical phenomena, such as detonation, effervescence, and precipitation, are owing to these changes. The sudden evolution of a large quantity of gaseous matter causes an explosion, as when gunpowder detonates. The slower disengagement of gas produces effervescence, as when marble is put into hydrochloric acid. A precipitate is owing to the formation of a new body which happens to be insoluble in the liquid in which its elements were dissolved.

4. *Change of colour* frequently attends chemical action. No uniform relation has been traced between the colour of a compound and that of its elements. Iodine, whose vapour is of a violet hue, forms a beautiful red compound with mercury, and a yellow one with lead. The black oxide of copper generally gives rise to green and blue coloured salts; while the salts of the oxide of lead, which is itself yellow, are for the most part colourless. The colour of precipitates is a

very important study, as it supplies a character by which most substances may be distinguished.

ON THE CIRCUMSTANCES THAT MODIFY AND INFLUENCE THE OPERATION OF AFFINITY.

Of the conditions which are capable of promoting or counteracting the tendency of chemical attraction, the following are the most important: cohesion, elasticity, quantity of matter, gravity, and contact with other bodies. To these may be added the agency of the imponderables.

Cohesion.—The first obvious effect of cohesion is to oppose affinity, by impeding or preventing that mutual penetration and close proximity of the particles of different bodies, which is essential to the successful exercise of their attraction. Bodies seldom act chemically in their solid state; their molecules do not come within the sphere of attraction, and therefore combination cannot take place, although their affinity may in fact be considerable. Liquidity, on the contrary, favours chemical action; it permits the closest possible approximation, while the cohesive power is comparatively so trifling as to oppose no appreciable barrier to affinity.

Cohesion may be diminished in two ways,—by mechanical division, or by the application of heat. The former aids by increasing the extent of surface; but it is not of itself in general sufficient, because the particles, however minute, still retain that degree of cohesion which constitutes solidity. Heat acts with greater effect, and never fails in promoting combination, whenever the cohesive power is a barrier to it. Its intensity should always be so regulated as to produce liquefaction. The fluidity of one of the substances frequently suffices for effecting chemical union, as is proved by the facility with which water dissolves many salts and other solid bodies. But the cohesive force is still in operation; for a solid is commonly dissolved in greater quantity when its cohesion is diminished by heat. The reduction of both substances to the liquid state is the best method for ensuring chemical action. The slight degree of cohesion possessed by liquids does not appear to cause any impediment to combination; for they commonly act as energetically on each other at low temperatures, or at a temperature just sufficient to cause perfect liquefaction, as when their cohesive power is still further diminished. It seems fair to infer, therefore, that very little, if any, affinity exists between two bodies which do not combine when they are intimately mixed in a liquid state.

The phenomena of crystallization are owing to the ascendency of cohesion over affinity. When a large quantity of salt has been dissolved in water by the aid of heat, part of the saline matter generally separates as the solution cools, because the cohesive power of the salt then becomes comparatively too powerful for chemical attraction. Its particles begin to cohere together, and are deposited in crystals, the process of crystallization continuing till it is arrested by the affinity of the liquid. A similar change happens when a solution made in the cold is gradually evaporated. The cohesion of the saline particles is no longer counteracted by the affinity of the liquid, and the salt therefore assumes the solid form.

Cohesion plays a still more important part. It sometimes determines the result of chemical action, probably even in opposition to affinity. Thus, on

mixing together a solution of two acids and one alkali, of which two salts may be formed, one soluble and the other insoluble, the alkali will unite with that acid with which it forms the insoluble compound, to the total exclusion of the other. This is one of the modifying circumstances employed by Berthollet to account for the phenomena of single elective attraction, and is certainly applicable to many of the instances to be found in the tables of affinity. When, for example, hydrochloric acid, sulphuric acid, and baryta are mixed together, sulphate of baryta is formed in consequence of its insolubility. Lime, which yields an insoluble salt with carbonic acid, separates that acid from ammonia, potassa, and soda, with all of which it makes soluble compounds.

A similar explanation may be given of many cases of double elective attraction. On mixing together in solution four substances, A, B, C, D, of which it is possible to form four compounds, AB and CD, or AC and BD, that compound will certainly be produced which happens to be insoluble. Thus, sulphuric acid, soda, nitric acid, and baryta may give rise either to sulphate of soda and nitrate of baryta, or to sulphate of baryta and nitrate of soda; but the first two salts cannot exist together in the same liquid, because the insoluble sulphate of baryta is instantly generated, and its formation necessarily causes the nitric acid to combine with the soda. In like manner a solution of nitrate of lime is decomposed by carbonate of ammonia, in consequence of the insolubility of carbonate of lime.

To comprehend the manner in which cohesion acts in these instances, it is necessary to consider what takes place when in the same liquid two or more compounds are brought together, which do not give rise to an insoluble substance. Thus, on mixing solutions of sulphate of potassa and nitrate of soda, no precipitate ensues; because the salts capable of being formed by double decomposition, sulphate of soda and nitrate of potassa, are likewise soluble. In this case it is possible either that each acid may be confined to one base, so as to constitute two neutral salts; or that each acid may be divided between both bases, yielding four neutral salts. It is difficult to decide this point in an unequivocal manner: but, judging from many chemical phenomena, there can, I apprehend, be no doubt that the arrangement last mentioned is the most frequent, and is probably universal whenever the relative forces of affinity are not very unequal. When two acids and two bases meet together in neutralizing proportion, it may therefore be inferred, that each acid unites with both the bases in a manner regulated by their respective forces of affinity, and that four salts are contained in solution. In like manner, the presence of three acids and three bases will give rise to nine salts; and when four of each are present, sixteen salts will be produced. This view affords the most plausible theory of the constitution of mineral waters, and of the products which they yield by evaporation.

The influence of insolubility in determining the result of chemical action may be readily explained on this principle. If nitric acid, sulphuric acid, and baryta are mixed together in solution, the base may be conceived to be at first divided between the two acids, the nitrate and sulphate of baryta to be generated. The latter, being insoluble, is instantly removed beyond the influence of the nitric acid, so that for an instant nitrate of baryta and free sulphuric acid remain in the liquid: but as the base left in solution is again divided between the two acids, a fresh quantity of the insoluble sulphate is generated; and this process of partition continues, until either the baryta or the sulphuric acid is withdrawn from the

solution. Similar changes ensue when nitrate of baryta and sulphate of soda are mixed.

The separation of salts by crystallization from mineral waters or other saline mixtures is explicable by a similar mode of reasoning. Thus, on mixing nitrate of potassa and sulphate of soda, four salts, according to this view, are generated,—namely, the sulphates of soda and potassa, and the nitrates of those bases; and if the solution be allowed to evaporate gradually, a point at length arrives when the least soluble of these salts, the sulphate of potassa, will be disposed to crystallize. As soon as some of its crystals are deposited, and thus withdrawn from the influence of the other salts, the constituents of these undergo a new arrangement, whereby an additional quantity of sulphate of potassa is generated; and this process continues until the greater part of the sulphuric acid and potassa has combined, and the compound is removed by crystallization. If the difference in solubility is considerable, the separation of salts may be often rendered very complete by this method.

The efflorescence of a salt is sometimes attended with a similar result. If carbonate of soda and chloride of calcium are mingled together in solution, the insoluble carbonate of lime subsides. But if carbonate of lime and sea-salt are mixed in the solid state, and a certain degree of moisture is present, carbonate of soda and chloride of calcium are slowly generated; and since the former, as soon as it is formed, separates itself from the mixture by efflorescence, its production continues progressively. The efflorescence of carbonate of soda, which is sometimes seen on old walls, or which in some countries is found on the soil, appears to have originated in this manner.

Elasticity.—From the obstacle which cohesion puts in the way of affinity, the gaseous state, in which the cohesive power is wholly wanting, might be expected to be peculiarly favourable to chemical action. The reverse, however, is the fact. Bodies evince little disposition to unite when presented to each other in the elastic form. Combination does indeed sometimes take place, in consequence of a very energetic attraction; but examples of an opposite kind are much more common. Oxygen and hydrogen gases, and chlorine and hydrogen, though their mutual affinity is very powerful, may be preserved together for any length of time without combining. This want of action seems to arise from the distance between the particles preventing that close approximation which is so necessary to the successful exercise of affinity. Hence many gases cannot be made to unite directly, which nevertheless combine readily while in their *nascent* state; that is, while in the act of assuming the gaseous form by the decomposition of some of their solid or fluid combinations.

Elasticity operates likewise as a decomposing agent. If two gases, the reciprocal attraction of which is feeble, suffer considerable condensation when they unite, the compound will be decomposed by very slight causes. Chloride of nitrogen, which is an oil-like liquid, composed of the two gases chlorine and nitrogen, affords an apt illustration of this principle, being distinguished for its remarkable facility of decomposition. Slight elevation of temperature, by increasing the natural elasticity of the two gases, or contact of substances which have an affinity for either of them, produces immediate explosion.

Many familiar phenomena of decomposition are owing to elasticity. All compounds that contain a volatile and a fixed principle are liable to be decomposed by a high temperature. The expansion occasioned by heat removes the elements

of the compound to a greater distance from each other, and thus, by diminishing the force of chemical attraction, favours the tendency of the volatile principle to assume the form which is natural to it. The evaporation of water from a solution of salt is an instance of this kind.

Many solid substances which contain water in a state of intimate combination part with it in a strong heat, in consequence of the volatile nature of that liquid. The separation of oxygen from some metals, by heat alone, is explicable on the same principle.

From these and some preceding remarks, it appears that the influence of heat over affinity is variable; for at one time it promotes chemical union, and opposes it at another. Its action, however, is always consistent. Whenever the cohesive power is an obstacle to combination, heat favours affinity either by diminishing the cohesion of a solid, or converting it into a liquid. As the cause of the gaseous state, on the contrary, it keeps at a distance particles which would otherwise unite; or, by producing expansion it tends to separate from one another substances which are already combined. There is one effect of heat which seems somewhat anomalous; namely, the combination which ensues in gaseous explosive mixtures on the approach of flame. The explanation given by Berthollet is probably correct,—that the sudden dilatation of the gases in the immediate vicinity of the flame acts as a violent compressing power to the contiguous portions, and thus brings them within the sphere of their attraction.

Some of the decompositions, which were attributed by Bergmann to the sole influence of elective affinity, may be ascribed to elasticity. If three substances are mixed together, two of which can form a compound which is less volatile than the third, the last will, in general, be completely driven off by the application of heat. The decomposition of the salts of ammonia by the pure alkalies or alkaline earths may be adduced as an example; and, for a like reason, all the carbonates are decomposed by nitric acid, and all the nitrates by sulphuric acid. This explanation applies equally well to some cases of double decomposition. It explains, for instance, why dry carbonate of lime will decompose nitrate of ammonia by the aid of heat; for carbonate of ammonia is more volatile than the nitrate either of ammonia or lime.

The influence of elasticity in determining the result of chemical action in these instances seems owing to the same cause which enables insolubility to be productive of similar effects. Thus, on mixing nitrate of ammonia with lime, the acid is divided between the two bases; some ammonia becomes free, which, in consequence of its elasticity, is entirely expelled by a gentle heat. The acid of the remaining nitrate of ammonia is again divided between the two bases; and if a sufficient quantity of lime is present, the ammoniacal salt will be completely decomposed. In like manner, the decomposition of potassa may be effected by iron, though the affinity of this metal for oxygen seems much inferior to that of potassium for oxygen. If potassa in the fused state be brought in contact with metallic iron at a white heat, the oxygen is divided between the two metals, and a portion of potassium set at liberty. But as potassium is volatile at a white heat, it is expelled at the instant of reduction; and thus, by its influence being withdrawn, an opportunity is given for the decomposition of an additional quantity of potassa.

Quantity of Matter.—The influence of quantity of matter over affinity is universally admitted. If one body, A, unites with another, B, in several proportions, that compound will be most difficult of decomposition which contains the

smallest quantity of B. Of the three oxides of lead, for instance, the peroxide parts most easily with its oxygen by the action of heat; a higher temperature is required to decompose the red oxide; and the protoxide will bear the strongest heat of our furnaces without losing a particle of its oxygen.

The influence of quantity over chemical attraction may be further illustrated by the phenomena of solution. When equal weights of a soluble salt are added in succession to a given quantity of water, which is capable of dissolving almost the whole of the salt employed, the first portion of the salt will disappear more readily than the second, the second than the third, the third than the fourth, and so on. The affinity of the water for the saline substance diminishes with each addition, till at last it is so weakened as to be unable to overcome the cohesion of the salt. The process then ceases, and a saturated solution results.

Quantity of matter is employed advantageously in many chemical operations. If a chemist wishes to displace a metallic oxide from an acid by the superior affinity of potassa for the latter, he frequently uses rather more of the alkali than is sufficient for neutralizing the acid. He employs an excess of the alkali, in order the more effectually to bring every particle of the substance to be decomposed in contact with the decomposing agent.

But Berthollet has attributed much greater influence to quantity of matter. It was the basis of his doctrine, developed in the *Statique Chimique*, that bodies cannot be wholly separated from each other by the affinity of a third substance for one element of a compound; and to explain why a superior chemical attraction does not produce the effect which might be expected from it, he contended that quantity of matter compensates for a weaker affinity. From the co-operation of several disturbing causes, Berthollet perceived that the force of affinity cannot be estimated with certainty by observing the order of decomposition; and he therefore had recourse to another method. He supposed the affinity of different acids for the same alkali to be in the inverse ratio of the ponderable quantity of each which is necessary for neutralizing equal quantities of the alkali. Thus, if two parts of one acid, A, and one part of another acid, B, are required to neutralize equal quantities of the alkali, C, it was inferred that the affinity of B for C was twice as great as that of A. He conceived, further, that as two parts of A produce the same neutralizing effect as one part of B, the attraction exerted by any alkali towards two parts of A ought to be precisely the same as for the one part of B; and he hence concluded that there is no reason why the alkali should prefer the small quantity of one to the large quantity of the other. On this he founded the principle that quantity of matter compensates for force of attraction.

Berthollet has here obviously confounded two things, namely, force of attraction and neutralizing power, which are really distinct. The relative weights of hydrochloric and sulphuric acids required to neutralize an equal quantity of any alkali, or, in other words, their capacities of saturation, are as 36·4 to 40, a ratio which remains constant with respect to all other alkalies. The affinity of these acids, according to Berthollet's rule, will be expressed by the inverse ratio of these numbers. But in taking this estimate, we have to make three assumptions, each of which is disputable. There is no proof, in the first place, that hydrochloric acid has a greater affinity for an alkali, such as potassa, than sulphuric acid. Such an inference would be directly opposed to the general opinion founded on the order of decomposition; and though that order, as we have shown, is by no means a satisfactory test of the strength of affinity, it would be

improper to adopt an opposite conclusion without having good reasons for so doing. Secondly, were it established that hydrochloric acid has the greater affinity, it does not follow that the attraction of those acids for potassa is in the inverse ratio of 36·4 to 40. And, thirdly, supposing this point settled, it is very improbable that the ratio of their affinities for one alkali will apply to all others; analogy would lead us to anticipate the reverse. Independently of these objections, Dulong has found that the principle of Berthollet is not in accord with the results of experiment.

Gravity.—The influence of gravity is perceptible when it is wished to make two substances unite, the densities of which are different. In a case of simple solution, a larger quantity of saline matter is found at the bottom than at the top of the liquid, unless the solution shall have been well mixed subsequently to its formation. In making an alloy of two metals which differ in density, a larger quantity of the heavier metal will be found at the lower than in the upper part of the compound, unless great care be taken to counteract the tendency of gravity by agitation. This force obviously acts, like the cohesive power, in preventing a sufficient degree of approximation.

Contact with other bodies.—The influence of contact of different substances in modifying affinity is observable either in the increased or diminished energy of chemical action. The former is always the result of a galvanic current, and has been treated of elsewhere: the latter is produced by the interposition of an indifferent body by which others are removed out of the sphere of their mutual action. Thus, on immersing a fragment of pure zinc into dilute sulphuric acid the chemical action is no sooner commenced than it is checked by the hydrogen which is liberated; this is effected by the minute globules of the gas collecting upon the surface of the zinc, and adhering firmly to it, preventing the zinc and dilute acid from coming into that close contact which is essential to chemical action. Some means must therefore be used to remove this intervening film of hydrogen, if a continuous action be desired: this is effected when the common zinc of commerce is used by the minute portions of other metals present in it as impurities, by which small but numerous galvanic currents are excited, and by their action the hydrogen is collected and makes its escape as globules of gas.

Imponderables.—The influence which heat exerts over chemical phenomena, and the modes in which it operates, have been already discussed. The chemical agency of galvanism has also been described. The effects of light will be most conveniently stated in other parts of the work. Electricity is frequently employed to produce the combination of gases with one another, and in some instances to separate them. It appears to act by the heat which it occasions, and therefore on the same principle as flame.

On the measure of affinity.—As the foregoing observations prove that the order of decomposition is not always a satisfactory measure of affinity, it becomes a question whether there are any means of determining the comparative forces of chemical attraction. When no disturbing causes operate, the phenomena of decomposition afford a sure criterion; but when the conclusions obtained in this way are doubtful, assistance may be frequently derived from other sources. The surest indications are procured by observing the tendency of different substances to unite with the same body under the same circumstances, and subsequently marking the comparative facility of decomposition when the compounds so formed are exposed to the same decomposing agent. Thus, on exposing silver,

lead, and iron, to air and moisture, the iron soon rusts, the lead is oxidized in a slight degree only, and the silver resists oxidation altogether. Iron is hence inferred to have the greatest affinity for oxygen, lead next, and silver the least. This conclusion is supported by concurring observations of a like nature, and confirmed by the circumstances under which the oxides of those metals part with their oxygen. Oxide of silver is reduced by heat alone; and oxide of lead is decomposed by charcoal at a lower temperature than oxide of iron.

It is inferred from the action of heat on the carbonate of potassa, baryta, lime, and oxide of lead, that potassa has a stronger attraction for carbonic acid than baryta, baryta than lime, and lime than oxide of lead. The affinity of different substances for water may be determined in a similar manner.

Of all chemical substances, our knowledge of the relative degrees of attraction of acids and alkalies for each other is the most uncertain. Their mutual action is affected by so many circumstances, that it is in most cases impossible, with certainty, to refer any effect to its real cause. The only methods that have been hitherto devised for remedying this defect are those of Berthollet and Kirwan. Both are founded on the capacities of saturation, and the objections which have been urged to the rule suggested by the former philosopher apply equally to that proposed by the latter. But this uncertainty is of no great consequence in practice. We know perfectly the order of decomposition, whatever may be the actual forces by which it is effected.

SECTION II.

ON THE PROPORTIONS IN WHICH BODIES UNITE, AND ON THE LAWS OF COMBINATION.

The study of the proportions in which bodies unite naturally resolves itself into two parts. The first includes compounds whose elements appear to unite in a great many proportions; the second comprehends those, the elements of which combine in a few proportions only.

I. The compounds contained in the first division are of two kinds. In one, combination takes place unlimitedly in all proportions; in the other, it occurs in every proportion within a certain limit. The union of water with alcohol and the liquid acids, such as the sulphuric, hydrochloric, and nitric, affords instances of the first mode of combination; the solutions of salts in water are examples of the second. One drop of sulphuric acid may be diffused through a gallon of water, or a drop of water through a gallon of the acid; or they may be mixed together in any intermediate proportions; and nevertheless in each case they appear to unite perfectly with each other. A hundred grains of water, on the contrary, will dissolve any quantity of sea-salt which does not exceed forty grains. Its solvent power then ceases, because the cohesion of the solid becomes comparatively too powerful for the force of affinity. The limit to combination is in such instances owing to the cohesive power; and but for the obstacle

which it occasions, the salt would most probably unite with water in every proportion.

All substances that unite in many proportions, give rise to compounds which have this common character, that their elements are united by a feeble affinity, and preserve, when combined, more or less of the properties which they possess in a separate state. In a scientific point of view, these combinations are of a minor importance; but they are exceedingly useful as instruments of research. They enable the chemist to present bodies to each other, under circumstances peculiarly favourable for acting with effect: the liquid form is thus communicated to them; while the affinity of the solvent or menstruum, which holds them in solution, is not sufficiently powerful to interfere with their mutual attraction.

II. The most interesting series of compounds is produced by substances which unite in a few proportions only; and which, in combining, lose more or less completely the properties that distinguished them when separate. Of these bodies, some form but one combination. Thus there is only one compound of boron and oxygen, and of chlorine and hydrogen. Others combine in two proportions. For example, two compounds are formed by mercury and oxygen, and by hydrogen and oxygen. Other bodies again unite in three, four, five, or even six proportions, which is the greatest number of compounds that any two substances are known to produce, except perhaps carbon and hydrogen, and those which belong to the first division.

The combination of substances that unite in a few proportions only, is regulated by the three following remarkable laws:—

First Law of Combination. The composition of bodies is fixed and invariable. A compound substance, so long as it retains its characteristic properties, always consists of the same elements united together in the same proportion. Sulphuric acid, for example, is always composed of sulphur and oxygen in the ratio of 16 parts of the former to 24 of the latter: no other elements can form it, nor can it be produced by its own elements in any other proportion. Water, in like manner, is formed of 1 part of hydrogen and 8 of oxygen; and were these elements to unite in any other ratio, some new compound, different from water, would be the product. The same observation applies to all other substances, however complicated, and at whatever period they were produced. Thus sulphate of baryta, whether formed ages ago by the hand of nature, or quite recently by the operations of the chemist, is always composed of 40 parts of sulphuric acid and 76·7 of baryta. This law, in fact, is universal and permanent. Its importance is equally manifest: it is the essential basis of chemistry, without which the science itself could have no existence.

Two views have been proposed by way of accounting for this law. The explanation now universally given is confined to a mere statement, that substances are disposed to combine in those proportions to which they are so strictly limited, in preference to any others; it is regarded as an ultimate fact, because the phenomena are explicable on no other known principle. A different doctrine was advanced by Berthollet, in his *Statique Chimique*, published in 1803. Having observed the influence of cohesion and elasticity in modifying the action of affinity as already described, he thought he could trace the operations of the same causes in producing the effect at present under consideration. As the solubility of a salt and of a gas in water is limited, in the former by cohesion, in the latter by elasticity, he conceived that the same forces would account for the unchange-

able composition of certain compounds. He maintained that within certain limits bodies have a tendency to unite in every proportion; and that combination is never definite and invariable, except when rendered so by the operation of modifying causes, such as cohesion, insolubility, elasticity, quantity of matter, and the like. Thus, according to Berthollet, sulphate of baryta is composed of 40 parts of sulphuric acid and 76·7 of baryta, not because those substances are disposed to unite in that ratio rather than in another, but because the compound so constituted happens to have great cohesive power.

These opinions were ably and successfully combated by Proust in several papers published in the *Journal de Phisique*, wherein he proved that the metals are disposed to combine with oxygen and with sulphur only in one or two proportions, which are definite and invariable; and a controversy ensued remarkable for the moderation with which it was conducted on both sides. The question is now no longer at issue. The great variety of facts, similar to those observed by Proust, which have since been established, has proved beyond a doubt that the leading principle of Berthollet is erroneous. The tendency of bodies to unite in definite proportions only, is indeed so great as to excite a suspicion that all substances combine in this way; and that the exceptions thought to be afforded by the phenomena of solution are rather apparent than real; for it is conceivable that the apparent variety of proportion, noticed in such cases, may arise from the mixture or combination of a few definite compounds with each other.

2. *Second Law of Combination. The relative quantities in which bodies unite, may be expressed by proportional numbers.* Thus, 8 parts of oxygen united with 1 part of hydrogen, 16 of sulphur, 35·4 of chlorine, 37·6 of selenium, and 108 parts of silver. Such are the quantities of these five bodies which are disposed to unite with 8 parts of oxygen; and it is found that when they combine with one another, they unite either in the proportions expressed by those numbers, or in multiples of them according to the third law of combination. Hydrosulphuric acid, for instance, is composed of 1 part of hydrogen and 16 of sulphur, and bisulphuret of hydrogen of 1 part of hydrogen to 32 of sulphur; 35·4 of chlorine unite with 1 of hydrogen, 16 of sulphur, and 108 of silver; and 39·6 parts of selenium with 1 of hydrogen, and 16 of sulphur.

From the occurrence of such proportional numbers has arisen the use of certain terms, as *Proportion*, *Combining Proportion*, *Proportional*, and *Chemical Equivalent*, or *Equivalent*, to express them. The latter term, introduced by Wollaston, and which is employed in this treatise, was suggested by the circumstance that the combining proportion of one body is, as it were, *equivalent* to that of another body, and may be substituted for it in combination. Among the tables at the end of the volume will be found one of the equivalents of elementary substances.

This law is not confined to elementary substances, since compound bodies have their combining proportions or equivalents, which may likewise be expressed in numbers. Thus, since water is composed of 1 eq. or 8 parts of oxygen, and 1 eq. or 1 of hydrogen, its combining proportion or equivalent is 9. The equivalent of sulphuric acid is 40, because it is a compound of one eq. or 16 parts of sulphur, and three eq. or 24 parts of oxygen; and in like manner, the eq. of hydrochloric acid is 36·4, because it is a compound of one eq. or 35·4 parts of chlorine, and one eq. or 1 part of hydrogen. The equivalent number of potassium is 39, and as that quantity combines with 8 of oxygen to form potassa, the equivalent of the latter is $39 + 8 = 47$. Now when these compounds unite,

one equivalent of the one combines with one, two, three, or more equivalents of the other, precisely as the simple substances do. Hydrate of potassa, for example, is constituted of 47 parts of potassa and 9 of water, and its equivalent is consequently 47 + 9, or 56. Sulphate of potassa is composed of 40 sulphuric acid + 47 potassa; and the nitrate of that alkali of 54 nitric acid + 47 of potassa. The equivalent of the former salt is therefore 87, and of the latter 101.

The composition of the salts affords a very instructive illustration of this subject; and to exemplify it still further, a list of the equivalents of a few acids and alkaline bases is annexed:—

Hydrofluoric Acid	19·7	Lithia	14
Phosphoric Acid	35·7	Magnesia	20·7
Hydrochloric	36·4	Lime	28·5
Sulphuric Acid	40·1	Soda	31·3
Nitric Acid	54·15	Potassa	47·15
Arsenic Acid	57·7	Strontia	51·8
Selenic Acid	63·6	Baryta	76·7

The alkalies here are shown to differ widely in neutralizing power; for the equivalent of each base expresses the quantity required to neutralize an equivalent of each of the acids. Thus 14 of lithia, 31·3 of soda, and 76·7 of baryta, combine with 64·15 of nitric acid, forming the neutral nitrates of lithia, soda, and baryta. The same fact is obvious with respect to the acids; for 40·1 of sulphuric, 54·15 of nitric, and 63.6 of selenic acid unite with 76·7 of baryta, forming a neutral sulphate, nitrate and selenate of baryta.

These circumstances afford a ready explanation of a curious fact, first noticed by the Saxon chemist Wenzel; namely, that when two neutral salts mutually decompose each other, the resulting compounds are likewise neutral. The cause of this fact is now obvious. If 71·3 parts of neutral sulphate of soda are mixed with 130·7 of nitrate of baryta, the 76·7 parts of baryta unite with 40 of sulphuric acid, and the 54 parts of nitric acid of the nitrate combine with the 31·3 of soda of the sulphate, not a particle of acid or alkali remaining in an uncombined condition.

Sulphate of Soda.		Nitrate of Baryta.	
Sulphuric acid	40	54	Nitric acid.
Soda	31·3	76·7	Baryta.
	71·3	130·7	

It matters not whether more or less than 71·3 parts of sulphate of soda are added; for if more, a small quantity of sulphate of soda will remain in solution; if less, nitrate of baryta will be in excess; but in either case the neutrality will be unaffected.

3. *Third Law of Combination. When one body,* A, *unites with another body,* B, *in two or more proportions, the quantities of the latter, united with the same quantity of the former, bear to each other a very simple ratio.* The progress of chemical research, in discovering new compounds and ascertaining their exact composition, has shown that these ratios of B may be represented by one or other of the two following series:—

1st Series. A unites with 1, 2, 3, 4, 5, &c. of B.

2d Series. A unites with 1, $1\frac{1}{2}$, 2, $2\frac{1}{2}$, &c. of B.

The first series is exemplified by the subjoined compounds.

Water is composed of	Hydrogen	1	Oxygen	8	1
Binoxide of Hydrogen	Do.	1	Do.	16	2
Carbonic Oxide	Carbon	6	Do.	8	1
Carbonic Acid	Do.	9	Do.	16	2
Nitrous Oxide	Nitrogen	14·15	Do.	8	1
Nitric Oxide	Do.	14·15	Do.	16	2
Hyponitrous Acid	Do.	14·15	Do.	24	3
Nitrous Acid	Do.	14·15	Do.	32	4
Nitric Acid	Do.	14·15	Do.	40	5

In all these compounds the ratio of the oxygen are expressed by whole numbers. In water the hydrogen is combined with half as much oxygen as in the binoxide of hydrogen, so that the ratio is as 1 to 2. The same relation holds in carbonic oxide and carbonic acid. The oxygen in the compounds of nitrogen and oxygen is in the ratio of 1, 2, 3, 4, and 5. In like manner the ratio of sulphur in the two sulphurets of mercury, and that of chlorine in the two chlorides of mercury, is as 1 to 2. So, in bicarbonate of potassa, the alkali is united with twice as much carbonic acid as in the carbonate; and the acid of the three oxalates of potassa is in the ratio of 1, 2, and 4.

The following compounds exemplify the second series:—

Protoxide of Iron	consists of Iron	28	Oxygen	8	1
Peroxide	Do.	28	Do.	12	1½
Protoxide of Manganese	Manganese	27·7	Do.	8	1
Sesqui-oxide	Do.	27·7	Do.	12	1½
Bin-oxide	Do.	27·7	Do.	16	2
Arsenious Acid	Arsenic	37·7	Do.	12	1½
Arsenic Acid	Do.	37·7	Do.	20	2½
Hypophosphorous Acid	Phosphorus	15·7	Do.	4	½
Phosphorus Acid	Do.	15·7	Do.	12	1½
Phosphoric Acid	Do.	15·7	Do.	20	2½

Both of these series, which together constitute the Third Law of Combination, result naturally from the operation of the second law. The first series arises from one equivalent of a body uniting with 1, 2, 3, or more equivalents of another body. The second series is a consequence of two equivalents of one substance combining with 3, 5, or more equivalents of another. Thus, if two equivalents of phosphorus unite both 3 and with 5 equivalents of oxygen, we obtain the ratio of $1\frac{1}{2}$ to $2\frac{1}{2}$, and should one equivalent of iron combine with one of oxygen, and another compound be formed of two equivalents of iron to three of oxygen, then the oxygen united with the same weight of iron would have the ratio, as in the table of 1 to $1\frac{1}{2}$. The compounds of manganese and phosphorus with oxygen afford examples of the same nature. Still more complex arrangements will be readily conceived, such as 3 equivalents of one substance to 4, 5, or more of another. But it is remarkable that combinations of this kind are very rare; and even their existence, though theoretically possible, has not been decidedly established. Even some of the compounds which are usually included in the second series belong properly to the first. The red oxide of lead, for instance, appears in its chemical relations not so much as a direct compound of lead and oxygen, but as a kind of salt formed by the union of the binoxide of lead with the protoxide of the same metal. On this supposition the two other oxides belong to the first series.

The merit of establishing the first law of combination seems due to Wenzel,

a Saxon chemist; and the second law is deducible from his experiments on the composition of the salts. His work, entitled *Lehre der Verwandtschaft*, was published in 1777. Bergmann and Richter, a few years after, confirmed the observations of Wenzel, though without adding materially in the way of generalization. Higgins in 1789 speculated on the atomic constitution of compound bodies in a manner which, if pursued, would have led to the discovery of Dalton. It is to the latter, science is indebted for deducing from the scattered facts which had been previously collected, a theory of chemical union, embracing the whole science, and giving it a consistency and form which before his time it had never possessed. In his hands the second law of combination first attained its full generality; but the discovery, which is more peculiarly his own, is that part of the third law of combination which is contained in the first of the two series above mentioned. The first public announcement of his views appears to have been made to the Philosophical Society of Manchester in 1803; and in 1808 they were explained in his New System of Chemical Philosophy. In the same year Wollaston and Thomson gave their evidence in support of the new doctrine, and other chemists have followed in the same path of inquiry. But of all who have successfully laboured in establishing the laws of combination, the most splendid contribution is that of the celebrated Berzelius. Struck with the perusal of the works of Richter, he commenced in 1807 an investigation into the Laws of Definite Proportion. Since that period his labours in this important field have been incessant, and every department of the science has been enriched by his skill and indefatigable industry. Whether we look to pneumatic chemistry, to the chemical history of the metals and of the salts, or to the composition of minerals, we are alike indebted to Berzelius. In all he has traced the laws of definite proportion, and by a multitude of exact analyses given to the laws of combination that certainty which accumulated facts can alone convey.

The utility of being acquainted with these important laws is manifest. Through their aid, and by remembering the equivalents of a few elementary substances, the composition of an extensive range of compound bodies may be calculated with facility. Thus by knowing that 6 is the eq. of carbon and 8 of oxygen it is easy to recollect the composition of carbonic oxide and carbonic acid; the first consisting of 6 parts of carbon + 8 of oxygen, and the second of 6 carbon + 16 of oxygen. The eq. of potassium is 39; and potassa, its protoxide, is composed of 39 of potassium + 8 of oxygen. From these few data, the composition of carbonate and bi-carbonate of potassa are given; the former being composed of 22 parts of carbonic acid + 47 potassa, and the latter of 44 carbonic acid + 47 potassa. This method acts as an artificial memory, the advantage of which, compared with the former practice of stating the composition in 100 parts, will be manifest by inspecting the following quantities and attempting to recollect them.

Carbonic Oxide.		Carbonic Acid.	
Carbon	42·86	Carbon	27·27
Oxygen	57·14	Oxygen	72·73

Carbonate of Potassa.		Bi-carbonate of Potassa.	
Carbonic acid	31·43	Carbonic acid	47·83
Potassa	68·57	Potassa	52·17

From the same data, calculations, which would otherwise be difficult or tedious, may be made rapidly and with ease, without reference to books, and frequently

by a simple mental process. The exact quantities of substances required to produce a given effect may be determined with certainty, thus affording information which is often necessary to the success of chemical processes, and of great consequence both in the practice of the chemical arts, and the operations of pharmacy.

The same knowledge affords a good test to the analyst by which he may judge of the accuracy of his result, and even sometimes correct an analysis which he has not the means of performing with rigid precision. Thus a powerful argument for the accuracy of an analysis is derived from the correspondence of its result with the laws of chemical union. On the contrary, if it form an exception to them, we are authorized to regard it as doubtful; and may hence be led to detect an error, the existence of which might not otherwise have been suspected. If an oxidized body be found to contain one equivalent of the combustible with 7·99 of oxygen, it is fair to infer that 8, or one equivalent of oxygen, would have been the result, had the analysis been perfect.

The composition of a substance may sometimes be determined by a calculation, founded on the laws of chemical union, before an analysis of it has been accomplished. When the new alkali lithia was first discovered, chemists did not possess it in sufficient quantity for determining its constitution analytically. But the neutral sulphates of the alkalies and alkaline earths are known to be composed of one equivalent of each constituent, and the oxides to contain one eq. of oxygen. If it be found, therefore, by analysis, that neutral sulphate of lithia is composed of 40 parts of sulphuric acid and 14 of lythia, it may be inferred, since 40 is one eq. of the acid, that 14 is the eq. for lithia; and that this oxide is formed of 8 parts of oxygen and 6 of lithium.

The method of determining equivalent numbers will be anticipated from what has already been said. The commencement is made by carefully analyzing a definite compound of two simple substances which possess an extensive range of affinity. Thus water, a compound of oxygen and hydrogen, is found to contain 8 parts of the former to 1 of the latter; and if it be assumed that water consists of 1 eq. of oxygen and 1 of hydrogen, the relative weights of these equivalents will be as 8 to 1. The chemist then selects for analysis such compounds as he believes to contain 1 eq. of each element, in which either oxygen or hydrogen, but not both, is present. Carbonic oxide and hydro-sulphuric acid are suited to his purpose: as the former consists of 8 parts of oxygen and 6 of carbon, and the latter of 1 part of hydrogen and 16 of sulphur, the equivalent of carbon is inferred to be 6, and that of sulphur 16. The equivalent of all the other elements may be determined in a similar manner.

In researches on chemical equivalents there are two kinds of difficulty, one involved in the processes for ascertaining the exact composition of compounds, and the other in the selection of the compounds which contain single equivalents. Important general precautions in the experimental part of the subject are the following:—1, to exert scrupulous care about the purity of materials; 2, to select methods which consist of a few simple operations only; 3, to repeat experiments, and with materials prepared at different times; 4, to arrive at the same conclusion by two or more processes independent of each other. In the selection of compounds of single equivalents there are several circumstances calculated to direct the judgment:—

1. If two substances combine in several proportions, the law of multiples usually effects the electro-negative element of a compound. Thus, in the 5

compounds of nitrogen and oxygen, in which oxygen is the — element, 14 parts of nitrogen are united with 8, 16, 24, 32, and 40 parts of oxygen; whereas, taking the quantity of oxygen as constant, 8 parts of oxygen are united with 14, 7, 4·66, 3·5, and 2·8 parts of nitrogen, in which the simple ratio of the first series does not exist. This circumstance induces the chemist always to search among the oxides of the same element for the lowest grade of oxidation, and in most cases to consider it as a compound of single equivalent. In some instances, however, the second degree of oxidation is formed of single equivalents, while the lowest oxide consists of 2 eq. of the + element and one of oxygen. Such compounds are called *dioxides* (page 114) and sometimes *suboxides*.

2. Metallic oxides, distinguished for strong alkalinity, or for acting as strong alkaline bases, are always protoxides. Dioxides rarely unite definitely with acids, and are remarkable for their ready conversion into protoxides with separation of metal. If the same metal yield several oxides, the protoxide is the strongest base; the highest grade of oxidation is frequently an acid, and the intermediate oxides are in general little distinguished either for alkalinity or acidity. Protoxides usually resist decomposition more obstinately than other oxides.

3. When a metal forms two oxides, the oxygen of which is in a ratio of 1 to $1\frac{1}{2}$, the first is usually the protoxide, and the second a compound of 2 eq. of the metal to three of oxygen. The oxides of iron and nickel are examples.

4. If two compounds resemble each other in their modes of combination, it is a strong presumption that their constitution is similar. Alumina and the peroxide of iron are remarkably allied in their chemical relations; and hence it is inferred, since the latter consists of 2 eq. of iron and 3 eq. of oxygen, that the former, whose composition would otherwise be very doubtful, is composed of 2 eq. of aluminium and 3 eq. of oxygen.

5. Mitscherlich has found, as is more fully stated in the article on crystallization, that certain compounds which resemble each other in composition and in their modes of combining, are likewise disposed in crystallizing to affect the same form. Hence it is a strong presumption that compounds which are analogous both in their crystalline figure and modes of combining, are also similar in their composition. In the oxide and acid of chromium the oxygen is in the ratio 1 to 2, and hence it was at first supposed that 1 eq. of chromium was united in the oxide with 1 eq. and in the acid with 2 eq. of oxygen. But the chromates resemble the sulphates in form and modes of combining, and the oxide of chromium bears the same analogy to alumina and peroxide of iron. The inference is, that oxide of chromium consists of 2 eq. of chromium and 3 eq. of oxygen, and chromic acid of 1 eq. of chromium and 3 eq. of oxygen.

6. Another guide in these inquiries is derived from the relation traced by Dulong and Petit between the equivalents of a body and its sp. heat. The coincidences pointed out at page 36 are sufficiently numerous to show an interesting relation which is sometimes useful in selecting between doubtful numbers; but the instances of failure are at present too frequent to admit of this principle being used except with much caution.

7. The ready decomposition by galvanism, observed by Faraday, of compounds which consist of single equivalents, and the resistance to the same agent of many others not so constituted, promises to become an indication of great value in determining eq. numbers. The facts as yet known respecting it will be found in the section on galvanism.

8. Great light is often thrown on the chemical constitution of a compound by a knowledge of the *volumes* of the substances of which it is composed. This subject, however, will be discussed in an after part of this section.

Since the equivalents merely express the relative quantities of different substances which combine together, it is in itself immaterial what figures are employed to express them. The only essential point is, that the relation should be strictly observed. Thus, the eq. of hydrogen may be assumed as 10; but then oxygen must be 80, carbon 60, and sulphur 160. We may call hydrogen 100 or 1000; or, if it were desirable to perplex the subject as much as possible, some high uneven number might be selected, provided the due relation between the different numbers were faithfully preserved. But such a practice would destroy the advantage above ascribed to the use of equivalents; and it is the object of every one to employ such as are simple, that their relation may be perceived by mere inspection. Thomson makes oxygen 1, so that hydrogen is eight times less than unity, or 0·125, carbon 0·75, and sulphur 2. Wollaston, in his scale of chemical equivalents, estimated oxygen at 10; and hence hydrogen is 1·25, carbon 7·5 and so on. According to Berzelius, oxygen is 100. And lastly, several other chemists, such as Dalton, Davy, Henry, and others, selected hydrogen as their unit; and therefore the eq. of oxygen is 8. One of these series may easily be reduced to either of the others by an obvious and simple calculation. The numbers adopted in this work refer to hydrogen as unity, and are given in the subjoined table.*

CHEMICAL EQUIVALENTS OF ELEMENTARY SUBSTANCES.

Elements.	Equivalents.	Elements.	Equivalents.	Elements.	Equivalents.
Alluminium	13.7	Gold	199.2	Potassium	39.15
Antimony	64.6	Hydrogen	1	Rhodium	52.2
Arsenic	37.7	Iodine	126.3	Selenium	39.6
Barium	68.7	Iridium	98.8	Silicium	7.5
Bismuth	71	Iron	28	Silver	108
Boron	10.9	Lead	103.6	Sodium	23.3
Bromine	78.4	Lithium	10	Strontium	43.8
Cadmium	55.8	Magnesium	12.7	Sulphur	16.1
Calcium	20.5	Manganese	27.7	Tellurium	32.3
Carbon	6.12	Mercury	202	Thorium	59.6
Cerium	46	Molybdenum	47.7	Tin	57.9
Chlorine	35.42	Nickel	29.5	Titanium	24.3
Chromium	28	Nitrogen	14.15	Tungsten	99.7
Cobalt	29.5	Osmium	99.7	Vanadium	68.5
Columbium	185	Oxygen	8	Uranium	217
Copper	31.6	Palladium	53.3	Yttrium	32.2
Fluorine	18.68	Phosphorus	15.7	Zinc	32.3
Glucinium	17.7	Platinum	98.8	Zirconium	33.7

The preceding table is constructed principally from the published tables of Berzelius, and partly from facts supplied by my own researches. The hypothesis that all equivalent numbers are simple multiples of the equivalent of hydrogen, has been elsewhere shown to be untenable. (Phil. Trans. 1833, Part ii. page 523.) Whenever the experimental quantity is nearly a whole number, the last may for many purposes be used as a sufficient approximation; and, accordingly, for such elements as carbon, sulphur, nitrogen, and potassium, which are often referred to in the way of illustration, I have generally adopted round numbers, as

* For a full table of equivalents, expressed on both the oxygen and hydrogen scales, refer to Appendix. (R.)

being shorter and more easily remembered than fractions. But on all occasions where exact calculations are concerned, the numbers given in the table should be employed.*

The useful instrument known by the name of the *Scale of Chemical Equivalents*, was originally devised by Dr. Wollaston, and is a table of equivalents comprehending all those substances which are most frequently employed by chemists in the laboratory; and it only differs from other tabular arrangements of the same kind, in the numbers being attached to a sliding rule, which is divided according to the principle of that of Gunter. From the mathematical construction of the scale, it not only serves the same purpose as other tables of equivalents, but in many instances supersedes the necessity of calculation. Thus, by inspecting the common table of equivalents, we learn that 87 parts, or one equivalent, of sulphate of potassa, contain 40 parts of sulphuric acid and 47 of potassa; but recourse must be had to calculation, when it is wished to determine the quantity of acid or alkali in any other quantity of the salt. This knowledge, on the contrary, is obtained directly by means of the scale of chemical equivalents. For example, on pushing up the slide until 100 marked upon it is in a line with the name sulphate of potassa on the fixed part of the scale, the numbers opposite to the terms sulphuric acid and potassa will give the precise quantity of each contained in 100 parts of the compound. In the original scale of Wollaston, for a particular account of which I may refer to the Philosophical Transactions for 1814, oxygen is taken as the standard of comparison; but hydrogen may be selected for that purpose with equal propriety, and scales of this kind have been prepared for sale by Reid of Edinburgh. A very complete scale of equivalents has been drawn up by Prideaux of Plymouth. (Phil. Mag. and Annals, viii. 430.)

ON THE ATOMIC THEORY.

The brief sketch which has been given of the laws of combination will, I trust, set in its true light the importance of that department of chemical science. It is founded on *experiment* alone, and the laws which have been stated are the mere expression of fact. It is not necessarily connected with any speculation, and may be kept wholly free from it. The notion that the laws of combination involve something uncertain or hypothetical, is a fallacy easily referable to its source. It was impossible to reflect on the regularity and constancy with which bodies obey these laws, without speculating about the cause of that regularity; and, consequently, the facts themselves were no sooner noticed, than an attempt was made to explain them. Accordingly, when Dalton published his discovery of those laws, he at once incorporated the description of them with his notion of their physical cause, and even expressed the former in language suggested by the latter. Since that period, though several British chemists of eminence, and in particular Wollaston and Davy, recommended and practised an opposite course, both subjects have been too commonly comprised under the name of *atomic theory*; hence it has often happened that beginners have rejected the whole as hypothetical, because they could not satisfactorily distinguish those parts which are founded on fact from those which are conjectural. All such perplexity would have been avoided, and this department of the science have been far better under-

* The recent researches of Dumas, Erdmann and Marchand, on the equivalents of oxygen, hydrogen, carbon, and lime, have revived the hypothesis alluded to in the text. The numbers in the table are, therefore, to be regarded as still open to revision. (R.)

stood, and its value more justly appreciated, had the discussion concerning the atomic constitution of bodies been always kept distinct from that of the phenomena which it is intended to explain. When employed in this limited sense, the atomic theory may be discussed in a few words.

Two opposite opinions have long existed concerning the ultimate elements of matter. It is supposed, according to one party, that every particle of matter, however small, may be divided into smaller portions, provided our instruments and organs were adapted to the operation. Their opponents contend, on the other hand, that matter is composed of certain ultimate particles of molecules, which by their nature are indivisible, and are hence termed *atoms* (from α *not*, and τεμνειν *to cut*). These opposite opinions have from time to time been keenly contested, and with variable success, according to the acuteness and ingenuity of their respective champions. But it was at last perceived that no positive data existed capable of deciding the question, and its interest therefore gradually declined. The progress of modern chemistry has revived attention to this controversy, by affording a far stronger argument in favour of the atomic constitution of matter than was ever advanced before, and one which is almost irresistible. For the assumption that all bodies consist of ultimate atoms, the weight of which differs in different kinds of matter, supplies a luminous explanation of the laws of chemical union, which do not appear explicable on any other supposition.

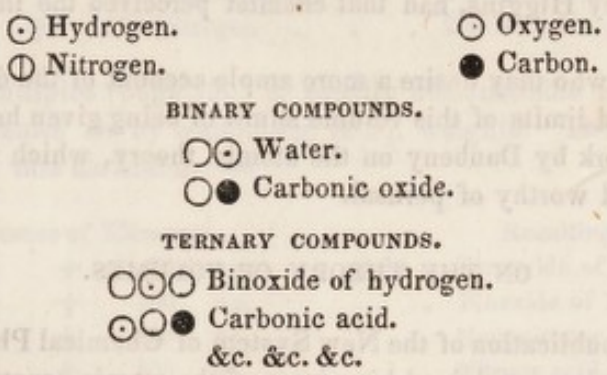
According to the atomic theory, every compound is formed of the atoms of its constituents. An atom of A may unite with 1, 2, 3, or more atoms of B. Thus, supposing water to be composed of 1 atom of hydrogen and 1 atom of oxygen, binoxide of hydrogen will consist of 1 atom of hydrogen and 2 atoms of oxygen. If carbonic oxide is formed of 1 atom of carbon and 1 atom of oxygen, carbonic acid will consist of 1 atom of carbon and 2 atoms of oxygen. If, in the compounds of nitrogen and oxygen, enumerated at page 130, the first or protoxide consist of 1 atom of nitrogen and 1 atom of oxygen, the four others will be regarded as compounds of 1 atom of nitrogen to 2, 3, 4, and 5 atoms of oxygen. From these instances it will appear that the law of multiple proportion is a necessary consequence of the atomic theory. There is also no apparent reason why 2 or more atoms of 1 substance may not combine with 2, 3, 4, 5, or more atoms of another; but, on the contrary, these arrangements are necessary in explanation of the not unfrequent occurrence of half equivalents, as formerly stated. (Page 130.) Such combinations will also account for the complicated proportion noticed in certain compounds, especially in many of those belonging to the animal and vegetable kingdoms.

In consequence of the satisfactory explanation which the laws of chemical union receive by means of the atomic theory, it has become customary to employ the term *atom* in the same sense as combining proportion or equivalent. For example, instead of describing water as a compound of 1 eq. of oxygen and 1 eq. of hydrogen, it is said to consist of 1 atom of each element. In like manner sulphate of potassa is said to be formed of 1 atom of sulphuric acid and 1 atom of potassa, the word in this case denoting as it were a compound atom, that is, the smallest integral particle of the acid or alkali; a particle which does not admit of being divided, except by the separation of its elementary or constituent atoms. The numbers expressing the proportions in which bodies unite must likewise indicate, consistently with this view, the relative weights of atoms; and accordingly these numbers are often called *atomic weights*. Thus, as water is composed of 8 parts of oxygen and 1 of hydrogen, it follows, on the supposition

of water consisting of 1 atom of each element, that an atom of oxygen must be 8 times heavier than an atom of hydrogen. If carbonic oxide be formed of an atom of carbon and an atom of oxygen, the relative weights of their atoms are as 6 to 8; and in short the chemical equivalents of all bodies may be considered as expressing the relative weights of their atoms.

The foregoing argument in favour of the atomic constitution of matter becomes much stronger when we trace the intimate connection which subsists among many substances, between their crystalline form and chemical composition. This subject, however, now known under the name of *isomorphism*, will be more conveniently discussed under the head of crystallization.

Dalton supposes the atoms of bodies to be spherical; and he has invented certain symbols to represent the mode in which he conceives they may combine together, as illustrated by the following figures:—



All substances containing only 2 atoms he called binary compounds, those composed of 3 atoms ternary compounds, of 4 quaternary, and so on.

There are several questions relative to the nature of atoms, most of which will perhaps never be decided. Of this nature are the questions which relate to the actual form, size, and weight of atoms, and to the circumstances in which they mutually differ. All that we know with any certainty is, that their weights do differ, and by exact analysis the relations between them may be determined. Peculiar views of the constitution of matter are held by Ampère, whose opinions are always acute and philosophical. He not only believes dissimilar atoms, as of oxygen and hydrogen, to be capable of uniting, but that 2 or more atoms of the same kind have a power of mutual attraction whereby they are arranged in groups of definite figure, which he calls *molecules*. These molecules, more or less intimately bound together by cohesion, give rise to the different states of bodies, the solid, liquid, and gaseous. Thus, oxygen gas is conceived not an assemblage of self-repulsive atoms of oxygen, but of molecules, each of which is a polyhedral solid made up of a constant number of atoms and repulsive to neighbouring molecules. In like manner he conceives the ultimate particles of compounds, as water and potassa, to be arranged in groups so as to constitute molecules. Similar views are maintained by Prout in his Bridgewater Treatise. This doctrine receives strong support from some phenomena of gaseous combination, and from the complex nature of organic compounds.

It is but justice to the memory of Higgins, to state that he first made use of the atomic hypothesis in chemical reasonings. In his "Comparative View of the Phlogistic and Antiphlogistic Theories," published in the year 1789, he observes (pages 36 and 37) that "in volatile vitriolic acid a single ultimate particle of sulphur is intimately united only to a single particle of dephlogisticated air;

and that, in perfect vitriolic acid, every single particle of sulphur is united to 2 of dephlogisticated air, being the quantity necessary to saturation;" and he reasons in the same way concerning the constitution of water and the compounds of nitrogen and oxygen. These remarks of Higgins do not appear to have had the slightest connection with the subsequent views of Dalton, who seems to have never seen the work of Higgins till after he had given an account of his own doctrine. The observations of Higgins, though highly creditable to his sagacity, do not affect Dalton's merit as an original observer. They were made, moreover, in so casual a manner, as not only not to have attracted the notice of his contemporaries, but to prove that Higgins himself attached no particular interest to them. Dalton's chief merit consists in having formed a complete theory of chemical union, and in the discovery of an essential and most important part of the doctrine, a merit which is solely and indisputably his; but in which he would have been anticipated by Higgins, had that chemist perceived the importance of his own opinions.

To the student who may desire a more ample account of the doctrine of atoms than the nature and limits of this volume admit of being given here, I may recommend a small work by Daubeny on the atomic theory, which in other respects will be found well worthy of perusal.

ON THE THEORY OF VOLUMES.

Soon after the publication of the New System of Chemical Philosophy in 1808, in which work Dalton explained his views of the atomic constitution of bodies, Gay-Lussac published in the *Memoires d'Arcueil* on the "Combination of Gaseous Substances with one another." He there proved that gases unite together by volume in very simple proportions, which he exemplified by the ratios in which the following gases unite:—

100	Hydrogen	to	50 Oxygen.
100	Ammoniacal	. . .	100 Hydrochloric acid gas.
100	do.	. . .	100 Fluoboric acid gas.
100	do.	. . .	200 do.
100	do.	. . .	100 Carbonic acid gas.
100	do.	. . .	200 do.

Various other examples were quoted, both from his own experiments and from those of others, all demonstrating the same fact. Thus ammonia was found by A. Berthollet to consist of 100 volumes of nitrogen gas and 300 volumes of hydrogen; sulphuric acid contains 100 volumes of sulphurous acid and 50 volumes of oxygen: and carbonic acid is formed by burning a mixture of 50 volumes of oxygen and 100 volumes of carbonic oxide.

From these and other instances Gay-Lussac established the fact, that gaseous substances unite in the simple ratio of 1 to 1, 1 to 2, 1 to 3, &c.; and this original observation has been confirmed by such a multiplicity of experiments, that it may be regarded as one of the best established laws in chemistry. Nor does it apply to gases merely, but to vapours also. For example, hydrosulphuric, sulphurous, and hydriodic acid gases are composed of

600 vol	hydrogen gas	and 100 vol.	vapour of	sulphur.
600	oxygen	100	. .	sulphur.
100	hydrogen	100	. .	iodine.

Another remarkable fact established by Gay-Lussac in the same essay is, that the volumes of compound gases and vapours always bear a very simple ratio to the volumes of their elements. This will appear from the following table, in which all the substances are supposed to be in the gaseous state:—

Volumes of Elements.				Volumes of resulting compounds.
100 Nitrogen	+	300 Hydrogen	yield	200 Ammonia.
50 Oxygen	+	100 Hydrogen	. . .	100 Water.
50 Oxygen	+	100 Nitrogen	. . .	100 Protoxide of Nitrogen.
100 Sulphur	+	600 Hydrogen	. . .	600 Hydrosulphuric acid.
100 Sulphur	+	600 Oxygen	. . .	600 Sulphurous acid.
100 Chlorine	+	100 Hydrogen	. . .	200 Hydrochloric acid.
100 Iodine	+	100 Hydrogen	. . .	200 Hydriodic acid.
100 Bromine	+	100 Hydrogen	. . .	200 Hydrobromic acid.
100 Cyanogen	+	100 Hydrogen	. . .	200 Hydrocyanic acid.
100 Oxygen	+	100 Nitrogen	. . .	200 Binoxide of Nitrogen.

The law of multiples (page 130) is equally demonstrable by means of combining or eq. volumes as by combining or eq. weights. The annexed tabular view will justify this statement:—

Volumes of Elements.				Resulting Compounds.
100 Nitrogen	+	50 Oxygen	yield	Protoxide of Nitrogen.
100 do.	+	100 do.	. . .	Binoxide of Nitrogen.
100 do.	+	150 do.	. . .	Hyponitrous acid.
100 do.	+	200 do.	. . .	Nitrous acid.
100 do.	+	250 do.	. . .	Nitric acid.
100 Hydrogen	+	50 do.	. . .	Water.
100 do.	+	100 do.	. . .	Binoxide of Hydrogen.
100 Carbon Vapour	+	50 do.	. . .	Carbonic oxide.
100 do.	+	100 do.	. . .	Carbonic acid.

It thus appears that the laws of combination may equally well be deduced from the volumes or from the weights of the combining substances, and that the composition of gaseous bodies may be expressed as well by measure as weight. In the subjoined table is a comparative view of equivalent weights and volumes, to which is added the respective sp. gravities in relation both to air and hydrogen: the facts respecting the vapours are drawn from an essay by Mitscherlich. (An. de Ch. et Ph. lv. 5.) In constructing the table 100 volumes of hydrogen are assumed as the unit to which the eq. vol. of other substances are compared, and as the volume occupied by a weight of hydrogen represented by its equivalent. The eq. vol. of other substances, considered as gases, are in like manner the volumes corresponding to their equivalents taken as weights. In all substances, whose sp. gr. and equivalents are the same compared to the sp. gr. and eq. of hydrogen as unity, the eq. vol. is 100. If the sp. gr. is smaller than its equivalent, as in mercury, this must arise from its eq. vol. being proportionally greater than the eq. vol. of hydrogen: and if the sp. gr. is greater than its equivalent, as in oxygen or sulphur, the eq. vol. is proportionally smaller than the eq. vol. of hydrogen. A simple rule of three, therefore, enables the eq. vol. to be calculated. Thus the eq. vol. of mercury is $\frac{202}{101} \times 100 = 200$; that of oxygen $\frac{8}{16} \times 100 = 50$; and that of sulphur is $\frac{16.10}{96.48} \times 100 = 16.66$, agreeably to the numbers which will be found in the table.

Gas and Vapours.	Specific Gravities.		Chemical Equivalents	
	Air as 1.	Hydrogen as 1.	By Vol.	By Weight.
Hydrogen	0·0690	1·00	100	1·00
Nitrogen	0·9727	14·12	100	14·15
Chlorine	2·4700	35·84	100	35·42
Carbon (hypothetical)	0·4215	6·12	100	6·12
Iodine	8·7011	126·30	100	126·30
Bromine	5·3930	78·40	100	78·40
Water	0·6202	9·00	100	9·00
Alcohol	1·6012	23·24	100	23·25
Sulphuric Ether	2·5822	37·50	100	37·50
Light Carburetted Hydrogen	0·5595	8·12	100	8·12
Olefiant Gas	0·9810	14·24	100	14·24
Carbonic Oxide	0·9727	14·12	100	14·12
Carbonic Acid	1·5239	22·12	100	22·12
Protoxide of Nitrogen	1·5239	22·12	100	22·15
Sulphurous Acid	2·2105	32·10	100	32·10
Sulphuric Acid (anhydrous)	2·7617	40·10	100	40·10
Cyanogen	1·8157	26·35	100	26·35
Hydrosulphuric Acid	1·1770	17·10	100	17·10
Binoxide of Nitrogen	1·0377	15·06	200	30·15
Mercury	6·9690	101·00	200	202·00
Ammonia	0·5898	8·56	200	17·15
Hydrochloric Acid	1·2695	18·42	200	36·42
Hydriodic Acid	4·3850	63·63	200	127·26
Hydrobromic Acid	2·7310	39·71	200	79·40
Hydrocyanic Acid	0.9423	13·67	200	27·35
Arsenuretted Hydrogen	2·6950	39·20	200	78·20
Sesquichloride of Arsenic	6·2950	91·36	200	181·66
Sesquiodide of Arsenic	15·6400	227·00	200	454·28
Protochloride of Mercury	8·2040	119·00	200	237·42
Bichloride of Mercury	9·4390	137·00	200	272·84
Bromide of Mercury	9·6650	140·26	200	280·40
Bibromide of Mercury	12·3620	179·40	200	358·80
Biniodide of Mercury	15·6700	227·40	200	454·52
Oxygen	1·1025	16·00	50	8·00
Arsenious Acid	13·6695	198·4	50	99·40
Phosphorus	4·3273	62·8	25	15·70
Arsenic	10·3620	150·8	25	37·7
Sulphur	6·6480	96·48	16.66	16·10
Bisulphuret of Mercury	5·3840	78·10	33.33	234·18

The observations which more immediately flow from the facts in the preceding table are these:—

1. The combining or eq. volumes of substances, both elementary and compound, are either equal or have the simple ratio of 1 to 1, 1 to 2, 1 to 3, &c. The same simplicity rarely exists among the equivalent weights.

2. On comparing the third and fifth columns, the corresponding numbers for the first 18 substances will be found nearly or quite identical. As those substances have the same uniting volume as hydrogen, which is the assumed unit of comparison, and as the sp. gravities are merely the weights of equal volumes, the numbers of the third column, were they quite exact, must coincide with those in the fifth: their want of identity indicates errors of observation.

3. The identity in the eq. volumes of the elementary gases, hydrogen, nitrogen, and chlorine, led to the notion that the eq. volumes of most other elements, such as carbon, sulphur, and phosphorus, might also be identical. *Assuming* that identity, the sp. gravity which those elements ought to have when gaseous, may easily be calculated. Thus, taking 1, 6·12, and 16·1 as the equivalents of hydrogen, carbon, and sulphur, then will their sp. gravities in the gaseous state, eq. volumes being supposed equal, be in the ratio of 1, 6·12, and 15·1. This method,

by which the hypothetical sp. gravity of carbon, as stated in the table, was obtained, was first indicated by Dr. Prout. (An. of Phil. vi. 321.) But though such hypothetical numbers may sometimes be used for the convenience of expressing the relation of uniting substances by measure, recent facts show how dangerous it would be to confide in them; for by the table it appears that the eq. volume of sulphurous vapour is one sixth of that of hydrogen, which renders the sp. gravity of the vapour of sulphur six times greater than the hypothetical number. Similar deviation is observable in phosphorus, arsenic, and mercury. In these cases, the real sp. gravity of a vapour is as much greater or less than the hypothetical as its eq. volume is less or greater than that of hydrogen.

4. The identity in the eq. volumes of hydrogen, nitrogen, and chlorine, suggested the idea that the atoms of all the elements are of the same magnitude; and this, coupled with the supposition that the self-repulsive energy of these atoms is equal, led to the opinion that equal volumes of the elements in the gaseous state must contain an equal number of atoms. This hypothesis, recommended by its simplicity, and supported by the fact that the volumes of gaseous substances vary according to the same law by varying temperature and pressure, was accordingly employed as a mode of determining the relative weights of atoms. As water consists of 50 measures of oxygen and 100 of hydrogen gas, it was inferred to be a compound of one atom of oxygen and two atoms of hydrogen; and consequently, taking 8 as the weight of an atom of oxygen, the weight of one atom of hydrogen is $\frac{1}{2}$ instead of 1, as in the table; or taking hydrogen as 1, the atom of oxygen is 16. On the same principle may the numbers which in the table represent the eq. weights of chlorine, bromine, iodine, and nitrogen, which have the same eq. volumes as hydrogen, be considered as the weights of two equivalents. The equivalents adopted by Davy in his Elements of Chemical Philosophy, as well as those of Berzelius, which are now in general use on the Continent, were framed in accordance with these views: this the British chemist requires to bear in mind, since the same numbers which Berzelius uses for 2 eq. of hydrogen, nitrogen, chlorine, bromine, and iodine, he considers as one equivalent. But the opinion of Davy and Berzelius must now either be abandoned, or maintained on other principles, since the late researches of Dumas and Mitscherlich have shown experimentally that eq. volumes of the elementary gases and vapours do not contain the same number of atoms.

5. The facts contained in the last and preceding tables supply material for calculating the sp. gravity of compound gases, by which means the accuracy of other conclusions respecting their composition may be verified. Thus analysis proves that ammoniacal gas is composed of 100 volumes of nitrogen and 300 of hydrogen gases, condensed into the space of 200 volumes: if so, its sp. gravity will be

$$\frac{0{\cdot}9727 + 3 \times 0{\cdot}069}{2} = \frac{1{\cdot}1797}{2} = 0{\cdot}5889.$$

The near agreement of this calculated number with that found by weighing the gas itself, proves that ammonia has really the constitution above assigned to it, and gives great probability that the sp. gravity of nitrogen and hydrogen gases is nearly correct.

Again, hydrochloric acid gas consists of 100 volumes of hydrogen and 100 of

chlorine gases united without any change of bulk. Hence its sp. gravity ought to be

$$\frac{2{\cdot}47 + 0{\cdot}069}{2} = 1{\cdot}2695.$$

Hydrocyanic acid vapour is formed of 100 volumes of hydrogen and 100 of cyanogen gases united without change of volume; and therefore its sp. gravity should be

$$\frac{1{\cdot}8157 + 0{\cdot}069}{2} = 0{\cdot}9423.$$

Considering olefiant gas as a compound of 200 volumes of hydrogen gas and 200 of the vapour of carbon condensed into 100, its sp. gravity will be $(2 \times 0{\cdot}069 + 2 \times 0{\cdot}4215) = (0{\cdot}1380 + 0{\cdot}8430) = 0{\cdot}9810$.

Aqueous vapour is composed of 100 volumes of hydrogen and 50 of oxygen gases condensed into the space of 100 volumes; and therefore its sp. gravity ought to be $0{\cdot}069 + 0{\cdot}5512$ (half the sp. gr. of oxygen) $= 0{\cdot}6202$.

Protoxide of nitrogen is formed of 100 volumes of nitrogen and 50 of oxygen gases condensed into 100 volumes, and hence its sp. gravity should be $0{\cdot}9727 + 0{\cdot}5512 = 1{\cdot}5239$.

Assuming carbonic oxide to be a compound of 100 volumes of carbon vapour and 50 of oxygen gas contracted in uniting into 100 volumes, its sp. gravity should be $0{\cdot}4215 + 0{\cdot}5512 = 0{\cdot}9727$.

As the different sp. gravities thus calculated are very nearly those found by direct experiment, there is a strong presumption that the elements of the calculations are correct.

The principle of these calculations is sufficiently obvious. The sp. gravities represent the weights of equal volumes of the gases; taking 100 as the standard volume of which the sp. gravity of each gas denotes the weight, then 50 volumes of a gas may be indicated by half, 25 volumes by a fourth, and 16·66 by a sixth of its sp. gravity. Thus hydrosulphuric acid is a compound of 100 volumes of hydrogen gas, and 16·66 ($\frac{100}{6}$) of the vapour of sulphur condensed it to 100 volumes, and therefore its sp. gravity is

$$0{\cdot}069 + \frac{6{\cdot}6480}{6} = 0{\cdot}069 + 1{\cdot}1080 = 1{\cdot}1770.$$

Sulphurous acid consists of 100 volumes of oxygen gas and 16·66 of the vapour of sulphur condensed into 100 volumes; and hence its sp. gravity is

$$1{\cdot}1025 + \frac{6{\cdot}6480}{6} = 1{\cdot}1025 + 1{\cdot}1080 = 2{\cdot}2105.$$

In these two gases the volume is the same as the hydrogen or oxygen which they contain, and therefore their sp. gravities are the sum of the weights of their elements. The same applies to water, protoxide of nitrogen, and carbonic oxide. In olefiant gas 400 volumes are condensed into 100, and therefore its sp. gravity is the sum of the sp. gravities of its elements. Hydrochloric acid gas occupies the same space as its elements, and therefore its sp. gravity is

found by taking the mean of their sp. gravities. The same remark applies to hydrocyanic acid. In ammonia 400 volumes are condensed into 200, and therefore the sum of the sp. gravities is halved.

As vapours are easily condensed by cold, and in many cases exist as such only at high temperatures, their sp. gravities may often be obtained by calculation more accurately than by experiment. Thus it is easier accurately to ascertain the sp. gravity of hydrogen and hydrosulphuric acid gases than of the vapour of sulphur; and therefore as soon as experiment has shown that the sp. gravity of that vapour is *somewhere about* 6·6480, then the precise number may be calculated. For as 100 volumes of hydrosulphuric acid gas contain 100 of hydrogen gas, the sp. gravity of the latter deducted from that of the former (1·177 — 0·069), gives 1·108 as the weight of combined sulphur. If the eq. volume of sulphur were 100, then must 1·108 be its sp. gravity; but as the number found experimentally is nearly six times 1·108, the inference is that the real sp. gravity is $6 \times 1{\cdot}108 = 6{\cdot}648$, and that its eq. volume is six times less than 100, or 16·66. The only assumption here is, that if the eq. volume of the vapour is not 100, it must be some multiple or submultiple of it by a whole number, consistently with the *theory of volumes*. In the construction of the preceding table I have given the sp. gravities of vapours calculated on these principles rather than the precise numbers given by experiment.

6. The volume of a compound gas in reference to the volumes of its components is determined by one of the following rules:—

1. One volume of gas united with one volume, yield two volumes of the compound.

2. The volume of the compound gas often has the volume of that gas which enters most largely into it by volume.

3. The volume of the compound gas is equal to the sum of the volumes of its components divided generally by 2, but sometimes by 4 or 8.

4. In a few cases the sum of the component volumes must be divided by 3.

[ON THE RELATIVE VOLUMES IN WHICH SOLIDS AND LIQUIDS RESPECTIVELY COMBINE.

[The recent researches of Schröder, Ammermuller, and Kopp, have brought to light several interesting facts in regard to the proportion, by *volume*, in which *solids and liquids* respectively combine, indicating laws of combination, in reference to the *volumes* of the solid and liquid ingredients, analogous in some respects to those already described, as applicable to the union of the gases. A few of the more prominent of these results are deserving of mention here, as well from their intrinsic interest as from the light they seem destined to shed on various important points of chemical theory.

[As the chemical equivalents or atomic weights of bodies represent the *proportion by weights* in which they enter into combination, so these numbers when divided by the specific gravities of the respective bodies to which they refer, will represent the *proportional volumes* in which they unite. The numbers thus resulting from the division of the equivalents, or atomic weights, by the specific gravities are called the equivalent, or atomic volumes. Thus the atomic weight of silver being 108·3, and its sp. gravity 10·5, we have the *equivalent volume of silver* $= \frac{108}{10.3} = 10{\cdot}40$. In like manner the atomic weight of potassium being

39·3 and its sp. gravity 0·865, we have the equivalent volume of potassium $= \frac{39{\cdot}3}{0{\cdot}865} = 45{\cdot}43$.

The following table includes the equivalent volumes of a number of the simple bodies, reduced to the hydrogen scale.*

TABLE OF EQUIVALENT VOLUMES.

Elements.	Eq. Vol.	Elements.	Eq. Vol.
Carbon	2·87	Iron	3·52
Sulphur	8·00	Cobalt	3·52
Phosphorus	8·08	Copper	3·52
Chlorine	12·80	Manganese	3·52
Bromine	12·80	Nickel	3·52
Iodine	12·80	Iridium	4·56
Chromium	5·52	Osmium	4·56
Molybdenum	5·52	Palladium	4·56
Tungsten	5·52	Platinum	4·56
Silver	10.40	Rhodium	4·56
Gold	5·20	Titanium	4·56
Sodium	23·31	Zinc	4·64
Potassium	46·64	Lead	9·12

From this table we see that the chlorine, chromium, iron, and iridium groups, have respectively the eq. volumes 12·80, 5·52, 3·52, and 4·56, while the eq. volumes of potassium and silver, are respectively double those of sodium and gold.

[The numbers in the above table are called by Kopp the *primative* atomic or equivalent volumes, to distinguish them from those which the same elements must, in many cases, be inferred to possess while they are actually in the state of combination. The latter often differ from the former, although related to them by some simple arithmetical rule, applicable to all the individuals of a particular group of compounds. The most important law, deduced from a comparison of equivalent volumes, is the following:—

The equivalent volumes of Isomorphous bodies are equal, or in some very simple ratio to each other.

This law, partially illustrated in the above table, has been shown by Kopp to be true of a large number of compound isomorphous bodies, among which are the following:—

1.

Alumina.
Sesquioxide of Iron.
Sesquioxide of Chromium.

2.

Carbonate of Zinc.
" Magnesia.
" Iron.
" Manganese.
" Lime.
Dolomite.

* The corresponding numbers in Kopp's and Schröder's tables are calculated according to the scale in which the eq. of oxygen is reckoned 100.

3.

Double Sulphate of Potassa and Ammonia.
" " " Alumina.
" " " Sesquioxide of Iron.
" " " Sesquioxide of Chromium.

4.

Sulphate of Zinc.
" Magnesia,
" Nickel.

[Where a gas, as oxygen or hydrogen, enters into the composition of a *solid* compound, it is obvious that we cannot compute its equivalent volume, as part of the compound, from its equivalent weight, and its sp. gravity in the *gaseous* condition, its sp. gravity in the solid form, being requisite for this purpose. In such cases the equivalent volume of the gaseous element is inferred from a comparison of the equivalent volume of the compound and the non-gaseous ingredient. Thus

Equivalent volume of Protoxide of Lead, or Ph O = 11·68
Do. do. of Lead, or Ph = 9·12
} Diff. = 2·56.

In the protoxide of lead, therefore, the eq. volume of the oxygen is, in this way, inferred to be 2·56.

It will readily appear, however, that this result is only correct upon the supposition that the lead exists in this compound in its primitive equivalent volume (9·12). Were it condensed to one half, or in any other way changed, the eq. vol. of the oxygen thus deduced would differ from the above. It is, however, an interesting fact that we obtain the same eq. vol. for the combined oxygen in a *large* number of analogous oxides, by adopting the same hypothesis in regard to eq. volumes of the other metals. Thus

Equivalent volume of Protoxide Zinc, or Zn O = 7·20
Do. do. of Zinc, or Zn = 4·64
} Diff. = 2·56.

Equivalent volume of Protoxide of Cadmium, or Cd O = 9·04
Do. do. of Cadmium, or Cd = 6·48
} Diff. = 2·56.

Equivalent volume of Protoxide of Copper, or Cu O = 6·08
Do. do. of Copper, or Cu = 3·52
} Diff. = 2·56.

Applying the same mode of calculation to the binoxides and sesquioxides, and still assuming the primitive equivalent volume of the metal to be retained by it while combined, we obtain in a large number of cases the same value as above, for the equivalent volume of the oxygen. Thus

Equivalent volume of Binoxide of Lead, or PhO_2 = 14·24
Do. do. of Lead, or Ph = 9·12
} 5·12 = 2 × 2·56.

Equivalent volume of Sesquioxide of Lead, or Ph_2O_3 = 25·92
Do. do. of Lead, or Ph = 9·12
} 7·68 = 3 × 2·56.

Equivalent volume of Sesquioxide of Iron, or Fe_2O_3 = 14·72
Do. do. of Iron, or Fe = 7·04
} 7·68 = 3 × 2·56.

[It is therefore a reasonable presumption from these facts, that the equivalent volume of the oxygen, as it exists in the various oxides referred to, is invariable, and is represented, according to the hydrogen scale, by 2·56. There is, however, a second class of oxides, such as the sesquioxide of chromium, ($Cr O_3$) in which the eq. vol. of the oxygen, as inferred by a similar process, is one half, and a third class, including the binoxide of copper (Cu_2O), in which it is twice

as great as that above given. Neither of these latter groups is as large as that first referred to. They, however, serve to indicate a law of dilatation and condensation on the part of the solid oxygen entering into these various compounds, of remarkable simplicity, the several combining volumes having the relation of the numbers 1, 2, 4.]

[Applying similar reasonings and calculations to the salts, we find that in the nitrates the (NO_6),* associated with the metallic base, has an invariable equivalent volume = 28·64 Thus

Equivalent volume of Nitrate of Lead, or Pb NO_6 = 37·76 } = 28·64.
Do. do. of Lead, or Pb = 9·12 }

Equivalent volume of Nitrate of Silver, or Ag NO_6 = 39.04 } = 28·64.
Do. do. of Silver, or Ag = 10·40 }

In the sulphates we find the eq. vol. of the SO_4 combined with the metal, to have two different values. For one class of the sulphates the eq. vol. of SO_4 is 18·88. Sulphate of copper, Cu SO_4, is an example of this class. For the other the eq. vol. is 14·88. Sulphate of lead, Pb SO_4, illustrates this. These two numbers are very nearly in the ratio of 4 to 5.]

[According to the researches of Kopp, the *equivalent volume of a compound is very rarely equal to the sum of the primitive equivalent volumes of its elements.* Hence the eq. volumes in which these elements exist in the compound are to be sought for by comparisons, such as those above given of the various compounds of analogous character. It will be seen, from the preceding results, that the changes of equivalent volume, due to the different combinations into which a given element enters, is, like the condensation or expansion in gaseous combination, governed by certain numerical laws peculiar to each group of compounds, although, according to Kopp, these condensations and rarefactions of the *solid* volumes, are not expressed by the same simple ratios, as in the case of the gases. This very interesting inquiry has, as yet, been too little advanced to furnish, in a positive form, any more general results than those above indicated; but there is good reason to hope for new and important generalizations in its further prosecution. (Pogg. Ann. xlvii.)]

CHEMICAL SYMBOLS.

The impracticability in many cases of contriving convenient names expressive of the constitution of chemical compounds, especially of minerals, suggested the employment of symbols as an abbreviated mode of denoting the composition of bodies. It was thought that the names of elementary substances, instead of being written at full length, might often be more conveniently indicated by the first letter of their names; and that the combination of elements with each other might be expressed by placing together, in some way to be agreed on, the letters which represent them. The advantage of such a symbolic language was felt so strongly by Berzelius, that he some years ago contrived a set of symbols, which he has since used extensively in his writings; and other eminent chemists as well as mineralogists, believing symbols to be useful, adopted those which Berzelius had proposed. The consequence is, that symbolic expressions, called *chemical formulæ*, are now so much resorted to, and are so identified with the language of chemistry, that essays of great value are in a measure as sealed books

* See general remarks on salts in a subsequent part of the work.

to those who cannot read symbols. It is therefore important that the chemical student, whatever he may think of the value of symbols, should not be unacquainted with them. Fortunately, the labour of a few minutes will enable him to understand the subject. The following table includes the symbols of all the elementary substances according to Berzelius.

Elements.	Symb.	Elements.	Symb.	Elements.	Symb.
Alluminium	Al	Gold (Aurum)	Au	Platinum	Pl
Antimony (Stibium)	Sb	Hydrogen	H	Potassium (Kalium)	K
Arsenic	As	Iodine	I	Rhodium	R
Barium	Ba	Iridium	Ir	Selenium	Se
Bismuth	Bi	Iron (ferrum)	Fe	Silicon	Si
Boron	B	Lantanum	Ln	Silver (Argentum)	Ag
Bromine	Br	Lead (Plumbum)	Pb	Sodium (Natrium)	Na
Cadmium	Cd	Lithium	L	Strontium	Sr
Calcium	Ca	Magnesium	Mg	Sulphur	S
Carbon	C	Manganese	Mn	Tellurium	Te
Cerium	Ce	Mercury (Hydrargyrum)	Hg	Thorium	Th
Chlorine	Cl	Molybdenum	Mo	Tin (Stannum)	Sn
Chromium	Cr	Nickel	Ni	Titanium	Ti
Cobalt	Co	Nitrogen	N	Tungsten (Wolfram)	W
Columbium (Tantalum)	Ta	Osmium	Os	Vanadium	V
Copper (Cuprum)	Cu	Oxygen	O	Uranium	U
Fluorine	F	Palladium	Pd	Yttrium	Y
Glucinium	G	Phosphorus	P	Zinc	Zn
				Zirconium	Zr

For the sake of uniformity, and to prevent confusion, it is much to be wished that these symbols, being now generally known, should be rigorously adhered to. Berzelius has properly selected them from Latin names, as being known to all civilized nations; and when the names of two or more elements begin with the same letter, the distinction is made by means of an additional letter.

The foregoing symbols are intended to represent the chemical eq. of the elements. Thus, the letters H, I, and Ba, stand for one eq. of hydrogen, iodine, and barium; and 2 H, 3 H, and 4 H, for 2, 3, and 4 eq. of hydrogen. Two eq. of an element are often denoted by placing a dash through or under its symbol: for instance, $\bar{H}$ or $\underline{H}$ means 2 H, and $\bar{P}$ or $\underline{P}$ signifies 2 P. Certain compounds are often, for the sake of brevity, denoted by single symbols in the same manner as the elements: thus an eq. of water, ammonia, and cyanogen, is sometimes expressed by Aq, Am, and Cy; but in general the formulæ for compound bodies are so contrived as to indicate the elements they contain, and the mode in which they are united. This may be done in several ways; but that which first suggests itself is, to connect together the symbols by the same signs as are used in Algebra. Thus the formulæ K + O, Ca + O, Ba + O, Mn + O, Fe + O, 2 Fe + 3 O, 3 H + N, 2 H + 2 C, C + 2 O, N + 5 O, S + 3 O, and H + Cl, denote single eq. of potassa, lime, baryta, protoxide of manganese, protoxide of iron, peroxide of iron, ammonia, olefiant gas, carbonic acid, nitric acid, sulphuric acid, and hydrochloric acid. The formula C + N + 6 O indicates the elements which are contained in an eq. of nitrate of potassa: in order to express further that the potassium is combined with only 1 eq. of oxygen, the remaining oxygen with the nitrogen, and the potassa with nitric acid, the symbols are placed thus, (K + O) + (N + 5 O,) the brackets containing the symbols of those elements which are supposed to be united. A number placed on the outside of a bracket multiplies the compound within it: thus (K + O) + (S + 3 O) is sulphate of potassa, and (K + O) + 2 (S + 8 O) is the bisulphate. All the elements con-

tained in a compound are thus visibly represented, and the chemist is able readily to trace all possible modes of combination, and to select that which is most in harmony with the facts and principles of his science. He may, and often does, thereby detect relations which might otherwise have escaped notice.

Another advantage attributable to such formulæ is, that they facilitate the comprehension of chemical changes. If hydrosulphuric acid acts upon the protoxide of lead, it is easy to say that the sulphur combines with the lead and the hydrogen with the oxygen; but the exact adaptation of the quantities for mutual interchange appears to me more clearly shown by symbols than by a description or a diagram, both of which are apt to produce confusion where the change to be explained is complex. In the simple instance alluded to, H + S reacts on Pb + O, and the products are Pb + S and H + O. When hydrosulphuric acid acts on bicyanuret of mercury, the result is bisulphuret of mercury and hydrocyanic acid: the substances which interchange elements are 2 (H + S) and Hg + 2 Cy; and the products are Hg + 2 S, and 2 (H + Cy). In more complicated changes the advantage of chemical formulæ is still more manifest, examples of which kind will be found in the section on cyanogen, and in other parts of this volume.

Useful as the algebraic chemical formulæ are for the purposes of studying chemical changes, they are sometimes found inconveniently long where the object is merely to express the composition of bodies, and accordingly Berzelius has introduced several abbreviations. For instance, he indicates degrees of oxidation by dots placed over the symbol, writing, $\dot{K}$, $\ddot{C}$, $\dddot{N}$, instead of K + O, C + 2O, N + 5O, for potassa, carbonic acid, and nitric acid. In like manner he denotes compounds of sulphur by commas, writing $\dot{K}$, $\ddot{Hg}$, $\dot{H}$ instead of K + S, Hg + 2 S, H + S, for sulphuret of potassium, bisulphuret of mercury, and hydrosulphuric acid. When the ratio is that of 2 to 3 he employs the symbol for two eq. above stated: thus $\underline{\ddot{Fe}}$, $\underline{\dddot{P}}$, $\underline{\dddot{As}}$, is used instead of 2 Fe + 3O, 2P + 5O, 2As + 5O, for an equivalent of peroxide of iron, phosphoric acid, and arsenic acid; and similarly we have $\underline{\ddot{As}}$, $\underline{\ddot{As}}$, instead of 2 As + 3 S, 2 As + 5 S for the sesquisulphuret and persulphuret of arsenic. These last formulæ are sometimes used to indicate two eq. instead of one; but as, agreeably to the atomic theory, the smallest possible particle of peroxide of iron consists of 2 atoms of iron and 3 of oxygen, the formula 2 Fe + 3 O ought to stand for 1 eq. only.

Berzelius often dispenses with the sign, +, and writes combined elements side by side, the sign of addition being understood instead of expressed. Thus he uses HO, KO, FeS, $\dot{Ca}\,\ddot{C}$, $\dot{Ba}\,\dddot{N}$, $\dot{K}\,\ddot{S}$ + $\dot{Ni}\,\ddot{S}$, instead of H + O, K + O, Fe + S, Ca + C, Ba + N, (K + S,) + (Ni + S), for water, potassa, sulphuret of iron, carbonate of lime, nitrate of baryta, and the double sulphate of potassa and oxide of nickel. Two or more equivalents of one constituent of a compound are denoted by numbers placed in the same position as the indices of powers in algebra: thus NH^3, NC^2, $\underline{\ddot{Fe}^2}$, H^3, is the abbreviation of N + 3H, N + 2C, $2\underline{\ddot{Fe}}$, + 3H for ammonia, cyanogen, and sesquihydrate of iron, a compound of 2 eq. of peroxide of iron and 3 of water. A number used before symbols, like coefficients in algebra, multiplies all the following symbols not separated from it by a + sign. Thus in 8 $\dot{Ca}\,\ddot{Si}$ + $\dot{K}\,\ddot{Si}^2$ + 16 aq. (which is

the formula for the mineral called apophyllite) the 8 denotes 8 eq. of $\dot{C}a\,\dddot{S}i$, or silicate of lime, which are united with 1 eq. of bisilicate of potassa, and 16 of water.

Berzelius also expresses the vegetable and animal acids by the first letter of their name, with a dash over it. Thus $\overline{T}$, $\overline{A}$, $\overline{C}$, $\overline{B}$, $\overline{G}$, $\overline{F}$, are the symbols for tartaric, acetic, citric, benzoic, gallic, and formic acids.

Several objections, some of which are of great weight, have been made to this system of symbols, and various modifications have been proposed by different authors. Among these, that which has been adopted by Liebig and Poggendorff in their chemical dictionary, combine more successfully than any other the requisite clearness, brevity, and generality, and will be used in this work. The following are the principles of this method. The numbers which are written before a symbol affect all that follow as far as the first full stop or sign of addition; while those which are written a little below and to the right hand, multiply only the symbol to which they are attached. Two symbols placed side by side are understood to be combined together; thus HO signifies water; KO potassa, &c. When two compounds are separated only by a comma, they are also to be considered as combined. Thus KO,HO is the symbol of hydrate of potash; KO,SO_3 that of sulphate of potash. When two salts or other complex compounds are combined, the + sign is used; thus $KO,SO_3 + HO,SO_3$ represents bisulphate of potash, a compound of sulphate of potash with hydrated sulphuric acid. In this system of notation, no dots are employed, nor is any abbreviation used to express two equivalents. For example, alumina, which Berzelius abbreviates thus, $\underline{\ddot{A}l}$, is represented by Al_2O_3, which is equally short, more easily written and printed, and which moreover has this advantage, that there is only one symbol used for each element; while the composition of allied compounds admits of a more ready comparison. If, for example, it is wished to show the analogy between the oxides and chlorides of phosphorus, this is at once done by writing their formulæ according to the method of Liebig and Poggendorff.

$$P_2O_3\ P_2O_5\ P_2Cl_3\ P_2Cl_5$$

Whereas if dots are employed for oxygen, the analogy is far from being so obvious:—

$$\underline{\dddot{P}\ \dddot{P}}\ \underline{PCl^3}\ \underline{PCl^5}$$

unless chlorine be, like oxygen, expressed in two ways; which, however, would embarrass the learner unnecessarily. By comparing the symbol for apophyllite, according to Berzelius, above given, with that for the same mineral, according to Liebig and Poggendorff, $8\ (CaO,SiO_3) + KO,2SiO_3 + 16$ aq., it will be seen that the latter is at least equally clear, and from the absence of dots, far less liable to error in printing or in reading. In the first limb of the above formula it is to be observed that the figure 8 multiplies all contained within the parenthesis. In like manner, crystallised alum is represented, according to Berzelius, by $\dot{K}\dddot{S} + \underline{\ddot{A}l}\,\dddot{S}^3 + 24\dot{H}$; and, on the method here preferred, by $KO,SO_3 + Al_2O_3$, $3SO_3 + 24HO$. For the reasons above mentioned, the method of Liebig and Poggendorff will be uniformly employed hereafter; but I have thought it right to explain that of Berzelius, that where it is met with it may be understood.

ISOMERIC BODIES.

It was formerly thought that the same elements united in the same ratio must always give rise to the same compound; but within these few years several examples have been discovered of two or even more substances containing the same elements in the same ratio, and yet exhibiting chemical properties distinct from each other. For such compounds Berzelius has suggested the general appellation of *isomeric*, from ισος *equal*, and μερος *part*, expressive of equality in the ingredients. Interesting instances of this kind are the two cyanic acids, which consist of cyanogen and oxygen in the same ratio, and have the same equivalent, yet differ widely in their chemical properties; and a similar example is afforded by the tartaric and paratartaric acids. Para from παρα *near to*, is prefixed in order to mark the relation to tartaric acid, a principle of nomenclature which is extended to other cases.

Unexpected as was the discovery of isomerism, it is quite consistent with our theories of chemical union, insomuch as the same elements may be grouped or combined in different ways, and thereby give rise to compounds essentially distinct. Thus the elements of sulphate of potassa may perhaps be united indiscriminately with each other, as expressed by the formula KSO_4; or they may form $KO + SO_3$; or $KS + O_4$; or $KO_2 + SO_2$; and other combinations might be made. The second of these is thought to be the real one; but no one can say that the others are impracticable. Again, the elements of peroxide of tin, Sn and 2O, may either form SnO_2, or $SnO + O$; and those of the peroxide of iron, 2Fe and 3O, may either be Fe_2O_3, or $FeO + FeO_2$, not to mention other possible combinations. The elements of alcohol are 4C, 6H, and 2O, which may be united indiscriminately as $H_6C_4O_2$, $H_6C_4 + 2O$, $H_5C_4O + HO$, or $H_4C_4 + 2HO$, besides others.

Some bodies consist of the same elements in the same ratio, and yet differ in their equivalents. A marked example is supplied by olefiant gas and etherine, the former of which contains 200 volumes of carbon vapour and 200 of hydrogen gas condensed into 100 volumes, and the latter of 400 volumes of carbon vapour and 400 of hydrogen gas, united so as to yield 100 volumes of etherine. The equivalent of olefiant gas is 14·24, and that of etherine 28·48, or exactly double. A similar case will be found in the description of cyanuric acid. The nature of these compounds is at once detected by their equivalents being unlike, and by the volume which they occupy as gases compared with the volumes of the elements of which they consist. Isomeric bodies of this kind are obviously much less intimately allied than those above described.

SECTION III.

OXYGEN.

History.—Discovered by Priestley in 1774, and by Scheele a year or two after, without previous knowledge of Priestley's discovery. It was termed *Dephlogisticated air* by Priestley, *Empyreal air* by Scheele, and *Vital air* by Condorcet.

The name it now bears, derived from the Greek words ὀξυς *acid* and γενναειν *to generate*, was proposed by Lavoisier, who considered it the sole cause of acidity.

Preparation.—From several sources, the peroxides of manganese, lead, and mercury, nitre, and chlorate of potassa, yield it in large quantities when they are exposed to a red heat. The substances commonly employed for the purpose are peroxide of manganese and chlorate of potassa. It may be procured from the former in two ways; either by heating it to redness in a gun-barrel, or in a retort of iron or earthenware; or by putting it in fine powder into a flask with about an equal weight of concentrated sulphuric acid, and heating the mixture by means of a lamp. To understand the theory of these processes, it is necessary to bear in mind the composition of the three following oxides of manganese:—

	Manganese.	Oxygen.	
Protoxide .	27·7 or 1 equiv.	+ 8 .	= 35·7
Sesquioxide .	27·7	+ 12 .	= 39·7
Peroxide .	27·7	+ 16 .	= 43·7

On applying a red heat to the last, it parts with half an equivalent of oxygen, and is converted into the sesquioxide. Every 43·7 grains of the peroxide will therefore lose, if quite pure, 4 grains of oxygen, or nearly 12 cubic inches; and one ounce will yield about 128 cubic inches of gas. [If more strongly heated it loses uniformly one third of its oxygen. That is three equivalents of the peroxide yield two equivalents of oxygen, and is thereby converted into the red oxide, a compound of the first two oxides. The change is expressed in symbols thus: $3MnO_2 = 2O$ & Mn_3O_4 or $MnO + Mn_2O_3$. Every 43·7 grains, therefore, of the peroxide, will lose about $5\frac{1}{3}$rd grains of oxygen or 16 cubic inches. Hence one pound will yield about 700 grains, or nearly 2000 cubic inches of gas.] With sulphuric acid the peroxide loses a whole eq. of oxygen, and is converted into the protoxide, which unites with the acid, forming a sulphate of the protoxide of manganese. Every 43·7 grains of peroxide yields 8 grains of oxygen and 35·7 of protoxide, which by uniting with one eq. (40) of the acid, forms 75·7 of the sulphate. The first of these processes is the most convenient in practice.

The gas obtained from peroxide of manganese, though hardly ever quite pure, owing to the presence of iron, carbonate of lime, and other earthy substances, is sufficiently good for ordinary purposes. It yields a gas of better quality, if previously freed from carbonate of lime by dilute hydrochloric or nitric acid; but when oxygen of great purity is required, it is better to obtain it from chlorate of potassa. For this purpose, the salt should be put into a retort of green glass, or of white glass made without lead, and be heated nearly to redness. It first becomes liquid, though quite free from water, and then, on increase of heat, is wholly resolved into pure oxygen gas, which escapes with effervescence, and into a white compound, called chloride of potassium, which is left in the retort. The composition of the chloric acid and potassa which constitute the salt is stated below:—

Chlorine .	35·42 or 1 eq.	Potassium .	39·15 or 1 eq.
Oxygen .	40 or 5 eq.	Oxygen .	8 or 1 eq.
Chloric acid .	75·42 or 1 eq.	Potassa .	47·15 or 1 eq.

Hence the oxygen which passes over from the retort, is derived partly from

the potassa and partly from the chloric acid; while chlorine and potassium enter into combination. Thus are 122·57 grains of the chlorate resolved into 74·57 grains of chloride of potassium, and 48 grains, or about 161 cubic inches of pure oxygen. The following equation briefly and clearly explains the change, $KO + ClO_5 = KCl + O_6$.*

Properties.—Colourless, tasteless, inodorous; feeble refractor of light; non-conductor of electricity; heavier than atmospheric air, sp. gr. being estimated at 1·1026 by Dulong and Berzelius, so that 100 cubic inches weigh at 60° and 30′ Bar. 34·193 grains. It is always gaseous when not combined with other ponderable matter; though even in its simplest form it is associated, like other elementary principles, with the agents productive of heat, light, and electricity. Like all gases it emits a strong heat when suddenly compressed: light also appears; but this is solely due to its chemical action on the oil with which the compressing tube is lubricated. It is the most perfect — electric, always appearing at the + electrode when any of its compounds are electrolized; is sparingly absorbed by water, which dissolves only 3 or 4 per cent. of the gas; is neither acid nor alkaline, as it does not change the colour of blue flowers, nor evince a disposition to unite directly either with acids or alkalies. It has a very powerful attraction for most simple substances; and there is not one of them, except perhaps the highly-negative fluorine, with which it may not be made to combine. The act of combining with oxygen is called *oxidation*, and bodies which have united with it are said to be *oxidized*. The compounds so formed are divided by chemists into acids and oxides. The former division includes those compounds which possess the general properties of acids; and the latter comprehends those which not only do not possess that character, but of which many are highly alkaline, and yield salts by uniting with acids. The phenomena of oxidation are variable. It is sometimes produced with great rapidity, and with evolution of heat and light. Ordinary combustion, for instance, is nothing more than rapid oxidation; and all inflammable or combustible substances derive their power of burning in the open air from their affinity for oxygen. On other occasions it takes place slowly, and without any appearance either of heat or light, as in the rusting of iron by moist air. Different as these processes may appear, oxidation is the result of both; and both depend on the same circumstance, namely, the presence of oxygen in the atmosphere.

All substances that are capable of burning in the open air, burn with far greater brilliancy in oxygen gas. A piece of wood, on which the least spark of light is visible, bursts into flame the moment it is put into a jar of oxygen; lighted charcoal emits beautiful scintillations; and phosphorus burns with so powerful and dazzling a light that the eye cannot bear its impression. Even iron and steel, which are not commonly ranked among the inflammables, undergo rapid combustion in oxygen gas.

The changes that accompany these phenomena are no less remarkable than the phenomena themselves. When a lighted taper is put into a vessel of oxygen gas, it burns for a while with increased splendour; but the size of the flame soon begins to diminish, and if the mouth of the jar be closed, the light will in a

* If the chlorate of potassa be previously mixed with about 1-10th of its weight of peroxide of manganese, it yields its oxygen at a lower temperature than when alone, and with uniform rapidity throughout the whole process. According to Balmain the peroxide of manganese remains undecomposed. (R.)

short time disappear entirely. The gas has now lost its characteristic property; for a second lighted taper, immersed in it, is instantly extinguished. This result is general. The burning of one body in a given portion of oxygen unfits it more or less completely for supporting the combustion of another; and the reason is manifest. Combustion is produced by the combination of inflammable matter with oxygen. The quantity of free oxygen, therefore, diminishes during the process, and is at length nearly or quite exhausted. The burning of all bodies, however inflammable, must then cease, because the presence of oxygen is necessary to its continuance. For this reason oxygen gas is called a supporter of combustion. Oxygen often loses its gaseous form as well as its other properties. If phosphorus or iron be burned in a jar of pure oxygen over water or mercury, the disappearance of the gas becomes obvious by the ascent of the liquid, which is forced up by the pressure of the atmosphere, and fills the vessel. Sometimes, on the contrary, the oxygen gas suffers diminution of volume only, or it may even undergo no change of bulk at all, as is exemplified by the combustion of the diamond.

The changes experienced by the burning body are equally striking. While the oxygen loses its power of supporting combustion, the inflammable substance lays aside its combustibility. It is then an oxidized body, and cannot be made to burn even by aid of the purest oxygen gas. It has also increased in weight. It is an error to suppose that bodies lose any thing while they burn. The materials of our fires and candles do indeed disappear, but they are not destroyed. Although they fly off in the gaseous form, and are commonly lost to us, it is not difficult to collect and preserve all the products of combustion. When this is done with the required care, the combustible matter is always found to weigh more after than before combustion; and the increase in weight is exactly equal to the quantity of oxygen which has disappeared during the process.

Oxygen gas is necessary to respiration. No animal can live in an atmosphere which does not contain a certain portion of uncombined oxygen; for an animal soon dies if put into a portion of air from which the oxygen has been previously removed by a burning body. Oxygen disappears during respiration. If a bird be confined in a limited quantity of atmospheric air, it will at first feel no inconvenience; but as a portion of oxygen is withdrawn at each inspiration, its quantity diminishes rapidly, so that respiration soon becomes laborious, and in a short time ceases altogether. Should another bird be then introduced into the same air, it will die in the course of a few seconds; or if a lighted candle be immersed in it, its flame will be extinguished. Respiration and combustion have therefore the same effect. An animal cannot live in an atmosphere which is unable to support combustion; nor, in general, can a candle burn in air which contains too little oxygen for respiration.

It is singular that, though oxygen, as a constituent of the atmosphere, is necessary to respiration, in a state of purity it is deleterious. When an animal, as a rabbit for example, breathes pure oxygen gas, no inconvenience is at first perceived; but after the interval of an hour or more the circulation and respiration become very rapid, and the system in general is highly excited. Symptoms of debility subsequently ensue, followed by insensibility; and death occurs in six, ten, or twelve hours. On examination after death, the blood is found highly florid in every part of the body, and the heart acts strongly even after the breathing has ceased. For these experiments we are indebted to Broughton.
Its eq. is = 8; *eq. vol.* = 50; *symb.* O.

THEORY OF COMBUSTION.

The only phenomena of combustion noticed by an ordinary observer, are the destruction of the burning body, and the developement of heat and light; but it has been demonstrated that in addition to these circumstances, oxygen gas invariably disappears, and a new compound consisting of oxygen and the combustible is generated. The term *combustion*, therefore, in its common signification, implies the rapid union of oxygen gas and combustible matter, accompanied with heat and light. As the evolution of heat and light is dependent on chemical action, the same phenomena may be expected in other chemical processes; and accordingly heat and light are frequently emitted quite independently of oxygen. Thus phosphorus takes fire, and a taper burns for a short time, in a vessel of chlorine; and several of the common metals, such as copper, antimony, and arsenic, in a state of fine division, become red hot when introduced into a jar of that gas. Potassium takes fire in cyanogen gas; and copper leaf or iron wire, if moderately heated, undergoes the same change in the vapour of sulphur. A mixture of iron filings and sulphur, when heated so as to bring the latter into perfect fusion, emits intense heat and light at the instant of combination; and a like effect, though in a far less degree, is produced by the action of concentrated sulphuric acid on pure magnesia. Most of these and similar examples, especially when one of the combining substances is gaseous, are frequently included under the idea of combustion; and they certainly belong to the same class of phenomena. In the subsequent observations, however, I shall employ the term in its ordinary sense; but the remarks concerning increase of temperature, whether with or without light, apply equally to all cases where heat is developed as a result of chemical action.*

For many years prior to the discovery of oxygen gas, the phenomena of combustion were explained on the Stahlian or phlogistic hypothesis. All combustible bodies, according to Stahl, contain a certain principle which he called *phlogiston*, to the presence of which he ascribed their combustibility. He supposed that when a body burns, phlogiston escapes from it; and that when the body has lost phlogiston, it ceases to be combustible, and is then a dephlogisticated or incombustible substance. A metallic oxide was consequently regarded as a simple substance, and the metal itself as a compound of its oxide with phlogiston. The heat and light which accompany combustion, were attributed to the rapidity with which phlogiston is evolved during the process.

The discovery of oxygen proved fatal to the Stahlian doctrine. Lavoisier had the honour of overthrowing it, and of substituting in its place the antiphlogistic theory. The basis of his doctrine has already been stated,—that combustion and oxidation in general consist in the combination of combustible matter with oxygen. This fact he established beyond a doubt. On burning phosphorus in a jar of oxygen, he observed that a considerable quantity of the gas disappeared, that the phosphorus gained materially in weight, and that the increase of the latter exactly corresponded to the loss of the former. An iron wire was burnt in a similar manner, and the weight of the oxidized iron was found equal to that of the wire originally employed, added to the quantity of oxygen which had disappeared. That the oxygen is really present in the oxidized body he proved by a very decisive experiment. Some liquid mercury was confined in a vessel of

* In its comprehensive sense, the term *combustion* is applied by chemists to all cases of *chemical combination* accompanied by the evolution of *heat and light*. (R.)

oxygen gas, and exposed to a temperature sufficient for causing its oxidation. The oxide of mercury, so produced, was put into a small retort and heated to redness, when it was reconverted into oxygen and fluid mercury, the quantity of the oxygen being exactly equal to that which had combined with the mercury in the first part of the operation.

To account for the production of heat and light during combustion, Lavoisier had recourse to Black's Theory of latent heat. Heat is always evolved when a substance, without change of form, passes from a rarer into a denser state, and also when a gas becomes liquid or solid, or a liquid solidifies; because a quantity of heat previously combined, or latent, within it, is then set free. Now this is precisely what happens in many instances of combustion. Thus water is formed by the burning of hydrogen, in which case two gases give rise to a liquid; and in forming phosphoric acid with phosphorus, or in oxidizing metals, oxygen is condensed into a solid. When the product of combustion is gaseous, as in the burning of charcoal, the evolution of heat is ascribed to the circumstance that the oxidized body contains a smaller quantity of combined heat, or has a smaller sp. heat, than the substances by which it is produced.

This is the weak point of Lavoisier's theory. Chemical action is very often accompanied by increase of temperature, and the heat evolved during combustion is only a particular instance of it. Any theory, therefore, by which it is proposed to account for the production of heat in some cases, ought to be applicable to all. When combustion, or any other chemical action, is followed by considerable condensation, in consequence of which the new body contains less insensible heat than its elements did before combination, it is obvious that heat will, in that case, be disengaged. But if this were the sole cause of the phenomenon, a rise of temperature should always be preceded by a corresponding diminution of sp. heat, and the extent of the former ought to be in a constant ratio with the degree of the latter. Now Petit and Dulong infer from their researches on this subject (An. de Ch. et Ph. x.), that the degree of heat developed during combination, bears no relation to the sp. heat of the combining substances; and that in the majority of cases, the evolution of heat is not attended by any diminution in the sp. heat of the compound. It is a well-known fact, that increase of temperature frequently attends chemical action, though the products contain much more insensible heat than the substances from which they were formed. This happens remarkably in the explosion of gunpowder, which is attended by intense heat; and yet its materials, in passing from the solid to the gaseous state, expand to at least 250 times their volume, and consequently render latent a large quantity of heat.

These circumstances leave no doubt that the evolution of heat during chemical action is owing to some cause quite unconnected with that assigned by Lavoisier; and if this cause operates so powerfully in some cases, it is fair to infer that part of the effect must be owing to it on those occasions, when the phenomena appear to depend on change of sp. heat alone. A new theory is therefore required to account for the chemical production of heat. But it is easier to perceive the fallacies of one doctrine, than to substitute another which shall be faultless; and it appears to me that chemists must, for the present, be satisfied with the simple statement, that energetic chemical action does of itself give rise to increase of temperature. Berzelius, in adopting the electro-chemical theory, regards the heat of combination as an electrical phenomenon, believing it to arise from the oppositely electrical substances neutralizing one another, in the same manner as

the electric equilibrium is restored during the discharge of a Leyden jar. Electrical action certainly appears to be an essential part of every chemical change, and it is probable that the heat developed during the latter may be due to the former; but this part of science is as yet too imperfect for indicating the precise mode by which the effect is produced.

The heat emitted during combustion varies with the nature of the material. The effect of the combustible gases in raising the temperature of water, according to the experiments of Dalton, is shown in the following table.—(Chemical Philosophy, ii. 309.)

Hydrogen, in burning, raises an equal volume of water	5° F.
Carbonic oxide	4½
Light carburetted hydrogen	18
Olefiant gas	27
Coal gas, varies with the quality of the gas from	10 to 16
Oil gas, varies also with the quality of the gas from	12 to 20

Dalton further states that generally the combustible gases give out heat nearly in proportion to the oxygen which they consume.

Despretz has given a notice of some experiments on the heat developed in combustion (An. de Ch. et Ph. xxxvii. 180). The substances burned were hydrogen, carbon, phosphorus, and several metals; and so much of each was employed as to require the same quantity of oxygen. When the combustion of hydrogen gas produced 2578 degrees of heat, carbon gave out 2967, and iron 5325. Phosphorus, zinc, and tin, emit quantities of heat very nearly the same as iron. Hence it follows that, for equal quantities of oxygen, hydrogen in burning evolves less heat than most other substances. These results do not accord with those of Dalton.

SECTION IV.

HYDROGEN.

Hist.—First correctly described in 1766 by Cavendish (Phil. Trans. lvi. 144), under the name of *inflammable air*. It had been previously confounded with other combustible gases, and it was by some called *phlogiston*, from the notion that it is the matter of heat. Its present name is derived from ὑδωρ *water*, and γενναειν *to generate*.

Prep.—Commonly in two ways. The first consists in passing the vapour of water over metallic iron heated to redness. This is done by putting iron wire into a gun-barrel open at both ends, to one of which is attached a retort containing pure water, and to the other a bent tube. The gun-barrel is placed in a furnace, and when it has acquired a full red heat, the water in the retort is made to boil briskly. The gas, which is copiously disengaged as soon as the steam comes in contact with the glowing iron, passes along the bent tube, and may be

collected in convenient vessels, by dipping the free extremity of the tube into the water of a pneumatic trough. The second and more convenient method consists in putting pieces of iron or zinc into dilute sulphuric acid, formed of one part of strong acid and four or five of water. Zinc is generally preferred. The hydrogen obtained in these processes is not absolutely pure. The gas evolved during the solution of iron has an offensive odour, ascribed by Berzelius to the presence of a volatile oil, which may be almost entirely removed by transmitting the gas through alcohol. The oil appears to arise from some compound being formed between hydrogen and the carbon which is always contained even in the purest kinds of common iron; and it is probable that a little carburetted hydrogen gas is generated at the same time. The zinc of commerce contains sulphur, and almost always traces of charcoal, in consequence of which it is contaminated with hydro-sulphuric acid, and probably with the same impurities, though in a less degree, as are derived from iron. A little metallic zinc is also contained in it, apparently in combination with hydrogen. All these impurities, carburetted hydrogen excepted, may be removed by passing the hydrogen through a solution of pure potassa. To obtain hydrogen of great purity distilled zinc should be employed.

Prop.—Colourless, inodorous, tasteless; always gaseous when uncombined; a powerful refractor of light; the lightest body in nature; and hence the best material for filling balloons. From its extreme lightness, it is difficult to ascertain its sp. gr. by weighing, because the presence of minute quantities of common air or watery vapour occasions considerable error. By the table of sp. gravities (page 140) it appears that hydrogen gas is just 16 times lighter than oxygen, an inference derived from the composition of water to be shortly stated: hence 100 C. I. 60° and 30 Bar. should weigh $\frac{1}{16} \times 34{\cdot}193 = 2{\cdot}1371$ grains, and its sp. gr. should be 0·06896.

It is neither acid nor alkaline. Water dissolves only $1\frac{1}{2}$ per cent. of its volume. It cannot support respiration: death ensues from deprivation of oxygen rather than from any noxious quality of the hydrogen, since an atmosphere composed of a due proportion of oxygen and hydrogen gases may be respired without inconvenience. Nor is it a supporter of combustion; for when a lighted candle, fixed on wire, is passed up into an inverted jar full of hydrogen gas, the light instantly disappears.

Hydrogen gas is inflammable in an eminent degree, though, like other combustibles, it requires the aid of a supporter of combustion, burning only where it is in contact with the air. Its combustion, when conducted in this manner, goes on tranquilly, and is attended with a yellowish blue flame and a very feeble light. The phenomena are different when the hydrogen is previously mixed with a due quantity of air. The approach of flame not only sets fire to the gas near it, but the whole is kindled at the same instant; and a flash of light passes through the mixture, followed by a violent explosion. The best proportion for the experiment is two measures of hydrogen to five or six of air. The explosion is far more violent when pure oxygen is used instead of atmospheric air, particularly when the gases are mixed together in the ratio of one measure of oxygen to two of hydrogen.

Oxygen and hydrogen gases cannot combine at ordinary temperatures, and may, therefore, be kept in a state of mixture without even gradual combination taking place between them. Hydrogen may be set on fire, when in contact with air or oxygen gas, by flame, by a solid body heated to bright redness, and by

the electric spark. If a jet of hydrogen gas be thrown upon recently prepared spongy platinum, this metal almost instantly becomes red hot, and then sets fire to the gas, a discovery which was made in the year 1824, by Professor Doebereiner, of Jena. The power of flame and electricity in causing a mixture of hydrogen with air or oxygen gas to explode, is limited. Mr. Cavendish found that flame occasions a very feeble explosion when the hydrogen is mixed with nine times its bulk of air; and that a mixture of four measures of hydrogen with one of air does not explode at all. An explosive mixture formed of two measures of hydrogen and one of oxygen gas, explodes from all the causes above enumerated. Biot found that sudden and violent compression likewise causes an explosion, apparently from the heat emitted during the operation; for an equal degree of condensation, slowly produced, has not the same effect. The electric spark ceases to cause detonation when the explosive mixture is diluted with twelve times its volume of air, fourteen of oxygen, or nine of hydrogen; or when it is expanded to sixteen times its bulk by diminished pressure. Spongy platinum acts just as rapidly as flame or the electric spark in producing explosion, provided the gases are quite pure, and mixed in the exact ratio of two to one.* Mr. Faraday finds that platinum foil, if perfectly clean, produces gradual, though rather rapid combination of the gases, often followed by explosion. (Phil. Trans. 1834.)

When the action of heat, the electric spark, and spongy platinum no longer cause explosion, a silent and gradual combination between the gases may still be occasioned by them. Sir H. Davy observed that oxygen and hydrogen gases unite slowly with one another, when they are exposed to a temperature above the boiling point of mercury, and below that at which glass begins to appear luminous in the dark. An explosive mixture, diluted with air to too great a degree to explode by electricity, is made to unite silently by a succession of electric sparks. Spongy platinum causes them to unite slowly, though mixed with one hundred times their bulk of oxygen gas.

A large quantity of heat is evolved during the combustion of hydrogen gas. Lavoisier concludes, from experiments made with his calorimeter, (Elements, vol. i.), that one pound of hydrogen occasions as much heat in burning as is sufficient to melt 295·6 pounds of ice. Dr. Dalton fixes the quuntity of ice at 320 pounds, and Dr. Crawford at 480. The most intense heat that can be produced, is caused by the combustion of hydrogen in oxygen gas. Dr. Hare, of Philadelphia, who first burned hydrogen for this purpose, collected the gases in separate gas-holders, from which a stream was made to issue through tubes communicating with each other, just before their termination. At this point, the jet of the mixed gases was inflamed. The effect of the combustion, though very great, is materially increased by forcing the two gases, in due proportion, into a strong metallic vessel, by means of a condensing syringe, and setting fire to a jet of the mixture as it issues. An apparatus of this kind, now known by the name of the oxy-hydrogen blow-pipe, was contrived by Mr. Newman, and employed by the late Professor Clarke in his experiments on the fusion of refrac-

* For a variety of facts respecting the causes which prevent the action of flame, electricity, and platinum in producing detonation, the reader may consult the Essay of M. Grotthus in the Ann. de Chimie, vol. xxxii.; Sir H. Davy's work on Flame; Dr. Henry's Essay in the Philosophical Transactions for 1824; and a paper by myself in the Edinburgh Philosophical Journal for the same year.

tory substances. On opening a stop-cock which confines the compressed gases, a jet of the explosive mixture issues with force through a small blowpipe tube, at the extremity of which it is kindled. In this state, however, the apparatus should never be used; for as the reservoir is itself full of an explosive mixture, there is great danger of the flame running back along the tube, and setting fire to the whole gas at once. To prevent the occurrence of such an accident, which would most probably prove fatal to the operator, Professor Cumming proposed that the gas, as it issues from the reservoir, should be made to pass through a cylinder full of oil or water before reaching the point at which it is to burn; and Dr. Wollaston suggested the additional precaution of fixing successive layers of fine wire gauze within the exit tube, each of which would be capable of intercepting the communication of flame. A modification of this apparatus has been devised by Mr. Gurney; but both his and Newman's are rendered unnecessary by the safety-tube lately proposed by Mr. Hemming. It consists of a brass cylinder, about 6 inches long, and 3-4ths of an inch wide, filled with very fine brass wire, in length equal to that of the tube. A pointed rod of metal, 1-8th of an inch thick, is then forcibly inserted through the centre of the bundle of wires in the tube, so as to wedge them tightly together. The interstices between the wires thus constitute very fine metallic tubes, the conducting power of which is so great as entirely to intercept the passage of flame. The mixed gases are supplied from a common bladder. (Phil. Mag. 3d S. i. 82.) A very intense heat may be safely and easily procured by passing a jet of oxygen gas through the flame of a spirit lamp, as proposed by the late Dr. Marcet. An elegant improvement on this principle has been devised by Mr. Daniell, by fixing a jet for conveying oxygen within another jet for hydrogen or coal gas, so that a current of oxygen may be introduced into the middle of the flame. (Phil. Mag. ii. 57. 3d Series.) The heat from this apparatus is quite sufficient for most purposes; and it may be still further increased by causing the gases to pass separately through heated tubes, in order that they may have a temperature of 400° or 500° on issuing from the jets.—On this principle is founded the patent of Mr. Dunlop, of the Carron Iron Works, for increasing the temperature of blast furnaces: the air which supports the combustion is previously heated by transmission through iron tubes kept at a low red heat, whereby the power of the furnaces is surprisingly increased, and a great saving in fuel and time is accomplished.

Its eq. is = 1; eq. vol. = 100; Symb. H. Compounds with oxygen:—

	By Weight.			By Volume.	
	Hydrogen.	Oxygen.	Equiv.	Hyd.	Oxy.
Water (Protoxide of Hydrogen)	1 or 1 eq. +	8 or 1 eq. =	9	100	50
Peroxide of Hydrogen	1 or 1 eq. +	16 or 2 eq. =	17	100	100

Water.—First proved by Cavendish to be the sole product of the combustion of hydrogen gas. He demonstrated it by burning oxygen and hydrogen gases in a dry glass vessel, when a quantity of pure water was generated, exactly equal in weight to that of the gases which had disappeared. This experiment, which is the synthetic proof of the composition of water, was afterwards made on a much larger scale in Paris by Vauquelin, Fourcroy, and Seguin. Lavoisier first demonstrated its nature analytically, by passing a known quantity of watery vapour over metallic iron heated to redness in a glass tube. Hydrogen gas was disengaged, the metal in the tube was oxidized, and the weight of the former,

added to the increase which the iron had experienced from combining with oxygen, exactly corresponded to the quantity of water decomposed.

Its composition by volume was demonstrated very satisfactorily by Nicholson and Carlisle: by resolving water into its elements by galvanism, and collecting them in separate vessels, they obtained precisely two measures of hydrogen and one of oxygen,—a result which has been fully confirmed by subsequent experimenters. The same fact was proved synthetically by Gay-Lussac and Humboldt, in their Essay on Eudiometry, published in the *Journal de Physique* for 1805. They found that when a mixture of oxygen and hydrogen is inflamed by the electric spark, those gases always unite in the exact ratio of one to two, whatever may be their relative quantity in the mixture. When one measure of oxygen is mixed with three of hydrogen, one measure of hydrogen remains after the explosion; and a mixture of two measures of oxygen and two of hydrogen leaves one measure of oxygen. When one volume of oxygen is mixed with two of hydrogen, both gases, if quite pure, disappear entirely on the electric spark being passed through them. The composition of water by weight was determined with great care by Berzelius and Dulong; and we cannot hesitate, considering the known dexterity of the operators, and the principle on which their method of analysis was founded, to regard their result as a nearer approximation to the truth than that of any of their predecessors. They state, as a mean of three careful experiments (Ann. de Ch. et Ph. xv.), that 100 parts of pure water consist of 11·1 of hydrogen, and 88·9 oxygen, which is the ratio of 1 to 8·009, very nearly that of 1 to 8 above stated.

The processes for procuring a supply of hydrogen gas will now be intelligible. The first is the method by which Lavoisier made the analysis of water. It is founded on the fact that iron at a red heat decomposes water, the oxygen of that liquid uniting with the metal, and the hydrogen gas being set free. That the hydrogen which is evolved when zinc or iron is put into dilute sulphuric acid must be derived from the same source, is obvious from the consideration, that of the three substances, iron, sulphuric acid, and water, the last is the only one which contains hydrogen. The product of the operation, besides hydrogen, is sulphate of the protoxide of iron, if iron is used, or of the oxide of zinc, when zinc is employed, according to the following equation; $HO + SO_3 + Fe = FeO + SO_3 + H$. The knowledge of the combining proportions of these substances will readily give the exact quantity of each product. These numbers are—

Water (8 oxy. + 1 hyd.)	9
Sulphuric acid	40·1
Iron	28
Protoxide of Iron (28 iron + 8 oxygen)	36
Sulphate of the protoxide of iron (40·1 + 36)	76·1

Hence for every 9 grains of water which are decomposed, 1 grain of hydrogen will be set free; 8 grains of oxygen will unite with 28 grains of iron, forming 36 of the protoxide of iron; and the 36 grains of protoxide will combine with 40·1 grains of sulphuric acid, yielding 76·1 of sulphate of the protoxide of iron. A similar calculation may be employed when zinc is used, merely by substituting the equivalent of zinc (32·5) for that of iron.—According to Mr. Cavendish, an ounce of zinc yields 676 cubic inches, and an equal quantity of iron 782 cubic inches of hydrogen gas.

The action of dilute sulphuric acid on metallic zinc affords an instance of what was once called *Disposing Affinity*. Zinc decomposes pure water at common temperatures with extreme slowness; but as soon as sulphuric acid is added, decomposition of the water takes place rapidly, though the acid merely unites with oxide of zinc. The former explanation was, that the affinity of the acid for oxide of zinc disposed the metal to unite with oxygen, and thus enabled it to decompose water; that is, the oxide of zinc was supposed to produce an effect previous to its existence. The obscurity of this explanation arises from regarding changes as consecutive, which are in reality simultaneous. There is no succession in the process; the oxide of zinc is not formed previously to its combination with the acid, but at the same instant. There is, as it were, but one chemical change, which consists in the combination at one and the same moment of zinc with oxygen, and of oxide of zinc with the acid; and this change occurs because these two affinities, acting together, overcome the attraction of oxygen and hydrogen for one another.*

Prop.—Transparent, colourless, inodorous, tasteless; powerful refractor of light; imperfect conductor of heat and electricity; very incompressible, its absolute diminution for a pressure of one atmosphere being only 51·3 millionths of its volume. (An. de Ch. et Ph. xxxvi. 140.) Its changes of form under varying temperatures have been already stated in the section on heat. Its sp. gr. is 1, being the unit to which the sp. gr. of all solids and liquids is referred as a convenient term of comparison. One cubic inch, at 62° and 30 Bar., weighs 252·458 grains. It is 815 times heavier than atmospheric air. The sp. gr. of aqueous vapour is 0·6202, and 100 C. I. (containing 100 hydrogen and 50 oxygen), at 212° and 30 Bar., weigh 14·96 grains; sp. gr. of ice is 0·92.

Owing partly to the extensive range of its own affinity, and partly to the nature of its elements, water is a chemical agent of great power. Of this, the preparation of hydrogen gas is an example; and indeed there are few complex changes, where oxygen and hydrogen are present, which do not give rise either to the production or decomposition of water. But, independently of the elements of which it is composed, it combines directly with many bodies. Sometimes it is contained in a variable ratio, as in ordinary solution; in other compounds it is present in a fixed definite proportion, as is exemplified by its union with several of the acids, the alkalies, and all salts that contain water of crystallization. These combinations are termed *hydrates*. Thus, concentrated sulphuric acid is a compound of one eq. of the real acid and one eq. of water; and its proper name is *hydrous sulphuric acid*, or *hydrate of sulphuric acid*. The prefix *hydro* has been sometimes used to signify the presence of water in definite proportion; but it is advisable, to prevent mistakes, to limit its employment to the compounds of hydrogen.

[Of late the investigations of chemists have shown that in relation to chemical compounds water performs at least 4 functions. 1st. That of a feeble acid when in combination with a base to which the term hydrate is more properly restricted. 2d. In combination with acids acting as a base forming *basic water*, as in the

* Most chemists now regard this case as simply one of *substitution*, in which the hydrogen of that portion of water which is intimately combined with the acid, is replaced by a metallic body, performing the same function. HO, SO_3 becoming, by the substitution of zinc for the hydrogen ZnO, SO_3. The large quantity of water present is useful to dissolve the sulphate of zinc as it is formed. (R.)

so called hydrated acids. 3d. In a neutral state, as a necessary constituent of certain neutral salts, and mutually replaceable in such salts by another neutral salt, and called saline or constitutional water. 4. In feeble union with neutral salts, and easily expelled by heat, the salt thereby losing its crystalline form and falling into powder; in this state called water of crystallization. For a full exposition of this subject see chapter on salts.]

The purest water which can be found as a natural product, is procured by melting freshly fallen snow, or by receiving rain in clean vessels at a distance from houses. But this water is not absolutely pure; for if placed under the exhausted receiver of an air-pump, or boiled briskly for a few minutes, bubbles of gas escape from it. The air obtained in this way from snow water is much richer than atmospheric air in oxygen gas. According to Gay-Lussac and Humboldt it contains 34·8 per cent. of oxygen, and the air separated by ebullition from rain water contains 32 per cent. All water which has once fallen on the ground becomes impregnated with more or less earthy or saline matters, and can be separated from them only by distillation. The distilled water, thus obtained, and preserved in clean well-stopped bottles, is absolutely pure. Recently boiled water has the property of absorbing a portion of all gases, when its surface is in contact with them; and the absorption is promoted by brisk agitation. The following table, from Henry's chemistry, shows the absorbability of different gases by water, deprived of all its air by ebullition.

100 C. I. water, at 60° and 30 Bar., absorb of

	Dalton and Henry.	Saussure.
Sulphuretted hydrogen	100 C. I.	253
Carbonic acid	100	106
Nitrous oxide	100	76
Olefiant gas	12·5	15.3
Oxygen	3·7	6·5
Carbonic oxide	1·56	6·2
Nitrogen	1·56	4·1
Hydrogen	1·56	4·6

The estimate of Saussure is in general too high. That of Dalton and Henry for nitrous oxide, according to the experiments of Davy, is considerably beyond the truth.

Its eq. is $=9$; eq. vol. 100; symb. H + O, or HO, or H, or aq. from aqua.

Peroxide or Binoxide.—Discovered by Thenard in 1818. Its preparation is founded on the fact that there are two oxides of barium, the peroxide and protoxide, the former of which is converted into the protoxide by the action of acids. When this process is conducted with the necessary precautions, the oxygen which is set free, instead of escaping in the form of gas, unites with the hydrogen of the water, and brings it to a maximum of oxidation. For a full detail of all the minutiæ of the process, the reader may consult the original memoir of Thenard;* the general directions are the following:—To six or seven ounces of water add so much pure concentrated hydrochloric acid as is sufficient to dissolve 230 grains of baryta; and after having placed the mixed fluids in a glass vessel surrounded with ice, add in successive portions 185 grains of peroxide of barium

* In the An. de Chim. et de Phys. vol. viii. ix. x. and l.; Annals of Philosophy, vol. xiii. and xiv.; and M. Thenard's Traité de Chimie.

reduced to powder, and stir with a glass rod after each addition. When the solution, which takes place without effervescence, is complete, sulphuric acid is added in sufficient quantity for precipitating the whole of the baryta in the form of an insoluble sulphate, leaving the hydrochloric acid in solution. Another portion of peroxide of barium, amounting to 185 grains, is then put into the liquid: the free hydrochloric acid instantly acts upon it, and as soon as it is dissolved, the baryta is again separated as a sulphate by the addition of sulphuric acid. The solution is then filtered, in order to separate the insoluble sulphate of baryta; and fresh quantities of peroxide of barium are added in succession, till about three ounces have been employed. The liquid then contains from 25 to 30 times its volume of oxygen gas. The hydrochloric acid which has served to decompose the peroxide of barium during the whole process, is now removed by the cautious addition of sulphate of oxide of silver, and the sulphuric acid afrerwards separated by solid baryta.

[M. Pelouse proposes a much easier process for the preparation of this compound. This consists in substituting hydrofluoric acid or fluosilicic acid for hydrochloric to decompose the peroxide of barium. By this means the baryta is deposited as an insoluble fluoride of barium, and the peroxide of hydrogen remains dissolved in the water. The change is thus simply expressed. $HF + BaO_2 = BaF + HO_2$.]

Peroxide of hydrogen, as thus prepared, is still diluted with a considerable quantity of water. To separate the latter, the mixed liquids are placed, with a vessel of strong sulphuric acid, under the exhausted receiver of an air-pump. As the water evaporates, the density of the residue increases, till at last it acquires the sp. gr. of 1·452. The concentration cannot be pushed further; for if kept under the receiver after reaching this point, the peroxide itself gradually but slowly volatilizes without change.

Prop.—A colourless, transparent liquid, inodorous, and of a metallic taste; volatilizes *in vacuo* less rapidly than water; retains its liquid form at all degrees of cold to which it has been exposed; at 59° is resolved into oxygen and water, and hence should be always kept in glass tubes surrounded by ice. It intermixes with water in all proportions; bleaches litmus and turmeric paper, whitens the skin and tongue, causing to both a pricking sensation, and thickens the saliva. The most remarkable of its properties is its facility of decomposition. Diffused daylight does not seem to exert any influence over it, and even the direct solar rays act upon it tardily. It effervesces from escape of oxygen at 59°, and the sudden application of a higher temperature, as that of 212°, gives rise to such rapid evolution of gas as to cause an explosion. Water, apparently by combining with the peroxide, renders it more permanent; but no degree of dilution can enable it to bear the heat of boiling water, at which temperature it is entirely decomposed. All the metals except iron, tin, antimony, and tellurium, have a tendency to decompose it, converting it into oxygen and water. A state of minute mechanical division is essential for producing rapid decomposition. If the metal is in mass, and the peroxide diluted with water, the action is slow. The metals which have a strong affinity for oxygen are oxidized at the same time, such as potassium, sodium, arsenic, molybdenum, manganese, zinc, tungsten, and chromium, while others, such as gold, silver, platinum, iridium, osmium, rhodium, palladium, and mercury, retain the metallic state.

It is decomposed at common temperatures by many of the metallic oxides. That some protoxides should have this effect, would be anticipated in conse-

quence of their tendency to pass into a higher state of oxidation. The protoxides of iron, manganese, tin, cobalt, and others, act on this principle, and are really converted into peroxides. The peroxides of barium, strontium, and calcium may likewise be formed by the action of peroxide of hydrogen on baryta, strontia, and lime. But it is a singular fact, of which no satisfactory explanation has been given, that some oxides decompose it without passing into a higher degree of oxidation. The peroxides of lead, mercury, gold, platinum, manganese, and cobalt, possess this property in the greatest perfection, acting on peroxide of hydrogen, when concentrated, with surprising energy. The decomposition is complete and instantaneous; oxygen gas is evolved so rapidly as to produce a kind of explosion; and such intense temperature is excited, that the glass tube in which the experiment is conducted becomes red-hot. The reaction is very great even when the peroxide of hydrogen is diluted with water. Oxide of silver occasions very perceptible effervescence when put into water which contains only 1-50th of its bulk of oxygen. All the metallic oxides, which are decomposed by a red heat, such as those of gold, platinum, silver, and mercury, are reduced to the metallic state when they act upon peroxide of hydrogen. This effect cannot be altogether ascribed to heat disengaged during the action; for oxide of silver suffers reduction when put into a very dilute solution of the peroxide, although the decomposition is not then attended by an appreciable rise of temperature.

While the tendency of metals and metallic oxides is to decompose the peroxide of hydrogen, acids have the property of rendering it more stable. In proof of this, let a portion of that liquid, somewhat diluted with water, be heated till it begins to effervesce from the escape of oxygen gas; let some strong acid, as the nitric, sulphuric, or hydrochloric, be then dropped into it, and the effervescence will cease on the instant. When a little finely divided gold is put into a weak solution of peroxide of hydrogen, containing only 10, 20, or 30 times its bulk of oxygen, brisk effervescence ensues; but on letting one drop of sulphuric acid fall into it, effervescence ceases instantly; it is reproduced by the addition of potassa, and is again arrested by adding a second portion of acid. The only acids that do not possess this property are those that have a low degree of acidity, as carbonic and boracic acids; or those which suffer a chemical change when mixed with peroxide of hydrogen, such as hydriodic, hydrosulphuric, and sulphurous acids. Acids appear to increase the stability of the peroxide in the same way as water does, namely, by combining chemically with it. Several compounds of this kind were formed by Thenard, before he was aware of the existence of the peroxide of hydrogen. They were made by dissolving peroxide of barium in some dilute acid, such as the nitric, and then precipitating the baryta by sulphuric acid. As nitric acid was supposed under these circumstances to combine with an additional quantity of oxygen, Thenard applied the term oxygenized nitric acid to the resulting compound, and described several other new acids under a similar title. But the subsequent discovery of peroxide of hydrogen put the nature of the oxygenized acids in a clearer light; for their properties are easily explicable on the supposition that they are composed, not of acids and oxygen gas, but of acids united with peroxide of hydrogen.

Peroxide of hydrogen was analysed by diluting a known weight of it with water, and then decomposing it by boiling the solution.

Its eq. is = 17; *symb.* H + 2O, or HO_2, or $\ddot{H}$.

SECTION V.

NITROGEN.

Hist.—First noticed by Rutherford of Edinburgh in 1772. Discovered to be a constituent of the atmosphere by Lavoisier in 1775, and by Scheele about the same time. It was termed azote, (α privative, and ζωη *life*,) by Lavoisier, from its inability to support respiration. The name of nitrogen is derived from its being an element of nitric acid.

Prep.—1. By burning a piece of phosphorus in a jar full of air inverted over water. The strong affinity of phosphorus for oxygen enables it to burn till the whole of that gas is consumed. The product of the combustion, metaphosphoric acid, is at first diffused through the residue in the form of a white cloud; but as this substance is rapidly absorbed by water, it disappears entirely in the course of half an hour. The residual gas is nitrogen, containing a small quantity of carbonic acid and vapour of phosphorus, both of which may be removed by agitating it briskly with a solution of pure potassa. Several other substances may be employed for withdrawing oxygen from atmospheric air. A solution of protosulphate of iron, charged with binoxide of nitrogen, absorbs the oxygen in the space of a few minutes. A stick of phosphorus produces the same effect in twenty-four hours, if exposed to a temperature of 60°. A solution of sulphuret of potassium or calcium acts in a similar manner; and a mixture of equal parts of iron filings and sulphur, made into a paste with water, may be employed with the same intention. Both these processes, however, are inconvenient from their slowness.—2. By exposing a mixture of fresh muscle and nitric acid of sp. gr. 1·20 to a moderate temperature. Effervescence then takes place, and a large quantity of gaseous matter is evolved, which is nitrogen mixed with a little carbonic acid. The latter must be removed by agitation with lime water; but the residue still retains a peculiar odour, indicative of the presence of some volatile principle which cannot be wholly separated from it. The theory of this process is somewhat complex, and will be considered more conveniently in a subsequent part of the work. 3. By transmitting chlorine gas through a solution of ammonia, when that alkali yields its hydrogen to the chlorine, and its nitrogen is evolved.

Prop.—Colourless, tasteless, inodorous; always gaseous when uncombined; sp. gr. 0·9722, so that 100 C.I. weigh 30.166 grains; no action on the blue colour of plants; water dissolves 1½ per cent. It is distinguished from other gases more by negative characters than by any striking quality. It is not a supporter of combustion; but, on the contrary, extinguishes all burning bodies that are immersed in it. No animal can live in it; but yet it exerts no injurious action either on the lungs or on the system at large, the privation of oxygen gas being the sole cause of death. It is not inflammable like hydrogen; though, under favourable circumstances, it may be made to unite with oxygen.

Considerable doubt exists as to the nature of nitrogen. Though ranked among the simple non-metallic bodies, some circumstances have led to the suspicion that it is compound; and this opinion has been warmly advocated by Davy and Berzelius. The chief argument in favour of this view is drawn from the phenomena that attend the formation of what is called the *ammoniacal amalgam*. From the metallic appearance of this substance, it was supposed to be a compound of mercury and a metal; and as one method of forming it is by the action of galvanism on a salt of ammonia, in contact with a globule of mercury, it follows that the metal, if present at all, must have been supplied by the ammonia. Now ammonia is composed of hydrogen and nitrogen; and as the former, from its small sp. gravity, can hardly be supposed to contain a metal, it was inferred that it must be present in the latter. Unfortunately for this argument, the supposed metal cannot be obtained in a separate state. The amalgam no sooner ceases to be under galvanic influence than its elements begin to separate spontaneously, and in a few minutes decomposition is complete, the sole products being ammonia, hydrogen, and pure mercury. Davy accounted for this change on the supposition that water is decomposed; that its oxygen reproduces nitrogen by uniting with the supposed metal; and that one part of its hydrogen forms ammonia by uniting with the nitrogen, while the remainder escapes in the form of gas. But Gay-Lussac and Thenard (Recherches Physico-Chimiques, vol. i.) declare that the amalgam resolves itself into mercury, ammonia, and hydrogen, even though perfectly free from moisture; and they infer from their experiments that it is composed of those three substances combined directly with each other. It hence appears that the examination of the ammoniacal amalgam affords no proof of the compound nature of nitrogen; nor was Davy's attempt to decompose that gas by aid of potassium, intensely heated by a galvanic current, attended with better success.

Its eq. is 14·15; *eq. vol.* = 100; *symb.* N.

The compounds of nitrogen treated of in this section are the following, exclusive of atmospheric air, which is regarded as a mechanical mixture:—

	By volume.		By weight.			
	Nit.	Oxy.	Nit.	Oxy.	Equiv.	Formulæ.
Nitrous oxide	100 .	50	14·15 +	8 =	22·15	N + O
Nitric oxide	100 .	100	14·15 +	16 =	30·15	N + 2O
Hyponitrous acid	100 .	150	14·15 +	24 =	38·15	N + 3O
Nitrous acid	100 .	200	14·15 +	32 =	46·15	N + 4O
Nitric acid	100 .	250	14·15 +	40 =	45·15	N + 5O

ON THE ATMOSPHERE.

The earth is everywhere surrounded by a mass of gaseous matter called the atmosphere, which is preserved at its surface by the force of gravity, and revolves together with it around the sun. It is colourless and invisible, excites neither taste nor smell when pure, and is not sensible to the touch unless when it is in motion. It possesses the physical properties of elastic fluids in a high degree. Its sp. gr. is unity, being the standard with which the density of all gaseous substances are compared. At 30 Bar. and 32° it is 769·4 times lighter than water, and 10462 than mercury; or at 62°, 815 times lighter than water, and nearly 11065 times lighter than mercury. The knowledge of its exact weight is

an essential element in many physical and chemical researches, and has been determined with very great care by Prout, who finds that 100 C. I. of pure and dry atmospheric air, at 60° and 30 Bar. weigh 31·0117 grains.

The pressure of the atmosphere was first noticed early in the 17th century by Galileo, and was afterwards demonstrated by his pupil Torricelli, to whom science is indebted for the invention of the barometer. Its pressure at the level of the sea is equal to a weight of about 15 pounds on every square inch of surface, and is capable of supporting a column of water 34 feet high, and one of mercury of 30 inches; that is, a column of mercury of one inch square and 30 inches long has the same weight (nearly 15 pounds) as a column of water of equal base and 34 feet long, and as a column of air of equal base reaching from the level of the sea to the extreme limit of the atmosphere. By the use of the barometer it was discovered that the atmospheric pressure is variable. It varies according to the elevation above the level of the sea, and on this principle the height of mountains is estimated. Supposing the density of the atmosphere to be uniform, a fall of one inch in the barometer would correspond to 11065 inches, or 922 feet of air; but in order to make the calculation with accuracy, allowance must be made for the increasing rarity of the air, and for various other circumstances which are detailed in works on meteorology. (Daniel's Meteorological Essays, 2nd edit. 376.) From causes at present not understood, the pressure varies likewise at the same place. On this depends the indications of the barometer as a weather-glass; for observation has fully proved, that the weather is commonly fair and calm when the barometer is high, and usually wet and stormy when the mercury falls.

Atmospheric air is highly compressible and elastic, so that its particles admit of being approximated to a great extent by compression, and expand to an extreme degree of rarity, when the tendency of its particles to separate is not restrained by external force. The volume of air and all other gaseous fluids, so long as they retain the elastic state, is inversely as the pressure to which they are exposed. Thus a portion of air which occupies 100 measures when compressed by a force of one pound, will be diminished to 50 measures when the pressure is doubled, and will expand to 200 measures when the compression is equal to half a pound. This law was first demonstrated in 1662 by the celebrated Boyle, and a second demonstration of it was given some years afterwards by the French philosopher Mariotte, apparently without being aware that the discovery had been previously made in England. It is hence frequently called the law of Mariotte. Till lately it had not been verified for very great pressures; but from the experiments of Oersted in 1825, who extended his observations to air compressed by a force equal to 110 atmospheres, it may be inferred to be quite general, except when the gaseous matter assumes the liquid form. (Ed. Journal of Science, iv. 224.) Gases vary from this law when they approach the point at which they assume the liquid form. At what pressure air becomes liquid is uncertain, since all attempts to condense it have hitherto been unsuccessful.

The extreme compressibility and elasticity of the air accounts for the facility with which it is set in motion, and the velocity with which it is capable of moving. It is subject to the laws which characterize elastic fluids in general. It presses, therefore, equally on every side; and when some parts of it become lighter than the surrounding portions, the denser particles rush rapidly into their place and force the more rarefied ones to ascend. The motion of air gives rise

to various familiar phenomena. A stream or current of air is wind, and an undulating vibration excites the sensation of sound.

The atmosphere is not of equal density at all its parts. This is obvious, from the consideration that those portions which are next the earth sustain the whole pressure of the atmosphere, while the higher strata bear only a part. The atmospheric column diminishes in length as the distance from the earth's surface increases; and, consequently, the greater the elevation, the lighter must be the air. It is not known to what height the atmosphere extends. From calculations founded on the phenomena of refraction, its height is supposed to be about 45 miles; and Wollaston estimated, from the law of expansion of gases, that it must extend to at least 40 miles with properties unimpaired by rarefaction. In speculating on its extent beyond that distance, it becomes a question whether the atmosphere is or is not limited to the earth. This subject was discussed with his usual sagacity by Wollaston in an Essay on the Finite Extent of the Atmosphere (Phil. Trans. 1822). Supposing the atmosphere unlimited, it should pervade all space, and accumulate about the sun, moon, and planets, forming around each an atmosphere, the density of which would depend on their respective forces of attraction. Now Wollaston inferred from astronomical observations made by himself and Kater, that there is no solar atmosphere; and the observations of other astronomers appear to justify the same inference with respect to the planet Jupiter. If the accuracy of these conclusions be admitted, it follows that our atmosphere is confined to the earth; and it may next be asked, by what means is its extent limited? Wollaston accounted for it by supposing the air, after attaining a certain degree of rarefaction, to possess such feeble elasticity, that the tendency of its particles to separate further from each other is counteracted by gravity. The unknown height at which this equilibrium between the two forces of elasticity and gravitation takes place, is the extreme limit of the atmosphere. The loss of elasticity may be ascribed to two powerful and concurring causes; namely, to the distance between the particles of air when highly rarefied, and to the extreme cold which prevails in the higher strata of the atmosphere.

The temperature of the atmosphere varies with its elevation. Gaseous fluids permit radiant matter to pass freely through them without any absorption, and therefore without their temperature being influenced by its passage. The atmosphere is not heated by transmitting the rays of the sun, but receives its heat solely from the earth, and chiefly by actual contact; so that its temperature becomes progressively lower, as the distance from the general mass of the earth increases. Another circumstance which contributes to the same effect, is the increasing tenuity of the atmosphere; for the temperature of rarefied air is less raised by a given quantity of heat, than that of the same portion of air when compressed, owing to its sp. heat being greater in the former state than in the latter. From the joint influence of both these causes it is found that, in ascending into the atmosphere, the temperature diminishes at the rate of one degree for about every 352 feet. The rate of decrease is probably much slower at considerable distances from the earth; but still there is no reason to doubt that the temperature continues to decrease with the increasing elevation. There must consequently, in every latitude, be a point where the thermometer never rises above 32°, and where ice is never liquefied. This point varies with the latitude, being highest within the tropics, and descending gradually as we advance towards

the poles. The following table, from the Supplement to the Encyclopedia Britannica, page 190, article Climate, shows the point of perpetual ice corresponding to different latitudes :—

Latitude.	English feet in height.	Latitude.	English feet in height.
0°	15,207	45°	7,671
5°	15,095	50°	6,334
10°	14,764	55°	5,034
15°	14,220	60°	3,818
20°	13,478	65°	2,722
25°	12,557	70°	1,778
30°	11,484	75°	1,016
35°	10,287	80°	457
40°	9,001	85°	117

Air was one of the four elements of the ancient philosophers, and their opinion of its nature prevailed generally, till its accuracy was rendered questionable by the experiments of Boyle, Hooke, and Mayow. The discovery of oxygen gas in 1774 paved the way to the knowledge of its real composition, which was discovered about the same time by Scheele and Lavoisier. The former exposed some atmospheric air to a solution of sulphuret of potassium, which gradually absorbed the whole of the oxygen. Lavoisier effected the same object by the combustion of iron wire and phosphorus.

The earlier analyses of the air did not agree very well with each other. According to the researches of Lavoisier, it is composed of 27 measures of oxygen and 73 of nitrogen. The analysis of Scheele gave a somewhat higher proportion of oxygen. Priestley found that the quantity of oxygen varies from 20 to 25 per cent.; and Cavendish estimated it only at 20. These discrepancies must have arisen from imperfections in the mode of analysis; for the proportion of oxygen has been found by subsequent experiments to be almost, if not exactly, that which was stated by Cavendish. The results of Scheele and Priestley are clearly referable to this cause. It is now known that the processes they employed cannot be relied on, unless certain precautions are taken of which these chemists were ignorant. Recently boiled water absorbs nitrogen; and consequently, if sulphuret of potassium be dissolved in that liquid by the aid of heat, the solution, when agitated with air, takes up a portion of nitrogen, and thereby renders the apparent absorption of oxygen too great. This inconvenience may be avoided by dissolving the sulphuret in cold unboiled water. Binoxide of nitrogen, employed by Priestley, removes all the oxygen in the course of a few seconds; but for reasons which will soon be mentioned, its indications are apt to be fallacious. The combustion of phosphorus, as well as the gradual oxidation of that substance, acts in a very uniform manner, and removes the whole of the oxygen completely. The residual nitrogen contains a little of the vapour of phosphorus, which increases the bulk of that gas by 1-40th, for which an allowance must be made in estimating the real quantity of nitrogen.

Since chemists have learned the precautions to be taken in the analysis of the air, a close correspondence has been observed in the results of their experiments upon it. The researches of Davy, Dalton, Gay-Lussac, Thomson, and others, leave no doubt that 100 measures of pure atmospheric air consist of 20 or 21 volumes of oxygen, and 80 or 79 of nitrogen. The most approved mode of

analysis consists in mixing with the air a quantity of hydrogen sufficient to convert all the oxygen present into water, and kindling the mixture by the electric spark. The combination may also be effected without detonation by means of spongy platinum. Water is formed, and is condensed; and since that liquid is composed of one volume of oxygen and two of hydrogen, one-third of the diminution must give the exact quantity of oxygen. This process is so easy of execution, and so uniform in its indications, that it is now employed nearly to the total exclusion of all others.

Such is the constitution of pure atmospheric air. But the atmosphere is never absolutely pure; for it always contains a certain variable quantity of carbonic acid and watery vapour, besides the odoriferous matter of flowers and other volatile substances, which are also frequently present. Saussure found carbonic acid in air collected at the top of Mont Blanc; and it exists at all altitudes which have been hitherto attained. Saussure, in a recent essay, states the proportion of this gas to vary at the same place within short intervals of time. It is greater in summer than in winter; and from observations made during spring, summer, and autumn, in the open fields, and in calm weather, its proportion is inferred to be always greater at night than in the day, and to be more abundant in gloomy than in bright weather. A very moist state of the ground, as after much rain, diminishes the quantity of carbonic acid, apparently by direct absorption. It is rather more abundant in elevated situations, as on the summits of high mountains, than in the plains: but its quantity is there nearly the same in day and night, in wet and dry weather, because the higher strata of the air are less influenced by vegetation, and the state of the soil. Saussure thinks also that a highly electrical state of the atmosphere tends to diminish the quantity of carbonic acid. He found that 10,000 parts of air contain 4·9 of carbonic acid as a mean, 6·2 as a maximum, and 3·7 as a minimum. (An. de Ch. et Ph. xxxviii. 411. xliv. 5.)

The chief chemical properties of the atmosphere are owing to the presence of oxygen gas. Air from which this principle has been withdrawn is nearly inert. It can no longer support respiration and combustion, and metals are not oxidized by being heated in it. Most of the spontaneous changes which mineral and dead organized matters undergo, are owing to the powerful affinities of oxygen. The uses of the nitrogen are in a great measure unknown. It was supposed to act as a mere diluent to the oxygen; but it most probably serves some useful purpose in the economy of animals, the exact nature of which has not been discovered.

The knowledge of the composition of the air, and of the importance of oxygen to the life of animals, naturally gave rise to the notion that the healthiness of the air, at different times, and in different places, depends on the relative quantity of this gas. It was therefore supposed that the purity of the atmosphere, or its fitness for communicating health and vigour, might be discovered by determining the proportion of the oxygen; and hence the origin of the term *Eudiometer*, which was applied to the apparatus for analyzing the air. But this opinion, though at first supported by the discordant results of the earlier analysts, was soon proved to be fallacious. On the contrary, the composition of air is not only constant in the same place, but is the same in all regions of the earth, and at all altitudes. Air collected at the summit of the highest mountains, such as Mont Blanc and Chimborazo, contains the same proportion of oxygen as that of the lowest valleys. The air of Egypt was found by Berthollet to be similar to that of France. The

air which Gay-Lussac brought from an altitude of 21,735 feet above the earth, had the same composition as that collected at a short distance from its surface. Even the miasms of marshes, and the effluvia of infected places, owe their noxious qualities to some principle of too subtile a nature to be detected by chemical means, and not to a deficiency of oxygen. Seguin examined the infectious atmosphere of an hospital, the odour of which was almost intolerable, and could discover no appreciable deficiency of oxygen, or other peculiarity of composition.

The question has been much discussed, whether the oxygen and nitrogen gases of the atmosphere are simply intermixed, or chemically combined with each other. Appearances are at first view greatly in favour of the latter opinion. Oxygen and nitrogen gases differ in density, and therefore it might be expected, were they merely mixed together, that the oxygen as the heavier gas ought, in obedience to the force of gravity, to collect in the lower regions of the air; while the nitrogen should have a tendency to occupy the higher. But this has nowhere been observed. If air be confined in a long tube preserved at perfect rest, its upper part will contain just as much oxygen as the lower, even after an interval of many months; nay, if the lower part of it be filled with oxygen, and the upper with nitrogen, these gases will be found in the course of a few hours to have mixed intimately with one another. The constituents of the air are, also, in the exact proportion for combining. By measure they are nearly in the simple ratio of 1 to 4, which agrees with the law of combination by volume; and by weight they are as 8 to 28, which corresponds to 1 eq. of oxygen and 2 of nitrogen.

Strong as are these arguments in favour of the chemical theory, it is nevertheless liable to objections which appear insuperable. The atmosphere possesses all the characters that should arise from a mechanical mixture. There is not, as in all other cases of chemical union, any change in the bulk, form, or other qualities of its elements. The nitrogen manifests no attraction for the oxygen. All bodies which have an affinity for oxygen abstract it from the atmosphere with as much facility as if the nitrogen were absent altogether. Even water effects this separation; for the air which is expelled from rain water by ebullition, contains more than 21 per cent. of oxygen. When oxygen and nitrogen gases are mixed together in the ratio of 1 to 4, the mixture occupies precisely 5 volumes, and has every property of pure atmospheric air. The refractive power of the atmosphere is precisely such as a mixture of oxygen and nitrogen gases ought to possess; and different from what would be expected were its elements chemically united. (Edinburgh Journal of Science, iv. 211.)

Since the elements of the air cannot be regarded as in a state of actual combination, it is necessary to account for the steadiness of their proportion on some other principle. It has been conceived that the affinity of oxygen and nitrogen for one another, though insufficient to cause their combination when mixed together at ordinary temperatures, might still operate in such a manner as to prevent their separation; that a certain degree of attraction is even then exerted between them, which is able to counteract the tendency of gravity. An opinion of this kind was advanced by Berthollet, in his *Statique Chimique*, and defended by Murray. This doctrine, however, is not satisfactory. It is conceivable that oxygen and nitrogen may attract each other in the way supposed: and it may be admitted that this supposition explains why these two gases continue in a state of perfect mixture. But still the explanation is unsatisfactory; and for the following reason:—Dalton took two cylindrical vessels, one of which was filled with carbonic acid, the other with hydrogen gas; the latter was placed perpen-

dicularly over the other, and a communication was established between them. In the course of a few hours hydrogen was detected in the lower vessel, and carbonic acid gas in the upper. If the upper vessel be filled with oxygen, nitrogen, or any other gas, the same phenomena will ensue: the gases will be found, after a short interval, to be in a state of mixture, and will at last be distributed equally through both vessels. Now this result cannot be ascribed to the action of affinity. Carbonic acid cannot be made to unite either with hydrogen, oxygen, or nitrogen; and therefore, it is gratuitous to assert that it has an affinity for them. Some other power must be in operation, capable of producing the mixture of gases with each other, independently of chemical attraction; and if this power can cause carbonic acid to ascend through a gas which is twenty-two times lighter than itself, it will surely explain why oxygen and nitrogen gases, the densities of which differ so little, should be intermingled in the atmosphere.

The explanation which Dalton has given of these phenomena is founded on the assumption, that the particles of one gas, though highly repulsive to each other, do not repel those of a different kind. Hence one gas should act as a vacuum with respect to another; and if a vessel full of carbonic acid communicate with another of hydrogen, the particles of each gas should insinuate themselves between the particles of the other, till they are equally diffused through both vessels. The particles of the carbonic acid do not indeed fill the space occupied by the hydrogen with the same velocity as if it were a real vacuum, because the particles of the hydrogen afford a mechanical impediment to their progress. The ultimate effect, however, is the same as if the vessel of hydrogen had been a vacuum. (Manchester Memoirs, vol. v.)

Though it would not be difficult to find objections to this hypothesis, it has the merit of being applicable to every possible case; which cannot, I conceive, be admitted of the other. It accounts not only for the mixture of gases, but for the equable diffusion of vapours through gases, and through each other. This view receives support from Graham's experiments on the diffusion of gases. (Phil. Trans. Edin. 1831.) When a gas is contained in a glass bell jar which has a crack or fissure in its sides, or communicates with the air by a narrow aperture, or is contained in a porous vessel, the gas gradually diffuses itself into the air, and air into the gas, each passing through the chink or other small opening at the same time, but in opposite directions. On ascertaining after an interval how much gas has escaped from, and how much air entered into, the vessel, it will be found that the respective quantities depend on the relative sp. gravities; and the same principle of intermixture equally applies when the apertures of communication are large, as when they are small. Each gas has a diffusiveness peculiar to itself, and which is greater as its sp. gr. is less. Graham determined the rate of diffusion for different gases by means of what he calls a *diffusion tube*, which is simply a graduated tube closed at one end by plaster of Paris, a substance, when moderately dry, possessed of the requisite porosity. He has been led by direct experiment to the following conclusion,—that "the diffusion or spontaneous intermixture of two gases in contact, is effected by an interchange in position of indefinitely small volumes of the gases, which volumes are not necessarily of equal magnitude, being, in the case of each gas, inversely proportional to the square root of the density of that gas." The relative diffusivenes of each gas may hence be represented by the reciprocal of the square root of its sp. gr. Thus, the sp. gr. of air being 1, its diffusiveness is 1 also; that of hydrogen is

$\frac{1}{\sqrt{0{\cdot}069}} = \frac{1}{0{\cdot}2627} = 3{\cdot}807$; that of oxygen $\frac{1}{\sqrt{1{\cdot}102}} = \frac{1}{1{\cdot}05} = 0{\cdot}9524$;

and that of nitrogen $\frac{1}{\sqrt{0{\cdot}972}} = 1{\cdot}014$:

so that the relative power of diffusion of air, hydrogen, oxygen, and nitrogen, is indicated by the numbers, 1, 3·807, 0·9524 and 1·014. In gases which are very sparingly soluble in water, and hence not condensable by the moisture of the plaster of Paris, the results of experiment coincide so exactly with the law, that Graham suggests its application to determine the sp. gr. of gases. Thus if g denote the diffusiveness of a gas, as found by careful experiment, and d its sp. gr.; then since, by the law of diffusion,

$$g = \frac{1}{\sqrt{d}}, \text{ we have } d = \frac{1}{g^2}.$$

It is obvious that these phenomena cannot be referred to any chemical principle, but are dependent on the mechanical constitution of gases. It has been lately shown in a very clever paper by T. Thomson of Clitheroe (Phil. Mag. 3rd Series, iv. 321), that the law of gaseous diffusion is included under Dalton's hypothesis, that one gas is as a vacuum with respect to another. For it is a law deduced from the physical properties of gaseous bodies, that the velocities of gases flowing under like circumstances into a vacuum are inversely as the square roots of their sp. gravities, which is precisely the same law that regulates their flow into each other.

There is still one circumstance for consideration respecting the atmosphere. Since oxygen is necessary to combustion, to the respiration of animals, and to various other natural operations, by all of which that gas is withdrawn from the air, it is obvious that its quantity would gradually diminish, unless the tendency of those causes were counteracted by some compensating process. To all appearance there does exist some source of compensation; for chemists have not hitherto noticed any change in the constitution of the atmosphere. The only source by which oxygen is known to be supplied, is the action of growing vegetables. A healthy plant absorbs carbonic acid during the day, appropriates the carbonaceous part of that gas to its own wants, and evolves the oxygen with which it was combined. During the night, indeed, an opposite effect is produced. Oxygen gas then disappears, and carbonic acid is eliminated; but it follows from the experiments of Priestley, Davy, and Daubeny, that plants during 24 hours yield more oxygen than they consume. Whether living vegetables make a full compensation for the oxygen removed from the air by the processes above mentioned, is uncertain. From the great extent of the atmosphere, and the continual agitation to which its different parts are subject by the action of winds, the effects of any deteriorating process would be very gradual, and a change in the proportion of its elements could be perceived only by observations made at very distant intervals.

Besides oxygen, nitrogen, carbonic acid, and traces of volatile organic substances, air, as already stated, always contains a greater or less amount of the vapour of water. The methods and instruments employed for determining its quantity have been described in the article Evaporation. As these instruments are termed hygrometers, the moisture of the atmosphere is often called hygro-

metric; and solid substances which absorb it are said to contain hygrometric water.

PROTOXIDE OF NITROGEN.

Hist.—*Dephlogisticated air* of Priestley, its discoverer; and the nitrous oxide of Davy, who studied it minutely. (Researches on the Nitrous Oxide, 1800.)

Prep.—It may be formed by exposing nitric oxide for some days to the action of iron filings, or other substances which have a strong affinity for oxygen, when the nitric oxide loses one half of its oxygen, and is converted into the protoxide; but the most convenient method is by nitrate of ammonia. This salt is prepared by neutralizing with carbonate of ammonia pure nitric acid diluted with about three parts of water, and concentrating by evaporation until a drop of the liquid let fall on a cold plate becomes a firm mass, adding a little ammonia towards the close to ensure neutrality. The salt after cooling is broken to pieces, introduced into a retort, and heated by a lamp or pan of charcoal: at first, below 400°, fusion ensues; and as the heat rises to 480° or 500°, rapid decomposition sets in, which continues until all the salt disappears. If a white cloud appears within the retort, due to some of the salt subliming undecomposed, the heat should be checked.

The sole products of this operation, when carefully conducted, are water and protoxide of nitrogen. The nature of the change will be readily understood by comparing the composition of nitrate of ammonia with that of the products derived from it. These, in round numbers, are as follows:—

Nitric Acid.	Ammonia.	Water.	Prot. of Nitrogen.
Nitrogen 14 or 1 eq.	Nitrogen 14 or 1 eq.	Hyd. 3 or 3 eq.	Nit. 38 or 2 eq.
Oxygen 40 or 5 eq.	Hydrogen 3 or 3 eq.	Oxy. 24 or 3 eq.	Oxy. 16 or 2 eq.
54	17	27	44

The same expressed in symbols is

$$N H_3 + N O_5 = 3 H O + 2 N O.$$

It thus appears that the hydrogen in the ammonia takes so much oxygen as is sufficient for forming water, and the residual oxygen converts the nitrogen both of the nitric acid and of the ammonia into protoxide of nitrogen: 71 grains of the salt will thus yield 44 grains of protoxide of nitrogen and 27 of water.

Prop.—Colourless, slightly agreeable odour, and sweetish taste; commonly gaseous, but at 45° and under a pressure of 50 atmospheres it is liquid; [under the same pressure, this liquid exposed to the intense cold of Thilorier's bath of solid carbonic acid and ether, becomes a transparent crystalline solid (page 53.)] sp. gr. of the gas = 1·5241, and 100 C. I. weigh 47·22 grains; no action on test paper. Recently boiled water at 60° dissolves nearly its own volume of the gas, and yields it unchanged by boiling: hence it cannot be preserved over cold water, and may by it be separated from gases which are insoluble in water. It is a supporter of combustion. Most substances burn in it with far greater energy than in the atmosphere. When a recently extinguished candle with a very red wick is introduced into it, the flame is instantly restored. Phosphorus, if previously kindled, burns in it with great brilliancy. Sulphur, when burning feebly, is extinguished by it; but if immersed while the combustion is lively, the size of the flame is considerably increased. With an equal bulk of hydrogen it forms a mixture which explodes violently by the electric spark or by flame. In all these cases the product of combustion is the same as when oxygen gas or atmospheric

air is used. The protoxide is decomposed; the combustible matter unites with its oxygen, and the nitrogen is set free. It suffers decomposition when a succession of electric sparks is passed through it, and a similar effect is caused by conducting it through a porcelain tube heated to incandescence. It is resolved, in both instances, into nitrogen, oxygen, and nitrous acid.

Davy discovered that it may be taken into the lungs with safety, and that it supports respiration for a few minutes. He breathed 9 quarts of it, contained in a silk bag, for three minutes, and 12 quarts for rather more than four; but no quantity could enable him to bear the privation of atmospheric air for a longer period. Its action on the system, when inspired, is very remarkable. A few deep inspirations are followed by most agreeable feelings of excitement, similar to the earlier stages of intoxication. This is shown by a strong propensity to laughter, by a rapid flow of vivid ideas, and an usual disposition to muscular exertion. These feelings, however, soon subside; and the person returns to his usual state without experiencing the langour or depression which so universally follows intoxication from spirituous liquors. Its effects, however, on different persons, are various; and in individuals of a plethoric habit it sometimes produces giddiness, headache, and other disagreeable symptoms.

When 100 measures of it are mixed with 100 of hydrogen and fired by electricity, 100 of nitrogen gas remain, and the sole other product is water. As 100 of hydrogen unite with 50 of oxygen, it follows that 100 measures of the protoxide contain 100 of nitrogen and 50 of oxygen gases. This result, obtained by Davy, has been confirmed by Henry, who analyzed it by means of carbonic oxide gas (An. Phil. N. S. viii. 299). Now,

100 cubic inches of	nitrogen gas	weigh . . .	30·166 grains
50 do.	oxygen	. . . .	17·054
These numbers added together amount to		. .	47·220

which must be the weight of 100 C. I. of the protoxide. Its composition by weight is determined by the same data, being 17·054 oxygen to 30·166 nitrogen, or 8 to 14 nearly, as already stated. *Its eq. is* = 22·15; *eq. vol.* = 100; *symb.* N + O, NO. or $\dot{N}$.

BINOXIDE OF NITROGEN.

Hist.—Discovered by Hales, but first carefully studied by Priestley, under the name of *nitrous gas*. It is also called *nitric oxide* and *deutoxide of nitrogen*.

Prep.—Preferably by the action of nitric acid, of sp. gr. 1·2, on metallic copper. Brisk effervescence takes place without the aid of heat, and the gas may be collected over water or mercury. The copper gradually disappears during the process; the liquid acquires a beautiful blue colour, and yields on evaporation a salt which is composed of nitric acid and oxide of copper. The chemical changes that occur are the following:—One portion of nitric acid suffers decomposition: part of its oxygen oxidizes the copper; while another part is retained by the nitrogen of the nitric acid, forming binoxide of nitrogen. The oxide of copper attaches itself to some undecomposed nitric acid, and forms the blue nitrate. Many other metals are oxidized by nitric acid, with disengagement of

a similar compound; but none, mercury excepted, yields so pure a gas as copper. The following equation expresses the reaction :—

$$Cu_3 + 4\,N\,O_5 = 3\,(Cu\,O.\,N\,O_5) + N\,O_2.$$

Prop.—Gaseous, not hitherto condensed into a liquid; colourless, tasteless, and inodorous; excites violent spasm of the glottis when an attempt is made to inhale it; sp. gr. = 1·0377, and 100 C. I. weigh 32·137 grains. Water at 60° dissolves about 11 per cent. It has no action on test paper; but if any free oxygen is present, it produces dense, suffocating, acid vapours of a red or orange colour, called *nitrous acid vapours*, which are freely absorbed by water, and render it acid. This character distinguishes it from all other gases, and is a good test of the presence of free oxygen. In some cases it supports combustion: burning sulphur and a lighted candle are extinguished by it; but charcoal and phosphorus, when in vivid combustion, burn in it with increased brilliancy. The product of the combustion is carbonic acid in the former case, and metaphosphoric acid in the latter, nitrogen being separated in both instances. With an equal bulk of hydrogen it forms a mixture which cannot be made to explode, but which is kindled by contact with a lighted candle, and burns rapidly with a greenish white flame, water and pure nitrogen gas being the sole products. The action of freshly ignited spongy platinum on a mixture of hydrogen and binoxide of nitrogen gases leads to the slow production of water and ammonia.

It is partially resolved into its elements by being passed through red-hot tubes, and a succession of electric sparks has a similar effect. It is converted into protoxide of nitrogen by substances which have a strong affinity for oxygen, such as moist iron filings, and a solution of sulphuret of potassium. Davy ascertained its composition by the combustion of charcoal (Elements of Chemical Philosophy, p. 200). Two volumes of the binoxide yielded one volume of nitrogen, and about one of carbonic acid; whence it was inferred to consist of equal measures of oxygen and nitrogen gases united without any condensation. Gay Lussac (Mémoires d'Arcueil) proved that this proportion is rigidly exact. He decomposed 100 measures of the gas, by heating potassium in it; when 50 measures of pure nitrogen were left, and the potassa formed corresponded to 50 measures of oxygen. The same fact has been lately proved by Henry (An. of Phil. N. S. viii. 299). Hence, as

50 cubic inches of oxygen gas weigh . . .	17·054 grains
50 do. nitrogen	15·083
100 cubic inches of the binoxide must weigh . .	32·137

From the invariable formation of red-coloured acid vapours, whenever binoxide of nitrogen and oxygen are mixed together, these gases detect the presence of each other with great certainty: and since the product is wholly absorbed by water, either of them may be entirely removed from any gaseous mixture by adding a sufficient quantity of the other. Priestley, who first observed this fact, supposed that combination takes place between them in one proportion only; and inferring on this supposition, that a given absorption must always indicate the same quantity of oxygen, he was led to employ binoxide of nitrogen in Eudiometry. But in this opinion he was mistaken. The discordant results obtained by his method soon excited suspicion of their accuracy; and the source

of error has since been discovered by the researches of Dalton and Gay-Lussac. It appears from the experiments of Gay-Lussac, and his results do not differ materially from those of Dalton, that for 100 measures of oxygen, 400 of the binoxide may be absorbed as a maximum, and 133 as a minimum; and that between these extremes, the quantity of the binoxide corresponding to 100 of oxygen is exceedingly variable. It does not follow from this, that oxygen and binoxide of nitrogen unite in every proportion within these limits. The true explanation is, that the mixture of these gases may give rise to three compounds, —hyponitrous, nitrous, and nitric acids; and that either may be formed almost, if not entirely, to the exclusion of the others, if certain precautions are adopted. But in the usual mode of operating, two if not all are generated at the same time, and in a proportion to each other which is by no means uniform. The circumstances that influence the degree of absorption, when a mixture of oxygen and binoxide of nitrogen is made over water, are the following:—1. The diameter of the tube; 2. The rapidity with which the mixture is made; 3. The relative proportion of the two gases; 4. The time allowed to elapse after mixing them; 5. Agitation of the tube; and lastly, The opposite conditions of adding the oxygen to the binoxide, or the binoxide to the oxygen.

The binoxide may, notwithstanding, be usefully employed in Eudiometry. Dalton operates (An. of Phil. x. 38, and Henry's Elements) by mixing the gases in a graduated tube about $\frac{1}{2}$ an inch wide over water, and waiting, without agitating the mixture, till decrease of volume is at an end, which usually occurs in less than 6 or 10 minutes. Every 27 measures which have disappeared, indicate 10 of oxygen. A large excess of the binoxide should be avoided; and if the gas under examination contain more than 20 per cent. of oxygen, it should be previously diluted with nitrogen. Gay-Lussac advises that 100 measures of the gas under examination should be introduced into a very wide tube or jar, and that an equal volume of the binoxide should then be added (Mém. d'Arcueil. ii. 247). The red vapours, which are instantly produced, disappear very quickly; and the absorption, after half a minute, or a minute at the most, may be regarded as complete. The residue is then transferred into a graduated tube and measured. One-fourth of the loss is oxygen.—Results very near the truth may be obtained by both methods.

If a current of the binoxide be conducted into a solution of protosulphate of iron, the gas is absorbed in large quantity, and the solution acquires a deep olive-brown colour, which appears almost black when fully saturated. This solution absorbs oxygen with facility. But it cannot be safely employed in Eudiometry; because the absorption of oxygen is accompanied, or at least very soon followed, by evolution of gas from the liquid itself. The binoxide is combined with the sulphate in the ratio of 1 eq. of the former to 4 eq. of the latter; and the gas may be recovered by exposure to a vacuum, the original salt being left unchanged (Péligot in An. de Ch. et Ph. liv. 17). On applying heat, part of the gas is evolved and part decomposed: the protoxide of iron takes oxygen both from the binoxide and from water, forming peroxide of iron; while the hydrogen of the decomposed water, and nitrogen of the binoxide combine together, and generate ammonia. Nitric acid is formed when the solution is exposed to the air or oxygen gas, but not otherwise (Davy). When a mixture of binoxide of nitrogen and sulphurous acid are brought into contact with a solution of potassa or ammonia, both gases are absorbed, and a peculiar acid is generated, which has been called by Pelouze, its discover, *nitrosulphuric acid.*

It is composed of 1 eq. of nitrogen, 1 of sulphur, and 4 of oxygen, 200 volumes of binoxide of nitrogen combining with 100 of sulphurous acid. The nitrosulphates are very prone to decomposition, a sulphate being formed with the evolution of protoxide of nitrogen: this ensues by the mere contact of certain substances, which do not themselves undergo any change, such as spongy platinum, silver and its oxide, charcoal powder, peroxide of manganese, and solutions of corrosive sublimate, lunar caustic, and the sulphates of the oxides of zinc, copper, and iron. The same effect is produced by an acid, as when an attempt is made to procure nitrosulphuric acid in a separate state, even the carbonic acid of the atmosphere being capable of causing the decomposition. The crystals of the nitrosulphates of potash and ammonia may be preserved in well-stopped bottles at ordinary temperatures; the solutions, on the contrary, are not stable above the freezing point, but the stability is much increased by an excess of alkali. On this is founded the best mode of preparing the nitrosulphates, which consists in transmitting binoxide of nitrogen through a strong solution of sulphite of ammonia or potash with an excess of alkali, when the corresponding nitrosulphate separates in colourless prismatic or acicular crystals. The dry crystals decompose at a moderate heat, namely, at 230° for the ammoniacal salt, and 266° for that of potash, the former giving rise to a slight explosion owing to the rapid evolution of protoxide of nitrogen. The decomposition of the nitrosulphate of potassa by heat is particularly interesting, from its forming sulphite of potassa and binoxide of nitrogen instead of sulphate of potassa and the protoxide, as occurs in every other instance. (Lieb. Ann. xv. 240.)

It is singular that both binoxide and protoxide of nitrogen, notwithstanding the absence of acidity, are capable of forming compounds of considerable permanence with the pure alkalies. The circumstances which give rise to the formation of these compounds will be stated in the description of nitre.

Its eq. is = 30·15; *eq. vol.* = 200; *symb.* N + 2O, NO_2, or $\ddot{N}$.

HYPONITROUS ACID.

Hist. and Prep.—First prepared by Gay-Lussac, who showed that on adding binoxide of nitrogen in excess to oxygen gas, confined in a glass tube over mercury, the absorption is always uniform, provided a strong solution of pure potassa is put into the tube before mixing the two gases: 50 measures of oxygen gas combine under these circumstances with 200 of the binoxide, forming an acid which unites with the potassa. As the binoxide contains half its volume of oxygen gas, the new acid must be composed of 100 measures of nitrogen and 150 of oxygen, as already stated. It is generated when the binoxide is kept for a considerable time, say three months, in a glass tube over mercury, with a strong solution of pure potassa, when the binoxide is resolved into hyponitrous acid, which unites with the alkali, while protoxide of nitrogen remains in the tube; and Dulong formed it by mixing 200 measures of binoxide of nitrogen with 50 of oxygen gas, both quite dry, and exposing the resulting orange fumes to intense cold, which condensed it into a liquid. It is the *nitrous* acid of Berzelius and other Continental chemists.

Prop.—At 0° it is a colourless liquid, and green at common temperatures. It is so volatile, that in open vessels the green fluid wholly and rapidly passes off in the form of an orange vapour, which is said by Mitscherlich to have a density

of 1·72. On admixture with water it is converted into nitric acid and binoxide of nitrogen, thus $3NO_3 = NO_5 + 2NO_2$, the latter escaping with effervescence; but when much nitric acid is present, the hyponitrous is changed into nitrous acid, the presence of which imparts several shades of colour, orange, yellow, green, and blue, according as its quantity is more or less predominant. One eq. of hyponitrous and one of nitric acid yield two eq. of nitrous acid:—Thus NO_3 and NO_5 obviously contain the elements for forming $2NO_4$.

Hyponitrous acid does not unite directly with alkalies, being then resolved principally into nitric acid and binoxide of nitrogen; but the hyponitrites of the alkalies and alkaline earths may be obtained by heating the corresponding nitrates to a gentle red heat; and the hyponitrite of the oxide of lead is formed by boiling a solution of the nitrate of that oxide with metallic lead.

Hyponitrous acid forms with water and sulphuric acid a crystalline compound, which is formed in large quantity during the manufacture of sulphuric acid, and the production of which is an essential part of that process. It is generated whenever moist sulphurous acid gas and nitrous acid vapour are intermixed, being instantly deposited in the form of white acicular crystals; and Gay-Lussac discovered that it may also be made by the direct action of anhydrous, nitrous and strong sulphuric acid. The first attempt to determine its composition analytically was by Henry, who found it to consist of 1 eq. of hyponitrous acid, 5 of sulphuric acid, and 5 of water. (Ann. of Phil. xxvii. 367.) G. De Claubry has lately repeated the analysis of the same compound in a state of more perfect dryness, and by what he considers a better method; and he gives as its constituents 2 eq. of hyponitrous acid, 4 of water, and 5 of sulphuric acid. (An. de Ch. et Ph. xlv. 284.) The theory of its production has been very carefully studied by De Claubry. It appears that when moist sulphurous and nitrous acids react on each other, the former is converted into sulphuric and the latter into hyponitrous acid, the oxygen lost by one being gained by the other, $NO_4 + SO_4 = NO_3 + SO_3$. A little nitrogen gas is always disengaged at the same time, which can only arise from a small portion of nitrous acid losing the whole of its oxygen. The action of sulphuric on nitrous acid is different: in this case the nitrous acid is resolved into nitric and hyponitrous acids, $2NO_4 = NO_5 + NO_3$, the latter uniting with sulphuric acid and most of its water to produce the crystalline solid, while the remainder of the water unites with the nitric acid. When the crystalline matter is put into water, the hyponitrous is resolved into nitrous acid and binoxide of nitrogen, both of which escape with effervescence, $2NO_3 = NO_4 + NO_2$. If much water is present, more or less of the nitrous acid is converted into nitric acid and the binoxide. Similar changes ensue when the crystals are exposed to the air, humidity being rapidly absorbed. This subject has also been examined by Bussy with similar results.*

Its eq. is = 38·15; *symb.* N + 3O, NO_3, or $\dddot{N}$.

NITROUS ACID.

Prep.—It is always formed when binoxide of nitrogen and oxygen gases are intermixed. Davy showed, by making the mixture in a dry glass vessel pre-

* From recent observations it would appear that the production of the crystalline compound, mentioned in the text, is not indispensable in the process of the manufacture of sulphuric acid, and that it is not a constant attendant upon that process. See Sulphuric Acid.—(R.)

viously exhausted, that nitrous acid vapour is formed by the action of 200 measures of the binoxide on 100 of oxygen gas; and hence, as 200 of the binoxide contains 100 of nitrogen and 100 of oxygen, nitrous acid was inferred to consist of 100 measures of nitrogen united with 200 of oxygen gas (page 166). This inference has been confirmed by the researches of Gay-Lussac and Dulong (An. de Ch. et Ph. i. and ii.), the former of whom also proved that its elements contract to 1-3rd of their volume, or in other words, 100 measures of nitrous acid vapour contain 100 of nitrogen acid gas and 200 of oxygen. The specific gravity of this vapour ought to be 3·1777, formed of 0·9727 the sp. gr. of nitrogen + 2·2050, twice the sp. gr. of oxygen. It is best prepared by heating to redness in an earthen retort the nitrate of oxide of lead, carefully dried; when nitric acid is resolved into nitrous acid and oxygen, and on receiving the products in a dry tube, surrounded by a mixture of ice and salt, the former is condensed. The following equation represents the decomposition:—

$$PbO, NO_5 = PbO + O + NO_4$$

Prop.—An anhydrous liquid of sp. gr. 1·451, and orange colour at 60°, yellow at 32°, and almost colourless at 0°; acid, pungent, and powerfully corrosive; and imparts a yellow stain to the skin. It is very volatile, boiling at 82°: in a stopped bottle it preserves its liquid form at 60°; but when exposed to the atmosphere it is rapidly dissipated in orange red fumes, which when once mixed with air or other gases require intense cold for condensation.

Nitrous acid vapour is characterized by its orange red colour, acid reaction, and by being absorbed by water with disengagement of binoxide of nitrogen and formation of nitric acid. It is quite irrespirable, exciting great irritation and spasm of the glottis, even when moderately diluted with air. A taper burns in it with considerable brilliancy. It extinguishes burning sulphur; but the combustion of phosphorus continues in it with great vividness.

Nitrous acid is a powerful oxidizing agent, readily giving oxygen to the more oxidable metals, and to most substances which have a strong affinity for it. The acid is decomposed at the same time, being commonly changed into binoxide of nitrogen, though sometimes the protoxide and even pure nitrogen gases are evolved. When transmitted through a red-hot porcelain tube, it suffers decomposition, and a mixture of oxygen and hydrogen gases is obtained.

When nitrous acid is mixed with a considerable quantity of water, it is instantly resolved into nitric acid, which unites with the water, and binoxide of nitrogen which escapes with effervescence. Three eq. of nitrous acid yield two eq. of nitric acid and one of the binoxide; for $3NO_4 = 2NO_5 + NO_2$. When a rather small quantity of water is used, the evolved binoxide, at first considerable, becomes less and less as successive quantities of nitrous acid are added, till at last the evolution of gas ceases altogether. The colour of the solution varies remarkably during the process: from being colourless the liquid acquires a blue tint, then passes into bluish green, green, yellow, and lastly orange. These different solutions contain different relative quantities of nitric acid, nitrous acid, and water, on which circumstance the varying shades of colour depend. Nitric and nitrous acids are disposed to unite with each other, and the influence of this attraction enables nitrous acid to sustain admixture with water without decomposition. Strong nitric acid will unite with a considerable quantity of nitrous acid, and thereby acquires an orange red tint. In a weaker nitric acid the water decomposes part of the nitrous acid, and the colour of the solution is orange or

yellow. As the strength of the nitric acid becomes weaker and weaker, the quantity of nitrous acid which it can protect from decomposition becomes less and less, and the colour of the solution varies from yellow to green and blue, and is at length colourless. These changes may be witnessed, not only by adding successive quantities of nitrous acid to water, and thereby at length producing a strong nitric acid, but commencing with the latter, saturating it with nitrous acid, and then successively diluting with water.

When nitrous acid is mixed with a very small quantity of water, no binoxide of nitrogen is disengaged, but the liquid becomes green, like the colour of hyponitrous acid. I have repeatedly obtained a similar liquid in preparing nitrous acid from nitrate of oxide of lead, when the materials were not adequately dried; and that green liquid, when allowed to dissipate in the air, leaves some nitric acid behind. From these facts it seems probable that in the decomposition of nitrous acid by water, the first change is the conversion of nitrous into nitric and hyponitrous acids, which last is subsequently changed, when the required quantity of water is present, into nitric acid and binoxide of nitrogen. It may thus well happen that hyponitrous acid contributes to produce the varying colours above described.

Some chemists consider nitrous acid as a compound of nitric and hyponitrous acids, rather than of nitrogen and oxygen. In fact, on adding nitrous acid to an alkaline solution, we obtain a nitrate and hyponitrite; a circumstance which has given rise to the notion that nitrous acid cannot act as a distinct acid.

Its eq. is 46·15; *eq. vol.* = 100; *symb.* N + 4O, NO_4, or $\dot{N}$.

NITRIC ACID.

Hist.—If a succession of electric sparks be passed through a mixture of oxygen and nitrogen gases confined in a glass tube over mercury, a little water being present, the volume of the gases will gradually diminish, and the water after a time will be found to have acquired acid properties. On neutralizing the solution with potassa, or what is better, by putting a solution of that alkali instead of water into the tube at the beginning of the experiment, a salt is obtained which possesses all the properties of nitrate of potassa. This experiment was performed in 1785 by Cavendish, who inferred from it that nitric acid is composed of oxygen and nitrogen, though the acid itself, under the name of *spirit of nitre*, had been long previously known. The best proportion of the gases was found to be seven of oxygen to three of nitrogen; but as some nitrous acid is always formed during the process, the exact composition of nitric acid cannot in this way be accurately determined.

Nitric acid may be formed much more conveniently by adding binoxide of nitrogen slowly over water to an excess of oxygen gas. Gay-Lussac proved that nitric acid may in this manner be obtained quite free from nitrous or hyponitrous acid; and that it is composed of 100 measures of nitrogen and 250 of oxygen, a result fully confirmed by Davy, Henry, Berzelius, and others.

Nitric acid cannot exist in an insulated state. Binoxide of nitrogen and oxygen gases never form nitric acid if mixed together when quite dry; and nitrous acid vapour may be kept in contact with oxygen gas without change, provided no water is present. The most simple form under which chemists have hitherto procured nitric acid is in solution with water; a liquid which, in its concentrated

state, is the nitric acid of the pharmacopœia. By manufacturers it is better known by the name of *aqua fortis*.

The nitric acid of commerce is procured by decomposing some salt of nitric acid by means of oil of vitriol, and common nitre, as the cheapest of the nitrates, is employed for the purpose. This salt, previously well dried, is put into a glass retort, and a quantity of the strongest oil of vitriol is poured upon it. On applying heat, ebullition ensues, owing to the escape of nitric acid vapours, which must be collected in a receiver kept cold by moist cloths. The heat should be steadily increased during the operation, and continued as long as any acid vapours come over.

Chemists differ as to the best proportions for forming nitric acid. The London College recommends equal weights of nitre and oil of vitriol; and the Edinburgh and Dublin colleges employ three parts of nitre to two of the acid. In the process of the London College the alkali of the nitre is left as a bisulphate in the retort; since one eq. of nitre (54 nitric acid and 47 potassa) is 100, and the nearly equal number 98 corresponds to 2 eq. of oil of vitriol, which contain 2 eq. of anhydrous sulphuric acid and 3 eq. of water. During the distillation the nitric acid passes over along with 1 eq. of water, and 1 eq. of water is retained by the bisulphate of potassa. The reaction may be thus expressed:—

$$KO, NO_5 + 2\,(HO, SO_3) = HO, NO_5 + (KO, HO, 2SO_3).$$

The presence of water is essential: nitric acid of 1·50 consists of real or anhydrous acid and water in the ratio of 1 eq. of each, and unless water in at least this proportion be supplied, a proportional quantity of nitric acid is resolved, at the moment of quitting the potassa, into oxygen and nitrous acid (Phillips, in Phil. Mag. ii. 430). If the mixture be introduced into the retort without soiling its neck, and the heat be cautiously raised, the product will be quite free from sulphuric acid; and therefore the second distillation from nitre, recommended in the pharmacopœia, is superfluous.

The proportions of the Edinburgh and Dublin Colleges are such, that the residual salt is a mixture of sulphate and bisulphate of potassa. The acid of the nitre does not receive from the oil of vitriol the requisite quantity of water, and hence part of it is decomposed, yielding towards the close of the operation an abundant supply of nitrous acid fumes. If the receiver be kept cool, nearly all these vapours are condensed, and the product is a mixture of nitric and nitrous acids, of a deep orange red colour, (the nitroso nitric acid of Berzelius) very strong and fuming, and of a greater sp. gr. though proportionally less in quantity, than that obtained by the foregoing process. The sp. gr. of the pale acid is 1·500; while that of the red acid is 1·520, or by previously drying the nitre and boiling the sulphuric acid, Hope states that it may be made so high as 1·54.

Some manufacturers decompose nitre with half its weight of sulphuric acid, thus employing the ingredients in the proportion of 1 eq. of each. In this case about half of the nitric acid is decomposed, and considerable loss sustained, unless the requisite quantity of water is previously mixed with the sulphuric acid, or water be placed in the receiver to condense the nitrous acid. Some of the nitre is likewise apt to escape decomposition; and the residue, consisting of neutral sulphate, which is much less soluble than the bisulphate, is removed from the retort with difficulty.

In none of the preceding processes, not even in the first, is the product quite

colourless: for at the commencement and close of the operation, nitrous acid fumes are disengaged, which communicate a straw yellow or an orange red tint, according to their quantity. If a very pale acid is required, two receivers should be used, one for condensing the colourless vapours of nitric acid, and another for the coloured products. The coloured acid is called nitrous acid by the College; but it is in reality a mixture or compound of nitric and nitrous acids, similar to what may be obtained by mixing anhydrous nitrous with colourless nitric acid. It is easy to convert the common mixed acid of the College into colourless nitric acid, by exposing the former to a gentle heat for some time, when all the nitrous acid will be expelled. But this process is rarely necessary, as the coloured acid may be substituted in most cases for that which is colourless. Where an acid of great strength is required, the former is even preferable.

Nitric acid frequently contains portions of sulphuric and hyrochloric acid. The former is derived from the acid which is used in the process, and the latter from sea-salt which is frequently mixed with nitre. These impurities may be detected by adding a few drops of a solution of chloride of barium and oxide of silver to separate portions of nitric acid, diluted with three or four parts of distilled water. If chloride of barium cause a cloudiness or precipitate, sulphuric acid must be present; if a similar effect be produced by nitrate of oxide of silver, the presence of hydrochloric acid may be inferred. Nitric acid is purified from sulphuric acid by redistilling it from a small quantity of nitrate of potassa, with the alkali of which the sulphuric acid unites, and remains in the retort. To separate hydrochloric acid, it is necessary to drop a solution of nitrate of oxide of silver into the nitric acid as long as a precipitate is formed, and draw off the pure acid by distillation.

Prop.—A strong, highly corrosive acid; in its purest and most concentrated state a colourless liquid, of sp. gr. 1·50 or 1·510, chemically combined with water, from which it cannot be separated without decomposition, or by uniting with some other body. An acid of sp. gr. 1·50 contains 25 per cent. of water, according to the experiments of Phillips, and 20·3 per cent. according to those of Ure.* Nitric acid of this strength emits dense, white, suffocating vapours when exposed to the atmosphere. It attracts watery vapour from the air, whereby its density is diminished. A rise of temperature is occasioned by mixing it with a certain quantity of water. When 58 measures of nitric acid of sp. gr. 1·5 are suddenly mixed with 42 of water, the temperature rises from 60° to 140°; and the mixture, on cooling to 60°, occupies the space of 92·65 measures instead of 100. From its strong affinity for water, it occasions snow to liquefy with great rapidity; and if the mixture is made in due proportion, intense cold will be generated. (Page 40.) It boils at 187°, and may be distilled without suffering material change. An acid of lower density than 1·42 becomes stronger by being heated; because the water evaporates more rapidly than the acid. An acid, on the contrary, which is stronger than 1·42 is weakened by the application of heat. It may be frozen by cold: the point of congelation varies with the strength of the acid. The strongest acid freezes at about 50° below zero. When diluted with half its weight in water, it becomes solid at $-1\frac{1}{2}^{\circ}$; but a little more water lowers its freezing point to —45°. It acts powerfully on oxidable substances, and is hence much employed by chemists for bringing bodies to their maximum of oxidation. Nearly all the metals are oxidized by it; and some of them, such

* See his Table in the Appendix, showing the strength of diluted acid of different densities.

as tin, copper, and mercury, are attacked with great violence. If flung on burning charcoal, it increases the brilliancy of its combustion in a high degree. Sulphur and phosphorus are converted into acids by its action. All vegetable substances are decomposed by it. In general the oxygen of the nitric acid enters into direct combination with the hydrogen and carbon of those compounds, forming water with the former, and carbonic acid with the latter. This happens remarkably in those compounds in which hydrogen and carbon are predominant, as in alcohol and the oils. It effects the decomposition of animal matters also. The cuticle and nails receive a permanent yellow stain when touched with it; and if applied to the skin in sufficient quantity it acts as a powerful cautery, destroying the organization of the part entirely.

When oxidation is effected through the medium of nitric acid, the acid itself is commonly converted into binoxide of nitrogen. This gas is sometimes given off nearly quite pure; but in general some nitrous acid, protoxide of nitrogen, or pure nitrogen, are evolved at the same time. The escape of nitrous acid in these cases seems owing, according to some late observations of Phillips, not so much to its direct formation, as to the binoxide at first formed acting on the nitric acid of the solution. Direct solar light deoxidizes nitric acid, resolving a portion of it into oxygen and nitrous acid. The former escapes as gas; the latter is absorbed by the nitric acid, and converts it into the mixed nitrous acid of the shops. When the vapour of nitric acid is transmitted through red-hot porcelain tubes, it suffers complete decomposition, and a mixture of oxygen and nitrogen gases is the product.

Nitric acid may also be deoxidized by transmitting a current of binoxide of nitrogen through it. That gas, by taking oxygen from the nitric, is converted into nitrous acid; and a portion of nitric acid, by losing oxygen, passes into the same compound. The nitrous acid, thus derived from two sources, gives a colour to the nitric acid, the depth and kind of which depend on the strength of the acid. On saturating with binoxide of nitrogen four separate portions of nitric acid of sp. gr. 1·15, 1·35, 1·40, and 1·50, the colour will be blue in the first, green in the second, yellow in the third, and brownish red in the fourth; and acid of 1·05 is not coloured at all. Phillips found that acid of density 1·497 acquired a density 1·541, that is, was made stronger, by saturation with the binoxide; but those acids which become green are much weakened, because nitrous acid vapour is mechanically carried off by those portions of binoxide which pass unabsorbed through the liquid.

Tests.—All the salts of nitric acid are soluble in water, and therefore it is impossible to precipitate that acid by any reagent. The presence of nitric acid, when uncombined, is readily detected by its strong action on copper and mercury, emitting ruddy fumes of nitrous acid, and by its forming with potassa a neutral salt, which crystallizes in prisms, and has all the properties of nitre. Gold leaf is a still more delicate test. When hydrochloric acid is added to the solution of a nitrate, chlorine is disengaged, and the liquid hence acquires the property of dissolving gold leaf; but as the action of hydrochloric acid on the salts of chloric, bromic, iodic, and selenic acids likewise yields a solution capable of dissolving gold, no inference can be drawn from the experiment, unless the absence of these acids shall have been previously demonstrated. Another character which may be useful is to mix the supposed nitric acid or nitrate with dilute sulphuric acid in a tube, add a few fragments of pure zinc, and set fire to the hydrogen as it issues: if nitric acid be present, the flame of the hydrogen

will have a greenish white tint, due to admixture with binoxide of nitrogen. This test occurred to my assistant, Mr. Balmain; and Mr. Maitland at the same time proposed alcohol instead of zinc with the same intention. A very delicate test has been proposed by O'Shaughnessy, founded on the orange red followed by a yellow colour, which nitric acid communicates to morphia. The supposed nitrate is heated in a test tube with a drop of sulphuric acid, and then a crystal of morphia is added. (Lancet, 1829-30.) It is advisable to try the process in a separate tube with the sulphuric acid alone, in order to prove the absence of nitric acid. But the most delicate test is the following, proposed by Derbanius de Richemont:—The suspected substance is mixed with pure sulphuric acid in a tube, and gently warmed, and a solution of green vitriol cautiously added. At the line of junction of the two liquids, the dark colour produced by the action of nitric acid on the protosulphate of iron is distinctly seen, even when only $\frac{1}{24000}$ of nitric acid is present.*

SECTION VI.

CARBON.

Hist. and Prep.—It occurs pure and crystallized in forms of the octohedral system in the diamond, a mineral of unknown origin, but probably derived from the slow decomposition of vegetable matter. It is sometimes a constituent of the rocks in the form of small tabular crystals called graphite, and in larger masses mixed with iron, as plumbago with which pencils are made, and in anthracite mixed with earth and metallic sulphurets. It is the essential principle of the different varieties of charcoal—the black mass left when most vegetable and animal matters are heated to redness in close vessels, and which contains any fixed principles originally present in its source. Common charcoal is made from wood and contains about 1-50th of its weight of alkaline and earthy salts, which constitute the ashes when wood-charcoal is burned. Coke is the charcoal from coal, ivory black or animal charcoal is that from bones, lamp-black from resin. Very pure varieties of charcoal may be formed from spirit of wine, turpentine, sugar, and starch.

Prop.—Carbon, as it exists in the diamond, is the hardest substance in nature; sp. gr. 3·52; it crystallizes in the regular system in forms which are frequently hemihedral, and are characterized by a perfect cleavage parallel to the faces of the octohedron; beautifully transparent and a powerful refractor of light; a non-conductor of heat and electricity. It is very unchangeable, resists the action of acids and alkalies, and bears the most intense heat in close vessels without fusing or undergoing any perceptible change. Heated to redness in the open air, it is entirely consumed. Newton first suspected it to be combustible from its great refracting power, a conjecture which was rendered probable by the experiments

* The bleaching effect which it exercises upon a boiling solution of the sulphate of Indigo, is another good test; provided, all traces of chlorine are absent.—(R.)

of the Florentine academicians in 1694. Lavoisier first proved it to contain carbon by throwing the sun's rays, concentrated by a powerful lens, upon a diamond contained in a vessel of oxygen gas. The diamond was consumed entirely, oxygen disappeared, and carbonic acid was generated. It has since been demonstrated by the researches of Guyton-Morveau, Smithson Tennant, Allen and Pepys, and Davy, that carbonic acid is the product of its combustion. Guyton-Morveau inferred from his experiments that the diamond is pure carbon, and that charcoal is an oxide of carbon. Tennant burned diamonds by heating them with nitre in a gold tube; and comparing his own results with those of Lavoisier on the combustion of charcoal, he concluded that equal weights of diamond and pure charcoal, in combining with oxygen, yield precisely equal quantities of carbonic acid. He was thus induced to adopt the opinion, that charcoal and the diamond are chemically the same substance; and that the difference in their physical character is solely dependent on a difference of aggregation.* This conclusion was confirmed by the experiments of Allen and Pepys†, and Davy‡, who compared the product of the combustion of the diamond with that derived from different kinds of charcoal. The latter chemist did indeed observe the production of a minute quantity of water during the combustion of the purest charcoal, indicative of a trace of hydrogen: but its quantity is so small, that it cannot be regarded as a necessary constituent. It proves only that a trace of hydrogen is retained by charcoal with such force, that it cannot be expelled by the temperature of ignition.

Charcoal, as obtained from wood, is hard and brittle, conducts heat very slowly, but is a good conductor of electricity; quite insoluble in water, is attacked with difficulty by nitric acid, and is little affected by any of the other acids, or by the alkalies. It undergoes little change from exposure to air and moisture, being less injured under these circumstances than wood. It is exceedingly refractory in the fire, if excluded from the air, supporting the most intense heat which chemists are able to produce without change.

It possesses the property of absorbing a large quantity of air or other gases at common temperatures, and of yielding the greater part of them again when it is heated. It appears from the researches of Saussure, that different gases are absorbed by it in different proportions. His experiments were performed by plunging a piece of red-hot charcoal under mercury, and introducing it when cool into the gas to be absorbed. He found that charcoal prepared from boxwood absorbs, during the space of 24 or 36 hours, of

Ammoniacal gas	90 times its volume.
Muriatic acid	85
Sulphurous acid	65
Sulphuretted hydrogen	81 (Dr. C. Henry.)
Nitrous oxide	40
Carbonic acid	35
Olefiant gas	35
Carbonic oxide	9·42
Oxygen	9·25
Nitrogen	7·5
Hydrogen	1·75

The absorbing power of charcoal, with respect to gases, cannot be attributed to chemical action; for the quantity of each gas which is absorbed bears no rela-

* Phil. Trans. 1797. † Ibid. 1807. ‡ Ibid. 1814.

tion whatever to its affinity for charcoal. The effect is in reality owing to the peculiar porous texture of that substance, which enables it, in common with most spongy bodies, to absorb more or less of all gases, vapours, and liquids with which it is in contact. This property is most remarkable in charcoal prepared from wood, especially in the compact varieties of it, the pores of which are numerous and small. It is materially diminished by reducing the charcoal to powder; and in plumbago, which has not the requisite degree of porosity, it is wanting altogether.

The porous texture of charcoal accounts for the general fact of absorption only; its power of absorbing more of one gas than of another, must be explained on a different principle. This effect, though modified to all appearance by the influence of chemical attraction, seems to depend chiefly on the natural elasticity of the gases. Those which possess such a great degree of elasticity as to have hitherto resisted all attempts to condense them into liquids, are absorbed in the smallest proportion; while those that admit of being converted into liquids by compression, are absorbed more freely. For this reason, charcoal absorbs vapours more easily than gases, and liquids than either.

Allen and Pepys determined experimentally the increase in weight experienced by different kinds of charcoal, recently ignited, after a week's exposure to the atmosphere. The charcoal from fir gained 13 per cent.; that from *lignum vitæ*, 9·6; that from box, 14; from beech, 16·3; from oak, 16·5; and from mahogany, 18. The absorption is most rapid during the first 24 hours. The substance absorbed is both water and atmospheric air, which the charcoal retains with such force, that it cannot be completely separated from them without exposure to a red heat. Vogel has observed that charcoal absorbs oxygen in a much greater proportion from the air than nitrogen. Thus, when recently ignited charcoal, cooled under mercury, was put into a jar of atmospheric air, the residue contained only 8 per cent. of oxygen gas; and if red-hot charcoal be plunged into water, and then introduced into a vessel of air, the oxygen disappears almost entirely. It is said that pure nitrogen may be obtained in this way. (Schweigger's Journal, iv.)

Charcoal likewise absorbs the odoriferous and colouring principles of most animal and vegetable substances. When coloured infusions of this kind are digested with a due quantity of charcoal, a solution is obtained, which is nearly if not quite colourless. Tainted flesh may be deprived of its odour by this means, and foul water be purified by filtration through charcoal. The substance commonly employed to decolorize fluids is animal charcoal reduced to a fine powder. It loses the property of absorbing colouring matters by use, but recovers it by being heated to redness.

Charcoal is highly combustible. When strongly heated in the open air, it takes fire, and burns slowly. In oxygen gas, its combustion is lively, and accompanied with the emission of sparks. In both cases it is consumed without flame, smoke, or residue, if quite pure; and carbonic acid gas is the product of its combustion.

Its eq. is = 6·12; *its vapour* (theoretical, p. 140) has a sp. gr. = 0·4215, and *eq. vol.* = 100, and 100 C. I. weigh 13·153 grains.

The composition of the compounds of carbon described in this section is as follows:—

	Carbon.		Oxygen.		Equiv.	Formulæ.
Carbonic Oxide	6·12 or 1 eq.	+	8 or 1 eq.	=	14·12	C + O or CO.
Carbonic Acid	6·12 or 1 eq.	+	16 or 2 eq.	=	22·12	C + 2O or CO_2.

Carbonic oxide gas is theoretically considered as a compound of 100 measures of the vapour of carbon and 50 of oxygen condensed into 100 measures; and carbonic acid gas, of 100 measures of the vapour of carbon and 100 of oxygen condensed into 100 measures.

CARBONIC ACID.

Hist.—Discovered by Black in 1757, and described by him in his inaugural dissertation on magnesia under the name of *fixed air*. He observed the existence of this gas in common limestone and magnesia, and found that it may be expelled from these substances by the action of heat or acids. He also remarked that the same gas is formed during respiration, fermentation, and combustion. Its composition was first demonstrated synthetically by Lavoisier, who burned carbon in oxygen gas, and obtained carbonic acid as the product. The same experiment has been repeated by Davy, Allen and Pepys, and others, with the result that in the combustion of diamond or other pure carbonaceous matter the oxygen undergoes no change of volume, or in other words, that carbonic acid gas contains its own volume of oxygen: hence the difference of the sp. gravities of carbonic acid and oxygen gases (1·524 — 1·1025), or 0·4215, gives the exact ratio of the quantities of carbon and oxygen combined, being 0·4215 to 1·1025, or 6·12 to 16. Smithson Tennant illustrated its nature analytically by passing the vapour of phosphorus over chalk, or carbonate of lime, heated to redness in a glass tube. The phosphorus took oxygen from the carbonic acid, charcoal in the form of a light black powder was deposited, and the phosphoric acid, which was formed, united with the lime.

Prep.—Conveniently by the action of hydrochloric acid, diluted with two or three times its weight of water, on fragments of marble, when carbonic acid gas escapes with effervescence, and chloride of calcium is left in solution.

Prop.—Commonly a colourless gas of a pungent odour and acidulous taste, condensable at 32° by a pressure of 36 atmospheres into a liquid, which congeals by the cold produced by its own evaporation, estimated at — 148°, and at that temperature is solid under the atmospheric pressure, being, until recently, the first instance of a solidified gas (page 53). The sp. gr. of the gas is 1·524, and 100 C. I. at 60° and 30 Bar. weigh 47·262 grains; the sp. gr. of the liquid at 32° is 0·83; it dilates remarkably from heat, its expansion being upwards of four times that of air, 20 volumes of the liquid at 32° occupying 29 volumes at 86°, and its sp. gr. varies from 0·9 to 0·6 as the temperature rises from — 4° to + 86°. When heated from 32° to 86° its elasticity rises from 36 to 73 atmospheres, being 0·68 atmospheres for each degree. It is insoluble in water and fat oils, but soluble in all proportions in ether, alcohol, naphtha, oil of turpentine, and bisulphuret of carbon. The evaporation of its ethereal solution causes an intense degree of cold, by which large quantities of mercury may be frozen. (Thilorier in Ann. de Ch. et Ph. lx. 427.)

Carbonic acid gas extinguishes burning substances of all kinds, and the combustion does not cease from the want of oxygen only. It exerts a positive influence in checking combustion, as appears from the fact, that a candle cannot burn in a gaseous mixture composed of four measures of atmospheric air, and one of carbonic aid.

It is not better qualified to support the respiration of animals; for its presence, even in moderate proportion, is soon fatal. An animal cannot live in air which contains sufficient carbonic acid for extinguishing a lighted candle; and

hence the practical rule of letting down a burning taper into old wells or pits before any one ventures to descend. If the light is extinguished, the air is certainly impure; and there is generally thought to be no danger, if the candle continues to burn. But some instances have been known of the atmosphere being sufficiently loaded with carbonic acid to produce insensibility, and yet not so impure as to extinguish a burning candle. (Christison on Poisons, 2nd ed. 707.) When an attempt is made to inspire pure carbonic acid, violent spasm of the glottis takes place, which prevents the gas from entering the lungs. If it be so much diluted with air as to admit of its passing the glottis, it then acts as a narcotic poison on the system. It is this gas which has often proved destructive to persons sleeping in a confined room with a pan of burning charcoal.

It is quite incombustible, and cannot be made to unite with an additional portion of oxygen. It is a compound, therefore, in which carbon is in its highest degree of oxidation.

Lime water becomes turbid when brought into contact with carbonic acid. The lime unites with the gas, forming carbonate of lime, which, from its insolubility in water, at first renders the solution milky, and afterwards forms a white flaky precipitate. Hence lime water is not only a valuable test of the presence of carbonic acid, but is frequently used to withdraw it altogether from any gaseous mixture that contains it.

Recently boiled water dissolves its own volume of carbonic acid gas at 60° and 30 Bar.; but it will take up much more if the pressure be increased. The quantity of the gas absorbed is in exact ratio with the compressing force; that is, water dissolves twice its volume when the pressure is doubled, and three times its volume when the pressure is trebled. A saturated solution may be made by transmitting a stream of the gas through a vessel of cold water during the space of half an hour, or still better by the use of a Woulfe's bottle or Nooth's apparatus, so as to aid the absorption by pressure. Water and other liquids, which have been charged with carbonic acid under great pressure, lose the greater part of the gas when the pressure is removed. The effervescence which takes place on opening a bottle of ginger beer, cider, or brisk champaigne, is owing to the escape of carbonic acid gas. Water, if fully saturated with carbonic acid gas, sparkles when it is poured from one vessel into another. The solution has an agreeably acidulous taste, and gives to litmus paper a red stain which is lost on exposure to the air. On the addition of lime water to it, a cloudiness is produced, which at first disappears, because the carbonate of lime is soluble in excess of carbonic acid; but a permanent precipitate ensues when the free acid is neutralized by an additional quantity of lime water. The water which contains carbonic acid in solution is wholly deprived of the gas by boiling. Removal of pressure from its surface by means of the air-pump has a similar effect.

The agreeable pungency of beer, porter, and ale, is in a great measure owing to the presence of carbonic acid; by the loss of which, on exposure to the air, they become stale. All kinds of spring and well water contain carbonic acid absorbed from the atmosphere, and to which they are partly indebted for their pleasant flavour. Boiled water has an insipid taste from the absence of carbonic acid.

Carbonic acid is always present in the atmosphere, even at the summit of the highest mountains, or at a distance of several thousand feet above the ground. Its presence may be demonstrated by exposing lime water in an open vessel to

the air, when its surface will soon be covered with a pellicle, which is carbonate of lime. The origin of the carbonic acid is obvious. Besides being formed abundantly by the combustion of all substances which contain carbon, the respiration of animals is a fruitful source of it, as may be proved by breathing for a few minutes into lime water; and it is also generated in all the spontaneous changes to which dead animal and vegetable matters are subject. The carbonic acid proceeding from such sources is commonly diffused equably through the air; but when any of these processes occur in low confined situations, as at the bottom of old wells, the gas is then apt to accumulate there, and form an atmosphere called *choke damp*, which is fatal to any animals that are placed in it. These accumulations happily never take place, except when there is some local origin for the carbonic acid; as, for example, when it is generated by fermentative processes going on at the surface of the ground, or when it issues directly from the earth, as happens at the Grotto del Cane in Italy, and at Pyrmont in Westphalia. There is no real foundation for the opinion that carbonic acid can separate itself from the great mass of the atmosphere, and accumulate in a low situation merely by the force of gravity. Such a supposition is contrary to the well-known tendency of gases to diffuse themselves equally through each other. It is also contradicted by observation; for many deep pits, which are free from putrefying organic remains, though otherwise favourably situated for such accumulations, contain pure atmospheric air.

Though carbonic acid is the product of many natural operations, chemists have not hitherto noticed any increase in the quantity contained in the atmosphere. The only known process which tends to prevent increase in its proportion, is that of vegetation. Growing plants purify the air by withdrawing carbonic acid, and yielding an equal volume of pure oxygen in return; but whether a full compensation is produced by this cause has not yet been satisfactorily determined.

Carbonic acid is contained in the earth. Many mineral springs, such as those of Tunbridge, Pyrmont, and Carlsbad, are highly charged with it. In combination with lime it forms extensive masses of rock, which geologists have found to occur in all countries, and in every formation.

Carbonic acid unites with alkaline substances, and the salts so constituted are called *carbonates*. Its acid properties are feeble, so that it is unable to neutralize completely the alkaline properties of potassa, soda, and lithia. For the same reason, all the carbonates, without exception, are decomposed by the hydrochloric and all the stronger acids; when carbonic acid is displaced, and escapes in the form of gas.

Its eq. is 22·12; *eq. vol.* = 100; *symb.* C + 2O, CO_2, or $\ddot{C}$.

CARBONIC OXIDE GAS.

Hist.—Priestley discovered it by igniting chalk in a gun-barrel, and afterwards obtained it by heating a mixture of chalk and iron filings. He supposed it to be hydrogen mixed with carbonic acid. Its real nature was pointed out by Cruickshank (Nicholson's Journal, 4to ed. v.), and about the same time by Clément and Désormes (An. de Chimie, xxxix.).

Prep.—1. By transmitting carbonic acid gas over red-hot fragments of charcoal contained in a tube of iron or porcelain. 2. By igniting alkaline or earthy carbonates with iron filings, charcoal, or some deoxidizing substance. 3. By

heating binoxalate of potassa with five or six times its weight of strong oil of vitriol in a retort. Effervescence soon ensues, owing to the escape of gas consisting of equal measures of carbonic acid and carbonic oxide gases; and on absorbing the former by an alkaline solution, the latter is left in a state of perfect purity. To comprehend the theory of the process it is necessary to premise, that oxalic acid is a compound of equal measures of carbonic acid and carbonic oxide, or at least its elements are in the proportion to form these gases; and that it cannot exist unless in combination with water or some other substance. Now the sulphuric acid unites both with the potassa and water of the binoxalate, and the oxalic acid being thus set free, is instantly decomposed. Oxalic acid may be substituted in this process for binoxalate of potassa. The following equation represents the reaction:—

$$KO, HO, 2C_2O_3 + 2SO_3 = KO, HO, 2SO_3 + 2CO + 2CO_2.$$

[4. By heating, in the same manner, one part of finely powdered ferrocyanide of potassium along with ten parts of oil of vitriol. The salt is entirely decomposed, and yields an abundant supply of pure carbonic oxide. (Fownes.*)]

Prop.—A colourless, inodorous gas; sp. gr. = 0·9727, and 100 C. I. at 60° and 30 Bar. weigh 30·207 grains; has neither acid nor alkaline properties; is sparingly dissolved by water, and does not render lime water turbid. It is inflammable. When a lighted taper is plunged into it, the taper is extinguished; but the gas itself is set on fire, and burns calmly at its surface with a lambent blue flame. The sole product of its combustion, when the gas is quite pure, is carbonic acid; a fact which proves that it does not contain any hydrogen. It cannot support respiration. It acts injuriously on the system; for if diluted with air, and taken into the lungs, it very soon occasions headache and other unpleasant feelings; and when breathed pure, it almost instantly causes profound coma.

A mixture of carbonic oxide and oxygen gases may be made to explode by flame, by a red-hot solid body, or by the electric spark. If mixed together in the ratio of 100 measures of carbonic oxide and rather more than 50 of oxygen, and the mixture is inflamed in Volta's Eudiometer by electricity so as to collect the product of the combustion, the whole of the carbonic oxide, together with 50 measures of oxygen, disappears, and 100 measures of carbonic acid gas occupy their place. From this fact, first ascertained by Berthollet, and since confirmed by subsequent observation, it follows that carbonic oxide contains half as much oxygen, and as much carbon, as carbonic acid. Accordingly its density should be 0·4215 (sp. gr. of carbon vapour) + 0·5512 (half the sp. gr. of oxygen gas) = 0·9727, which is the number found experimentally by Dulong and Berzelius.

The two first processes mentioned for generating carbonic oxide will now be intelligible. The principle of the methods is to bring carbonic acid at a red heat in contact with some substance which has a strong affinity for oxygen. This condition is fulfilled by igniting chalk, or any carbonate which can bear a red heat without decomposition, such as the carbonates of baryta, strontia, soda, potassa, or lithia, with half its weight of iron filings or charcoal. The carbonate is reduced to the caustic state, and its carbonic acid is converted into carbonic oxide by yielding oxygen to the iron or charcoal. When the former is used, oxide of iron is the product; when charcoal is employed, the charcoal itself is

* Memoirs Chem. Soc. Lond., i. p. 215.

oxidized, and yields carbonic oxide. This gas may likewise be generated by heating to redness a mixture of almost any metallic oxide with one-sixth of its weight of charcoal powder. The oxides of zinc, iron, or copper, are the cheapest and most convenient. In all these processes it is essential that the ingredients be quite free from moisture and hydrogen, otherwise some carburetted hydrogen gas would be generated. The product should always be washed with lime water to separate it from carbonic acid.

Henry has ascertained that when a succession of electric sparks is passed through carbonic acid confined over mercury, a portion of that gas is converted into carbonic oxide and oxygen. When a mixture of hydrogen and carbonic acid gases is electrified, a portion of the latter yields one half of its oxygen to the former; water is generated, and carbonic oxide produced. On electrifying a mixture of equal measures of carbonic oxide and protoxide of nitrogen, both gases are decomposed without change of volume, and the residue consists of equal measures of carbonic acid and nitrogen gases. The carbonic oxide should be in very slight excess, in order to ensure the success of the experiment. On this fact is founded Henry's method of analyzing protoxide of nitrogen, and testing its purity, as will be more particularly mentioned in the fourth part of the work.

[Carbonic oxide combines also with chlorine and several other elementary bodies, and forms compounds in which it appears to act the part of an element, and is on this account viewed as the radical of a series of bodies, which will be treated of in the third part of this work under the head of compound or organic radicals.]

Its eq. is 14·12; *eq. vol.* = 100; *symb.* C + O, CO, or Ċ.

SECTION VII.

SULPHUR.

Hist.—It occurs as a mineral production in some parts of the earth, particularly in the neighbourhood of volcanoes, as in Italy and Sicily. It is commonly found in a massive state; but it is sometimes met with crystallized in the form of a right rhombic octohedron. It exists much more abundantly in combination with several metals, such as silver, copper, antimony, lead, and iron. It is procured in a large quantity by exposing iron pyrites to a red heat in close vessels.

Prop.—A nearly tasteless, brittle solid; colour greenish yellow; odour when rubbed peculiar; sp. gr. 1·99; non-conductor of electricity and heat. Its point of fusion is 232°; between 232° and 280° it possesses the highest degree of fluidity, is then of an amber colour, and if cast into cylindrical moulds, forms the common roll sulphur of commerce. It begins to thicken near 320°, and acquires a reddish tint; and at temperatures between 428° and 482°, it is so tenacious that the vessel may be inverted without causing it to change its place. From 482° to its boiling point it again becomes liquid, but never to the same extent as when at 248°. When heated to at least 428°, and then poured into water, it becomes a ductile mass, which may be used for taking the impression of seals.

Fused sulphur has a tendency to crystallize in cooling. A crystalline arrangement is perceptible in the centre of common roll sulphur; and by good management regular crystals may be obtained. For this purpose several pounds of sulphur should be melted in an earthen crucible; and when partially cooled, the outer solid crust should be pierced, and the crucible quickly inverted, so that the inner and as yet fluid parts may gradually flow out. On breaking the solid mass, when quite cold, crystals of sulphur will be found in its interior.

Sulphur is very volatile. It begins to rise slowly in vapour, even before it is completely fused. At 550° or 600° it volatilizes rapidly, and condenses again unchanged in close vessels. Common sulphur is purified by this process; and if the sublimation be conducted slowly, the sulphur collects in the receiver in the form of detached crystalline grains, called *flowers of sulphur*. In this state, however, it is not quite pure, for the oxygen of the air within the apparatus combines with a portion of sulphur during the process, and forms sulphurous acid. The acid may be removed by washing the flowers repeatedly with water.

The sp. gr. of sulphur vapour was found by Dumas to lie between 6·51 and 6·617, and by Mitscherlich 6·9 (An. de Ch. et Ph. lv. 8.): its sp. gr. by calculation (page 140) is 6·648. Hence, could the vapour continue as such at 60° and 30 Bar., 100 cubic inches should weigh 206·17 grains.

Sulphur is insoluble in water. It dissolves readily in boiling oil of turpentine. The solution has a reddish brown colour like melted sulphur, and if fully saturated deposits numerous small crystals in cooling. Its best solvent is liquid bisulphuret of carbon. It is also soluble in alcohol, if both substances are brought together in the form of vapour. The sulphur is precipitated from the solution by the addition of water.

Sulphur, like charcoal, retains a portion of hydrogen so obstinately that it cannot be wholly freed from it either by fusion or sublimation. Davy detected its presence by exposing sulphur to the strong heat of a powerful galvanic battery, when some hydrosulphuric acid gas was disengaged. The hydrogen, from its minute quantity, can only be regarded in the light of an accidental impurity, and as in no wise essential to the nature of sulphur.

When sulphur is heated in the open air to 300° or a little higher, it kindles spontaneously, and burns with a faint blue light. In oxygen gas its combustion is far more vivid; the flame is much larger, and of a bluish white colour. Sulphurous acid is the product in both instances;—no sulphuric acid is formed even in oxygen gas unless moisture be present.

Crystals of native sulphur, which have been formed by the condensation of sulphurous vapour, as well as those which are deposited from a solution of sulphur in any menstruum, possess forms which are either identical, or connected by being referable to the same crystalline axes. Such, on the contrary, as are produced by the cooling of fused sulphur in the manner above described, belong to a different system of crystallization. The condition determining the form is temperature: if the crystal be formed below 232°, it belongs to the right prismatic system; if at that point, to the oblique prismatic. This is proved by the influence of temperature on a crystal of either system: a crystal of fusion when first formed is perfectly clear and transparent, but kept at common temperatures, it soon becomes opaque, and presents the appearance of the roll sulphur of commerce: the same change occurs when a native crystal is placed in a solution of a salt which boils at 232°. The opacity is in both cases produced by a new arrangement of the particles of sulphur, by which, without any change in the

exterior form, the internal structure of the crystal is altered to correspond to the crystallization peculiar to the temperature.

The *eq. of* sulphur is 16·1; *eq. vol.* 16·66; *symb.* S.

The compounds of sulphur described in this section are composed as follows:—

	Sulphur.	Oxygen.	Equiv.	Formulæ.
Sulphurous acid	16·1 or 1 eq.	+ 16 or 2 eq.	= 32·1	S + 2O or SO_2
Sulphuric acid	16·1 or 1 eq.	+ 24 or 3 eq.	= 40·1	S + 3O or SO_3
Hyposulphurous acid	32·2 or 2 eq.	+ 16 or 2 eq.	= 48·2	2S + 2O or S_2O_2
Hyposulphuric acid	32·2 or 2 eq.	+ 40 or 5 eq.	= 72·2	2S + 5O or S_2O_5.
Sulphuretted Hyposulphuric acid	48·3 or 3 eq.	+ 40 or 5 eq.	= 88·3	3S + 5O or S_3O_5.
Bisulphuretted Hyposulphuric acid	64·4 or 4 eq.	+ 40 or 5 eq.	= 104·4	4S + 5O or S_4O_5.

Taking 16·56 as the eq. vol. of the vapour of sulphur, the weight of which is represented by 1·108 (page 140), these compounds, by measure, are thus constituted:—

	Sulp.	Oxy.	Cond. into.	Densities.
Sulphurous acid	16·66	+ 100	100	1·108 + 1·1025 = 2·2105
Sulphuric acid	16·66	+ 150	100	1·108 + 1·6537 = 2·7617
Hyposulphurous acid	33·33	+ 100	unknown.	
Hyposulphuric acid	33·33	+ 250	unknown.	

SULPHUROUS ACID.

Hist. and Prep.—Discovered as a gas by Priestley. It is the sole product of the combustion of sulphur in air or dry oxygen gas, and is freely evolved, mixed with carbonic acid, when chips of wood, straw, cork, oil, or most other organic matters are heated in strong sulphuric acid, which yields oxygen to the carbon and hydrogen of those substances, and is thereby converted into sulphurous acid. Nearly all the metals, with the aid of heat, have a similar effect: one portion of the acid yields oxygen to the metal, and is thus reduced to sulphurous acid; while the metallic oxide, at the moment of its formation, unites with sulphuric acid. A very pure gas may thus be obtained by means of copper or mercury.

Prop.—Commonly gaseous, colourless, of a pungent suffocating odour, being that emitted by burning sulphur; taste, acid, sp. gr. 2·2105, and 100 C. I. at 60° and 30 Bar. weigh 68·691 grains; it is liquid at 45° under the pressure of two atmospheres, and at 0° under that of one atmosphere. The gas extinguishes all burning bodies which are immersed into it, and is not inflammable. It does not support respiration, but causes violent irritation and spasm of the glottis; and even when diluted with air, it excites cough when inspired, and causes a peculiar uneasiness about the chest. Water at 60° and 30 Bar. dissolves 33 times its volume, the solution having the peculiar odour of the gas, and yielding it unchanged by ebullition. It has considerable bleaching properties; at first it reddens litmus paper, and then slowly bleaches it: but most vegetable colours, as of the rose and violet, are speedily removed by it without being first reddened. The colouring principle is not destroyed, but may be restored by a stronger acid or by an alkali.

Davy proved that sulphurous acid gas contains exactly its own volume of oxy-

gen (Elements, p. 273), and consequently the difference in the weights or sp. gr. of these gases (2·2105 — 1.1025 = 1·108) gives the weight of sulphur combined with oxygen. The sulphur and oxygen are thus found to be in the ratio of 1·108 to 1·1025, or 16·1 to 16.

Liquid sulphurous acid is easily obtained by transmitting the dry pure gas through a glass tube surrounded by a freezing mixture of snow and salt. Its sp. gr. is 1·45; it boils at 14°, and from the rapidity of its evaporation causes intense cold; it conducts electricity (Kemp). When exposed to cold in the moist state, a crystalline solid is formed, which contains 20 per cent. of water, and probably consists of one eq. of the acid to 14 eq. of water.

Though sulphurous acid cannot be made to burn by the approach of flame, it has a very strong attraction for oxygen, uniting with it under favourable circumstances, and forming sulphuric acid. The presence of moisture is essential to this change. A mixture of sulphurous acid and oxygen gases, if quite dry, may be preserved over mercury for any length of time without chemical action; but if a little water be admitted, the sulphurous acid gradually unites with oxygen, and sulphuric acid is generated. Many of the chemical properties of sulphurous acid are owing to its affinity for oxygen. The solutions of metals which have a weak affinity for oxygen, such as gold, platinum, and mercury, are completely decomposed by it, those substances being precipitated in the metallic form. Nitric acid converts it instantly into sulphuric acid by yielding some of its oxygen. Peroxide of manganese causes a similar change, and is itself converted into protoxide of manganese, which unites with the resulting sulphuric acid.

Sulphurous acid gas may be passed through red-hot tubes without decomposition. Several substances which have a strong affinity for oxygen, such as hydrogen, carbon, and potassium, decompose it at the temperature of ignition.

Sulphurous acid combines with metallic oxides, and forms salts which are called *sulphites*, which are decomposed by sulphuric acid, and then emit the characteristic odour of sulphurous acid.

Its eq. is 32·1; *eq. vol.* = 100; *symb.* S + 2O, SO_2, or $\ddot{S}$.

SULPHURIC ACID.

Hist. and Prep.—Sulphuric acid, or *oil of vitriol* as it is often called, was discovered by Basil Valentine towards the close of the 15th century. It is procured for the purposes of commerce by two methods. One of these has been long pursued in the manufactory at Nordhausen in Germany, and consists in decomposing sulphate of oxide of iron (green vitriol) by heat. This salt contains 6 eq. of water of crystallization; and when strongly dried by the fire, it crumbles down into a white powder, which, according to Thomson, contains 1 eq. of water. On exposing this dried protosulphate to a red heat, its acid is wholly expelled, the greater part passing over unchanged into the receiver, in combination with the water of the salt. Part of the acid, however, is resolved by the strong heat employed in the distillation into sulphurous acid and oxygen. The former escapes as gas throughout the whole process; the latter only in the middle and latter stages, since, in the beginning of the distillation, it unites with the protoxide of iron. Peroxide of iron is the sole residue.

The acid, as procured by this process, is a dense, oily liquid of a brownish tint. It emits copious white vapours on exposure to the air, and is hence called *fuming sulphuric acid*. Its sp. gr. is 1·896 or 1·90. According to Thomson it

consists of 80 parts or 2 eq. of anhydrous acid, and 9 parts or 1 eq. of water. On putting this acid into a glass retort, to which a receiver surrounded by snow is securely adapted, and heating it gently, a transparent colourless vapour passes over, which condenses into a white crystalline solid. This substance is pure anhydrous sulphuric acid. It is tough and elastic; liquefies at 66° and boils at a temperature between 104° and 122°, forming, if no moisture is present, a transparent vapour. Exposed to the air, it unites with watery vapour, and flies off in the form of dense white fumes. [It has so strong an affinity for water that when dropped into that liquid it hisses like a hot iron, from the violence of the combination. It has no acid action on litmus or vegetable blues, unless moisture is present. When intensely heated it is resolved into sulphurous acid and oxygen.] The residue of the distillation is no longer fuming, and is in every respect similar to the common acid of commerce.

The other process for forming sulphuric acid, which is practised in Britain and in most parts of the Continent, is by burning sulphur previously mixed with one-eighth of its weight of nitrate of potassa. The mixture is burned in a furnace so contrived that the current of air, which supports the combustion, conducts the gaseous products into a large leaden chamber, the bottom of which is covered to the depth of several inches with water. The nitric acid yields oxygen to a portion of sulphur, and converts it into sulphuric acid, which combines with the potassa of the nitre; while the greater part of the sulphur forms sulphurous acid by uniting with the oxygen of the air. The nitric acid, in losing oxygen, is converted, partly perhaps into nitrous acid, but chiefly into binoxide of nitrogen, which, by mixing with air at the moment of its separation, gives rise to the red nitrous acid vapours. The gaseous substances, present in the leaden chamber, are therefore sulphurous and nitrous acids, atmospheric air, and watery vapour. The explanation of the mode in which these substances react on each other, so as to form sulphuric acid, was suggested by the experiments of Clément and Désormes (An. de Ch. lix.), and Davy (Elements, p. 276). When dry sulphurous acid gas and nitrous acid vapour are mixed together in a glass vessel quite free from moisture, no change ensues; but if a few drops of water be added, in order to fill the space with aqueous vapour, the white crystalline compound, described at page 179, is immediately produced. Clément and Désormes believed it to consist of sulphuric acid, binoxide of nitrogen, and water; and Davy, of sulphurous acid, nitrous acid, and water. But the observation that the same compound may be made with sulphuric and anhydrous nitrous acids, and that when decomposed by water both nitrous acid and binoxide of nitrogen are disengaged, led Gay-Lussac to the opinion which now seems to be fully substantiated by experiment. A consistent account may, therefore, be given of what really takes place within the leaden chambers.—The mutual reaction of humidity, sulphurous acid, and nitrous acid, gives rise to the crystalline compound of sulphuric acid, hyponitrous acid, and water; and when this solid falls into the water of the chamber, it is instantly decomposed, sulphuric acid is dissolved, and nitrous acid and binoxide of nitrogen escape with effervescence. The nitrous acid thus set free, as well as that reproduced by the binoxide uniting with the oxygen of the atmosphere, is again intermixed with sulphurous acid and humidity, and thus gives rise to a second portion of the crystalline solid, which undergoes the same change as the first. A certain portion of nitric acid is usually formed by the action of water on the nitrous acid; but the presence of sulphuric acid in that water tends to prevent the free decomposition of nitrous

acid which pure water produces. Nay, when the water becomes pretty strongly acid, the nitric acid at first generated is reduced, by absorbed sulphurous acid, into the hyponitrous, which unites with sulphuric acid, and remains even after concentration: it is the cause of the evolution of binoxide of nitrogen which usually ensues when common oil of vitriol is diluted, the hyponitrous acid being then decomposed by the water (Dana). When the water of the chamber is sufficiently charged with acid, it is drawn off, and concentrated by evaporation. It hence appears that the oxygen, by which the sulphurous is converted into sulphuric acid, is in reality supplied by the air; that the combination is effected, not directly, but through the medium of nitrous acid; and that a small quantity of nitrous acid is sufficient for the production of a large quantity of sulphuric acid. The decomposition of the crystalline solid by water seems owing to the strong affinity of that liquid for sulphuric acid.

[An improvement has recently been made in the chamber process for the manufacture of sulphuric acid, by which a larger product is obtained than by the old mode of burning a mixture of sulphur and nitrate of potassa. The method generally adopted at present is that of passing sulphurous acid and nitric acid vapours along with steam, simultaneously into the leaden chamber. The sulphurous acid is formed by the combustion of sulphur, in a properly constructed furnace, on the floor of which there is a tripod supporting an iron capsule containing the materials for nitric acid, viz: oil of vitriol and nitrate of potassa. The heat from the combustion of the sulphur, evolves the nitric acid vapours, which together with the sulphurous acid are carried by a tube into the chamber, where these acid vapours meet with the steam from a small steam boiler, which is admitted near the same point. According to the foregoing theory the changes in the chamber are to be looked upon as the same, for the nitric acid vapour is equivalent to nitric oxide or nitrous acid, as the immediate effect of the sulphurous acid is to reduce the nitric acid to a lower degree of oxidation.]

[In a recent memoir by M. Peligot, it is shown that the conversion of the sulphurous acid into sulphuric is the consequence of a decomposition of nitric acid, and that the action of the white crystalline compound above referred to, has no concern in the chamber process when in *regular* operation. This compound is then not formed. The process is conceived to be as follows:—The sulphurous acid is oxidized directly at the expense of the nitric acid which thus becomes nitrous acid; water, however, decomposes the latter into nitric and hyponitrous acids; the latter is again decomposed by contact with a large quantity of water into nitric acid and nitric oxide, which, in the presence of atmospheric air, yields nitrous acid; which is again resolved into nitric and hyponitrous acids, &c.

The nature of these successive reactions is clearly expressed by the following equations:

$$\begin{aligned} NO_5, Aq. + SO_2 &= SO_3, Aq. + NO_4 \\ 2NO_4 + Aq. &= NO_3 + NO_5 \\ 3NO_3 + Aq. &= 2NO_2 + NO_5 \\ NO_2 + 2O &= NO_4, \&c. \end{aligned}$$

The nitric acid is thus constantly regenerated, and the sulphurous acid acts upon this exclusively, and in a peculiar manner to deprive it of one equivalent of oxygen. (Ann. de Chim. et de Phys. lxi. p. 263.)]

Besides hyponitrous acid, as above stated, it contains potassa, and the oxide

of lead and sometimes iron, the first derived from the nitre employed in making it, and the two latter from the leaden chamber. To separate them, the acid should be distilled from a glass or platinum retort: the former may be safely used by putting into it some fragments of platinum leaf, which cause the acid to boil freely on applying heat, without danger of breaking the vessel. Arsenious acid, derived from arsenic in the sulphur used in the manufacture, has been lately detected in most of the oil of vitriol made in Germany; and from that source arsenic is introduced into preparations for which such acid is employed, as into phosphorus and hydrochloric acid. The arsenic is discovered by diluting with water and transmitting through the solution hydrosulphuric acid gas, which causes orpiment to be formed. The oil of vitriol may be purified from arsenious acid by adding a little hydrated peroxide of iron before distilling.

Prop.—As obtained by the second process, pure sulphuric acid is a dense, colourless, oily fluid, which boils at 620° F., and has a sp. gr. in its most concentrated form, of 1·847 or a little higher, never exceeding 1·850. [It consists of 40 parts or 1 eq. anhydrous acid and 9 parts or 1 eq. water, (HO, SO_3.)] Mitscherlich found the density of its vapour to be 3. It is one of the strongest acids with which chemists are acquainted, and when undiluted is powerfully corrosive. It decomposes all animal and vegetable substances by the aid of heat, causing deposition of charcoal and formation of water. It has a strong sour taste, and reddens litmus paper, even though greatly diluted. It unites with alkaline substances, and separates all other acids more or less completely from their combinations with the alkalies.

In a very concentrated state it dissolves small quantities of sulphur, and acquires a blue, green, or brown tint. Tellurium and selenium are also sparingly dissolved, the former causing a crimson, and the latter a green colour. By dilution with water, these substances subside unchanged; but if heat is applied, they are oxidized at the expense of the acid, and sulphurous acid gas is disengaged. Charcoal also appears soluble to a small extent in sulphuric acid, communicating at first a pink, and then a dark reddish brown tint.

It has a very great affinity for water, and the combination takes place with production of intense heat. When four parts by weight of the acid are suddenly mixed with one of water, the temperature of the mixture rises, according to Ure, to 300°. By its attraction for water it causes the sudden liquefaction of snow; and if mixed with it in due proportion (p. 40), intense cold is generated. It absorbs watery vapour with avidity from the air, and on this account is employed in the process for freezing water by its own evaporation. Its action in destroying the texture of the skin, and in decomposing animal and vegetable substances in general, seems dependent on its affinity for water.

To ascertain the quantity of real acid present in liquid acid of different strengths, dilute a known weight of the acid moderately with water, and, while warm, add pure anhydrous carbonate of soda, until the solution is exactly neutral. Every 53·3 parts of carbonate of soda, required to produce this effect, correspond to 40·1 parts of real sulphuric acid. If minute precision is not desired, the strength of the acid may be estimated by its sp. gr. according to the table of Ure inserted in the Appendix.

Sulphuric acid of commerce freezes at — 15°, yielding, often, six sided tabular crystals. Diluted with water so as to have a sp. gr. of 1·78, it congeals even above 32°, and remains in the solid state, according to Keir, till the temperature rises to 45°. [This is a second hydrate, containing 2 eq. of water and 1 eq. of

acid. The dilute acid when evaporated at a temperature not above 400°, loses water and is reduced to the same hydrate. At a higher heat, this second eq. of water is expelled; but the first can only be removed by the substitution of a stronger base. A third hydrate is believed to be formed, having the sp. gr. of 1·63, containing 3 equivalents of water, when a dilute acid is evaporated in vacuo at the temperature of 212°.—Including the Nordhausen acid, there are then four definite hydrates of sulphuric acid, represented by the following formulæ:—

Nordhausen acid,	$HO, 2\,SO^3$
Oil of Vitriol, (sp. gr. 1·850)	HO, SO_3
Acid of sp. gr. 1·78,	$HO, SO_3 + HO$
Acid of sp. gr. 1·63	$HO, SO_3 + 2\,HO$

When mixed with rather more than its weight of water, its freezing point is lowered to — 36°.

The composition of sulphuric acid as before given is founded on the observation of Gay-Lussac, that when the vapour of sulphuric acid is passed through a small porcelain tube heated to redness, it is resolved into two measures of sulphurous acid gas and one of oxygen. Berzelius has confirmed this conclusion by directly converting a known weight of sulphur into sulphuric acid.

Chemists possess an unerring test of the presence of sulphuric acid. If a solution of chloride of barium is added to a liquid containing sulphuric acid, it causes a white precipitate, sulphate of baryta, which is characterized by its insolubility in acids and alkalies.

Sulphuric acid does not occur free in nature, except occasionally in the neighbourhood of volcanoes. In combination, particularly with lime and baryta, it is very abundant.

Hydrosulphurous Acid.—It may be formed either by digesting sulphur in a solution of any sulphite, or by transmitting a current of sulphurous acid into a solution of sulphuret of calcium or strontium. In the former case, the sulphurous acid takes up an additional quantity of sulphur, and a salt of hyposulphurous acid is obtained; and in the latter, the sulphurous acid gives part of its oxygen to the metal, and its remaining oxygen unites with sulphur. Three equivalents of sulphurous acid and two of sulphuret of calcium contain the elements for forming two eq. of hyposulphite of lime, one eq. of sulphur being deposited. A convenient solution for this purpose is made by boiling 3 parts of slaked lime and one of sulphur with 20 parts of water for one hour, and decanting the clear liquid from the undissolved portions; but when this solution is used, the deposite of sulphur is abundant. Herschel states that hydrosulphurous acid may be formed by the action of sulphurous acid on iron filings; but the nature of the change is not well understood.

The salts of hyposulphurous acid were first described by Gay-Lussac (An. de Ch. lxxxv.) under the name of *Sulphuretted Sulphites*. Thomson in his System of Chemistry suggested that the acid of these salts might be regarded as a compound of one equivalent of sulphur and one of oxygen, and proposed for it the name of *hyposulphurous* acid; and the subsequent researches of Herschel (Phil. Journal, i. 8 and 396) accorded so entirely with this opinion, that it was universally adopted. But it appears from the experiments of Rose, that though the ratio of its elements is as 16 to 8, the equivalent of the acid, or the quantity required to neutralize one eq. of an alkali, is not 24, but 48; and hence that its

smallest molecule must be formed of 2 atoms of sulphur united with 2 atoms of oxygen (Pog. Ann. xxi. 431.)

Prop.—It cannot exist permanently in a free state. On decomposing a hyposulphite by any stronger acid, such as the sulphuric or hydrochloric, the hyposulphurous acid, at the moment of quitting the base, resolves itself into sulphurous acid and sulphur. Herschel succeeded in obtaining free hyposulphurous acid, by adding a slight excess of sulphuric acid to a dilute solution of hyposulphite of strontia; but its decomposition very soon took place, even at common temperatures, and was instantly effected by heat. Most of the hyposulphites are soluble in water, and have a bitter taste. The solution precipitates the nitrates of the oxides of silver and mercury black, as sulphuret of the metals; and salts of baryta and oxide of lead are thrown down as white insoluble hyposulphites of those bases. That of baryta is soluble without decomposition in water acidulated with hydrochloric acid. The solution of all the neutral hyposulphites has the peculiar property of dissolving recently precipitated chloride of silver in large quantity, and forming with it a liquid of an exceedingly sweet taste. *Its eq. is* 48·2; *sym.* 2S + 2O or $S_2 O_2$.

Hyposulphuric acid.—It was discovered in 1819 by Welter and Gay-Lussac (An. de Ch. et Ph. x.), and is formed by transmitting a current of sulphurous acid gas through water containing peroxide of manganese in fine powder; when by a new arrangement of their elements,

2 eq. Sulp. acid and 1 eq. Perox. Mang. yield 1 eq. Protox. Mang. & 1 eq. Hyposulp. acid,
$2SO_2$ MnO_2 MnO S_2O_5

hyposulphate of protoxide of manganese remaining in solution. During the action heat is freely evolved, and in consequence sulphuric acid is also generated; but if the peroxide of manganese be pure and the materials kept cool, the formation of sulphuric acid is almost completely prevented. To the liquid, after filtration, a solution of pure baryta or sulphuret of barium in slight excess is added, whereby the manganese is thrown down as an oxide or sulphuret, sulphuric acid as sulphate of baryta, and a solution of hyposulphate of baryta is obtained: the excess of baryta is got rid of by a free current of carbonic acid gas, and then heating the solution. The hyposulphate of baryta crystallizes by evaporation, and on decomposing a solution of that salt by a quantity of sulphuric acid exactly sufficient for precipitating the baryta, the hyposulphuric acid is left in solution.

Prop.—Taste sour; distinct acid reaction; neutralizes alkalies; inodorous, and thus distinguished from sulphurous acid; forms soluble salts with baryta, strontia, lime, and oxide of lead, by which it is distinguished from sulphuric acid. It cannot be obtained free from water. Its solution, if confined with a vessel of sulphuric acid under the exhausted receiver of an air-pump, may be concentrated till it has a density of 1·347; but if an attempt is made to condense it still further, the acid is decomposed, sulphurous acid gas escapes, and sulphuric acid remains in solution. A similar change is still more readily produced if the evaporation is conducted by heat.

Welter and Gay-Lussac analyzed hyposulphuric acid by exposing neutral hyposulphate of baryta to heat. At a temperature a little above 212° this salt suffers complete decomposition; sulphurous acid gas is disengaged, and neutral sulphate of baryta is obtained. It was thus ascertained that 72 grains of hyposulphuric acid yield 32 grains of sulphurous, and 40 of sulphuric acid; from which

it is inferred that hyposulphuric acid is composed either of an equivalent of each of those acids combined with each other, or of 2 eq. of sulphur and 5 of oxygen. *Its eq. is* 72·2; *sym.* 2S + 5O or $S_2 O_5$.

[*Sulphuretted Hyposulphuric Acid.*—A salt containing this new acid was accidentally discovered by M. Langlois in the preparation of hyposulphite of potassa. It is prepared by digesting the bisulphate of potassa along with sulphur and water without boiling. The salt thus formed crystallizes easily, and is resolved by heat into sulphurous acid, sulphur and sulphate of potassa. Perchloric acid removes the potassa, and the new acid is thereby isolated. The acid solution slowly decomposes, and when heated yields sulphurous acid, sulphur and sulphuric acid; $S_3 O_5 = SO_2$; S and SO_3.—*Its eq. is* 88·3; *sym.* $S_3 O_5$. (Ann. Chim. de Phys. 3, sec. iv. p. 77.)]

[*Bisulphuretted Hyposulphuric Acid.*—Discovered by M. Fordos and Gellis. When iodine is dissolved in a solution of the hyposulphite of baryta, the clear solution which is obtained is found to contain both iodide of barium, and the baryta salt of this new acid. The former is dissolved by alcohol, and the latter is left pure. The baryta is removed by the cautious addition of dilute sulphuric acid, and the new acid is obtained dissolved in water. It resembles the two preceding acids in being exceedingly prone to change, and like the last, is resolved by heat into the same substances, but the quantity of sulphur separated is exactly twice as great; $S_4 O_5 = SO_2$, S_2 & SO_3.—*Its eq. is* 104·4; *sym.* $SO_4 O_5$. (Ann. Chim. de Phys. iv. p. 454.)]

SECTION VIII.

PHOSPHORUS.

Hist. and Prep.—Phosphorus (φωσφόρος, from φῶς *light* and φέρειν *to carry*), so called from its property of shining in the dark, was discovered about the year 1669 by Brandt, an alchemist of Hamburgh. It was originally prepared from urine; but Scheele, after Gahn's discovery of bones containing phosphate of lime, extracted it from that source. The bones are first ignited in an open fire till they become white, so as to destroy their animal matter, and burn away the charcoal derived from it, in which state they contain nearly 4-5ths of phosphate of lime. They are then reduced to a fine powder, and digested for a day or two with half their weight of strong sulphuric acid, with the addition of so much water as will give the consistence of a thin paste. Decomposition of the phosphate of lime is thus effected, and two new salts formed, the sparingly soluble sulphate and a soluble superphosphate of lime. The latter is dissolved in warm water, and the solution, after being separated by filtration from the sulphate of lime, is evaporated to the consistence of syrup, mixed with a fourth of its weight of powdered charcoal, and strongly heated in an earthen retort well luted with clay. The beak of the retort is put into water, in which the phosphorus, as its vapour

passes over, is condensed. When first obtained it is usually of a reddish brown colour, owing to the presence of phosphuret of carbon formed during the process. It may be purified by fusion in hot water, and being pressed while liquid through chamois leather, or by a second distillation.

In this process the oxygen of that part of the phosphoric acid which constitutes superphosphate, unites with charcoal, giving rise to carbonic acid and carbonic oxide gases; and phosphate of lime in the state of bone earth, together with redundant charcoal, remains in the retort. The lime acts an important part in fixing the phosphoric acid, which if not so combined would distil over before the heat was high enough for its decomposition. In extracting phosphorus from urine, the phosphoric acid should be thrown down by acetate of the oxide of lead, and the insoluble salt converted by the action of sulphuric acid into the superphosphate, which is decomposed by charcoal as in the former process.

Prop.—When pure, transparent, and almost colourless. At common temperatures it is a soft solid of sp. gr. 1·77; is easily cut with a knife, and the cut surface has a waxy lustre: at 108° it fuses, and at 550° is converted into vapour, which, according to Dumas, has a sp. gr. of 4·355. It is soluble by the aid of heat in naphtha, in fixed and volatile oils, in the chloride of sulphur, sulphuret of carbon, and sulphuret of phosphorus. On its cooling from solution in the latter, Mitscherlich obtained it in regular dodecahedral crystals. By the fusion and slow cooling of a large quantity of phosphorus, M. Frantween has obtained very fine crystals of an octohedral form, and as large as a cherry-stone. Thenard has remarked that when phosphorus is fused at 150°, and suddenly cooled by being plunged into cold water, it appears black; but by fusion and slow cooling it recovers its original aspect.

It is exceedingly inflammable. Exposed to the air at common temperatures, it undergoes slow combustion, emits a white vapour of a peculiar alliaceous odour, appears distinctly luminous in the dark, and is gradually consumed. On this account, phosphorus should always be kept under water. The disappearance of oxygen which accompanies these changes is shown by putting a stick of phosphorus in a jar full of air, inverted over water. The volume of the gas gradually diminishes; and if the temperature of the air is at 60°, the whole of the oxygen will be withdrawn in the course of 12 or 24 hours. The residue is nitrogen gas, containing about 1-40th of its bulk of the vapour of phosphorus. It is remarkable that the slow combustion of phosphorus does not take place in pure oxygen, unless its temperature be about 80°. But if the oxygen be diluted with nitrogen, hydrogen, or carbonic acid gases, the oxidation occurs at 60°; and it takes place at temperatures still lower in a vessel of pure oxygen, rarefied by diminished pressure. Mr. Graham finds that the presence of certain gaseous substances, even in minute quantity, has a remarkable effect in preventing the slow combustion of phosphorus: thus at 66° it is entirely prevented by the presence, (Quart. Jour. of Science, N. S. vi. 83.)

	Volumes of air.
of 1 volume of olefiant gas in - - -	450
1 ditto of vapour of sulphuric ether in -	150
1 ditto of vapour of naphtha in - -	1820
1 ditto of vapour of oil of turpentine in -	4444

and by an equally slight impregnation of the vapour of the other essential oils.

Their influence is not confined to low temperatures. Phosphorus becomes faintly luminous in the dark, in mixtures of

1	volume of air	and	1	volume	of olefiant gas at	200° F.
1	- -	and	1	ditto	of vapour of ether at	215°
111	- -	and	1	ditto	of vapour of naphtha at	170°
156	- -	and	1	ditto	of vapour of turpentine at	186°

It may be sublimed at its boiling temperature, in air containing a considerable proportion of the vapour of oil of turpentine, without diminishing the quantity of oxygen present, provided the heat be gradually and uniformly applied. Mr. Graham has also remarked, that the oxidation of phosphorus in the air is promoted by the presence of hydrochloric acid gas.

A very slight degree of heat is sufficient to inflame phosphorus in the open air. Gentle pressure between the fingers, friction, or a temperature not much above its point of fusion, kindles it readily. It burns rapidly even in the air, emitting a splendid white light, and causing intense heat. Its combustion is far more rapid in oxygen gas, and the light proportionally more vivid.

When phosphorus is kept for a long time under water, especially if exposed to light, its surface acquires a thin coating of white matter, which some have described as an oxide, and others as a hydrate of phosphorus. It seems, according to Rose, to be neither an oxide nor a hydrate, but phosphorus in a peculiar mechanical state, which deprives it of its usual action upon light, and renders it opaque. (Pog. Annalen, xxvii. 565.)

Repeated researches by Berzelius have shown that the oxygen in phosphorus and phosphoric acids is in the ratio of 3 to 5, a result conformable to experiments on the same subject by Dulong, and admitted by most chemists. It is hence inferred that the smallest molecule of phosphoric acid contains 5 atoms of oxygen. Also Berzelius finds that 31·4 parts of phosphorus require 40 of oxygen for forming phosphoric acid: if this acid consist of one atom of phosphorus and five atoms of oxygen, 31·4 will represent one atom of phosphorus; or if the acid contain two atoms to five, the atom of phosphorus will be half 31·4 or 15.7. It is doubtful which view is preferable, and I therefore continue to use the latter.

Its equivalent is therefore 15·7; eq. vol. = 25; symb. P.

The compounds of phosphorus described in this section are the following:—

	Phosp.		Oxy.	Equiv.	Formulæ.
Oxide of Phosphorus	47·1 or 3 eq.	+	8 or 1 eq.	= 55·1	3P + O or P_3O
Hypophosphorous acid	31·4 or 2 eq.	+	8 or 1 eq.	= 39·4	2P + O or P_2O
Phosphorous acid	31·4 o 2 eq.	+	24 or 3 eq.	= 55·4	2P + 3O or P_2O_3
Phosphoric acid Pyrophosphoric acid Metaphosphoric acid	31·4 or 2 eq.	+	40 or 5 eq.	= 71·4	2P + 5O or P_2O_5

COMPOUNDS OF OXYGEN AND PHOSPHORUS.

Oxide.—When a jet of oxygen gas is thrown upon phosphorus while in fusion under hot water, combustion ensues, phosphoric acid is formed, and a number of red particles collect, which have been examined by M. Pelouze, who has shown them to be an oxide of phosphorus. The red matter left when phosphorus is burned, is probably of the same nature.

This, the only known oxide of phosphorus, is of a red colour, without taste or odour, and is insoluble in water, ether, alcohol, and oil. It is permanent in the

air, even at 662° F., but takes fire at a low red heat. Heated to redness in a tube, phosphorus is expelled, and metaphosphoric acid remains. It takes fire in chlorine gas, and is rapidly oxidized by nitric acid. It does not appear to possess any alkaline character. (An. de Ch. et Ph. l. 83.) Its equivalent is 55·1; symb. $3P + O$, or P_3O.

Hypophosphorous Acid.—This acid was discovered in 1816 by Dulong. (An. de Ch. et Ph. ii.) When water acts upon the phosphuret of barium the elements of both enter into a new arrangement, giving rise to phosphuretted hydrogen, phosphoric acid, hypophosphorous acid, and baryta. The former escapes in the form of gas, and the two latter combine with the baryta. Hypophosphite of baryta, being soluble, dissolves in the water, and may consequently be separated by filtration from the phosphate of baryta, which is insoluble. On adding a sufficient quantity of sulphuric acid for precipitating the baryta, hypophosphorous acid is obtained in a free state, and on evaporating the solution, a viscid liquid remains, highly acid and even crystallizable, which is a *hydrate of hypophosphorous acid.* When exposed to heat in close vessels, it undergoes the same kind of change as hydrated phosphorous acid.

Prop.—It is a powerful deoxidizing agent. It unites with alkaline bases; and it is remarkable that all its salts are soluble in water. The hypophosphites of potassa, soda, and ammonia, dissolve in every proportion in rectified alcohol; and hypophosphite of potassa is even more deliquescent than chloride of calcium. They are all decomposed by heat, and yield the same products as the acid itself. They are conveniently prepared by precipitating hypophosphite of baryta, strontia, or lime, with the alkaline carbonates; or by directly neutralizing these carbonates with hypophosphorous acid. The hypophosphite of baryta, strontia, and lime, are formed by boiling these earths in the caustic state in water together with fragments of phosphorus. The same change occurs as during the action of water on phosphuret of barium. The composition of this acid, as stated at page 203, is on the authority of Rose. (Poggen. Annalen, ix. 367.) Its eq. is 39·4; symb. $2P + O$, $\dot{P}$, or P_2O.

Phosphorous Acid.—Prep.—When phosphorus is burned in air highly rarefied, imperfect oxidation ensues, and metaphosphoric and phosphorous acids are generated, the latter being obtained in the form of a white volatile powder. It may be procured more conveniently by subliming phosphorus through powdered bichloride of mercury contained in a glass tube; when a limpid liquid comes over, which is a compound of chlorine and phosphorus. (Davy's Elements, p. 288.) This substance and water mutually decompose each other: the hydrogen of water unites with the chlorine, and forms hydrochloric acid; while the oxygen attaches itself to the phosphorus, and thus phosphorous acid is produced. The solution is then evaporated to the consistence of syrup to expel the hydrochloric acid; and the residue, which is hydrate of phosphorous acid, becomes a crystalline solid on cooling. It is also generated during the slow oxidation of phosphorus in atmospheric air. The product attracts moisture from the air, and forms an oil-like liquid. Dulong thinks that a distinct acid is produced in this case, which he calls *phosphatic acid;* but the opinion of Davy, that it is merely a mixture of phosphoric and phosphorous acids, is, in my opinion, perfectly correct.

Prop.—When obtained by the first process, it is anhydrous. Heated in the open air, it takes fire and forms metaphosphoric acid; but in close vessels it is resolved into metaphosphoric acid and phosphorus. The action of the hydrate

under the latter circumstances is different, owing to the reaction of the elements of the water and acid, by which metaphosphoric acid and a gaseous compound of phosphorus and hydrogen are produced. The nature of this gas will be more particularly noticed in the section on phosphureted hydrogen. It dissolves readily in water, has a sour taste, and smells somewhat like garlic. It unites with alkalies, and forms salts which are termed *phosphites*. The solution of phosphorous acid absorbs oxygen slowly from air, and is converted into phosphoric acid. From its tendency to unite with an additional quantity of oxygen, it is a powerful deoxidizing agent; and hence, like sulphurous acid, precipitates mercury, silver, platinum, and gold, from their saline combinations in the metallic form. Nitric acid converts it into phosphoric acid.

Its eq. is 55·4; *symb.* 2P + 3O, $\dddot{\underline{P}}$, or P_2O_3.

Phosphoric Acid.—Hist.—It was shown in the year 1827 by Dr. Clark, now Professor of Chemistry in Aberdeen, that under the term *phosphoric acid* had previously been confounded two distinct acids, one of which he proposed to distinguish by the name *pyrophosphoric acid* (from πυρ *fire*), to indicate that it is phosphoric acid modified by heat; and very lately Mr. Graham has described another modification of phosphoric acid, to which he has given the provisional name of metaphosphoric (from μετα *together with*), implying phosphoric acid and something besides; but this name is rather unfortunate, since it is applied to the only one of the three modifications which can be obtained free from water. Perhaps paraphosphoric (from παρα *near to*) would be more appropriate. These three acids contain phosphorus and oxygen in the same ratio, and have the same equivalent, so that they may be considered as isomeric bodies (page 150); but that difference in the arrangement of their elements on which their peculiarities may be presumed to depend is very slight, since they are easily convertible into each other. Mr. Graham, indeed, supposes the difference to arise solely from a disposition to unite in different proportions with water and alkaline bases; but this view scarcely suffices as an explanation, because it does not account for the peculiar *disposition* which causes their distinctive characters. (Phil. Trans. 1833, Part. ii., and Phil. Mag. 3rd Series, iv. 401.)

Prep.—Phosphoric acid has hitherto been obtained only in combination with water or some alkaline base. One of the best modes for procuring it, is to oxidize phosphorus by strong nitric acid; but in this process care is necessary, as the action is sometimes very violent, and the escape of binoxide of nitrogen gas ungovernably rapid. It is safely conducted by adding fragments of phosphorus, or the so-called phosphatic acid, to strong nitric acid contained in a platinum crucible partially closed by its cover. Gentle heat is applied so as to commence, and, when necessary, to maintain moderate effervescence; and when one portion of phosphorus disappears, another is added, till the whole of the nitric acid is exhausted. The solution is then evaporated to dryness, and exposed to a red heat to expel the last traces of nitric acid. This should always be done in vessels of platinum, since phosphoric acid acts chemically upon those of glass or porcelain, and is thereby rendered impure. In this case, as in some other instances of the oxidation of combustibles by nitric acid, water is decomposed; and while its oxygen unites with phosphorus, its hydrogen combines with nitrogen of the nitric acid. A portion of ammonia, thus generated, is expelled by heat in the last part of the process.

Phosphoric acid may be prepared at a much cheaper rate from bones. For this

purpose, superphosphate of lime, obtained in the way already described, should be boiled for a few minutes with excess of carbonate of ammonia. The lime is thus precipitated as a phosphate, and the solution contains phosphate, together with a little sulphate, of ammonia. The liquid, after filtration, is evaporated to dryness, and then ignited in a platinum crucible, by which means the ammonia and sulphuric acid are expelled.

In both the foregoing processes phosphoric acid exists only in solution; for on heating to redness, in order to expel ammonia in the one case, and nitric acid in the other, metaphosphoric acid is generated. To reproduce the phosphoric acid, the residue in the crucible requires to be dissolved in water and boiled for a few minutes.

Prop.—Phosphoric acid is colourless, intensely sour to the raste, reddens litmus strongly, and neutralizes alkalies; but it does not destroy the texture of the skin, like sulphuric and nitric acids. Its solution may be evaporated at a temperature of 300° without decomposition, and when thus concentrated it assumes a dark colour, is as thick as treacle when cold, and consists of 71·4 parts or 1 eq. of phosphoric acid and 27 parts or 3 eq. of water. Mr. Graham obtained this hydrate in thin crystalline plates, which were extremely deliquescent, by keeping it for seven days *in vacuo* along with sulphuric acid. On heating this hydrate for several days to 415°, it lost nearly two-thirds of an equivalent of water, and then principally consisted of pyrophosphoric acid with two equivalents of water. At a still higher temperature metaphosphoric acid began to be formed: and at a red heat the conversion was complete. But after ignition it still contains water, amounting, according to Rose, to 9·44 per cent., which is more than an equivalent of water to one of metaphosphoric acid.

Phosphoric acid is remarkable for its tendency to unite with alkaline bases, in such proportions that the oxygen of the base and of the acid is as 3 to 5; or, in other words, it is prone to form subsalts, in which one equivalent of acid is combined with three equivalents of base. It manifests the same character in regard to water, and ceases to be phosphoric acid unless three equivalents of water to one of acid are present: it even appears that the water acts the part of a base, hence called *basic* water, and that the aqueous solution is not a mere solution of phosphoric acid, but of triphosphate of water, a sort of salt composed of one equivalent of acid and three equivalents of water. Part of this basic water enters along with soda into the constitution of two of the phosphates of soda, the water and soda together forming the three equivalents of base required by one equivalent of the acid. This point will be more fully described in the history of the phosphates.

When phosphoric acid is neutralized by ammonia and mixed with nitrate of oxide of silver, the yellow phosphate of that oxide subsides; a character by which it is distinguished from pyrophosphoric and metaphosphoric acids, as well as from all other acids except the arsenious. A certain test between phosphoric and arsenious acids is, that the former is neither changed in colour nor precipitated when a stream of sulphuretted hydrogen gas is transmitted through it; while the latter, with the required precautions, first acquires a yellow tint, and then yields a yellow precipitate.

Its eq. is 71·4; *symb.* $2P + 5O$, $\dot{\underline{P}}$, or P_2O_5: but as it cannot exist uncombined, it is best denoted by $X_3P_2O_5$, where X represents an equivalent of water or any base.

Pyrophosphoric Acid.—This acid is formed by exposing concentrated phosphoric acid for some time to a heat of 415°. Its general characters resemble phosphoric acid; but when neutralized by ammonia and mixed with nitrate of oxide of silver it yields a snow-white granular precipitate, pyrophosphate of that oxide, by which it is distinguished from phosphoric and metaphosphoric acids. In solution with cold water pyrophosphoric acid passes gradually, and at a boiling temperature rapidly, into phosphoric acid. Its salts, while neutral, are very permanent; but when boiled with either of the stronger acids in water, they are quickly converted more or less completely into phosphates.

Pyrophosphoric acid is remarkable for its tendency to unite with two equivalents of a base. Its aqueous solution probably contains a dipyrophosphate of water, that is, 1 eq. of the acid with 2 eq. of water, expressed by $2HO + P_2O_5$, or $2HO.\ P_2O_5$. This basic water is readily displaced by 2 eq. of stronger bases, such as soda; or if 1 eq. only of soda be added, then the soda and water together make up the two eq. of base, the formula of the salt being $NaO,\ HO.\ P_2O_5$. The readiest mode of obtaining a pyrophosphate is to heat phosphoric with any fixed base in the ratio of one to two of their equivalents. This was done by Dr. Clark in the experiments by which he established the existence of pyrophosphoric acid. (Brewster's Journal, vii. 298.) Phosphate of soda is a compound of 1 eq. phosphoric acid, 2 eq. soda, 1 eq. basic water, and 24 eq. water of crystallization, its formula being $2NaO,\ HO.\ P_2O_5 + 24HO$: on drying this salt its water of crystallization is expelled, there remains $2NaO,\ HO.\ P_2O_5$, which is still a phosphate, but on heating to redness the basic water is expelled, and $2Na.\ P_2O_5$, pyrophosphate of soda, remains. By being forced to unite with 2 eq. of base, the acid acquires a disposition to do so on all occasions.

Its eq. is 71·4: symb. $X_2.\ P_2O_5$, X being used as above.

Metaphosphoric Acid.—This acid is obtained by burning phosphorus in dry air or oxygen gas, or heating to redness a concentrated solution of phosphoric or pyrophosphoric acids. By the former method the acid is a white solid, and anhydrous; in the latter it is a hydrate, or probably a metaphosphate of water, composed of 1 eq. acid and 1 eq. of water, its formula being $HO.\ P_2O_5$. The water in this compound cannot be expelled by fire, since on attempting to do so by a violent heat, the whole is sublimed. In an open crucible it volatilizes at a temperature by no means high.

The peculiarity of this acid is to combine with one equivalent of a base. On exposing the anhydrous acid to the air it rapidly deliquesces, and at the same time acquires its basic water, which can only be replaced by an equivalent quantity of soda or some other alkaline base. The water is also driven off by fusion with siliceous or aluminous substances with which the acid unites and forms very fusible compounds. The pure hydrated acid is of itself very fusible, and on cooling concretes into a transparent brittle solid, being known under the name of *glacial phosphoric acid*, which is highly deliquescent, and can hence only be preserved in its glassy state in bottles carefully closed.

The metaphosphoric resembles pyrophosphoric acid in the facility with which its aqueous solution passes into phosphoric acid. On the contrary, both of the other acids are converted into metaphosphates when heated to redness in contact with no more than one equivalent of certain fixed bases, such as potassa and soda. This acid when free occasions precipitates in solutions of the salts of baryta, and most of the earths and metallic oxides, and forms an insoluble compound with albumen. The metaphosphate of baryta and oxide of silver both fall

in gelatinous flakes of a grey colour. *Its eq. is* 71·4; *symb.* $P_2 O_5$, or X. $P_2 O_5$

In an admirable paper on the constitution of the organic acids, Liebig has shown, that, if we adopt the view first suggested by Davy, and afterwards by Dulong, namely, that the hydrated acids, as well as the hydracids, are all compounds of hydrogen, we can easily understand how the three forms of phosphoric acid differ from each other. On this view, just as hydrochloric acid is H,Cl, hydrated sulphuric acid is H,SO_4. In like manner metaphosphoric acid is H, P_2O_6; pyrophosphoric acid is H_2,P_2O_7, and common phosphoric acid is H_3,P_2O_8. They are thus distinct compounds, as is evident from the differences among their salts. When the hydrogen in them is replaced, equivalent for equivalent, by a metal, a salt is formed; and we thus see how the salts of metaphosphoric acid contain 1 eq. of metal, those of pyrophosphoric acid 2 eq., and those of common phosphoric acid 3 eq. of metal. The first is a monobasic acid, the second a bibasic, and the third a tribasic acid. The memoir of Liebig just referred to (Ann. der Pharm. vol. xxvi.) has placed beyond question the existence of polybasic acids; that is, acids which combine with more than one equivalent of base to form neutral salts. This subject will be more fully discussed hereafter.

SECTION IX.

BORON.

Hist. and Prep.—Sir H. Davy discovered the existence of *Boron* in 1807 by exposing boracic acid to the action of a powerful galvanic battery; but he did not obtain a sufficient supply of it for determining its properties. Gay-Lussac and Thenard* procured it in greater quantity in 1808 by heating boracic acid with potassium. The boracic acid is by this means deprived of its oxygen, and boron is set free. The easiest and most economical method of preparing this substance, according to Berzelius, is to decompose borofluoride of potassium or sodium by means of potassium. (Annals of Philosophy, xxvi. 128.)

Prop.—It is a dark olive-coloured substance, which has neither taste nor smell, and is a non-conductor of electricity. It is insoluble in water, alcohol, ether, and oils. It does not decompose water whether hot or cold. It bears intense heat in close vessels, without fusing or undergoing any other change except a slight increase of density. Its sp. gr. is about twice as great as that of water. It may be exposed to the atmosphere at common temperatures without change; but if heated to 600°, it suddenly takes fire, oxygen gas disappears, and boracic acid is generated. It is very difficult to oxidize all the boron by burning, because the boracic acid fuses at the moment of being formed, and by glazing the surface of the unburned boron protects it from oxidation. It also passes into boracic acid when heated with nitric acid, or with any substance that yields oxygen with facility.

* Recherches Physico-Chimiques, vol. i.

According to the experiments of Davy and Berzelius, boron in burning unites with 68 per cent. of oxygen; and the latter, from the composition of borax, estimates the oxygen in boracic acid at 68·8 per cent. In this, as in some other cases, where a combustible unites with oxygen in one proportion only, it is difficult with any certainty to assign the true atomic constitution of the compound. Boracic acid may be a compound of boron and oxygen in the ratio of 1 atom to 1 atom, in that of 1 to 2 as supposed by Thomson, or of 1 to 3. When dry boracic acid is heated with charcoal in chlorine gas, it is decomposed, and two volumes of chloride of boron and three of carbonic oxide gas are produced. The latter contains $1\frac{1}{2}$ volumes of oxygen, and the former has been proved by Dumas to be composed of 3 volumes of chlorine united with 1 volume of the vapour of boron, the density of which is estimated at ·751, its eq. vol. being 100. From this it may be deduced that the constitution of boracic acid is BO_3, which has also been recently adopted by Berzelius (Pog. An. xxiv. 561.) Hence *its eq.* is 10·9; *eq. vol.* = 100; *symb.* B.

Boracic Acid.—Hist. and Prep.—This is the only known compound of boron and oxygen. As a natural product it is found in the hot springs of Lipari, in those of Sasso in the Florentine territory, and in considerable quantities in the hot volcanic lagoons of Tuscany, whence a large supply is at present obtained. It is a constituent of several minerals, among which the datolite and boracite may in particular be mentioned. It also occurs abundantly under the form of impure borax or tinkal, a native compound of boracic acid and soda. It is prepared for chemical purposes by adding sulphuric acid to a solution of purified borax in about four times its weight of boiling water, till the liquid acquires a distinct acid reaction. The sulphuric acid unites with the soda; and the boracic acid is deposited, when the solution cools, in a confused group of shining scaly crystals. It is then thrown on a filter, washed with cold water to separate the adhering sulphate of soda and sulphuric acid, and still further purified by solution in boiling water and re-crystallization. But even after this treatment it is apt to retain a little sulphuric acid; on this account, when required to be absolutely pure, it should be fused in a platinum crucible, and once more dissolved in hot water and crystallized.

Prop.—In the crystallized state it is a hydrate, which contains 43·62 per cent. of water, being a ratio of 34·9 parts or 1 eq. of the anhydrous acid to 27 parts or 3 eq. of water. Its formula is therefore BO_3+3HO. This hydrate dissolves in 25·7 times its weight of water at 60°, and in three times at 212°. Boiling alcohol dissolves it freely, and the solution, when set on fire, burns with a beautiful green flame; a test which affords the surest indication of the presence of boracic acid. Its sp. gr. is 1·479. It has no odour, and its taste is rather bitter than acid. It reddens litmus paper feebly, and effervesces with alkaline carbonates. Faraday has noticed that it renders turmeric paper brown like the alkalies. From the weakness of the acid properties of boracic acid, all the borates, when in solution, are decomposed by the stronger acids; and the neutral borates of potash and soda are deprived of half their base by carbonic acid, at common temperatures.

When hydrous boracic acid is exposed to a gradually increasing heat in a platinum crucible, its water of crystallization is wholly expelled, and a fused mass remains which bears a white heat without being sublimed. On cooling, it forms a hard, colourless, transparent glass, which is anhydrous boracic acid. If the water of crystallization be driven off by the sudden application of a strong heat,

a large quantity of boracic acid is carried away during the rapid escape of watery vapour. The same happens, though in a less degree, when a solution of boracic acid in water is boiled briskly. Vitrified boracic acid should be preserved in well-stopped vessels; for if exposed to the air it absorbs water, and gradually loses its transparency. Its sp. gravity is 1·803. It is exceedingly fusible, and communicates this property to the substances with which it unites. For this reason borax is often used us a flux.

Its *eq. is* 34·9; *symb.* B+3O, $\dddot{B}$, or BO_3.

SECTION X.

SILICON.

Hist.—That silicic acid or silica is composed of a combustible body united with oxygen, was demonstrated by Davy; for on bringing the vapour of potassium in contact with pure silicic acid heated to whiteness, a silicate of potassa resulted, through which was diffused the inflammable base of silicic acid in the form of black particles like plumbago. To this substance, on the supposition of its being a metal, the term *silicium* was applied. But though this view has been adopted by most chemists, so little was known with certainty concerning the real nature of the base of silica, that Thomson inclined to the opinion of its being a non-metallic body, and accordingly associated it in his system of chemistry with carbon and boron under the name of *silicon*. The recent researches of Berzelius appear almost decisive of this question. A substance which has not the metallic lustre, and is a non-conductor of electricity, cannot be regarded as a metal.

Prep.—Pure silicon was first procured by Berzelius in the year 1824 by the action of potassium on fluosilicic acid gas, but it is more conveniently prepared from the double fluoride of silicon and potassium or sodium, previously dried by a temperature near that of redness. When this compound is heated in a glass tube with potassium, the latter unites with fluorine, and silicon is separated. The heat of a spirit-lamp is sufficient for the purpose, and the decomposition takes place, accompanied with feeble detonation, before the mixture becomes red-hot. When the mass is cold, the soluble parts are removed by the action of water; the first portions of which produce disengagement of hydrogen gas, owing to the presence of some silicuret of potassium. The silicon thus procured is chemically united with a little hydrogen, and at a red heat burns vividly in oxygen gas. In order to render it quite pure, it should be first heated to redness, and then digested in dilute hydrofluoric acid to dissolve adherent particles of silicic acid. (An. of Phil. xxvi. 116.)

Prop.—Silicon, obtained in this manner, has a dark nut-brown colour, without the least trace of metallic lustre. It is a non-conductor of electricity. It is incombustible in air and in oxygen gas; and may be exposed to the flame of the blowpipe without fusing or undergoing any other change. It is neither dis-

solved nor oxidized by the sulphuric, nitric, hydrochloric, or hydrofluoric acids; but a mixture of the nitric and hydrofluoric acids dissolves it readily even in the cold.

It is not changed by ignition with chlorate of potassa. In nitre it does not deflagrate until the temperature is raised so high that the acid is decomposed; and then the oxidation is effected by the affinity of the disengaged alkali for silicic acid co-operating with the attraction of oxygen for silicon. For a similar reason it burns vividly when brought into contact with carbonate of potassa or soda, and the combustion ensues at a temperature considerably below that of redness. It explodes in consequence of a copious evolution of hydrogen gas, when it is dropped upon the fused hydrate of potassa, soda, or baryta.

Berzelius ascertained, by oxidizing a known weight of silicon, that 100 parts of silicic acid are composed of 48·4 of silicon and 51·6 of oxygen. Now, if silicic acid, as Thomson supposes, be composed of single atoms of its elements, then the equivalent of silicon will be 7·5; but if, as Berzelius believes, the smallest molecule of that acid contain 3 atoms of oxygen united with 1 atom of silicium, the equivalent of silicium would be 22·5. The latter view is supported by very strong analogies. Its *equivalent* is therefore 22·5; *symb.* Si.

Silicic Acid.—Hist. and Prep.—This compound, known also by the names of *silica* and *siliceous earth*, exists abundantly in nature. It enters into the composition of most of the earthy minerals; and under the name of quartz rock, forms independent mountainous masses. It is the chief ingredient of sandstones, flint, calcedony, rock crystal, and other analagous substances. It may indeed be procured, of sufficient purity for most purposes, by igniting transparent specimens of rock crystal, throwing them while red-hot into water, and then reducing them to powder.

Prop.—Pure silicic acid, in this state, is a light white powder, which feels rough and dry when rubbed between the fingers; is both insipid and inodorous; the sp. gr. is 2·69. It is fixed in the fire, and very infusible; but fuses before the oxy-hydrogen blowpipe with greater facility than lime or magnesia. It is quite insoluble in water; but Berzelius has shown, that if presented to water while in the nascent state, it is dissolved in large quantity. On evaporating the solution gently, a bulky gelatinous hydrate separates, which is partially decomposed by a very moderate temperature, but does not part with all its water except at a red heat.

Silicic acid has no action on test paper; but in all its chemical relations it manifests the properties of an acid, and displaces carbonic acid by the aid of heat from the alkalies. Its combinations with the fixed alkalies are effected by mixing pure sand with carbonate of potassa or soda, and heating the mixture to redness. During the process, carbonic acid is expelled, and a silicate of the alkali is generated. The nature of the product depends upon the proportions which are employed. On igniting one part of silicic acid with three of carbonate of potassa, a vitreous mass is formed, which is deliquescent, and may be dissolved completely in water. This solution, which was formerly called *liquor silicum*, has an alkaline reaction, and absorbs carbonic acid on exposure to the atmosphere, by which it is partially decomposed. Concentrated acids precipitate the silicic acid as a gelatinous hydrate; but if a considerable quantity of water is present, and the acid is added gradually, the alkali may be perfectly neutralized without any separation of silicic acid. When a solution of this kind is evaporated to dryness,

the silicic acid is rendered quite insoluble, and may thus be obtained in a pure form.

But if the proportion of silicic acid and alkali be reversed, a transparent brittle compound results, which is insoluble in water, is attacked by none of the acids excepting the hydrofluoric, and possesses the well-known properties of glass. Every kind of ordinary glass is a silicate, and all its varieties are owing to differences in the proportion of the constituents, to the nature of the alkali, or to the presence of foreign matters. Thus, green bottle glass is made of impure materials, such as river sand, which contains iron, and the most common kind of kelp or pearl-ashes. Crown glass for windows is made of a purer alkali, and sand which is free from iron. Plate glass, for looking-glasses, is composed of sand and alkali in their purest state; and in the formation of flint-glass, besides these pure ingredients, a considerable quantity of litharge or red lead is employed. A small portion of peroxide of manganese is also used, in order to oxidize carbonaceous matters contained in the materials of the glass; and nitre is sometimes added with the same intention. Ordinary flint-glass, according to Faraday, contains 51·93 per cent. of silicic acid, 33·28 of oxide of lead, and 13·77 of potassa; proportions which correspond to 1 eq. of potassa, 1 eq. of oxide of lead, and nearly 4 eq. of silicic acid. Flint-glass, accordingly, is a double salt, consisting chiefly of bisilicate of potassa, and bisilicate of oxide of lead.

Its eq. is 46·5; *symb.* Si + 3O, $\dot{S}i$, or $S\dot{O}$.

SECTION XI.

SELENIUM.

Hist. and Prep.—This substance was discovered in 1818 by Berzelius, who called it selenium, from Σελήνη *the Moon*, suggested by its having at first been mistaken for the metal tellurium. (An. de Ch. et Ph. ix. 160, and An. of Phil. xiii. 401.) It has hitherto been obtained in very small quantity, and occurs for the most part in combination with some varieties of iron pyrites. Stromeyer has also detected it, as a sulphuret of selenium, among the volcanic products of the Lipari isles. It is found likewise at Clausthal in the Hartz, combined, according to Stromeyer and Rose, with several metals, such as lead, cobalt, silver, mercury, and copper. Berzelius found it in the sulphur obtained by sublimation from the iron pyrites of Fahlun. In a manufactory of sulphuric acid, at which this sulphur was employed, it was observed that a reddish-coloured matter always collected at the bottom of the leaden chamber; and on burning this substance, Berzelius perceived a strong and peculiar odour, similar to that of decayed horseradish, which induced him to submit it to a careful examination, and thus led to the discovery of selenium. For the extraction of selenium from the native sulphuret, Magnus proposes to mix it with eight times its weight of peroxide of manganese, and to expose the mixture to a low red heat in a glass retort, the

beak of which dips into water. The sulphur, oxidized at the expense of the manganese, escapes in the form of sulphurous acid; while the selenium either sublimes as such or in the state of selenious acid. Should any of the latter be carried over into the water, it would there be reduced by the sulphurous acid.

Prop.—Selenium in many of its physical and chemical properties, is closely allied to sulphur. At common temperatures, is a brittle opaque solid body, without taste or odour. It has a metallic lustre and the aspect of lead, when in mass; but it is of a deep red colour when reduced to powder. Its sp. gr. is between 4·3 and 4·32. At 212° it softens, and is then so tenacious, that it may be drawn out into fine threads which are transparent, and appear red by transmitted light. It becomes quite fluid at a temperature somewhat above that of boiling water. It boils at about 650°, forming a vapour which has a deep yellow colour, but is free from odour. It may be sublimed in close vessels without change, and condenses again into dark globules of a metallic lustre, or as a cinnabar-red powder, according as the space in which it collects is small or large. Berzelius at first regarded it as a metal; but since it is an imperfect conductor of heat and electricity, it more properly belongs to the class of the simple non-metallic bodies.

Selenium is insoluble in water. It suffers no change from mere exposure to the atmosphere; but if heated in the open air, it combines readily with oxygen, and two compounds, oxide of selenium and selenious acid are generated. If exposed to the oxidizing part of the blowpipe flame, it tinges the flame with a light blue colour, and exhales a strong odour like that of decayed horse-radish, so strong that 1-50th of a grain is said to be sufficient to scent the air of a large apartment. By this character the presence of selenium, whether alone or in combination, may always be detected.

Berzelius has shown that selenic acid is composed of 24 parts of oxygen and 39·6 of selenium. This substance, also, has three grades of oxidation, the oxygen in the two last of which is in the ratio of 2 and 3; and the highest grade, selenic acid, has in all its chemical relations a singularly close analogy to sulphuric acid. From these facts it is inferred that selenic acid is composed of 1 atom of selenium and 3 atoms of oxygen. *Its eq. is* 39·6; *symb.* Se.

The compounds of selenium described in this section are the following:—

	Selenium.		Oxygen.	Equiv.	Formulæ.
Oxide of Selenium (probably)	39·6 or 1 eq.	+	8 or 1 eq.	= 47·6	SeO.
Selenious Acid . .	39·6	+	16 or 2 eq.	= 55·6	SeO_2.
Selenic Acid . .	39·6	+	24 or 3 eq.	= 63·6	SeO_3.

Oxide of Selenium.—This compound is formed in greatest abundance by heating selenium in a limited quantity of atmospheric air, and by washing the product to separate selenious acid, which is generated at the same time. It is a colourless gas, which is very sparingly soluble in water, and does not possess any acid properties. It is the cause of the peculiar odour which is emitted during the oxidation of selenium.

Selenious Acid.—This acid is most conveniently prepared by digesting selenium in nitric or nitro-hydrochloric acid till it is completely dissolved. On evaporating the solution to dryness, a white residue is left, which is selenious acid. By increase of temperature, the acid itself sublimes, and condenses again unchanged into long four-sided needles. [It is also obtained by passing a current of oxygen over selenium strongly heated in a glass tube, the selenium takes fire, and burns with a bluish green flame at the point and edges, while selenious acid is con-

densed in the cooler parts of the tube.] It attracts moisture from the air, whereby it suffers imperfect liquefaction. It dissolves in alcohol and water. It has distinct acid properties, and its salts are called *selenites*.

Selenious acid is readily decomposed by all substances which have a strong affinity for oxygen, such as sulphurous and phosphorous acids. When sulphurous acid, or an alkaline sulphite, is added to a solution of selenious acid, a red-coloured powder, pure selenium, is thrown down, and the sulphurous is converted into sulphuric acid. Hydrosulphuric acid also decomposes it; and an orange-yellow-precipitate subsides, which is a sulphuret of selenium.

Selenic Acid.—Hist.—The preceding compound, discovered by Berzelius, was till lately the only known acid of selenium, and has been described in elementary works under the name of selenic acid; but the recent discovery of another acid of selenium containing more oxygen than the other, has rendered necessary a change of nomenclature. The existence of selenic acid was first noticed by M. Nitzsch, assistant of Mitscherlich, and its properties have been examined and described by the Professor himself. (Edin. Journal of Science, viii. 294.)

Prep.—This acid is prepared by fusing nitrate of potassa or soda with selenium, a metallic seleniuret, or with selenious acid or any of its salts. Seleniuret of lead, as the most common ore of selenium, will generally be employed; but it is very difficult to obtain pure selenic acid by its means, because it is commonly associated with metallic sulphurets. The ore is first treated with hydrochloric acid to remove any carbonate that may be present; and the insoluble part, which is about a third of the mass, is mixed with its own weight of nitrate of soda, and thrown by successive portions into a red-hot crucible. The lead is thus oxidized, and the selenium converted into selenic acid, which unites with soda. The fused mass is then acted on by hot water, which dissolves only seleniate of soda, together with nitrate and nitrite of soda; while the insoluble matter, when well washed, is quite free from selenium. The solution is next made to boil briskly, when anhydrous seleniate of soda is deposited; while, on cooling, nitrate of soda crystallizes. On renewing the ebullition and subsequent cooling, fresh portions of seleniate and nitrate are procured; and these successive operations are repeated, until the former salt is entirely separated. This process is founded on the fact, that seleniate of soda, like the sulphate of the same base, is more soluble in water of about 90° than at higher or lower temperatures. The nitrite of soda, formed during the fusion, is purposely reconverted into nitrate by digestion with nitric acid.

The seleniate of soda thus procured always contains a little sulphuric acid, derived from the metallic sulphurets of the ore; and it is not possible to separate this acid by crystallization. All attempts to separate it by means of baryta were likewise fruitless; and the only method of effecting this object is by reducing the selenic acid into selenium. This is done by heating a mixture of seleniate of soda with hydrochlorate of ammonia, when the sodium unites with chlorine, all the hydrogen with oxygen, and selenium and nitrogen are set free. This change will be more readily followed when stated in symbols;—thus

$$NaO, SeO_3, NH_3 \text{ and } HCl, \text{ yield } N, Se, 4HO \text{ and } NaCl.$$

The selenium which sublimes is quite free from sulphur. It is then converted by nitric acid into selenious acid, which should be neutralized with soda, and fused with nitre or nitrate of soda. The pure seleniate of soda, separated from

the nitrate according to the foregoing process, is subsequently dissolved in water, and obtained in crystals by spontaneous evaporation.

To procure the acid in a free state, seleniate of soda is decomposed by nitrate of oxide of lead. The seleniate of that oxide, which is as insoluble as the sulphate, after being well washed, is exposed to a current of hydrosulphuric acid gas, which precipitates all the lead as a sulphuret, but does not decompose the selenic acid. The excess of the gas is driven off by heat, and pure selenic acid remains diluted with water. The absence of fixed substances may be proved by its being volatilized by heat without residue; and if free from sulphuric acid, it gives no precipitate with chloride of barium after being boiled with hydrochloric acid. Any nitric acid which may be present is expelled by concentrating the solution by means of heat.

Prop.—It is a colourless liquid, which may be heated to 536° without appreciable decomposition; but above that point decomposition commences, and it becomes rapid at 554°, giving rise to disengagement of oxygen and selenious acid. When concentrated by a temperature of 329°, its sp. gr. is 2·524; at 512° it is 2·60, and at 545° it is 2·625, but a little selenious acid is then present. When procured by the process above described, selenic acid always contains water, but it is very difficult to ascertain its precise proportion. Some acid, which had been heated higher than 536°, contained, subtracting the quantity of selenious acid present, 15·75 per cent. of water, which approximates to the ratio of one equivalent of water and one of the acid. It is certain that selenic acid is decomposed by heat before parting with all the water which it contains.

Selenic acid has a powerful affinity for water, and emits as much heat in uniting with it as sulphuric acid does. Like this acid it is not decomposed by hydrosulphuric acid, and hence this gas may be employed for decomposing seleniate of the oxides of lead or copper. With hydrochloric acid the change is peculiar; for on boiling the mixture mutual decomposition ensues, water and selenious acid are formed, and chlorine is set free; so that the solution, like *aqua regia*, is capable of dissolving gold and platinum. Selenic acid dissolves zinc and iron with disengagement of hydrogen gas, and copper with formation of selenious acid. It dissolves gold also, but not platinum. Sulphurous acid has no action on selenic acid, whereas selenious acid is easily reduced by it. Consequently, when it is wished to precipitate selenium from selenic acid, it must be boiled with hydrochloric acid before sulphurous acid is added.

Mitscherlich has observed, that selenic and sulphuric acids are not only analogous in composition and in many of their properties, but that the similarity runs through their compounds with alkaline substances, their salts resembling each other in chemical properties, constitution, and form.

SECTION XII.

CHLORINE.

Hist.—The discovery of chlorine was made in the year 1774 by Scheele, while investigating the nature of manganese, and he described it under the name of *dephlogisticated marine acid.* The French chemists called it *oxygenized muriatic*

acid, a term which was afterwards contracted to *oxy-muriatic acid*, from an opinion proposed by Berthollet that it is a compound of *muriatic acid* and *oxygen*. In 1809 Gay-Lussac and Thenard published an abstract of some experiments upon this substance, which subsequently appeared at length in their Recherches Physico-Chimiques, wherein they stated that oxy-muriatic acid might be regarded as a simple body, though they gave the preference to the doctrine advanced by Berthollet. Davy engaged in the inquiry about the same time; and after having exposed oxy-muriatic acid to the most powerful decomposing agents which chemists possess, without being able to effect its decomposition, he communicated to the Royal Society an essay, in which he denied its compound nature; and he maintained that, according to the true logic of chemistry, it is entitled to rank with simple bodies. This view, which is commonly termed the *new theory of chlorine*, though strongly objected to at the time it was first proposed, is now universally received by chemists. The grounds of preference will hereafter be briefly stated.

Prep.—Chlorine gas is obtained by the action of hydrochloric acid on peroxide of manganese. The most convenient method of preparing it is by mixing concentrated hydrochloric acid, contained in a glass flask, with half its weight of finely powdered peroxide of manganese. Effervescence, owing to the escape of chlorine, takes place even in the cold; but the gas is evolved much more freely by the application of a moderate heat. It should be collected by displacement of air in dry bottles. The tube conducting the gas reaches to the bottom of the bottle, where the chlorine, being heavier than air, accumulates, and displaces it. When the bottle is full, which is known by the colour of the gas appearing at the mouth of the bottle, it is stopped with a greased stopper, and another bottle put in its place. As some hydrochloric acid gas commonly passes over with it, the chlorine should not be considered quite pure, till after being transmitted through water.

The theory of this process will be readily understood by first viewing the elements which act on each other, namely,—

Manganese .	27·7 or 1 eq.	Mn		Chlorine .	70·84 or 2 eq.	2Cl
Oxygen .	16 2 eq.	2 O		Hydrogen .	or 2 eq.	2H
Perox. of Mang.	43·7 or 1 eq.	Mn + 2O		Hydrochl. acid	72·84 or 2 eq.	2 (H + Cl);

and then inspecting the products derived from them, namely,

Manganese .	27·7	Hydrogen	2	Chlorine 35·42 or 1 eq.	
Chlorine .	35·42	Oxygen	16		
Chloride of Mang.	63·12	Water	18.		

In symbols,

MnO_2 and 2HCl yield MnCl, 2HO, and Cl.

The affinities which determine these changes are the mutual attraction of oxygen and hydrogen, and of chlorine and manganese.

When it is an object to prepare chlorine at the cheapest rate, as for the purposes of manufacture, the preceding process is modified in the following manner. Three parts of sea-salt are intimately mixed with one of peroxide of manganese, and to this mixture two parts of sulphuric acid, diluted with an equal weight of water, are added. By the action of sulphuric acid on sea-salt, hydrochloric acid is disengaged, which reacts, as in the former case, upon the peroxide of man-

ganese; so that, instead of adding hydrochloric acid directly to the manganese, the materials for forming it are employed. In this process, however, the sulphates of soda and protoxide of manganese are generated, instead of chloride of manganese. Thus the materials which act on each other are MnO_2, NaCl, and $2SO_3$; and the products MnO. SO_3, NaO. SO_3, and Cl.

Prop.—Chlorine (from χλωρος *green*) is a yellowish-green coloured gas, which has an astringent taste, and a disagreeable odour. It is one of the most suffocating of the gases, exciting spasm and great irritation of the glottis, even when considerably diluted with air. When strongly and suddenly compressed, it emits both heat and light, the latter being solely due, as in the case of air and oxygen, to the chlorine acting chemically on the oil with which the compressing apparatus is lubricated (An. de Ch. et Ph. xliv. 181). According to Davy, 100 cubic inches of dry chlorine at 30 B. and 60° F. weigh between 76 and 77 grains. Gay-Lussac and Thenard found the density of pure and dry chlorine to be 2·47, which gives 76·599 grains as the weight of 100 cubic inches at 60° F. and 30 B. Under the pressure of about four atmospheres it is a limpid liquid of a bright yellow colour, which does not freeze at the temperature of zero, and which assumes the gaseous form with the appearance of ebullition when the pressure is removed. Kemp finds that this liquid is a non-conductor of electricity.

Cold recently boiled water, at the common pressure, absorbs twice its volume of chlorine, and yields it again when heated. The solution, which is made by transmitting a current of chlorine gas through cold water, has the colour, taste, and most of the other properties of the gas itself. When moist chlorine gas is exposed to a cold of 32°, yellow crystals are formed, which consist of water and chlorine in definite proportions. They are composed, according to Faraday, of 35·42 parts or 1 eq. of chlorine, and 90 parts or 10 eq. of water. It experiences no chemical change from the action of the imponderables. Thus it is not affected chemically by intense heat, by strong shocks of electricity, or by a powerful galvanic battery. Davy exposed it also to the action of charcoal heated to whiteness by galvanic electricity, without separating oxygen from it, or in any way affecting its nature. Light does not act on dry chlorine; but if water be present, the chlorine decomposes that liquid, unites with the hydrogen to form hydrochloric acid, and oxygen gas is set at liberty. This change takes place quickly in sunshine, more slowly in diffused daylight, and not at all when light is wholly excluded. Hence the necessity of keeping moist chlorine gas, or its solution, in a dark place.

Chlorine unites with some substances with evolution of heat and light, and is hence termed a suporter of combustion. On plunging a lighted taper into chlorine gas, it burns for a short time with a small red flame, and emits a large quantity of smoke. Phosphorus takes fire in it spontaneously and burns with a pale white light. Several of the metals, such as tin, copper, arsenic, antimony, and zinc, when introduced into chlorine in the state of powder or in fine leaves, are suddenly inflamed. In all these cases the combustible substances unite with chlorine.

Chlorine has a very powerful attraction for hydrogen; and many of the chemical phenomena to which it gives rise are owing to this property. A striking example is its power of decomposing water by the action of light, or at a red-heat; the same effect is produced on most compound substances, of which hydrogen is an element. For the same reason, when chlorine, water, and some

other body which has a strong affinity for oxygen, are presented to one another, water is usually resolved into its elements, its hydrogen attaching itself to the chlorine, and its oxygen to the other body. Thus chlorine is, indirectly, one of the most powerful oxydizing agents which we possess.

When any compound of chlorine and an inflammable is exposed to the influence of galvanism, the inflammable body goes over to the —, and chlorine to the + pole of the battery. This establishes a close analogy between oxygen and chlorine, both of them being supporters of combustion, and both negative electrics.

Though formerly called an acid, it possesses no acid properties. It has not a sour taste, does not redden the blue colour of plants, and shows comparatively little disposition to unite with alkalies. Its strong affinity for the metals is sufficient to prove that it is not an acid; for chemists are not acquainted with any instance of an acid combining directly in definite proportion with a metal. Its action on the pure alkalies leads to complicated changes, which will be considered while speaking of the oxides of chlorine.

One of the most important properties of chlorine is its bleaching power. All animal and vegetable colours are speedily removed by chlorine; and when the colour is once discharged, it can never be restored. Davy proved that chlorine cannot bleach unless water is present. Thus dry litmus paper suffers no change in dry chlorine; but when water is admitted, the colour speedily disappears. It is well known also that hydrochloric acid is always generated when chlorine bleaches. From these facts it is inferred that water is decomposed during the process; that its hydrogen unites with chlorine, and that decomposition of the colouring matter is occasioned by the oxygen which is liberated. The bleaching property of binoxide of hydrogen and of chromic and permanganic acids, of which oxygen is certainly the decolorizing principle, leaves little doubt of the accuracy of the foregoing explanation.

Chlorine is useful, likewise, for the purposes of fumigation. The experience of Guyton-Morveau is sufficient evidence of its power in destroying the volatile principles given off by putrefying animal matter; it probably acts in a similar way on contagious effluvia. A peculiar compound, formed by the action of chlorine on soda, has been lately introduced for this purpose by Labaraque.

Chlorine is in general easily recognized by its colour and odour. Chemically it may be detected by its bleaching property, added to the circumstance that a solution of nitrate of oxide of silver occasions in it a dense white precipitate (a compound of chlorine and metallic silver), which becomes dark on exposure to light, is insoluble in acids, and dissolves completely in pure ammonia. The whole of the chlorine, however, is not thrown down; for the oxygen of the oxide of silver unites with a portion of the chlorine, and converts it into chloric acid.

Those compounds of chlorine which are not acid, are termed *chlorides* or *chlorurets*. The former expression, from the analogy between chlorine and oxygen, is perhaps the more appropriate.

Berzelius inferred the equivalent of chlorine from the oxygen lost by chlorate of potassa when decomposed by heat, and the quantity of chlorine found in the residual chloride of potassium. I investigated the same subject by examining into the composition of the nitrate of the oxide and chloride of silver, of the protoxide and chloride of lead, and of the peroxide and chlorides of mercury. These researches concur in showing 36, the eq. of chlorine commonly adopted

in this country, to be erroneous. The number inferred from the sp. gr. of chlorine and hydrogen gases is 35·84; but, unfortunately, the densities of these gases are not known with the precision required for an application of this nature.

Its eq. is 35·42; *eq. vol.* = 100; *symb.* Cl.

The composition of the compounds described in this section is as follows :—

	Chlorine.			Equiv.	Formulæ.
Hydrochloric Acid	35·42	1 eq. + Hydrogen	1	1 eq. = 36·42	HCl.
Hypochlorous Acid	35·42	+ Oxygen	8	1 eq. = 43·42	Clo.
Chlorous Acid	35.42	+ Ditto	32	4 eq. = 67·42	ClO_4.
Chloric Acid	35·42	+ Ditto	40	5 eq. = 75·42	ClO_5.
Perchloric Acid	35·42	+ Ditto	56	7 eq. = 91.42	ClO_7.
Quadrochloride of Nitrogen	141·68	4 eq. + Nitrogen	14·15	1 eq. = 155·83	NCl_4.
Protochloride of Carbon	35·42	1 eq. + Carbon	6·12	1 eq. = 41·54	CCl.
Dichloride of Carbon	35·42	1 eq. + Ditto	12·24	2 eq. = 47·66	C_2Cl.
Perchloride of Carbon	106·26	3 eq. + Carbon	12·24	2 eq. = 118·50	C_2Cl_3.
Dichloride of Sulphur	35·42	1 eq. + Sulphur	32·2	2 eq. = 67·62	SCl.
Bichloride of Sulphur	70	2 eq. + Ditto	16·1	1 eq. = 86·1	SCl_2.
Sesquichloride of Phosphorus	106·26	3 eq. + Phospho.	31·4	1 eq. = 137·66	P_2Cl_3.
Perchloride of Phosphorus	175	5 eq. + Ditto	31·4	1 eq. = 206·4	P_2Cl_5.
Chlorocarbonic Acid Gas	35·42	1 eq. + Carb. ox.	14·12	1 eq. = 49·54	Co + Cl.
Terchloride of Boron	106·26	3 eq. + Boron	10·9	1 eq. = 117·16	BCl_3.
Terchloride of Silicon	106·26	3 eq. + Silicon	22·5	1 eq. = 128·76	$Sicl_3$.

Hydrochloric, Chlorohydric, or Muriatic Acid.—Hist. and Prep.—A concentrated aqueous solution of this acid has been long known under the names of spirit of salt, and of marine or muriatic acid ; but in its purer form of gas it was discovered in 1772 by Priestley. It may be conveniently prepared by putting an ounce of strong hydrochloric acid solution into a glass flask, and heating it by means of a lamp till the liquid boils, when the gas is freely evolved, and may be collected over mercury. Another method of preparing it is by the action of concentrated sulphuric acid on an equal weight of sea-salt. Brisk effervescence ensues at the moment of making the mixture, and on the application of heat a large quantity of hydrochloric acid gas is disengaged. In the former process, hydrochloric acid previously dissolved in water is simply expelled from the solution by heat. The explanation of the latter process is more complicated. Sea-salt was formerly supposed to be a compound of hydrochloric acid and soda; and, on this supposition, the soda was believed merely to quit the hydrochloric and unite with sulphuric acid. But the researches of Gay-Lussac, Thenard, and Davy, proved that it consists of chlorine and sodium combined in the ratio of their equivalents. The nature of its action with sulphuric acid will be understood by comparing the elements concerned in the change before and after it has occurred :—

Hydrous Sulp. Acid.		Chloride of Sodium.		Sulph. of Soda.		Hydrochloric Acid.	
Real Acid	41·1	Chlorine	35·42	Acid	40·1	Chlorine	35.42
Water	Hyd. 1, Oxy. 8	Sodium	23·3	Soda	Sod. 23·3, Oxy. 8	Hydrogen	1

or in symbols,

$$SO_3, HO + NaCl = SO_3, NaO + HCl.$$

Thus it appears that single equivalents of water, sulphuric acid, and chloride of sodium, yield sulphate of soda and hydrochloric acid. The water of the sulphuric acid is essential; so much so, indeed, that chloride of sodium is not decomposed at all by anhydrous sulphuric acid.

Hydrochloric acid may be generated by the direct union of its elements. When equal measures of chlorine and hydrogen are mixed together, and an electric spark is passed through the mixture, instantaneous combination takes place, heat and light are emitted, and hydrochloric acid is generated. A similar effect is produced by flame, by a red-hot body, and by spongy platinum. Light also causes them to unite. A mixture of the two gases may be preserved without change in a dark place; but if exposed to the diffused light of day, gradual combination ensues, which is completed in the course of 24 hours. The direct solar rays produce, like flame and electricity, sudden inflammation of the whole mixture, accompanied with explosion; and, according to Brande, the vivid light emitted by charcoal intensely heated by galvanic electricity acts in a similar manner.

This acid is most commonly used in the form of a concentrated aqueous solution, which is made by transmitting a current of the gas into water as long as any of it is absorbed. All the Pharmacopœias give directions for conducting the process. That adopted by the Edinburgh College is practically good. The proportions they recommend are equal weights of sea-salt, water, and sulphuric acid, more acid being purposely employed than is sufficient to form a neutral sulphate with the soda, so that the more perfect decomposition of the sea-salt may be insured. The acid, to prevent too violent effervescence at first, is mixed with one-third of the water; and when the mixture has cooled, it is poured upon the salt previously introduced into a glass retort. The distillation is continued to dryness; and the gas, as it escapes, is conducted into the remainder of the water. The theory of the process has been already explained. The residue is a mixture of sulphate and bisulphate of soda. The sp. gr. of the acid solution obtained by this process is 1·170.

Prop.—It is a colourless gas, has a pungent odour and an acid taste. Under a pressure of 40 atmospheres, and at the temperature of 50°, it is liquid. Sp. gr. 1·2695. It is quite irrespirable, exciting violent spasm of the glottis; but when diluted with air, it is far less irritating than chlorine. All burning bodies are extinguished by it, nor is the gas itself inflammable.

It is not chemically changed by mere heat. It is readily decomposed by galvanism, hydrogen appearing at the —, and chlorine at the + pole. It is also decomposed by ordinary electricity. The decomposition, however, is incomplete; for though one electric spark resolves a portion of the gas into its elements, the next shock in a great measure effects their reunion. It is not affected by oxygen under common circumstances; but if a mixture of oxygen and hydrochloric acid gases is electrified, the oxygen unites with the hydrogen of the acid to form water, and chlorine is set at liberty. For this and the preceding fact we are indebted to the researches of Henry.

One of the most striking properties of hydrochloric acid gas is its powerful attraction for water. A dense white cloud appears whenever it escapes into the air, owing to its combining with the aqueous vapour of the atmosphere. A piece of ice put into a jar full of the gas confined over mercury liquefies on the instant, and the whole of the gas disappears in the course of a few seconds. On opening a long wide jar of hydrochloric acid gas under water, the absorption of

the gas takes place so instantaneously, that the water is forced up into the jar with the same violence as into a vacuum. Considerable increase of temperature takes place during the absorption, and therefore the apparatus should be kept cool by ice. Davy states (Elements, p. 252) that water at the temperature of 40° absorbs 480 times its volume of the gas, and that the solution has a sp. gr. of 1·2109. Thomson finds that one cubic inch of water at 69° absorbs 418 cubic inches of gas, and occupies the space of 1·34 cubic inch. The solution has a sp. gr. of 1·1958, and one cubic inch of it contains 311.04 cubic inches of hydrochloric acid gas. The quantity of real acid contained in solutions of different densities may be determined by ascertaining the quantity of pure marble dissolved by a given weight of each. Every 50·6 grains of marble correspond to 36·42 of real acid. The following table, from Thomson's "Principles of Chemistry," is constructed according to this rule. The first and second columns show the atomic constitution of each acid.

Table exhibiting the Specific Gravity of Muriatic acid of determinate strengths.

Atoms of Acid.	Atoms of Water.	Real Acid in 100 of the liquid.	Specific Gravity.	Atoms of Acid.	Atoms of Water.	Real Acid in 100 of the liquid.	Specific Gravity.
1	6	40·559	1·203	1	14	22·700	1·1060
1	7	37·000	1·179	1	15	21·512	1·1008
1	8	33·945	1·162	1	16	20·442	1·0960
1	9	31·346	1·149	1	17	19·474	1·0902
1	10	29·134	1·139	1	18	18·590	1·0860
1	11	27·206	1·1285	1	19	17·790	1·0820
1	12	25·517	1·1197	1	20	17·051	1·0780
1	13	24·026	1·1127				

Hydrochloric acid of commerce has a yellow colour, and is always impure. Its usual impurities are nitric acid, sulphuric acid, oxide of iron, and occasionally sulphurous acid. The latter, according to Girardin, may be detected by the addition of some crystals of the protochloride of tin, which decomposes the sulphurous acid and precipitates a brown powder containing sulphur in combination with tin. The presence of nitric acid may be inferred if the hydrochloric acid has the property of dissolving gold leaf. Iron may be detected by ferrocyanide of potassium, and sulphuric acid by chloride of barium, the suspected hydrochloric acid being previously diluted with three or four parts of water. The presence of nitric acid is provided against, by igniting the sea-salt, as recommended by the Edinburgh College, in order to decompose any nitre which it may contain. The other impurities may be avoided by employing Woulfe's Apparatus. A few drachms of water are put into the first bottle to retain the chloride of iron and sulphuric acid which pass over, and the hydrochloric acid gas is condensed in the second.

A strong solution of pure hydrochloric acid is a colourless liquid, which emits white vapours when exposed to the air, is intensely sour, reddens litmus paper strongly, and neutralizes alkalies. It combines with water in every proportion, and causes increase of temperature when mixed with it, though in a much less degree than sulphuric acid. It freezes at 60° F.; and boils at 110°, or a little higher, giving off pure hydrochloric acid gas in large quantity.

[The strongest acid which can be easily procured, as represented in the table, contains 6 atoms of water. When this liquid is evaporated in the open air, it abandons a quantity of acid gas, and according to Graham becomes a compound

containing 12 atoms of water. Dalton found that when the concentrated acid was heated in a retort, its boiling point gradually rose to 230°, at which temperature the residual acid distilled over unchanged, and had a sp. gr. of 1·094. This acid Dr. Clark found to contain 16·4 atoms of water to 1 of acid.]

Hydrochloric acid is decomposed by substances which yield oxygen readily. Thus several peroxides, such as those of manganese, cobalt, and lead, effect its decomposition. Chloric, iodic, bromic, nitric, and selenic acids act on the same principle. A mixture of nitric and hydrochloric acids, in the ratio of one measure of the former to two of the latter, has long been known under the name of *Aqua regia*, as a solvent for gold and platinum. When these acids are mixed together, the solution instantly becomes yellow; and on heating the mixture, pure chlorine is evolved, and the colour of the solution deepens. On continuing the heat, chlorine and nitrous acid vapours are disengaged. At length the evolution of chlorine ceases, and the residual liquid is found to be a solution of hydrochloric and nitrous acids, which is incapable of dissolving gold. The explanation of these facts is, that nitric and hydrochloric acids decompose one another, giving rise to the production of water and nitrous acid, and the separation of chlorine; while hydrochloric and nitrous acids may be heated together without mutual decomposition. It is hence inferred that the power of nitro-hydrochloric acid in dissolving gold is owing to the chlorine which is liberated. (Davy in the Quarterly Journal, vol. i.)

Hydrochloric acid is distinguished by its odour, volatility, and strong acid properties. With nitrate of oxide of silver it yields the same precipitate as chlorine; but no chloric acid is generated, because the oxygen of the oxide of silver unites with the hydrogen of the hydrochloric acid, and the chlorine in consequence is entirely precipitated. Notwithstanding that nitrate of oxide of silver yields the same precipitate with chlorine and hydrochloric acid, there is no difficulty in distinguishing between them, for the bleaching property of the former is a sure ground of distinction.

The composition of hydrochloric acid has been determined by Davy, and Gay-Lussac and Thenard. Their experiments concur in proving that chlorine and hydrogen unite in equal volumes, and that the hydrochloric acid, which is the sole and constant product, occupies the same space as the gases from which it is formed. From these facts the composition of hydrochloric acid is easily inferred. For, as

	Grains.
50 cubic inches of Chloride weigh	38·299
50 " " of Hydrogen	1·0699
100 C. I. of Hydrochloric acid gas must weigh . .	39·3689

These numbers are in the ratio of 1 to 35·84, being nearly that of single eq. of hydrogen and chlorine. Hence *its eq. is* 36·42; *eq. vol.* = 100; *symb.* H + Cl, or HCl.

COMPOUNDS OF CHLORINE AND OXYGEN.

The leading character of these compounds is derived from the circumstance that chlorine and oxygen, the attraction of which for most elementary substances is so energetic, have but a feeble affinity for each other. These principles, con-

sequently, are never met with in nature in a state of combination. Indeed, they cannot be made to combine directly; and when they do unite, very slight causes effect their separation. Chemists have long been doubtful as to the exact number of the compounds of chlorine and hydrogen. The recent labours of Balard and Martens have established the existence of four, all of which they have shown to possess acid properties. Their names and constitutions are given in the subjoined table.

	By weight.		By volume.	
	Chl.	Oxy.	Chl.	Oxy.
Hypochlorous acid	35·42	8	2	1
Chlorous acid	35·42	32	2	4
Chloric acid	35·42	40	2	5
Perchloric acid	35·42	56	2	7

According to the practice of most British chemists, two volumes of chlorine, as also two volumes of hydrogen and of nitrogen, are considered as respectively corresponding to one equivalent or one atom; whereas one volume of oxygen corresponds to one equivalent. Berzelius, with many continental chemists, considering the atoms of all elements to possess the same volume, regard the four preceding compounds as composed of 2 atoms or 2 eqs. of chlorine combined with 1, 4, 5, and 7 atoms or eqs. of oxygen.

Hypochlorous Acid.—Hist. and Prep.—Davy, in 1811, discovered a gaseous compound, which was described by him in the Philosophical Transactions of the same year under the name of Euchlorine. This gas, which until recently has been considered to be the protoxide of chlorine, is made by the action of hydrochloric acid on the chlorate of potassa; and its production is explicable by the fact, that hydrochloric and chloric acids mutually decompose each other. When hydrochloric acid and chlorate of potassa are mixed together, more or less of the potassa is separated by the hydrochloric from the chloric acid, and the latter being set at liberty, reacts on free hydrochloric acid. The result depends upon the relative quantities of the materials. If hydrochloric acid be in excess, the chloric acid undergoes complete decomposition. For each eq. of chloric acid, 5 eq. of hydrochloric acid are decomposed: the 5 eq. of oxygen contained in the former, unite with the hydrogen of the latter, producing 5 eq. of water; while the chlorine of both acids is disengaged. If, on the contrary, chlorate of potassa be in excess, the chloric acid is deprived of part of its oxygen only; the products are water and the euchlorine of Davy. The chloric and hydrochloric acids react on each other in the ratio of 1 eq. to 2, or what is the same thing, in that of 4 eq. to 8 eq.; thus

$$4ClO_5 + 8HCl = 8HO + 12ClO.$$

The gas thus obtained, though containing chlorine and oxygen in the ratio of atom to atom, is not, as was supposed by Davy, a distinct compound, but is a mixture of chlorine and chlorous acid. For this fact, which has long been suspected, we are indebted to the researches of Soubeiran. On transmitting a stream of euchlorine through a tube nearly full of calomel, the free chlorine is readily absorbed; on subsequently exploding the purified gas, he obtained one volume

of chlorine to two volumes of oxygen, being the exact composition of chlorous acid. The product of the last decomposition is therefore

$$3ClO_4 + 9Cl, \text{ and not } 12ClO.$$

The experiments of Soubeiran have been confirmed by the discoveries of Balard.

If a stream of chlorine gas be passed into a solution of the pure alkalies, or be allowed to act upon the alkaline earths in the form of hydrates, a bleaching substance is procured which has been commonly viewed as a direct compound of chlorine and an alkaline base. It consists, however, according to Balard, of a mixture of a metallic chloride and the hypochlorite of the alkali employed (An. de Ch. et Ph. lvii. 225). The process recommended for obtaining the pure acid is to pour into bottles filled with chlorine gas peroxide of mercury in fine powder, and mixed with twice its weight of distilled water: by brisk agitation the chlorine is rapidly and completely absorbed, if a slight excess of the peroxide be used. By this process one portion of the peroxide of mercury, HgO_2, is decomposed, both its constituents combining with chlorine, the mercury forming corrosive sublimate, $HgCl_2$, and the oxygen hypochlorous acid. The latter remains in solution in the water; while the former, by combining with undecomposed peroxide of mercury, forms the sparingly soluble oxychloride of mercury, which is separated by filtration. The hypochlorous acid being volatile, is obtained in a pure but diluted state by distillation. The temperature which is used for this purpose should be kept considerably below 212°, as the hypochlorous acid decomposes rapidly at that heat: the process is, therefore, best performed under reduced pressure. A more concentrated solution of the acid is obtained by submitting the first products to a second distillation.

Prop.—As thus obtained, hypochlorous acid is a transparent liquid of a slightly yellow colour when concentrated. Its odour is strong and penetrating, and different though somewhat similar to chlorine. Its action on the skin is exceedingly active, the effect being similar to but greater than that produced by nitric acid. It is a highly bleaching compound. In a concentrated state it is very unstable, a slow decomposition taking place at common temperatures, by which chlorine is evolved and chloric acid produced. This change is promoted by light, and is effected almost instantly by exposure for a few moments to the direct rays of the sun. It is also decomposed by agitation with angular bodies; and on throwing into the acid a portion of pounded glass, a brisk effervescence is observed from the escape of chlorine.

It is one of the most powerful oxidizing agents. Its action in this respect, however, is various, and is principally observed in relation to the simple non-metallic elements. Thus sulphur and phosphorus are readily brought to their highest state of oxidation, and even selenium is converted into selenic acid, an effect which the nitric acid cannot accomplish. Iodine and bromine are also instantly changed into iodic and bromic acids. Its action on the more perfect metals, on the contrary, is slight: iron and silver, however, are remarkable exceptions to this rule; for when either of them is brought in a finely divided state in contact with hypochlorous acid, the latter suffers instantaneous decomposition. When iron is used, it is oxidized at the expense of the acid, and chlorine is evolved; with silver the oxygen escapes, and the chlorine unites exclusively with the metal. The decomposition of hypochlorous acid may also be produced by metallic mercury, but the decomposition is unattended by the evolution of either gas. Both

the chloride and oxide of mercury are produced, and instantly unite to form the oxychloride.

Balard has also succeeded in obtaining hypochlorous acid in the gaseous form. A small quantity of a concentrated solution is introduced into a bell jar over mercury, and fragments of dry nitrate of lime are successively added. The nitrate of lime being highly deliquescent, unites with the water, and the acid gas escapes with effervescence: the presence of the saline solution is essential, as it prevents the decomposition of the gas by the mercury.

[M. Pelouse has found that when chlorine, and the common crystallized red oxide of mercury, both quite dry, are presented to each other, the reaction is such as not to form hypochlorous acid, but simply chloride of mercury, with the liberation of free oxygen gas. When, however, the oxide used is prepared by precipitation, and subsequent exposure to a temperature of about 550° F. this acid is readily produced. By passing over the oxide so prepared, and placed in a glass tube, a gentle current of dry chloride gas an active reaction ensues, chloride of mercury is formed, which remains in the tube, and hypochlorous acid gas is evolved, which may be collected, by displacement, from the open end of the tube, so bent as to reach to the bottom of a dry flask, or bottle. By exposure to the cold arising from a mixture of ice and snow, the hypochlorous acid gas condenses as a deep red liquid, which is slowly dissolved by water, and readily decomposed by heat, often with explosive violence. (Ann. de Ch. et Ph. 3rd se. p. 179.)]

The gas is of a yellowish green colour, and is very similar to chlorine in appearance. It unites rapidly with water, which absorbs at least 100 times its own volume of gas. It detonates by a slight increase of temperature; and though less explosive than the chlorous acid, there is a probability of an accident in transferring it from one vessel to another. The results of explosion are oxygen and chlorine; and Balard found that 100 measures produced 100 of chlorine and 50 of oxygen. From these data its sp. gr. is 3·0212; *its eq.* 43·42; *eq. vol.*= 100; *symb.* Cl + O, $\dot{C}l$ or ClO.

Chlorous Acid.—Hist. and Prep.—This compound was discovered by Davy in 1815 (Phil. Trans.), and soon after by Count Stadion of Vienna. It is formed by the action of sulphuric acid on chlorate of potassa. A quantity of this salt, not exceeding 50 or 60 grains, is reduced to powder, and made into a paste by the addition of strong sulphuric acid. The mixture, which acquires a deep yellow colour, is placed in a glass retort, and heated by warm water, the temperature of which is kept under 212° F. A bright yellowish green gas of a richer colour than chlorine is disengaged, which has an aromatic odour without any smell of chlorine, is absorbed rapidly by water, to which it communicates its tint. This gas, which has long been described as the peroxide of chlorine, must now be called chlorous acid, as it has been shown to possess acid properties, and to form definite compounds with the alkaline bases.

The chemical changes which take place in the process are explained in the following manner. The sulphuric acid decomposes some of the chlorate of potassa, and sets chloric acid at liberty. The chloric acid, at the moment of separation, resolves itself into peroxide of chlorine and oxygen; the last of which, instead of escaping as free oxygen gas, goes over to the acid of some undecomposed chloride of potassa, and converts it into perchloric acid. The products are bisulphate and perchlorate of potassa, and chlorous acid. It is

most probable, from the data contained in the preceding table, that every 3 eq. of chloride acid yield 1 eq. of perchloric acid and 2 eq. of chlorous acid.

Prop.—Chlorous acid unites readily with the alkalies and alkaline earths, forming salts which are more stable than those of the hypochlorous acid. They are produced by transmitting the gas into the alkaline solutions, which may thus be rendered perfectly neutral (Martens, An. de Ch. et Ph. lxi. 293.) All the salts hitherto examined are soluble in water, and are possessed, like the acid itself, of bleaching properties. The neutral salts pass readily into a metallic chloride and chlorate of the base, particularly such as the chlorite of potassa, which form a sparingly soluble chlorate. This change does not so readily ensue when alkali is in excess. The proportion in which the chloride and chlorate are produced indicate that 6 eq. of chlorite are decomposed, by which 1 eq. of metallic chloride and 5 eq. of chlorate are produced: thus 6KO ClO_4 yields KCl and 5 KO ClO_5. The solution of the pure acid gradually yields chloric acid and chlorine. It is a powerful oxidizing agent, and in this respect is very similar to the hypochlorous acid. It causes a precipitate with nitrate of silver; but it is best recognized by the evolution of chlorous acid gas on the addition of an acid to its salts.

Phosphorus takes fire when introduced into the gas, and occasions an explosion. It explodes violently when heated to a temperature of 212°, emits a strong light, and undergoes a greater expansion than protoxide of chlorine. According to Davy, whose result is confirmed by Gay-Lussac, 40 measures of the gas occupy after explosion the space of 60 measures; and of these, 20 are chlorine and 40 oxygen. The peroxide is therefore composed of 35·42 parts, or 1 eq. of chlorine, united with 32 or 4 eq. of oxygen; and its sp. gr. must be 23·375.

Its *eq. is* 67·42; *eq. vol.* = 100; *symb.* Cl + 4O, $\dot{Cl}$, or ClO_4.

Chloric Acid.—Prep.—If a current of chlorine gas be transmitted into a strong solution of pure potassa, a portion of the alkali is decomposed, and chloride of potassium and hypochlorite of potassa are generated. On bringing the solution to the boiling point, the latter salt is decomposed. The changes which occur are complicated, and give rise to the evolution of oxygen, and the formation of chlorate of potassa and chloride of potassium. According to the experiments of Morin and Soubeiran, which accord entirely with the observations of Balard, 9 eq. of hypochlorite of potassa produce 1 eq. of chlorate of potassa, 8 eq. of chloride of potassium, and 12 eq. of oxygen; or thus,

$$9(KO+ClO) \text{ yield } (KO+Clo_5), 8KCl, \text{ and } 12O.$$

Hence for every eq. of chlorate, 17 eq. of chloride are formed.

When to a dilute solution of chlorate of baryta a quantity of weak sulphuric acid, exactly sufficient for combining with the baryta, is added, the insoluble sulphate of baryta subsides, and pure chloric acid remains in the liquid. This acid, the existence of which was originally observed by Mr. Chenevix, was first obtained in a separate state by Gay-Lussac.

Prop.—Chloric acid reddens vegetable blue colours, has a sour taste, and forms neutral salts, called *chlorates* (formerly *hyperoxymuriates*,) with alkaline bases. It possesses no bleaching properties, a circumstance by which it is distinguished from chlorine, hypochlorous, and chlorous acids. It gives no precipitate in solution of nitrate of oxide of silver, and hence cannot be mistaken for hydrochloric

acid. Its solution may be concentrated by gentle heat till it acquires an oily consistence without decomposition: in this state of highest concentration it acquires a yellowish tint, emits an odour of nitric acid, sets fire to paper and other dry organic matter, and converts alcohol into acetic acid. When sharply heated in a retort, part of the acid is resolved into chlorine and oxygen; but another portion, acquiring oxygen from that which is decomposed, is converted into perchloric acid, and then passes over into the receiver in the form of a dense colourless liquid (Serullas.) Chloric acid is easily decomposed by deoxidizing agents. Sulphurous acid, for instance, deprives it of oxygen, with formation of sulphuric acid and evolution of chlorine. By the action of hydrosulphuric acid, water is generated, while sulphur and chlorine are set free. The power of hydrochloric acid in effecting its decomposition has already been explained.

Chloric acid is readily known by forming a salt with potassa, which crystallizes in tables and has a pearly lustre, deflagrates like nitre when flung on burning charcoal, and yields peroxide of chlorine by the action of concentrated sulphuric acid. Chlorate of potassa, like most of the chlorates, gives off pure oxygen when heated to redness, and leaves a residue of chloride of potassium. By this mode Gay-Lussac ascertained the composition of chloric acid, as stated in the preceding table. (An. de Chimie, xci.)

Its *eq. is* 75·42; *symb.* $Cl + 5O$, $\dot{\dot{C}}l$, or ClO_5.

Perchloric Acid.—The saline matter which remains in the retort after forming chlorous acid, is a mixture of perchlorate and bisulphate of potassa; and by washing it with cold water, the bisulphate is dissolved, and the perchlorate is left. Perchloric acid may be prepared from this salt by mixing it in a retort with half its weight of sulphuric acid, diluted with one-third of water, and applying heat to the mixture. At the temperature of about 284° F. white vapours rise, which condense as a colourless liquid in the receiver. This is a solution of perchloric acid.

The existence of perchloric acid was first ascertained by Count Stadion, who found it to be a compound of 2 volumes or 1 eq. of chlorine and 7 of oxygen; and this view of its constitution has been confirmed by Gay-Lussac, Serullas, and Mitscherlich. (An. de Ch. et Ph. viii. ix. xlvi. 297, and xlix. 113.) According to Serullas, it is a very stable compound: it may be heated with hydrochloric or sulphuric acid without change, does not set fire to organic substances, and is not decomposed by alcohol. When concentrated it has a density of 1·65, in which state it emits vapour when exposed to the air, absorbs hygrometric moisture powerfully, and boils at 392° F. By admixture with strong sulphuric acid and distilling, Serullas obtained it in the solid form, both massive and in elongated prisms. It hisses when thrown into water, like red-hot iron when quenched.

Of all the salts of perchloric acid, that with potassa is the most insoluble, requiring 65 times its weight of water at 60° for solution. This salt is readily and safely formed by adding chlorate of potassa, well dried and in fine powder, in small portions at a time, to an equal weight of concentrated sulphuric acid, gently warmed in an open vessel. The chlorous acid gas escapes without danger, and the chlorate is entirely converted into perchlorate and bisulphate of potassa, the latter of which, being very soluble, is easily removed by cold water. Serullas finds that chlorate of potassa, when decomposed by a low heat, is converted into chloride of potassium and perchlorate of potassa; but the temperature

must be carefully managed, otherwise the perchlorate itself would be resolved into oxygen and chloride of potassium. The perchlorate thus procured is purified by solution in hot water and crystallization.* It is distinguished from chlorate of potassa by not acquiring a yellow tint on the addition of hydrochloric acid. The primary form of its crystals, according to Mitscherlich, is a right rhomboidal prism isomorphus with premanganate of potassa.

Its eq. is 91·42; *symb.* Cl + 7O, Cl, or ClO_7.

[In reference to the oxygen compounds of chlorine it must be observed that our knowledge is far from being entirely complete. The recent elaborate researches of Gay-Lussac and Millon have tended to prove the existence of a greater number than has been heretofore recognized, and to modify our views respecting their constitution. These researches are still in progress and require confirmation. The following table presents the composition of these compounds according to the views of Millon.

Hypochlorous Acid,	ClO		
Chlorous Acid,	ClO_3		
Hypochloric Acid,	ClO_4	$= Cl_4O_{16}$	$= 3ClO_3 + ClO_7$
Chloric Acid,	ClO_5	$= Cl_2O_{10}$	$= ClO_3 + ClO_7$
Chlorochloric Acid,	Cl_3O_{13}	$= 2ClO_3 + ClO_7$	
Chloroperchloric Acid,	Cl_3O_{17}	$= ClO_3 + 2ClO_7$	
Perchloric Acid,	ClO_7]		

Quadrochloride of Nitrogen.—Hist. and Prep.—This compound was discovered by Dulong in 1811. Its elements have a feeble mutual affinity, and do not unite when presented to each other in their gaseous form. The condition which leads to their union is the decomposition of ammonia by chlorine, during which hydrochloric acid is generated by chlorine combining with the hydrogen of ammonia; while the nitrogen of that alkali, in its nascent state, enters into combination with another portion of chlorine. A convenient mode of preparing the quadrochloride of nitrogen is the following. An ounce of hydrochlorate of ammonia is dissolved in 12 or 16 ounces of hot water; and when the solution has cooled to the temperature of 90°, a glass bottle with a wide mouth, full of chlorine, is inverted in it. The solution gradually absorbs the chlorine, and acquires a yellow colour; and in about 20 minutes globules of a yellow fluid are seen floating like oil upon its surface, which, after acquiring the size of a small pea, sink to the bottom of the liquid. The drops of the chloride, as they descend, should be collected in a small saucer of lead, placed for that purpose under the mouth of the bottle. It is also readily obtained by suspending a fragment of sal-ammonia in a solution of hypochlorous acid.

Prop.—It is one of the most explosive compounds yet known, having been the cause of serious accidents both to its discoverer and to Davy. (Phil. Trans. 1813; An. de Ch. lxxxvi.) Its specific gravity is 1·653. It does not congeal in the intense cold produced by a mixture of snow and salt. It may be distilled

* All possibility of danger, as first shown by Professor Penny, is avoided by adding the chlorate to dilute nitric acid, and applying a gentle heat. The change which occurs is similar to that which takes place when sulphuric acid is used; but in this case the oxygen and chlorine are evolved merely in a state of mixture, and not in union as an explosive compound. The resulting salts, nitrate and perchlorate of potassa, are readily separated by water, on account of the much greater solubility of the former.—(R.)

at 160°; but at a temperature between 200° and 212° it explodes. It appears from the investigation of Messrs. Porrett, Wilson, and Kirk, that its mere contact with some substances of a combustible nature causes detonation even at common temperatures. This result ensues particularly with oils, both volatile and fixed. I have never known olive oil fail in producing the effect. The products of the explosion are chlorine and nitrogen. (Nicholson's Journal, xxxiv.)

Sir H. Davy analyzed chloride of nitrogen by means of mercury, which unites with chlorine, and liberates the nitrogen. He inferred from his analysis that its elements are united in the proportion of four measures of chlorine to one of nitrogen; and it hence follows that, by weight, it consists of 4 eq. of chlorine and 1 eq. of nitrogen. [Chemists are, however, still undecided, respecting the true constitution of this substance. From the researches of Millon, Kane, and others, it would appear to contain hydrogen, and may be a compound of chlorine and amidogen:—represented thus, NH_2, Cl.]

Perchloride of Carbon.—Hist. and Prep.—The discovery of this compound is due to Mr. Faraday. When olefiant gas (a compound of carbon and hydrogen) is mixed with chlorine, combination takes place between them, and an oil-like liquid is generated, which consists of chlorine, carbon, and hydrogen. On exposing this liquid in a vessel full of chlorine gas to the direct solar rays, the chlorine acts upon and decomposes the liquid, hydrochloric acid is set free, and the carbon, at the moment of separation, unites with the chlorine. (Phil. Trans. 1821.)

Prop.—Perchloride of carbon is solid at common temperatures, has an aromatic odour approaching to that of camphor, is a non-conductor of electricity, and refracts light very powerfully. Its sp. gr. is exactly double that of water. It fuses at 320°, and after fusion it is colourless and very transparent. It boils at 360°, and may be distilled without change, assuming a crystalline arrangement as it condenses. It is sparingly soluble in water, but dissolves in alcohol and ether, especially by the aid of heat. It is soluble also in fixed and volatile oils.

It burns with a red light when held in the flame of a spirit-lamp, giving out acid vapours and smoke; but the combustion ceases as soon as it is withdrawn. It burns vividly in oxygen gas. Alkalies do not act upon it; nor is it changed by the stronger acids, such as the hydrochloric, nitric, or sulphuric acids, even with the aid of heat. When its vapour, mixed with hydrogen, is transmitted through a red-hot tube, charcoal is separated, and hydrochloric acid gas evolved. On passing its vapour over the peroxides of metals, such as that of mercury and copper, heated to redness, a chloride of the metal and carbonic acid are generated. Protoxides, under the same treatment, yield carbonic oxide gas and metallic chlorides. Most of the metals decompose it also at the temperature of ignition, uniting with its chlorine, and causing deposition of charcoal.

The composition of the perchloride of carbon was inferred by Faraday from the proportions of chlorine and olefiant gas employed in its production, and from the quantity of chloride of copper and carbonic acid generated when its vapour was transmitted over oxide of copper at a red heat.

Its eq. is 118·50; *symb.* 2C + 3Cl, or $C_2 Cl_3$.

Protochloride of Carbon.—When the vapour of the perchloride is passed through a red-hot glass or porcelain tube, filled with fragments of rock crystal to increase the quantity of heated surface, partial decomposition occurs, chlorine gas escapes, and a vapour which, analyzed by Faraday, by means of oxide of copper, proved to be protochloride of carbon. At common temperatures it is a limpid colourless

liquid, which has a density of 1·5526, does not congeal at 0° F., and at 160° or 170° is converted into vapour. It may be distilled repeatedly without change; but when exposed to a red heat, some of it is resolved into its elements. In its chemical relations it is very analogous to perchloride of carbon.

Its eq. is 41·54; *symb.* C + Cl, or C Cl.

Dichloride of Carbon.—The first sample of this substance yet obtained was brought from Sweden by M. Julin, and is said to have been formed during the distillation of nitric acid from crude nitre and sulphate of iron. It occurs in small, soft, adhesive fibres of a white colour, which have a peculiar odour, somewhat resembling spermaceti. It fuses on the application of heat, and boils at a temperature between 350° and 450° F. At 250° it sublimes slowly, and condenses again in the form of long needles. It is insoluble in water, acids, and alkalies; but is dissolved by hot oil of turpentine or by alcohol, and forms acicular crystals as the solution cools. It burns with a red flame, emitting much smoke and fumes of hydrochloric acid gas. It has since been obtained among the products of the action of chlorine, aided by light, on some organic compounds.

The nature of this substance is shown by the following circumstances. When its vapour is exposed to a red heat, evolution of chlorine gas ensues, and charcoal is deposited. A similar deposition of charcoal is produced by heating it with phosphorus, iron, or tin; and a chloride is formed at the same time. Potassium burns vividly in its vapour with formation of chloride of potassium and separation of charcoal. On detonating a mixture of its vapour with oxygen gas over mercury, a chloride of that metal and carbonic acid are generated. By these means Phillips and Faraday ascertained its composition (An. of Phil. xviii. 150). *Its eq. is* 47·66; *symb.* 2C + Cl, or C_2 Cl.

Chlorocarbonic Acid Gas.—Hist. and Prep.—This compound was discovered in 1819 by John Davy, who described it in the Philosophical Transactions for that year, under the name of *phosgene gas.* (From φως *light*, and γενναω *to produce.*) It is made by exposing a mixture of equal measures of dry chlorine and carbonic acid gases to sunshine, when rapid but silent combination ensues, and they contract to one half their volume. Diffused day-light also affects their union slowly; but they do not combine at all when the mixture is wholly excluded from light.

Prop.—It is colourless gas, has a strong odour, and reddens dry litmus paper. It combines with four times its volume of ammoniacal gas, forming a white solid salt; so that it possesses the characteristic property of acids. It is decomposed by contact with water. One equivalent of each compound undergoes decomposition; and as the hydrogen of the water unites with chlorine, and its oxygen with carbonic oxide, the products are carbonic and hydrochloric acids. When tin is heated in this gas, chloride of tin is generated, and carbonic oxide gas set free, which occupies exactly the same space as the chlorocarbonic acid which was employed. A similar change occurs when it is heated in contact with antimony, zinc, or arsenic.

As chlorocarbonic acid gas contains its own volume of each of its constituents, it follows that 100 cubic inches of that gas at the standard temperature and pressure must weigh 106·806 grains; namely, 76·599 of chlorine added to 30·207 of carbonic oxide. Its sp. gr. is therefore 3·4427, and it consists of 35·42 parts or 1 eq. of chlorine, and 14·15 parts or 1 eq. of carbonic oxide.

Its eq. is 49·54; *symb.* C + O + Cl, or CO Cl.

Dichloride of Sulphur.—This compound was discovered in the year 1804 by

Thomson,* and was afterwards examined by Berthollet.† It is most conveniently prepared by passing a current of chlorine gas over flowers of sulphur gently heated, until nearly all the sulphur disappears. Direct combination ensues, and the product, distilled off from uncombined sulphur, is obtained under the form of a liquid which appears red by reflected, and yellowish green by transmitted light. Its density is 1·687. It is volatile below 200°, boils at 280°, yielding vapour which has a density of 4·70, and condenses again without change in cooling. When exposed to the air it emits acrid fumes, which irritate the eyes powerfully, and have an odour somewhat resembling sea-weed, but much stronger. Dry litmus paper is not reddened by it, nor does it unite with alkalies. It acts with energy on water:—mutual decomposition ensues, with formation of hydrochloric and hyposulphurous acids, and deposite of sulphur, by which the water is rendered cloudy. From a recent analysis by Rose it consists of 35·42 parts or 1 eq. of chlorine, and 32.2 parts or 2 eq. of sulphur (Pog. An. xxi. 431.)

Its eq. is 67·62; *symb.* 38 + Cl, or S_2 Cl.

Rose maintains that the preceding is the only chloride of sulphur, arguing that the chloride analyzed by Davy was merely dichloride of sulphur holding chloride in solution. Dumas, on the other hand, contends, that when sulphur is acted on by excess of chlorine, a chloride of sulphur is really obtained, which is apt to retain traces of the dichloride, and can only be purified by repeated distillation at about 140° F. This chloride is a liquid of a deep reddish brown tint, and has a density of 1·62. It boils at 147°, and the density of its vapour is between 3·67 and 3.70. By decomposition in water it should yield hydrochloric and hyposulphurous acids. (An. de Ch. et Ph. xlix. 205.)

Perchloride of Phosphorus.—There are two definite compounds of chlorine and phosphorus, the nature of which was first satisfactorily explained by Davy (Elements, p. 290). When phosphorus is introduced into a jar of dry chlorine, it inflames, and on the inside of the vessel a white matter collects, which is *perchloride of phosphorus.* It is very volatile, a temperature much below 212° being sufficient to convert it into vapour. Under pressure it may be fused, and it yields transparent prismatic crystals in cooling.

Water and perchloride of phosphorus mutually decompose each other; and the sole products are hydrochloric and phosphoric acids. Now, in order that these products should be formed, consistently with the constitution of phosphoric acid, as stated at page 206, the perchloride must consist of 31·4 parts or 2 eq. of phosphorus, and 177·1 parts or 5 eq. of chlorine. One equivalent of the chloride and 5 eq. of water will then mutually decompose each other without any element being in excess, and yield 1 eq. of phosphoric, and 5 eq. of hydrochloric acid. This proportion is not far from the truth; for, according to Davy, one grain of phosphorus is united in the perchloride with six of chlorine.

Its eq. is 206·4; *symb.* 2P + 5 Cl, or P_2Cl_5.

Sesquichloride of Phosphorus may be made either by heating the perchloride with phosphorus, or by passing the vapour of phosphorus over corrosive sublimate contained in a glass tube. It is a clear liquid like water, of sp. gr. 1·45; emits acid fumes when exposed to the air, owing to the decomposition of watery vapour; but when pure it does not redden dry litmus paper. On mixing it with water, mutual decomposition ensues, heat is evolved, and a solution of hydrochloric and phosphorous acids is obtained. It hence appears to consist of 31·4

* Nicholson's Journal, vol. vi. † Memoires de Arcueil, vol. i.

parts or 2 eq. of phosphorus, and 106·26 parts or 3 eq. of chlorine. *Its eq. is* 137·66; *symb.* 2P + 3Cl, or P_2Cl_3.

When hydrosulphuric acid gas is transmitted through a vessel containing perchloride of phosphorus, hydrochloric acid is disengaged, and a liquid produced which, according to Serullas, is a compound of three equivalents of chlorine, one of phosphorus, and one of sulphur. (An. de Ch. et Ph. xlii. 25.)

Terchloride of Boron.—Davy noticed that recently prepared boron takes fire spontaneously in an atmosphere of chlorine, and emits a vivid light; but he did not examine the product. Berzelius remarked, that if the boron has been previously heated, whereby it is rendered more compact, the combustion does not take place till heat is applied. This observation led him to expose boron, thus rendered dense, in a glass tube to a current of dry chlorine; and to heat it gently as soon as the atmospheric air was completely expelled, in order to commence the combustion. The resulting compound proved to be a colourless gas; and on collecting it over mercury, which absorbed free chlorine, he procured the chloride of boron in a state of purity. This gas is rapidly absorbed by water; but double decomposition takes place at the same instant, giving rise to hydrochloric and boracic acids as the sole products: from this fact is inferred the composition of the chloride; for 1 eq. of terchloride of boron or B + 3 Cl, and 3 eq. of water or 3(H + O), correspond to 1 eq. of boracic acid or B + 3O, and 3 eq. of hydrochloric acid or 3(H + Cl). The watery vapour of the atmosphere occasions a similar change; so that when the gas is mixed with air containing hygrometric moisture, a dense white cloud is produced. The sp. gr. of the gas, according to Dumas, is 3·942. It is soluble in alcohol, and communicates to it an ethereal odour, apparently by the action of hydrochloric acid. It unites with ammoniacal gas, forming a fluid volatile substance, the nature of which is unknown.—(Annals of Phil. xxvi. 129.)

Dumas finds that chloride of boron may be generated by the action of dry chlorine on a mixture of charcoal and boracic acid, heated to redness in a porcelain tube. Although neither charcoal nor chlorine can, when acting alone, decompose boracic acid, they do so readily by their united effort. According to Dumas, two volumes of chloride of boron, and three of carbonic oxide gas are formed. From these data chloride of boron may be considered as composed of 3 eq. vol. of chlorine and 1 eq. vol. of boron condensed into two volumes. Its sp. gr. is 4·079 (Dumas).

Despretz also appears to have invented a similar process. (Philos. Magazine and Annals, i. 469.)

Its eq. is 117·16; *eq. vol.* = 200; *symb.* B + 3Cl, or BCl_3.

Terchloride of Silicon.—When silicon is heated in a current of chlorine gas, it takes fire, and is rapidly volatilized. The product of the combustion condenses into a liquid, which appears to be naturally colourless, but to which an excess of chlorine communicates a yellow tint. This fluid is very limpid and volatile, and evaporates almost instantaneously in open vessels in the form of a white vapour. It boils at 124°, and bears a cold of zero without becoming solid. It has a suffocating odour not unlike that of cyanogen, and when put into water is converted into hydrochloric and silicic acids, the latter being easily obtained in a gelatinous form (Berzelius).

It may also be prepared by the method proposed by Oersted, which has been so successfully applied in the formation of other chlorides. It consists in mixing about equal parts of hydrated silicic acid and starch into a paste with oil,

heating the mass in a covered crucible so as to char the starch, introducing the mixture in fragments into a porcelain tube, and then transmitting through it a current of dry chlorine gas while the tube is kept at a red heat. The chlorine unites with silicium, while the charcoal and oxygen combine. The volatile chloride is then agitated with mercury to separate the free chlorine, and purified by distillation.

Its eq. is 128·76; *symb.* Si + 3Cl., or $SiCl_3$.

Chloro-nitrous Gas.—When fused chloride of sodium, potassium, or calcium, in powder, is treated with as much strong nitric acid as is sufficient to wet it, mutual decomposition ensues, and a new gas, composed of chlorine and binoxide of nitrogen, is generated. Its discoverer, Mr. E. Davy, describes it as a gas of a pale reddish yellow colour, of an odour similar to that of chlorine, though less pungent, and possessed of bleaching properties. It fumes on exposure to the air, and is freely absorbed by water. It is decomposed by sulphur, phosphorus, mercury, and most metals, and by substances in general which have an affinity for chlorine. It consists, according to Davy, of equal volumes of chlorine and binoxide of nitrogen, united without any condensation.

In the mutual decomposition of chloride of sodium and nitric acid, the products appear to be chloro-nitrous and chlorine gases, and nitrate of soda. Their formation must obviously depend on sodium being oxidized at the expense of nitric acid, while part of the chlorine unites, at the moment of separation from the sodium, with binoxide of nitrogen. (Phil. Mag. ix. 355.) Theoretically, it should be mixed with twice its volume of chlorine, the presence of which must materially obscure the properties of the new gas.

ON THE NATURE OF CHLORINE.

The change of opinion which has gradually taken place among chemists concerning the nature of chlorine, is a remarkable fact in the history of the science. The hypothesis of Berthollet, unfounded as it is, prevailed at one time universally. It explained phenomena so satisfactorily, and in a manner so consistent with the received chemical doctrine, that for some years no one thought of calling its correctness into question. A singular reverse, however, has taken place; and this hypothesis, though it has not hitherto been rigidly demonstrated to be erroneous, has within a short period been generally abandoned, even by persons who, from having adopted it in early life, were prejudiced in its favour. The reason of this will readily appear on comparing it with the opposite theory, and examining the evidence in favour of each.

Chlorine, according to the new theory, is maintained to be a simple body, because, like oxygen, hydrogen, and other analogous substances, it cannot be resolved into more simple parts. It does not indeed follow that a body is simple because it has not hitherto been decomposed; but as chemists have no other mode of estimating the elementary nature of bodies, they must necessarily adopt this one, or have none at all. Hydrochloric acid, by the same rule, is considered to be a compound of chlorine and hydrogen. For when exposed to the agency of galvanism, it is resolved into these substances; and by mixing the two gases in due proportion, and passing an electric spark through the mixture, hydrochloric acid gas is the product. Chemists have no other kind of proof of the composition of water, of potassa, or of any other compound.

Very different is the evidence in support of the theory of Berthollet. Accord-

ing to that view, hydrochloric acid gas is composed of *absolute muriatic acid* and water or its elements; chlorine consists of *absolute muriatic acid* and oxygen; and *absolute muriatic acid* is a compound of a certain unknown base and oxygen gas. Now all these propositions are gratuitous. For, in the first place, hydrochloric acid gas has not been proved to contain water. Secondly, the assertion that chlorine contains oxygen is opposed to direct experiment, the most powerful deoxidizing agents having been unable to elicit from that gas a particle of oxygen. Thirdly, the existence of such a substance as *absolute muriatic acid* is wholly without proof, and therefore its supposed base is also imaginary.

But this is not the only weak point of the doctrine. Since chlorine is admitted by this theory to contain oxygen, it was necessary to explain how it happens that no oxygen can be separated from it. For instance, on exposing chlorine to a powerful galvanic battery, oxygen gas does not appear at the positive pole, as occurs when other oxidized bodies are subjected to its action; nor is carbonic acid or carbonic oxide evolved, when chlorine is conducted over ignited charcoal. To account for the oxygen not appearing under these circumstances, it was assumed that *absolute muriatic acid* is unable to exist in an uncombined state, and therefore cannot be separated from one substance except by uniting with another. This supposition was thought to be supported by the analogy of certain compounds, such as nitric and oxalic acids, which appear to be incapable of existing except when combined with water or some other substance. The analogy, however, is incomplete; for the decomposition of such compounds, when an attempt is made to procure them in an insulated state, is manifestly owing to the tendency of their elements to enter into new combinations.

Admitting the various assumptions which have been stated, most of the phenomena receive as consistent an explanation by the old as by the new theory. Thus, when hydrochloric acid gas is resolved by galvanism into chlorine and hydrogen, it may be supposed that *absolute muriatic acid* attaches itself to the oxygen of the water, and forms chlorine; while the hydrogen of the water goes to the opposite pole of the battery. When chlorine and hydrogen enter into combination, the oxygen of the former may be said to unite with the latter; and that hydrochloric acid gas is generated by the water so formed combining with the *absolute muriatic acid* of the chlorine. The evolution of chlorine, which ensues on mixing hydrochloric acid and peroxide of manganese, is explained on the supposition that *absolute muriatic acid* unites directly with the oxygen of the black oxide of manganese.

It will not be difficult, after these observations, to account for the preference shown to the new theory. In an exact science, such as chemistry, every step of which is required to be matter of demonstration, there is no room to hesitate between two modes of reasoning, one of which is hypothetical, and the other founded on experiment. Nor is there, in the present instance, temptation to deviate from the strict logic of the science; for there is not a single phenomenon which may not be fully explained on the new theory, in a manner quite consistent with the laws of chemical action in general.

It was supposed, indeed, at one time, that the sudden decomposition of water, occasioned by the action of that liquid on the compounds of chlorine with some simple substances, constitutes a real objection to the doctrine; but it will afterwards appear, that the acquisition of new facts has deprived this argument of all its force. While nothing therefore can be gained, much may be lost by adopting the doctrine of Berthollet. If chlorine is regarded as a compound body, the

same opinion, though in direct opposition to the result of observation, ought to be extended to iodine and bromine; and as other analogous substances may hereafter be discovered, in regard to which a similar hypothesis will apply, it is obvious that this view, if proper in one case, may legitimately be extended to others. One encroachment on the method of strict induction would consequently open the way to another, and thus the genius of the science would eventually be destroyed.

An able attempt was made some years ago by the late Dr. Murray, to demonstrate the presence of water or its elements as a constituent part of hydrochloric acid gas, and thus to establish the old theory to the subversion of the new. The arguments which he used, though plausible and ingenious, were successfully combated by Sir H. and Dr. Davy. The only experiment which strictly bears upon the question—that, namely, where hydrochloric acid and ammoniacal gases were mixed together, goes far to demonstrate the absence of combined water in hydrochloric acid gas, and thereby to establish the views of Davy.*

SECTION XIII.

IODINE.

Hist.—Iodine was discovered in the year 1812 by M. Courtois, a manufacturer of saltpetre at Paris. In preparing carbonate of soda from the ashes of sea-weeds, he observed that the residual liquor corroded metallic vessels powerfully; and on investigating the cause of the corrosion, he noticed that sulphuric acid threw down a dark-coloured matter, which was converted by the application of heat into a beautiful violet vapour. Struck with its appearance, he gave some of the substance to M. Clément, who recognized it as a new body, and in 1813 described some of its leading properties in the Royal Institute of France. Its real nature was soon after determined by Gay-Lussac and Davy, each of whom proved that it is a simple non-metallic substance, exceedingly analogous to chlorine.†

Iodine is frequently met with in nature in combination with potassium or sodium. Under this form it occurs in many salt and other mineral springs, both in England, on the Continent, and in North America. It has been detected in the water of the Mediterranean, in the oyster and some other marine molluscous animals, in sponges, and in most kinds of sea-weed. In some of these productions, such as the *Fucus serratus* and *Fucus digitatus*, it exists ready formed, and according to Fyfe (Edin. Philos. Journal, i. 254) may be separated by the action of water; but in others it can be detected only after incineration. Marine animals and plants doubtless derive from the sea the iodine which they contain.

* In Nicholson's Journal, vols. xxxi. xxxii. and xxxiv. Edinburgh Philos. Trans. vol. viii. and Philos. Trans. for 1818.

† The original papers on this subject are in the Annales de Chimie, vols. lxxxviii. xc. and xci.; and in the Philos. Trans. for 1814 and 1815.

Vauquelin found it also in the mineral kingdom, in combination with silver. (An. de Ch. et Ph. xxix.)

Prep.—The iodine of commerce is procured from the impure carbonate of soda, called kelp, which is prepared in large quantity on the northern shores of Scotland, the Hebrides, and west coast of Ireland, by incinerating sea-weeds. The kelp is employed by soap-makers for the preparation of carbonate of soda; and the dark residual liquor remaining after that salt has crystallized, contains a considerable quantity of iodine, combined with sodium or potassium. By adding a sufficient quantity of sulphuric acid, hydriodic acid is first generated, and then decomposed. The iodine sublimes when the solution is boiled, and may be collected in cool glass receivers. A more convenient process is to employ a moderate excess of sulphuric acid, and then add to the mixture some peroxide of manganese, which acts on hydriodic in the same way as on hydrochloric acid (Phil. Mag. L. Ure). Another method, proposed by Soubeiran, is by adding to the ley from kelp a solution made with the sulphates of protoxides of copper and iron in the ratio of one of the former to $2\frac{1}{4}$ of the latter, as long as a white precipitate appears. The diniodide of copper is thus thrown down; and it may be decomposed either by peroxide of manganese alone, or by manganese and sulphuric acid. By means of the former, the iodine passes over quite dry; but a strong heat is requisite.

Prop.—Iodine, at common temperatures, is a soft friable opaque solid of a bluish-black colour, and metallic lustre. It occurs usually in crystalline scales, having the appearance of micaceous iron ore; but it sometimes crystallizes in large rhomboidal plates, the primitive form of which is a rhombic octohedron. The crystals are best prepared by exposing to the air a solution of iodine in hydriodic acid. Its sp. gr. according to Gay-Lussac, is 4·948; but Thomson found it only 3·0844. At 225° it is fused, and enters into ebullition at 347°; but when moisture is present, it is sublimed rapidly even below the degree of boiling water, and suffers a gradual dissipation at low temperatures. Its vapour is of an exceedingly rich violet colour, a character to which it owes the name of *Iodine*. (From Ἰώδης, violet-coloured.) This vapour is remarkably dense, its sp. gr. by calculation, page 140, being 8·7011, or 8·716 as directly observed by Dumas. Hence 100 cubic inches, at the standard temperature and pressure, must weigh 269·84 grains.

It is a non-conductor of electricity, and, like oxygen and chlorine, is a — electric. It has a very acrid taste, and its odour is almost exactly similar to that of chlorine, when much diluted with air. Its acts energetically on the animal system as an irritant poison, but is employed medicinally in very small doses with advantage.

It is very sparingly soluble in water, requiring about 7000 times its weight of that liquid for solution. It communicates, however, even in this minute quantity, a brown tint to the menstruum. Alcohol and ether dissolve it freely, and the solution has a deep reddish-brown colour.

Iodine possesses an extensive range of affinity. It destroys vegetable colours, though in a much less degree than chlorine. It manifests little disposition to combine with metallic oxides; but it has a strong attraction for the pure metals, and for most of the simple non-metallic substances, producing compounds which are termed *Iodides* or *Iodurets*. It is not inflammable; but under favorable circumstances may, like chlorine, be made to unite with oxygen. A solution of the pure alkalies acts upon it and gives rise to decomposition of water; whether an hypo-iodite and iodide are first produced, as in the case of chlorine, has not

yet been determined, but on the application of heat an iodate and iodide are formed.

Pure iodine is not influenced chemically by the imponderables. Exposure to the direct solar rays, or to strong shocks of electricity, does not change its nature. It may be passed through red-hot tubes, or over intensely ignited charcoal, without any appearance of decomposition; nor is it affected by the agency of galvanism. Chemists, indeed, are unable to resolve it into more simple parts, and consequently it is regarded as an elementary principle.

The violet hue of the vapour of iodine is for many purposes a sufficiently sure indication of its presence. A far more delicate test, however, was discovered by Colin and Gaultier de Claubry. They found that iodine has the property of uniting with starch, and of forming with it a compound insoluble in cold water, which is recognized with certainty by its deep blue colour. This test, according to Stromyer, is so delicate, that a liquid containing 1 — 450,000th of its weight of iodine receives a blue tinge from a solution of starch. Two precautions should be observed to insure success. In the first place, the iodine must be in a free state; for it is the iodine itself only, and not its compounds, which unites with starch. Secondly, the solution should be quite cold at the time of adding the starch; for hot water dissolves the blue compound, and forms a colourless solution. [A solution of bichloride of palladium, as first ascertained by Lasaigne, is also an exceedingly delicate test for iodine in any of its soluble compounds. It indicates its presence by forming a dark brown precipitate of iodide of palladium.]

Berzelius determined the equivalent of iodine by exposing fused iodide of silver to a current of chlorine gas, whereby the iodine was expelled and chloride of silver generated. Through the known composition of chloride of silver he inferred that of the iodide, and thence found the eq. of iodine. *It is* 126·3; *eq. vol.* = 100; *symb.* I.

The composition of the compounds of iodine described in this section is as follows:—

	Iodine.		Equiv.	Formulæ
Hydriodic Acid	126·3 1 eq. + 1	1 eq. hydrogen	=127.3.	H + I or HI.
Oxide of Iodine } Iodous Acid }	Composition unknown.			
Iodic Acid	126·3 1 eq. + 40	5 eq. oxygen	=166·3.	IO_5.
Periodic Acid	126·3 1 eq. + 56	7 eq. do.	=182·3.	IO_7.
Protochloride of Iodine	126·3 1 eq. + 35·42	1 eq. chlorine	=161·72.	ICl.
Terchloride do.	126·3 1 eq. + 106·26	3 eq. do	=232·56.	ICl_3.
Perchloride do.	Composition doubtful.			
Protiodide of Phos.	126·3 1 eq. + 15·7	1 eq. phosphs.	=142·0.	PI
Sesquiodide do.	378·9 3 eq. + 31.4	2 eq. do.	=410·3	P_2I_3.
Periodide do.	631·5 5 eq. + 31·4	2 eq. do.	=662·9.	P_2I_5.
Iodide of Sulphur	Composition unknown.			
Iodide of Carbon	Composition unknown.			
Periodide of Carbon	Composition unknown.			
Teriodide of Nitrogen	378·9 3 eq. + 14·15	1 eq. nitrogen	=293·05.	NI_3.

Hydriodic Acid.—Iodohydric Acid.—Prep.—This compound is formed by the direct union of its elements, when a mixture of hydrogen gas and iodine vapour are transmitted through a porcelain tube at a red heat. A more convenient pro-

cess, and by which it is obtained in a pure state, is by the action of water on the periodide of phosphorus. Any convenient quantity of the iodide is put into a small glass retort, together with a little water, and a gentle heat is applied. Mutual decomposition ensues; the oxygen of the water unites with phosphorus, and its hydrogen with iodine, giving rise to the formation of phosphoric and hydriodic acids, the latter of which passes over in the form of a colourless gas. The preparation of the iodide requires care; since phosphorus and iodine act so energetically on each other by mere contact, that the phosphorus is generally inflamed, and a great part of the iodine expelled in the form of vapour. This inconvenience is avoided by putting the phosphorus into a tube sealed at one end, about twelve inches long, displacing the air by a current of dry carbonic acid gas, then gradually adding the iodine, and promoting the action towards the close by a gentle heat. The materials should be well dried with bibulous paper, and the iodide preserved in a well-stopped dry vessel; for even atmospheric humidity gives rise to copious white fumes of hydriodic acid. The proportions usually employed are one part of phosphorus to about twelve of iodine. Another process has been recommended by F. d'Arcet, which consists in evaporating hypophosphorous acid until it begins to yield phosphuretted hydrogen, mixing it with an equal weight of iodine, and applying a gentle heat. Hydriodic acid gas of great purity is then rapidly disengaged; its production depending, as in the former process, on the decomposition of water.

Prop.—Hydriodic acid gas has a very sour taste, reddens vegetable blue colours without destroying them, produces dense white fumes when mixed with atmospheric air, and has an odour similar to that of hydrochloric acid gas. [Condensed into a liquid which may be frozen into a solid like ice under the influence of intense cold and pressure. (Page 53.)] The salts which it forms with alkalies are called *hydriodates*. Like hydrochloric acid gas, it cannot be collected over water; for that liquid dissolves it in large quantity.

It is decomposed by several substances which have a strong affinity for either of its elements. Thus oxygen gas, when heated with it, unites with its hydrogen, and liberates the iodine. Chlorine effects the decomposition instantly; hydrochloric acid gas is produced, and the iodine appears in the form of vapour. With strong nitrous acid it takes fire, and the vapour of iodine is set free. It is also decomposed by mercury. The decomposition begins as soon as hydriodic acid gas comes in contact with mercury, and proceeds steadily, and even quickly if the gas is agitated, till nothing but hydrogen remains. Gay-Lussac ascertained by this method that 100 measures of hydriodic acid gas contain precisely half their volume of hydrogen. Assuming it to consist of equal volumes of hydrogen gas and iodine vapour united without any condensation, then, since

			Grains.
50 cubic inches of the vapour of iodine weigh	. . .		134·92
50	do.	hydrogen gas	1·0684
100 cubic inches of hydriodic acid gas should weigh	. .		135·9884.

These numbers are obviously in the ratio of 1 to 126·3, the eq. of iodine and hydrogen. On the same principles the density of the gas should be 4·3850, which is probably more correct than 4·443, a number found experimentally by Gay-Lussac (An. de Ch. xci. 16.) From these coincidences there is no doubt

that 100 measures of hydriodic acid gas contain 50 measures of hydrogen gas and 50 of the vapour of iodine.

When the gas is conducted into water till that liquid is fully charged with it, a colourless acid solution is obtained, which emits white fumes on exposure to the air, and has a sp. gr. of 1·7. It may be prepared also by transmitting a current of hydrosulphuric acid gas through water in which iodine in fine powder is suspended; or by adding sulphuric acid in atomic proportion to a solution of iodide of barium (Glover.) The iodine, from having a greater affinity than sulphur for hydrogen, decomposes the hydrosulphuric acid; and hence sulphur is set free, and hydriodic acid produced. As soon as the iodine has disappeared and become colourless, it is heated for a short time to expel the excess of hydrosulphuric acid, and subsequently filtered to separate free sulphur.

The solution is readily decomposed. On exposure during a few hours to the atmosphere, the oxygen of the air forms water with the hydrogen of the acid, and sets iodine free. The solution is found to have acquired a yellow tint from the presence of uncombined iodine, and a blue colour is occasioned by the addition of starch. Nitric and sulphuric acid likewise decompose it by yielding oxygen, the former being at the same time converted into nitrous, and the latter into sulphurous acid. Chlorine unites directly with the hydrogen of the hydriodic acid, and hydrochloric acid is formed. The separation of iodine in all these cases may be proved in the way just mentioned. These circumstances afford a sure test of the presence of hydriodic acid, whether free or in combination with alkalies. All that is necessary, is to mix a cold solution of starch with the liquid, previously concentrated by evaporation if necessary, and then add a few drops of strong sulphuric acid. A blue colour will make its appearance if hydriodic acid is present.

Its eq. is 127·3; *eq. vol.* = 200; *symb.* H + I, or HI.

Oxide of Iodine and Iodous Acid.—On mixing the vapour of iodine and oxygen gas considerably heated, the violent tint of the former disappears, and a yellow matter of the consistence of solid oil is generated, which Sementini regards as oxide of iodine; and if the supply of oxygen be kept up after its formation, it is converted into a yellow liquid, which he supposes to be iodous acid. From the mode in which the process is described, there can scarcely be a doubt that some compound of iodine and oxygen is thus formed; but its composition and properties have not been satisfactorily made out. (Quarterly Journ. of Science, N. S. i. 478.) On dissolving iodine in a rather dilute solution of soda, until the solution begin to acquire a red tint, permanent crystals are obtained by spontaneous evaporation, in six-sided prisms, which dissolve in cold water without change, but by the action of water moderately heated, or by alcohol, are converted into iodate of soda and iodide of sodium. On the addition of an acid, iodine and iodic acid were set at liberty. From these facts Mitscherlich infers the crystals to be iodite of soda. (An. de Ch. et Ph. xxx. 84.) They are more probably the hypo-iodite.

Iodic Acid.—Hist. and Prep.—This acid was discovered at about the same time by Gay-Lussac and Davy; but the latter first succeeded in obtaining it in a state of perfect purity. When iodine is brought into contact with the euchlorine of Davy, immediate action ensues; the chlorine unites with one portion of iodine, and the oxygen with another, forming two compounds, a volatile orange-coloured matter, chloride of iodine, and a white solid substance, which is *iodic acid*. On applying heat, the former passes off in vapour, and the latter remains (Phil.

Trans. for 1815). Serullas has obtained it, in the form of hexagonal laminæ, by evaporating in a warm place its solution either in water, or in sulphuric or nitric acids. The method which he found most convenient is by forming a solution of iodate of soda in a considerable excess of sulphuric acid, keeping it at a boiling temperature for twelve or fifteen minutes, and then setting it aside to crystallize (Ann. de Ch. et Ph. xliii. 216). Iodic acid may also be formed by dissolving perchloride of iodine in water, and gradually adding a large quantity of strong sulphuric acid, a rise of temperature being at the same time prevented by the application of cold. Iodic acid will then be precipitated. The action of strong alcohol on moist perchloride produces the same result: water and the perchloride decomposed, and hydrochloric and iodic acids formed. The latter is left undissolved by the alcohol. Another process, suggested by Mr. Connell, of Edinburgh, is by boiling iodine in nitric acid. For this purpose a pure acid of density 1·5 should be introduced with about a fifth of its weight of iodine into a tube sealed at one end, about an inch wide and 15 inches long, and these materials be kept at a boiling temperature for at least twelve hours. As the iodine rises and condenses on the sides of the tube, it should be restored to the liquid, either by agitation, or by help of a glass rod. As soon as the iodine disappears, the nitric acid is dissipated by cautious evaporation. It is also obtained, as remarked by Balard, by the oxidizing effect of hypochlorous acid on iodine; the latter unites with the oxygen of the acid, and the chlorine escapes in the gaseous state.

Prop.—This compound, which was termed *oxiodine* by Davy, is *anhydrous iodic acid.* It is a white semitransparent solid, which has a strong astringent sour taste, but no odour. Its sp. gr. is considerable, as it sinks rapidly in sulphuric acid. When heated to the temperature of about 500° F. it is fused, and at the same time resolved into oxygen and iodine. In a dry air it is unchanged; but in a moist atmosphere it absorbs humidity, forming a hydrated acid, and eventually deliquesces. In water it is very soluble, and the solution has a distinct acid reaction: the bleaching power ascribed to it by Davy is said by Hiley not to be a property of pure iodic acid. (Lancet for July, 1833.) On evaporating the solution, a thick mass of the consistence of paste is left, which is hydrous iodic acid; and which, by the cautious application of heat, may be rendered anhydrous. It acts powerfully on inflammable substances. With charcoal, sulphur, sugar, and similar combustibles, it forms mixtures which detonate when heated. It enters into combination with metallic oxides, and the resulting salts are called *iodates.* These compounds, like the chlorates, yield pure oxygen by heat, and deflagrate when thrown on burning charcoal.

Iodic acid forms with the pure alkalies salts which are soluble in water; but with lime, baryta, strontia, and the oxides of lead and silver, it yields compounds of very sparing solubility. It is readily detected by the facility with which it is deoxidized, an effect readily produced by the sulphurous, phosphorous, hydriodic, and hydro-sulphuric acids. Iodine in each case is set at liberty, and may be detected as usual by starch. Hydrochloric and iodic acids decompose each other, water and chloride of iodine being generated.

Davy ascertained the composition of iodic acid by determining the quantity of oxygen which the acid loses when decomposed by heat; Gay-Lussac arrived at the same result by heating iodate of potassa, when pure oxygen was given off and iodide of potassium remained. *Its eq.* is 166·3; *symb.* $I + 5O$, $\dot{I}$, or IO_5.

Periodic Acid.—Hist. and Prep.—This compound has been lately discovered by Ammermüller and Magnus. (Pogg. Annalen, xxviii. 514.) When pure soda is mixed with a solution of iodate of soda, and chlorine gas is transmitted into it to saturation, a sparingly soluble white pulverulent salt is generated, which subsides after heating, and if necessary, concentrating the solution. This salt is a periodate of soda, the production of which appears to depend on the formation of chloride of sodium, and the union of the oxygen of the soda with the iodine of the iodic acid. For each equivalent of periodic acid, 2 eqs. of chloride of sodium should be generated; since the materials IO_5, 2NaO, 2Cl, just suffice for yielding IO_7, and 2NaCl. On dissolving the periodate of soda in dilute nitric acid, and adding nitrate of oxide of silver, the periodate of this oxide of a greenish-yellow colour subsides, which should be washed with water acidulated with nitric acid. This yellow salt is soluble in hot dilute nitric acid, and separates again on cooling in small shining straw-yellow crystals, which by digestion with warm water acquire, without dissolving, a reddish-brown almost black colour. If the nitric acid solution of the yellow salt is so far concentrated by evaporation that it crystallizes while still warm, orange-coloured crystals subside. These three salts are readily analyzed by exposure to a red heat in a glass tube, when iodine and metallic silver remain in the tube, and oxygen gas along with water, when water is present, is expelled. Their composition is as follows:—

	Oxide of Silver.	Periodic Acid.	Water.	Formulæ.
Yellow Salt	232 2 eq.	182·3 1 eq.	27 3 eq.	IO_7,2AgO, 3aq.
Red Salt	232 2 eq.	182·3 1 eq.	18 2 eq.	IO_7,2AgO, 2aq.
Orange Salt	116 1 eq.	182·3 1 eq.	0	IO_7,AgO.

The two former are therefore hydrated subperiodates of oxide of silver, and the latter a neutral periodate. This neutral salt has the peculiarity, that by pure cold water it is converted into the yellow subsalt, while the water takes up exactly half of its acid without a trace of silver. By this means a pure solution of periodic acid may be obtained.

Prop.—Periodic acid is analogous in composition to perchloric acid, and has decided acid properties. Its solution may be boiled without decomposition, and on evaporation the acid yields crystals, which do not change by exposure to the air. By hydrochloric acid it is reduced to iodic acid with disengagement of chlorine, and the same change will of course be produced by substances which decompose iodic acid. When the heat is increased beyond 212°, (the precise point is not stated,) periodic acid loses oxygen, and iodic acid remains. Thus is periodic more easy of decomposition than iodic acid. *Its eq.* is 182·3; *symb.* $\dddot{I} + 7O$, $\dddot{I}$, or IO_7.

Chlorides of Iodine.—Chlorine is absorbed at common temperatures by dry iodine with evolution of heat, and a solid compound of iodine and chlorine results, which was discovered both by Davy and Gay-Lussac. The colour of the product is orange-yellow when the iodine is fully saturated with chlorine, but is of a reddish-orange if iodine is in excess. It is converted by heat into an orange-coloured liquid, which yields a vapour of the same tint on increase of temperature. It deliquesces in the open air, and dissolves freely in water. Its solution is colourless, very sour to the taste, and reddens vegetable blue colours, but afterwards destroys them. From its acid properties Davy gave it the name

of *chloriodic acid*. Gay-Lussac, on the contrary, calls it *chloride of iodine*, conceiving that the acidity of its solution arises from the presence of hydrochloric and iodic acids, which he supposes to be generated by decomposition of water. From the observations of Serullas and Dumas, it appears that there exist two compounds of chlorine and iodine, by the different action of which on water the discordant opinions of Davy and Gay-Lussac may be explained.

This subject has lately been examined by Soubeiran. He has distinguished a compound of three eq. of chlorine and one eq. of iodine, but doubts the existence of the perchloride of iodine of Davy and Gay-Lussac (Journal de Pharmacie, Feb. 1837). This compound and a protochloride appears, however, to have been previously described by Kane (Phil. Mag. x. 430). The protochloride was obtained by passing a current of chlorine gas into water, in which iodine was diffused. A deep reddish-yellow solution is formed, which gives off fumes irritating to the eyes and nose, has a peculiar smell of both its constituents, and first reddens and then bleaches litmus paper. This terchloride was obtained by repeatedly distilling the protochloride; it may also be procured by adding to the protochloride a strong solution of corrosive sublimate, which throws down iodine. The perchloride is supposed to contain 5 eq. of chlorine and 1 eq. of iodine, from giving rise, when decomposed by water, to hydrochloric and iodic acids.

Teriodide of Nitrogen.—From the weak affinity that exists between iodine and nitrogen, these substances cannot be made to unite directly. But when iodine is put into a solution of ammonia, the alkali is decomposed; its elements unite with different portions of iodide, and thus cause the formation of hydriodic acid and iodide of nitrogen. The latter subsides in the form of a dark powder, which is characterized, like quadrochloride of nitrogen, by its explosive property. It detonates violently as soon as it is dried; and slight pressure, while moist, produces a similar effect. Heat and light are emitted during the explosion, and iodine and nitrogen are set free. According to the experiments of M. Colin, iodide of nitrogen consists of one eq. of nitrogen and three of iodine.

It is conveniently made, according to Serullas, by saturating alcohol of 0·852 with iodine, adding a large quantity of pure ammonia, and agitating the mixture. On diluting with water, teriodide of nitrogen subsides, which should be washed by repeated affusion of water and decantation. As thus prepared it is very finely divided, and may be pressed under water without detonating; but if, subsequently to its formation, it is put in contact with pure ammonia, it will afterwards detonate with the same facility as that prepared in the usual manner. Water and teriodide of nitrogen mutually decompose each other, giving rise to the formation of hydriodic and iodic acids and ammonia. The change takes place slowly in cold water; but it is completed in a few minutes, and with scarcely any disengagement of nitrogen, when gentle heat is applied. When a little nitric or sulphuric acid is used, ammonia and iodic acid are alone produced. (An. de Ch. et Ph. xlii. 201.)

Its eq. 393·05; *symb.* $N + 3I$, or NI_3.

Iodides of Phosphorus.—Iodine and phosphorus combine readily in the cold, evolving so much heat as to kindle the phosphorus, if the experiment is made in the open air; but in close vessels no light appears. One of these compounds, apparently a protiodide, is formed of one part of phosphorus and 7 or 8 parts of iodine. It has an orange colour, fuses at 212°, sublimes unchanged by heat, and

is decomposed by water, with the elements of which it gives rise to hydriodic and phosphorous acids, while phosphorus is set free. *Its eq. is* 142·0; *symb.* P + I, or PI.

The sesquiodide is formed by the action of 1 part of phosphorus and 12 of iodine. It appears as a dark grey crystalline mass, fusible at 84°, and yields with water hydriodic and phosphorous acids, from which circumstance its elements are supposed to be in the ratio of 2 eq. of phosphorus to 3 eq. of iodine. *Its eq. is* 410·3; *symb.* 2P + 3I, or P_2I_3.

The periodide is prepared with 1 part of phosphorus and 20 of iodine, and is a black compound, fusible at 114°. As by the action of water it yields hydriodic and phosphoric acids only, it is inferred to contain phosphorus and iodine in the ratio of 2 eq. to 5 eq. Thus

1 eq. periodide Phos. & 5 eq. water	yield	1 eq. Phos. Acid. & 5 eq. Hydriodic Acid.
P_2I_5+5HO		P_2O_5+5HI.

Its eq. is 662·9; *symb.* 2P + 5I, or P_2I_5.

Iodide of Sulphur.—This compound is formed by heating gently 4 parts of iodine with 1 of sulphur. The product has a dark colour and radiated appearance, like antimony, its elements are easily disunited by heat.

SECTION XIV.

BROMINE.

Bromine was discovered in 1826 by Balard of Montpellier. The name originally applied to it was *muride*, but the term *brome* or *bromine*, from βρωμος *graveolentia*, signifying a strong or rank odour, has since been substituted (An. of Phil. xviii. 381).

Bromine in its chemical relations bears a close analogy to chlorine and iodine, and has hitherto been always found in nature associated with the former, and sometimes also with the latter. It exists in sea-water in the form of bromide of sodium or magnesium. Its relative quantity, however, is very minute; and even the uncrystallizable residue called *bittern*, left after chloride of sodium has been separated from sea-water by crystallization, contains it in small proportion. It may apparently be regarded as an essential ingredient of the saline matter of the ocean; for it has been detected in the waters of the Mediterranean, Baltic, North Sea, and Frith of Forth. It has also been found in the waters of the Dead Sea, and in a variety of salt springs in Germany. Daubeny has detected it in several mineral springs in England, and states that it is rarely wanting in those springs which contain much common salt, except that of Droitwich in Worcestershire. Balard found that it exists in marine plants growing on the shores of the Mediterranean, and has procured it in appreciable quantity from the ashes of sea-weeds that furnish iodine. He has likewise detected its presence in the ashes of some animals, especially in those of the *Janthina violacea*, one of the testaceous mollusca.

Prep.—Bromine is usually extracted from bittern, and its mode of preparation is founded on the property which chlorine possesses of decomposing hydrobromic acid, uniting with its hydrogen, and setting bromine at liberty. Accordingly, on adding chlorine to bittern, the free bromine immediately communicates an orange-yellow tint to the liquid; and on heating the solution to its boiling point, the red vapours of bromine are expelled, and may be condensed by being conducted into a tube surrounded with ice. It was this change of colour produced by chlorine that led to the discovery of bromine. The method recommended by Balard for procuring this substance, as well as for detecting the presence of hydrobromic acid, is to transmit a current of chlorine gas through bittern, and then to agitate a portion of sulphuric ether with the liquid. The ether dissolves the whole of the bromine, from which it receives a beautiful hyacinth-red tint, and on standing it rises to the surface. When the ethereal solution is agitated with caustic potassa, its colour entirely disappears, owing to the formation of bromide of potassium and bromate of potassa, the former of which is obtained in cubic crystals by evaporation. The bromine may then be set free by means of chlorine, or still better by sulphuric acid and the peroxide of manganese. The process should be conducted in a retort, the beak dipping into cold water, which collects the bromine driven over by heat. Balard has subsequently improved the process so much, that it is now produced in considerable quantity, and sold in Paris as an article of commerce.

Prop.—At common temperatures bromine is a liquid, the colour of which is blackish-red when viewed in mass and by reflected light, but appears hyacinth-red when a thin stratum is interposed between the light and the observer. Its odour, which somewhat resembles that of chlorine, is very disagreeable, and its taste powerful. Its sp. gr. is about 3. By a temperature between zero and -4° it is congealed, and in that state is brittle. Its volatility is considerable; for at common temperatures it emits red-coloured vapours, which are very similar in appearance to those of nitrous acid; and at $116{\cdot}5^\circ$ it enters into ebullition. The sp. gr. of its vapour was found by Mitscherlich to be 5·54, and the number calculated (p. 140) from its equivalent is 5·3930: 100 cubic inches at 60° and 30 inches B. should weigh 167·25 grains. It is a non-conductor of electricity, and undergoes no chemical change whatever from the agency of the imponderables. It may be transmitted through a red-hot glass tube, and be exposed to the agency of galvanism, without evincing the least trace of decomposition. Like oxygen, chlorine, and iodine, it is a negative electric. It is soluble in water, alcohol, and ether, the latter being its best solvent. It does not redden litmus paper, but bleaches it rapidly like chlorine; and it likewise discharges the blue colour from a solution of indigo. Its vapour extinguishes a lighted taper; but before going out, it burns for a few seconds with a flame which is green at its base and red at its upper part. Some inflammable substances take fire by contact with bromine, in the same manner as when introduced into an atmosphere of chlorine. It acts with energy on organic matters, such as wood or cork, and corrodes the animal texture; but if applied to the skin for a short time only, it communicates a yellow stain, which is less intense than that produced by iodine, and soon disappears. To animal life it is highly destructive, one drop of it placed on the beak of a bird having proved fatal.

From the close resemblance observable between chlorine and bromine, Balard was of course led to examine its relations with hydrogen, and found that these substances may readily be made to unite; the product of the combination being

a gas very similar to hydrochloric and hydriodic acid gases, whence it has received the name of *hydrobromic* acid gas. In its action on metals, also, bromine presents the closest similarity to that which chlorine exerts on the same substances. Antimony and tin take fire by contact with bromine; and its union with potassium is attended with such intense heat as to cause a vivid flash of light, and often to burst the vessel in which the experiment is performed. Its affinity for metallic oxides is feeble. By the action of alkalies it is resolved into hydrobromic and bromic acids, suffering the same kind of change as chlorine or iodine when similarly treated.

According to all the experiments hitherto made, bromine appears to be an element. It is so very similar in most aspects to chlorine and iodine, and in the order of its chemical relations is so constantly intermediate between them, that Balard at first supposed it to be some unknown compound of these substances. There seems, however, to be no good ground for the supposition; but, on the contrary, an experiment performed by De la Rive affords a very strong argument against it. He finds that when a compound of bromine and iodine is mixed with starch, and exposed to the influence of galvanism, bromine appears at the + and iodine at the — wire, where the starch acquires a blue tint. On making the experiment with bromine containing a little bromide of iodine, the same appearance ensues; but if iodine is not previously added, the starch does not receive a tint of blue.

Bromine is in most cases easily detected by means of chlorine; for this substance displaces bromine from its combination with hydrogen, metals, and most other bodies. The appearance of its vapour or the colour of its solution in ether will then render its presence obvious. Like chlorine, it forms a crystalline hydrate when exposed to 32° F. in contact with water. The crystals are octohedral, of a beautiful red tint, and suffer decomposition at 54°. (Löwig.)

Berzelius determined the equivalent of bromine in the same way as that of iodine, namely, by heating a known weight of bromide of silver in a current of chlorine gas, so as to displace the bromine and obtain chloride of silver.

Its eq. is 78·4; *eq. vol.* = 100; *symb.* Br.

The compounds of bromine described in this section are as follows:—

	Bromine.		Equiv.		Formulæ.
Hydrobromic Acid .	78·4	1 eq. + Hydrogen	1	1 eq. = 79·4.	HBr.
Bromic Acid . .	78·4	1 eq. + Oxygen	40	5 eq. = 118·4.	BrO_5.
Chloride of Bromine	Composition uncertain.				
Bromides of Iodine	Composition uncertain.				
Bromide of Sulphur	Composition uncertain.				
Protobromide of Phosp.	78·4	1 eq. + phosph.	15.7	1 eq. = 94·1.	PBr.
Perbromide of Phosp.	392	5 eq. + do.	31·4	2 eq. = 423·4.	P_2B_5.
Bromide of Carbon	Composition uncertain.				
Terbromide of Silicon	235·2	3 eq. + Silicon	22·5	1 eq. = 257·7.	$SiBr_3$.

Hydrobromic Acid, Bromohydric Acid.—Prep.—No chemical action takes place between the vapour of bromine and hydrogen gas at common temperatures, not even by the agency of the direct solar rays; but on introducing a lighted candle, or a piece of red-hot iron, into the mixture, combination ensues in the vicinity of the heated body, though without extending to the whole mixture, and w ithout explosion. The combination is readily effected by the action of bromine on some of the gaseous compounds of hydrogen. Thus, on mixing the vapour of

bromine with hydriodic acid, hydrosulphuric acid, or phosphuretted hydrogen gases, decomposition ensues, and hydrobromic acid gas is generated. It may be conveniently made for experimental purposes by a process similar to that for forming hydriodic acid. A mixture of bromine and phosphorus, slightly moistened, yields, by the aid of gentle heat, a large quantity of pure hydrobromic acid gas, which should be collected either in dry glass bottles, or over mercury.

Prop.—It is a colourless gas, has an acid taste, and pungent odour. It irritates the glottis powerfully, so as to excite cough, and when mixed with moist air, yields white vapours, which are denser than those occasioned under the same circumstances by hydrochloric acid gas. [May be liquified and converted into a solid by cold and pressure (page 53)]. It undergoes no decomposition when transmitted through a red-hot tube, either alone, or mixed with oxygen. It is not affected by iodine; but chlorine decomposes it instantly, with production of hydrochloric acid gas, and deposition of bromine. It may be preserved without change over mercury; but potassium and tin decompose it with facility, the former at common temperatures, and the latter by the aid of heat. It is very soluble in water. The aqueous solution may be made by treating bromine with hydrosulphuric acid dissolved in water, or still better, by transmitting a current of hydrobromic acid gas into pure water. The liquid becomes hot during the condensation, acquires great density, increases in volume, and emits white fumes when exposed to the air. This acid solution is colourless when pure, but possesses the property of dissolving a large quantity of bromine, and then receives the tint of that substance.

Chlorine decomposes the solution of hydrobromic acid in an instant. Nitric acid likewise acts upon it, though less suddenly, occasioning the disengagement of bromine, and probably the formation of water and nitrous acid. Nitro-hydrobromic acid is analogous to *aqua regia*, and possesses the property of dissolving gold. The elements of sulphuric and hydrobromic acids react on each other in a slight degree; and hence, on decomposing bromide of potassium by sulphuric acid, the hydrobromic is generally mixed with a little sulphurous acid gas.

The composition of hydrobromic acid gas is easily inferred from the two following facts. 1. On decomposing hydrobromic acid gas by potassium, a quantity of hydrogen remains, precisely equal to half the volume of the gas employed; and, 2, when hydriodic acid gas is decomposed by bromine, the resulting hydrobromic acid occupies the very same space as the gas which is decomposed. Hence hydrobromic is analogous to hydriodic and hydrochloric acid gases, in containing equal measures of bromine vapour and hydrogen gas united without any change of volume; and since

			Grains.
50	cubic inches of	Bromine vapour weigh	83·64
50	do.	Hydrogen gas	1·0684
100	do.	Hydrobromic acid must weigh . .	84·7084

These numbers are in the ratio of 1 to 78·4, which is the composition of the gas by weight. Its sp. gr. is 2·731.

Since bromine decomposes hydriodic, and chlorine hydrobromic acid, bromine, in relation to hydrogen, is intermediate between chlorine and iodine; for it has a stronger affinity for hydrogen than iodine, and a weaker than chlorine. The affinity of bromine and oxygen for hydrogen appears nearly similar; for while

oxygen cannot detach hydrogen from bromine, bromine does not decompose watery vapour.

The salts of hydrobromic acid are termed *hydrobromates*. Like the free acid, they are decomposed, and the presence of bromine is detected, by means of chlorine. On mixing a soluble bromide with the nitrates of the protoxides of lead, silver, and mercury, white precipitates are obtained, which are very similar in appearance to the chlorides of those metals, but which are metallic bromides. On the addition of chlorine, the vapour of bromine is evolved.

Its eq. is 79·4; *eq. vol.* = 200; *symb.* H + Br, or H Br.

Bromic Acid.—Prep.—The only compound yet known of bromine and oxygen is that formed by the action of bromine on potassa, when a change exactly similar to that produced by chlorine (page 226) ensues, whereby bromide of potassium and bromate of potassa are generated; and the latter, being much less soluble than the former, is readily separated by evaporation. The bromate of the other alkalies and alkaline earths may be prepared in a similar manner.

The acid may be procured in a separate state by decomposing a dilute solution of bromate of baryta with sulphuric acid, so as to precipitate the whole of the baryta. The resulting solution of bromic acid may be concentrated by slow evaporation until it acquire the consistence of syrup; but on raising the temperature, in order to expel all the water, one part of the acid is volatilized, and the other resolved into oxygen and bromine. A similar result took place when the evaporation was conducted *in vacuo* with sulphuric acid; and accordingly all attempts to procure anhydrous bromic acid have hitherto failed.

Prop.—Bromic acid has scarcely any odour, but its taste is very acid, though not at all corrosive. It reddens litmus paper powerfully at first, and soon after destroys its colour. It is not affected by nitric or sulphuric acids except when the latter is highly concentrated, in which case bromine is set free, and effervescence, probably owing to the escape of oxygen gas, ensues. From the analysis of bromate of potassa, bromic acid is obviously similar in constitution to iodic, chloric, and nitric acids; that is, it consists of one equivalent of bromine united with five of oxygen. Its salts are analogous to the chlorates and iodates. Thus bromate of potassa is converted by heat into bromide of potassium, with disengagement of pure oxygen gas, deflagrates like nitre when thrown on burning charcoal, and forms with sulphur a mixture which detonates by percussion. The acid of the bromates is decomposed by deoxidizing agents, such as sulphurous and hydrosulphuric acids, in the same manner as the acids of the iodates. The bromates likewise suffer decomposition from the action of hydrobromic and hydrochloric acids.

Bromate of potassa is said not to precipitate the salts of lead, but to occasion a white precipitate with nitrate of silver, and a yellowish white with protonitrate of mercury; characters which, if true, serve as a good test to distinguish bromate from iodate and chlorate of potassa.

Its eq. is 118·4; *symb.* Br + 5O, $\dot{\dot{\text{B}}}\text{r}$, or BrO_5.

Chloride of Bromine.—This compound may be formed at common temperatures by transmitting a current of chlorine through bromine, and condensing the disengaged vapours by means of a freezing mixture. The resulting chloride is a volatile fluid of a reddish yellow colour, much less intense than that of bromine; its odour is penetrating, and causes a discharge of tears from the eyes; and its taste very disagreeable. Its vapour is a deep yellow, like chlorous acid, and it

enables metals to burn as in an atmosphere of chlorine, doubtless giving rise to the formation of metallic chlorides and bromides.

Chloride of bromine is soluble in water without decomposition; for the solution possesses the colour, odour, and bleaching properties of the compound, and discharges the colour of litmus paper without previously reddening it. By the action of the alkalies it is decomposed, being converted, by means of the elements of water, into hydrochloric and bromic acids.

Bromide of Iodine.—These substances act readily on each other, and appear capable of uniting in two proportions. The protobromide is a solid, convertible by heat into a reddish-brown vapour, which, in cooling, condenses into crystals of the same colour, and of a form resembling that of fern leaves. An additional quantity of bromine converts these crystals into a fluid, which in appearance is like a strong solution of iodine in hydriodic acid. This compound dissolves without decomposition in water, but with the alkalies yields hydrobromic and iodic acids. The existence of two bromides of iodine can scarcely be regarded as satisfactorily established.

Bromide of Sulphur.—On pouring bromine on sublimed sulphur, combination ensues, and a fluid of an oily appearance and reddish tint is generated. In odour it somewhat resembles chloride of sulphur, and like that compound emits white vapours when exposed to the air; but its colour is deeper. It reddens litmus paper faintly when dry, but strongly if water is added. Cold water acts slowly upon bromide of sulphur; but at a boiling temperature the action is so violent that a slight detonation occurs, and three compounds, hydrobomic, hydrosulphuric, and sulphuric acids are formed. The formation of these substances is of course attributable to decomposition of water, and the union of its elements with bromine and sulphur. Bromide of sulphur is likewise decomposed by chlorine, which unites with sulphur, and displaces bromine.

The composition of bromide of sulphur is unknown. It dissolves an excess both of chlorine and sulphur, and its elements separate from each other so readily, that it has hitherto been impracticable to procure a definite compound.

Bromide of Phosphorus.—When bromine and phosphorus are brought into contact in a flask filled with carbonic acid gas, they act suddenly on each other with evolution of heat and light, and two compounds are generated; one, a crystalline solid, which is sublimed and collects in the upper part of the flask; and the other, a fluid, which remains at the bottom. The former contains the most bromine, and the latter is supposed by Balard to consist of single equivalents of its elements.

The protobromide retains its liquid form even at 52° F. It is readily converted into vapour by heat, and on exposure to the air emits penetrating fumes. It reddens litmus paper faintly, an effect which is probably owing to the presence of moisture. With water it acts energetically and with free disengagement of heat, hydrobromic acid gas being evolved when only a few drops of water are employed; but if a large quantity is used, the gas is dissolved, and the acid solution leaves by evaporation a residuum, which burns slightly when dried, and is converted into phosphoric acid.

The perbromide is yellow in its solid state; but with gentle heat it becomes a red-coloured liquid, which by increase of temperature is converted into a vapour of the same tint. On cooling after fusion it yields rhombic crystals: but when its vapour is condensed, the crystals are acicular. It is decomposed by metals, probably with the formation of metallic bromides and phosphurets. It emits

dense penetrating fumes on exposure to the air, and with water gives rise to the production of hydrobromic and phosphoric acids. Hence its elements should be in the ratio of 2 eqs. of phosphorus to 5 eqs. of bromine.

Chlorine has a greater affinity for phosphorus than bromine, and decomposes both the bromides with evolution of the vapour of bromine. These compounds are not decomposed by iodine; but, on the contrary, bromine decomposes iodide of phosphorus.

Terbromide of Silicon.—This compound was made by Serullas in precisely the same mode as that described by forming the terchloride. When purified from free bromine by mercury, and re-distilled, it is a colourless liquid, which emits dense vapours in an open vessel, being decomposed by the moisture of the air, and is denser than strong sulphuric acid. At 302° it enters into ebullition, and freezes at 10°. Potassium, when gently heated, acts on it with such energy that detonation ensues. By water it is resolved into hydrobromic and silicic acids. (Phil. Mag. and Annals, xi. 295.) *Its eq. is* 257·7; *symb.* Si + 3Br, or Si Br_3.

SECTION XV.

FLUORINE.

The substance to which this name is applied, though long known to exist in various compounds, has only recently been obtained in an insulated form, and therefore the properties peculiar to it in that state are but imperfectly known. It was first procured by Baudrimont by passing fluoride of boron over minium heated to redness, and receiving the gas in a dry vessel. As it is mixed with a large quantity of oxygen, his present method is to treat a mixture of fluoride of calcium and peroxide of manganese with strong sulphuric acid. This process, however, does not give a pure gas, as hydrofluoric and fluosilicic acid gases are at the same time evolved. The presence of the latter do not prevent the observation of some of the properties of fluorine. It is a gas of a yellowish-brown colour; its odour resembles chlorine and burnt sugar; it bleaches. It does not act on glass, but combines directly with gold (Phil. Mag. x. 149). The latter fact is confirmed by the observations of Messrs. Knox, who have succeeded so far in the preparation of fluorine as to leave no doubt of its existence as a coloured gas (Phil. Mag. x. 107). Its sp. gr. is 1·289. From the nature of its compounds it appears to belong to the class of negative electrics, and, like oxygen and chlorine, to have a powerful affinity for hydrogen and metallic substances. Berzelius determined its eq. by finding that 100 parts of pure fluoride of calcium yield with sulphuric acid 175 parts of sulphate of lime. *Its eq. is* 18·68; *eq. vol.* = 100; symb. F.

The compounds of fluorine described in this section are the following:—

	Fluorine.	Equiv.	Formulæ.
Hydrofluoric acid	18·68 1 eq. + Hydrogen	1.	1 eq. = 19·68. HF.
Fluoboric acid	56·08 3 eq. + Boron	10·9	1 eq. = 66·98. BF_3.
Fluosilicic acid	56·08 3 eq. + Silicon	22·5	1 eq. = 78.58 SiF_3.

Hydrofluoric Acid.—Fluohydric Acid.—Hist. and Prep.—This acid was first procured in its pure state in the year 1810 by Gay-Lussac and Thenard, and described in the second volume of their *Recherches Physico-Chimiques*. It is prepared by acting on the mineral called *fluor-spar*, which is a fluoride of calcium, carefully separated from siliceous earth and reduced to fine powder, with twice its weight of concentrated sulphuric acid. The mixture is made in a leaden retort; and on applying heat, an acid and highly corrosive vapour distils over, which must be collected in a receiver of the same metal surrounded with ice. As the materials swell up considerably during the process, owing to a quantity of vapour forcing its way through a viscid mass, the retort should be capacious. At the close of the operation pure hydrofluoric acid is found in the receiver, and the retort contains dry sulphate of lime. The chemical changes are precisely the same as in the formation of hydrochloric acid gas at page 220, fluorine being substituted for chlorine and calcium for sodium. Thus in symbols CaF and HO, SO_3 = HF and CaO, SO_3. If the oil of vitriol is of sufficient strength, all its water is decomposed, and the resulting hydrofluoric acid is anhydrous.

Prop.—It is at 32° a colourless fluid, and remains in that state at 59° if preserved in well-stopped bottles; but when exposed to the air, it flies off in dense white fumes, which consist of the acid vapour combined with the moisture of the atmosphere. Its sp. gr. is 1·0609; but its density may be increased to 1·25 by gradual additions of water. Its affinity for this liquid far exceeds that of the strongest sulphuric acid, and the combination is accompanied with a hissing noise, as when red-hot iron is quenched by immersion in water.

Its vapour is much more pungent than chlorine or any of the irritating gases. Of all known substances, it is the most destructive to animal matter. When a drop of the concentrated acid of the size of a pin's head comes in contact with the skin, instantaneous disorganization ensues, and deep ulceration of a malignant character is produced. On this account the greatest care is requisite in its preparation. It acts energetically on glass. The transparency of the glass is instantly destroyed, heat is evolved, and the acid boils, and in a short time entirely disappears. A colourless gas, commonly known by the name of *fluo-silicic acid gas*, is the sole product. This compound is always formed when hydrofluoric acid comes in contact with a siliceous substance. For this reason it cannot be preserved in glass; but must be prepared and kept in metallic vessels. Those of lead, from their cheapness, are often used; but vessels of silver or platinum are preferable. In consequence of its powerful affinity for siliceous matter, hydrofluoric acid may be employed for etching on glass; and when used with this intention, it should be diluted with three or four times its weight of water.

Hydrofluoric acid has all the usual characters of a powerful acid. It has a strong sour taste, reddens litmus paper, and neutralizes alkalies, either forming salts termed *hydrofluates*, or most generally giving rise to metallic fluorides. All these compounds are decomposed by strong sulphuric acid with the aid of heat, and the hydrofluoric acid while escaping may be detected by its action on glass.

On some of the metals it acts violently, especially on the bases of the alkalies. Thus when potassium is brought in contact with the concentrated acid, an explosion attended with heat and light ensues; hydrogen gas is disengaged, and a white compound, fluoride of potassium, is generated. It is a solvent for some elementary principles which resist the action even of nitro-hydrochloric acid. Thus it dissolves silicon, zirconium, and columbium, with evolution of hydrogen gas; and when mixed with nitric acid, it proves a solvent for silicon which has

been condensed by heat, and for titanium. Nitro-hydrofluoric acid, however, is incapable of dissolving gold and platinum. Several oxidized bodies, which are not attacked by sulphuric, nitric, or hydrochloric acid, are readily dissolved by hydrofluoric acid. As examples of this fact, several of the weaker acids, such as silica, or silicic acid, titanic, columbic, molybdic, and tungstic acids may be enumerated. (Berzelius.)

A different view of the compounds of fluorine was originally taken by Gay-Lussac and Thenard, and is still held by some chemists. They adopted the opinion that hydrofluoric acid is a compound of a certain inflammable principle and oxygen, and applied to it the name of *fluoric acid*, previously introduced by Scheele. Fluor-spar on this view is a fluate of lime, and when this salt is decomposed by oil of vitriol, the fluoric is merely displaced by the sulphuric acid, and the former passes off combined with the water of the latter. What I have described as anhydrous hydrofluoric acid is, according to this hypothesis, hydrated fluoric acid; and when acted upon by potassium, this metal is oxidized at the expense of the water, and potassa thus generated unites with fluoric acid, forming, not fluoride of potassium, but fluate of potassa. The equivalent of fluoric acid, as inferred from the analysis of Berzelius, is 10·68; for 39·18 parts or one equivalent of fluor-spar is supposed to contain 28·5 parts of lime (20·5 calcium and 8 oxygen), thus leaving 10·68 as the equivalent of the acid.

The theory, according to which fluor-spar is a compound of fluorine and calcium, originated as a suggestion with M. Ampère of Paris, and was afterwards supported experimentally by Davy. It was found that pure hydrofluoric acid evinces no sign of containing either oxygen or water. Charcoal may be intensely heated in the vapour of the acid without the production of carbonic acid. When hydrofluoric acid was neutralized with dry ammoniacal gas, a white salt resulted, from which no water could be separated; and on treating this salt with potassium, no evidence could be obtained of the presence of oxygen. On exposing the acid to the agency of galvanism, there was a disengagement at the negative pole of a small quantity of gas, which from its combustibility was inferred to be hydrogen; while the platinum wire of the opposite side of the battery was rapidly corroded, and became covered with a chocolate coloured powder. Davy explained these phenomena by supposing that hydrofluoric acid was resolved into its elements; and that fluorine, at the moment of arriving at the positive side of the battery, entered into combination with the platinum wire which was employed as a conductor. Unfortunately, however, he did not succeed in obtaining fluorine in an insulated state. Indeed, from the noxious vapours that arose during the experiment, it was impossible to watch its progress, and examine the different products with that precision which is essential to the success of minute chemical inquiries, and which Davy has so frequently displayed on other occasions.

Though these researches led to no conclusive result, they afforded so strong a presumption in favour of the opinion of Ampère and Davy, that it was adopted by several other chemists. This view has received strong additional support from the experiments of M. Kuhlman. (Quarterly Journal of Science for July 1827, p. 255.) It was found by this chemist that fluor-spar is not in the slightest degree decomposed by the action of anhydrous sulphuric acid, whether at common temperatures or at a red heat. The experiment was made both by transmitting the vapour of anhydrous sulphuric acid over fluor-spar heated to redness in a tube of platinum, and by putting the mineral into the liquid acid. In

neither case did decomposition ensue; but when the former experiment was repeated, with the difference of employing concentrated hydrous instead of anhydrous sulphuric acid, evolution of hydrofluoric acid was produced. M. Kuhlman also transmitted hydrochloric acid gas over fluor-spar at a red heat, when hydrofluoric acid was disengaged, without any evolution of hydrogen, and chloride of calcium remained. I am aware of no satisfactory explanation of these facts, except by regarding fluor-spar as a compound of fluorine and calcium, and hydrofluoric acid as a compound of fluorine and hydrogen. I shall accordingly adopt this view in the subsequent pages, and never employ the term fluoric acid except when explaining phenomena according to the theory of Gay-Lussac.

Its eq. is 19·68; *symb.* H + F, or HF.

Fluoboric Acid.—Prep.—The chief difficulty in determining the nature of hydrofluoric acid arises from the water of the sulphuric acid which is employed in its preparation. To avoid this source of uncertainty, Gay-Lussac and Thenard made a mixture of vitrified boracic acid and fluor-spar, and exposed it in a leaden retort to heat, under the expectation that as no water was present, anhydrous fluoric acid would be obtained. In this, however, they were disappointed; but a new gas came over, to which they applied the term *fluoboric acid gas*. A similar train of reasoning led Davy about the same time to the same discovery; though the French chemists had the advantage in priority of publication. Another process given by Dr. Davy, is to mix 1 part of vitrified boracic acid and 2 of fluor-spar with 12 parts of strong sulphuric acid, heating the mixture gently in a glass flask (Phil. Trans. 1812); but the gas thus developed contains a considerable quantity of fluosilicic acid. Fluoboric acid gas may also be formed by heating a strong solution of hydrofluoric and boracic acids in a metallic retort.

In the decomposition of fluor-spar by vitrified boracic acid, the former and part of the latter undergo an interchange of elements. The fluorine uniting with boron gives rise to fluoboric acid gas; and by the union of calcium and oxygen lime is generated, which combines with boracic acid, and is left in the retort as borate of lime. Fluoboric acid gas, therefore, is composed of boron and fluorine. Those who adopt the theory of Gay-Lussac give a different explanation, and regard this gas as a compound of fluoric and boracic acids. The lime of fluor-spar is supposed to unite with one portion of boracic acid, and fluoric acid at the moment of separation with another, yielding borate of lime and fluoboric acid gas.

Prop.—It is a colourless gas, has a penetrating pungent odour, and extinguishes flame on the instant. Its sp. gr., according to Thomson, is 2·3622. It reddens litmus paper as powerfully as sulphuric acid, and forms salts with alkalies which are called *fluoborates*. It has a singularly great affinity for water. When mixed with air or any gas which contains watery vapour, a dense white cloud, a combination of water and fluoboric acid appears, thus affording an extremely delicate test of the presence of moisture in gases. Water acts powerfully on this gas, absorbing, according to Dr. Davy, 700 times its volume, during which the water increases in temperature and volume. The solution is limpid, fuming, and very caustic. On the application of heat, part of the gas is disengaged; but afterwards the whole solution is distilled.

Gay-Lussac and Thenard and Dr. Davy were of opinion that fluoboric acid gas is dissolved by water without decomposition; but Berzelius denies the accuracy of their observation. On transmitting the gas into water until the liquid

acquires a sharply sour taste, but is far from being saturated, a white powder begins to subside; and, on cooling, a considerable quantity of boracic acid is deposited in crystals. It appears that in a certain state of dilution, part of the fluoboric acid and water mutually decompose each other, with formation of boracic and hydrofluoric acids. The latter unites, according to Berzelius, with undecomposed fluoboric acid, forming what he has called *boro-hydrofluric acid*. On concentrating the liquid by evaporation, the boracic and hydrofluoric acids decompose each other, and the original compound is reproduced.

Fluoboric acid gas does not act on glass, but attacks animal and vegetable matters with energy, converting them like sulphuric acid into a carbonaceous substance. The action is most probably owing to its affinity for water.

When potassium is heated in fluoboric acid gas, the metal takes fire, and a chocolate coloured solid, wholly devoid of metallic lustre, is formed. This substance is a mixture of boron and fluoride of potassium, from which the latter is dissolved by water, and the boron is left in a solid state.

The composition of fluoboric acid gas has not hitherto been determined by direct experiment. Dr. Davy ascertained that it unites with an equal measure of ammoniacal gas, forming a solid salt; and that it also combines with twice and three times its volume of ammonia, yielding liquid compounds. In the former salt the relative weights of the constituent gases are in the ratio of their specific gravities; and if the compound consists of one equivalent of each, it will be constituted of,

Fluoboric acid gas	2·3622	68·04	one eq.
Ammoniacal gas	0·5898	17	one eq.

so that the equivalent of the acid may be assumed in round numbers to be 68. Now supposing this acid to be formed of three eqs. of fluorine and one of boron, its eq. will be 64·04, a number which approximates to the preceding. This view is consistent with the composition of boracic as given at page 210, and with the conversion of fluoboric acid by water into hydrofluoric and boracic acids.

Its symb. is B + 3F, or BF_3.

Fluosilicic Acid.—Prep.—This gas is formed whenever hydrofluoric and silicic acids come in contact; and hence pure hydrofluoric acid can be prepared in metallic vessels only, and with fluor-spar that is free from rock crystal. The most convenient method of procuring it is to mix in a retort one part of pulverized fluor-spar with its own weight of sand or pounded glass, and two parts of strong sulphuric acid. On applying a gentle heat, fluosilicic acid gas is disengaged with effervescence, and may be collected over mercury.

The chemical changes attending this process are differently explained, according to the view which is taken concerning the nature of the product. In regarding fluor-spar as a compound of fluoric acid and lime, the former at the moment of being set free is thought to unite directly with silicic acid, thereby giving rise to a compound of silicic and fluoric acids. But for reasons already stated, fluor-spar is not considered as fluate of lime; and therefore this view cannot be admitted. It is inferred, on the contrary, that when, by the action of sulphuric acid on fluoride of calcium, hydrofluoric acid is generated, the elements of this acid react on those of silicic acid, and give rise to the production of water and fluosilicic acid gas. This gas is therefore a fluoride of silicon. It may occur to some whether hydrofluoric acid does not unite directly with silicic acid; but this

idea is inconsistent with the proportion in which the elements of the gas are found to be united.

Prop.—It is a colourless gas which extinguishes flame, destroys animals that are immersed in it, and irritates the respiratory organs powerfully. It does not corrode glass vessels provided they are quite dry. When mixed with atmospheric air it forms a white cloud, owing to the presence of watery vapour. Its sp. gr. according to Thomson, is 3·6111; and 100 cubic inches of it at 60°, and when the barometer stands at 30 inches, weigh 111·985 grains.

Water acts powerfully on fluosilicic acid gas, of which it condenses, according to Dr. Davy, 365 times its volume (Phil. Trans. for 1812). The gas suffers decomposition at the moment of contact with water, silicic acid in the form of a gelatinous hydrate being deposited, which when well washed is quite pure. The liquid, which has a sour taste, and reddens litmus paper, contains the whole of the hydrofluoric acid, together with two-thirds of the silicic acid which was originally present in the gas (Berzelius). By conducting fluosilicic acid gas into a solution of ammonia, complete decomposition ensues:—hydrofluoric acid unites with the alkali, forming hydrofluate of ammonia, and all the silicic acid is deposited. On this fact is founded the mode of analyzing fluosilicic acid gas adopted by Dr. Davy and Thomson.

The solution which is formed by fully saturating water with fluosilicic acid gas is powerfully acid, and emits fumes on exposure to the air. It is commonly known by the name of *silicated fluoric acid*; but a more appropriate term is *silico-hydrofluoric acid*. [It is called by Berzelius *hydrofluosilicic acid*, but preferably by Prof. Hare *fluohydrosilicic acid*.] According to the experiments of Berzelius, it appears to be a definite compound of hydrofluoric and fluosilicic acids in the ratio of 3 eqs. of the former to two of the latter, and is thus expressed, $3\,HF + 2SiF_3$. If evaporated before separation from the silicic acid deposited by the action of water on fluosilicic acid gas, this compound is reproduced. But if the solution is poured off from the silicic acid thus deposited, and then evaporated, fluosilicic acid gas is at first evolved, and subsequently hydrofluoric acid and water are expelled. The evaporation of silico-hydrofluoric acid *in vacuo* is attended by a similar change, so that this acid cannot be obtained free from water. It does not corrode glass; but when evaporated in glass vessels, the production of free hydrofluoric acid of course gives rise to corrosion.

On neutralizing silico-hydrofluoric acid with ammonia, and gently evaporating to dryness, all the silicic acid is rendered insoluble. By exactly neutralizing with carbonate of potassa, a sparingly soluble double fluoride of silicon and potassium subsides; the precipitation is still more complete with chloride of barium, when the insoluble fluoride of silicon and barium is generated. A variety of similar compounds may be obtained either by double decomposition, or by the action of silico-hydrofluoric acid on metallic oxides.

Its eq. is 78·58; *symb.* Si + 3F, or SiF_3.

ON THE COMPOUNDS OF THE SIMPLE NON-METALLIC ACIDIFIABLE COMBUSTIBLES WITH EACH OTHER.

SECTION I.

HYDROGEN AND NITROGEN.—AMMONIACAL GAS.

Hist. and Prep.—The aqueous solution of ammonia, under the name of *spirit of hartshorn*, has been long known to chemists; but its existence as a gas was first noticed by Priestley, who described it in his works under the title of *alkaline air*. It is often called the *volatile alkali*; but the terms ammonia and ammoniacal gas are now usually employed. Although a product of the decomposition of organic substances, it has been thought better to describe it here, from its great importance in inorganic chemistry.

An abundant supply of ammoniacal gas may be obtained from any salt of ammonia by the action of a pure alkali or alkaline earth; but hydrochlorate of ammonia and lime, from economical considerations, are always employed. The proportions to which I give the preference are equal parts of hydrochlorate of ammonia and well-burned quicklime, considerable excess of lime being taken, in order to decompose the hydrochlorate more expeditiously and completely. The lime is slaked by the addition of water; and as soon as it has fallen into powder, it should be placed in an earthen pan and be covered till it is quite cold, in order to protect it from the carbonic acid of the air. It is then mixed in a mortar with the hydrochlorate of ammonia, previously reduced to a fine powder; and the mixture is put into a retort or other convenient glass vessel. Heat is then applied, and the temperature gradually increased as long as free evolution of gas continues. The residue consists of chloride of calcium and lime.

The gas, thus liberated, must be collected over mercury, as it is most rapidly absorbed by water. Advantage is taken of this property to prepare what is commonly though incorrectly termed liquid ammonia. For this purpose a current of gas is transmitted into distilled water, which is kept cool by means of ice or moist cloths, and the process is continued as long as any gas is absorbed. A highly concentrated solution of ammonia is thus obtained. The most convenient method of preparing ammoniacal gas for purposes of experiment is by applying a gentle heat to the concentrated solution, contained in a glass vessel. It soon enters into ebullition, and a large quantity of pure ammonia is disengaged.

Prop.—Ammonia is a colourless gas, which has a strong pungent odour, and acts powerfully on the eyes and nose. It is quite irrespirable in its pure form, but when diluted with air, it may be taken into the lungs with safety. Burning bodies are extinguished by it, nor is the gas inflamed by their approach. Am-

monia, however, is inflammable in a low degree; for when a lighted candle is immersed in it, the flame is somewhat enlarged, and tinged of a pale yellow colour at the moment of being extinguished; and a small jet of the gas will burn in an atmosphere of oxygen. A mixture of ammoniacal and oxygen gases detonates by the electric spark; water being formed, and nitrogen set free. A little nitric acid is generated at the same time, except when a smaller quantity of oxygen is employed than is sufficient for combining with all the hydrogen of the ammonia. (Henry, Phil. Trans. 1809.)

Ammoniacal gas at the temperature of 50° and under a pressure equal to 6·5 atmospheres becomes a transparent colourless liquid. [In the experiments of Mr. Faraday it was converted into a transparent crystalline solid (page 53.)] It is also liquefied, according to Guyton-Morveau, under the common pressure, by a cold of —70°; but there is no doubt that the liquid which he obtained was a solution of ammonia in water.

It has all the properties of an alkali in a very marked manner. Thus it has an acrid taste, and gives a brown stain to turmeric paper; though the yellow colour soon reappears on exposure to the air, owing to the volatility of the alkali. It combines also with acids, and neutralizes their properties completely. All these salts suffer decomposition by being heated with the fixed alkalies or alkaline earths, such as potassa or lime, the union of which with the acid of the salt causes the separation of its ammonia. None of the ammoniacal salts can sustain a red heat without being dissipated in vapour or decomposed, a character which manifestly arises from the volatile nature of the alkali. If combined with a volatile acid, such as the hydrochloric, the compound itself sublimes unchanged by heat; but when united with an acid, which is fixed at a low red heat, such as the phosphoric, the ammonia alone is expelled. It is here considered that the salts of ammonia are formed by its direct union with acids. Another, and a very scientific view has been adopted by Berzelius. When an electric current is passed through a weak solution of ammonia, it is decomposed by the secondary action, hydrogen from decomposed water being evolved at the negative electrode and nitrogen at the positive (Faraday, Phil. Trans. 1834). But if a portion of mercury form the negative electrode, no hydrogen is evolved, and the mercury is rapidly converted into a light porous substance, which has the lustre and all the characters of an amalgam. As soon as it is removed from the influence of the electric current, rapid decomposition ensues, mercury is reproduced, and hydrogen and ammoniacal gases are evolved in the ratio of one measure of the former to two of the latter, according to the observations of Gay-Lussac and Thenard. The production of this compound is explained by Berzelius on the supposition that ammonia by uniting with an additional eq. of hydrogen, forms a compound, which has all the properties of a metal; he therefore calls it ammonium. The oxide of ammonium, the composition of which is represented by the formula $NH_4 + O$, he considers to be the base of the ammoniacal salts. This view is supported by several facts, which will be considered when treating of the salts.

Hydrogen and nitrogen gases do not unite directly, and therefore chemists have no synthetic proof of the constitution of ammonia. Its composition, however, has been determined analytically with great exactness. When a succession of electric sparks is passed through ammoniacal gas, it is resolved into its elements; and the same effect is produced by conducting it through porcelain tubes heated to redness. A. Berthollet analyzed ammonia in both ways, and ascertained that 200 measures of that gas, on being decomposed, occupy the space of

400 measures, 300 of which are hydrogen, and 100 nitrogen. Henry has made an analysis of ammonia by means of electricity, and his experiment proves beyond a doubt that the proportions above given are rigidly exact. (Annals of Philosophy, xxiv. 346.)

	Grains.
Now since 150 cubic inches of hydrogen weigh . .	3·205
and 50 of nitrogen	15·083
200 cubic inches of ammonia must weigh . .	18·288

and it is composed by weight of

Hydrogen . .	3·205 .	3 .	or 3 equivalents.
Nitrogen . .	15·083 .	14·15 .	or 1 equivalent.

The sp. gr. of ammonia, according to this calculation, is 0·5898, a number which agrees closely with those ascertained directly by Davy and Thomson.

Ammoniacal gas has a powerful affinity for water. Owing to this attraction, a piece of ice, when introduced into a jar full of ammonia, is instantly liquefied, and the gas disappears in the course of a few seconds. Davy, in his Elements, stated that water at 50°, and when the barometer stands at 29·8 inches, absorbs 670 times its volume of ammonia, and that the solution has a sp. gr. of 0·875 According to Thomson, water at the common temperature and pressure takes up 780 times its bulk. By strong compression, water absorbs the gas in still greater quantity. Heat is evolved during its absorption; and a considerable expansion, independently of the increased temperature, occurs at the same time.

The concentrated solution of ammonia is a clear colourless liquid, of sp. gr. 0·936. It possesses the peculiar pungent odour, taste, alkalinity, and other properties of the gas itself. On account of its great volatility it should be preserved in well-stopped bottles, a measure which is also required to prevent the absorption of carbonic acid. At a temperature of 130° it enters into ebullition, owing to the rapid escape of pure ammonia; but the whole of the gas cannot be expelled by this means, as at last the solution itself evaporates. It freezes at about the same temperature as mercury.

The following table, from Davy's Elements of Chemical Philosophy, shows the quantity of real ammonia contained in 100 parts of solutions of different sp. gravities at 59° F. and when the barometer stands at 30 inches. The sp. gr. of water is supposed to be 10,000:—

Table of the quantity of real Ammonia in solutions of different densities.

100 parts of sp. gravity.		Of real Ammonia.	100 parts of sp. gravity.		Of real Ammonia.
8750	contain	32·5	9435	contain	14·53
8875		29·25	9476		13·46
9000		26·00	9513		12·40
9054		25·37	9545		11·56
9166		22·07	9573		10·82
9255		19·54	9597		10·17
9326		17·52	9619		9·60
9385		15·88	9692		9·50

The presence of free ammoniacal gas may always be detected by its odour, by its temporary action on yellow turmeric paper, and by its forming dense white fumes, hydrochlorate of ammonia, when a glass rod moistened with hydrochloric acid is brought near it.

Besides ammonia and ammonium, another compound of nitrogen and hydrogen is believed to exist, the composition of which is represented by the formula, NH_2. It is only known in combination, and has been named *Amide, or Amidogen.* Its compounds, which are important, will be described in treating of organic chemistry.

Its eq. is 17·15; *eq. vol.* = 200; *symb.* N + 3H, or NH_3.

SECTION II.

COMPOUNDS OF HYDROGEN AND CARBON.

Chemists have for several years been acquainted with two distinct compounds of carbon and hydrogen, viz. carburetted hydrogen and olefiant gases; but late researches have enriched the science with several other compounds of a similar nature, to which much interest is attached. They are remarkable for their number, for supplying some instructive instances of isomerism, and for their tendency to unite with and even neutralize powerful acids, without, in their uncombined state, manifesting any ordinary signs of alkalinity. Several of them are particularly distinguished by their chemical affinities; for although compound, they exhibit in their combinations with other substances the characteristics of an element. They have hence been called the compound radicals. These compound radicals are closely associated both with the organic and inorganic chemistry. In the latter they must hold a place, as being compounds formed by the direct union of two elements; and in the former they are the roots or radicals of the various organic products.

Light Carburetted Hydrogen.—Hist.—This gas is sometimes called *heavy inflammable air*, the *inflammable air of marshes*, and *hydrocarburet.* Agreeably to the principles of chemical nomenclature, taking carbon as the electro-negative element, it is a *dicarburet of hydrogen;* but it is generally termed *light carburetted hydrogen.* It is formed abundantly in stagnant pools during the spontaneous decomposition of dead vegetable matter; and it may readily be procured by stirring the mud at the bottom of them, and collecting the gas, as it escapes, in an inverted glass vessel. In this state it is found to contain 1-20th of carbonic acid gas, which may be removed by means of lime water or a solution of pure potassa, and 1-15th or 1-20th of nitrogen. This is the only convenient method of obtaining it.

Prop.—Colourless, tasteless, nearly inodorous; always gaseous when uncombined; does not change the colour of litmus or turmeric paper. Water, according to Henry, absorbs about 1-60th of its volume. It extinguishes all burning bodies, and is unable to support the respiration of animals. It is highly inflammable; and when a jet of it is set on fire, it burns with a yellow flame, and with a much

stronger light than is occasioned by hydrogen gas. With a due proportion of atmospheric air or oxygen gas it forms a mixture which detonates powerfully with the electric spark, or by the contact of flame. The sole products of the explosion are water and carbonic acid.

Dalton first ascertained the real nature of light carburetted hydrogen; and it has since been particularly examined by Thomson, Davy, and Henry. When 100 measures are detonated with rather more than twice their volume of oxygen gas, the whole of the inflammable gas and precisely 200 measures of the oxygen disappear, water is condensed, and 100 measures of carbonic acid are produced. Now 100 measures of carbonic acid gas contain (page 188) 100 of carbon vapour and 100 of oxygen gas, just half the oxygen which had been employed; and the remaining oxygen requires 200 measures of hydrogen to form water. Hence as, at 60° F. and 30 inches Bar.,

			Grains.
100	cubic inches of	carbon vapour weigh . . .	13·153
200	do.	hydrogen gas	4·2636
100	do.	light carburetted hydrogen must weigh	17·4166

These weights are obviously in the ratio of 2 to 6·12, as already assigned; and the sp. gr. of such a gas ought to be 0·5594, which is nearly the quantity found experimentally by Thomson and Henry.

Light carburetted hydrogen is not decomposed by electricity, nor by being passed through red-hot tubes, unless the temperature is very intense, in which case some of the gas does suffer decomposition, each volume yielding two volumes of pure hydrogen gas and a deposite of charcoal. Mixed with chlorine, no action takes place at common temperatures, when quite dry, even if exposed to the direct solar rays. If moist, and the mixture is kept in a dark place, still no action ensues: but if light be admitted, particularly sunshine, decomposition follows. The nature of the products depends upon the proportion of the gases. If four measures of chlorine and one of light carburetted hydrogen are present, carbonic and hydrochloric acid gases will be produced: two volumes of chlorine combine with two volumes of hydrogen contained in the carburetted hydrogen, and the other two volumes of chlorine decompose so much water as will likewise give two volumes of hydrogen, forming hydrochloric acid; while the oxygen of the water unites with the carbon, and converts it into carbonic acid. If there are three instead of four volumes of chlorine, carbonic oxide will be generated instead of carbonic acid, because one-half less water will be decomposed (Henry). If a mixture of chlorine and light carburetted hydrogen is electrified or exposed to a red heat, hydrochloric acid is formed, and charcoal deposited.

Its eq. is 8·12; *eq. vol.* = 100; *symb.* H_2C.

It was first ascertained by Henry (Nicholson's Journal, vol. xix.); and his conclusions have been fully confirmed by the subsequent researches of Davy, that the *fire-damp* of coal-mines consists almost solely of light carburetted hydrogen. This gas often issues in large quantity from between beds of coal, and by collecting in mines, owing to deficient ventilation, gradually mingles with atmospheric air, and forms an explosive mixture. The first unprotected light which then approaches, sets fire to the whole mass, and an explosion ensues. These accidents, which were formerly so frequent and so fatal, are now comparatively rare, owing to the employment of the safety-lamp. For this invention we are

indebted to Davy, who established the principles of its construction by a train of elaborate experiment and close reasoning, which may be regarded as one of the happiest efforts of his genius (Essay on Flame).

Davy commenced the inquiry by determining the best proportion of air and light carburetted hydrogen for forming an explosive mixture. When the inflammable gas is mixed with 3 or 4 times its volume of air, it does not explode at all. It detonates feebly when mixed with 5 or 6 times its bulk of air, and powerfully when 1 to 7 or 8 is the proportion. With 14 times its volume it still forms a mixture which is explosive; but if a larger quantity of air be admitted, a taper burns in it only with an enlarged flame.

The temperature required for causing an explosion was next ascertained. It was found that the strongest explosive mixture may come in contact with iron or other solid bodies heated to redness, or even to whiteness, without detonating, provided they are not in a state of actual combustion; whereas the smallest point of flame, owing to its higher temperature, instantly causes an explosion.

The last important step in the inquiry was the observation that flame cannot pass through a narrow tube. This led to the discovery, that the power of tubes in preventing the transmission of flame is not necessarily connected with any particular length; and that a very short one will have the effect, provided its diameter is proportionally reduced. Thus, a piece of fine wire gauze, which may be regarded as an assemblage of short narrow tubes, is quite impermeable to flame; and consequently, if a common oil lamp be completely surrounded with a cage of such gauze, it may be introduced into an explosive atmosphere of fire-damp and air, without kindling the mixture. This simple contrivance, which is appropriately termed the *safety-lamp*, not only prevents explosion, but indicates the precise moment of danger. When the lamp is carried into an atmosphere charged with fire-damp, the flame begins to enlarge; and the mixture, if highly explosive, takes fire as soon as it has passed through the gauze, and burns on its inner surface, while the light in the centre of the lamp is extinguished. Whenever this appearance is observed, the miner must instantly withdraw: for though the flame should not be able to communicate with the explosive mixture on the outside of the lamp, as long as the texture of the gauze remains entire, yet the heat emitted during the combustion is so great, that the wire, if exposed to it for a few minutes, would suffer oxidation, and fall to pieces.

The peculiar operation of small tubes in obstructing the passage of flame admits of a very simple explanation. Flame is gaseous matter heated so intensely as to be luminous; and Davy has shown that the temperature necessary for producing this effect is far higher than the white heat of solid bodies. Now, when flame comes in contact with the sides of very minute apertures, as when wire gauze is laid upon a burning jet of coal gas, it is deprived of so much heat that its temperature instantly falls below the degree at which gaseous matter is luminous; and consequently, though the gas itself passes freely through the interstices, and is still very hot, it is no longer incandescent. Nor does this take place when the wire is cold only;—the effect is equally certain at any degree of heat which the flame can communicate to it. For since the gauze has a large extent of surface, and from its metallic nature is a good conductor of heat, it loses heat with great rapidity. Its temperature, therefore, though it may be heated to whiteness, is always so far below that of flame, as to exert a cooling influence over the burning gas, and reduce its heat below the point at which it is incandescent.

These principles suggest the conditions under which Davy's lamp would cease to be safe. If a lamp with its gauze red-hot be exposed to a *current* of explosive mixture, the flame may possibly pass so rapidly as not to be cooled below the point of ignition, and in that case an accident might occur with a lamp which would be quite safe in a calm atmosphere. It has been lately shown by Messrs. Upton and Roberts, lamp manufacturers of London, that flame may in this way be made to pass through the safety-lamp as commonly constructed; and I am satisfied, from having witnessed some of their experiments, that the observation is correct. This then may account for accidents in coal-mines where the safety-lamp is constantly employed. An obvious mode of avoiding such an evil is to diminish the apertures of the gauze; but this remedy is nearly impracticable from the obstacle which very fine gauze causes to the diffusion of light. A better method is to surround the common safety-lamp with a glass cylinder, allowing air to enter solely at the bottom of the lamp through wire gauze of extreme fineness, placed horizontally, and to escape at top by a similar contrivance. Upton and Roberts have constructed a lamp of this kind, through which I have in vain tried to cause the communication of flame, and which appears to me perfectly secure: should an accident break the glass, their lamp would be reduced to a safety-lamp of the common construction. Davy's lamp thus modified gives a much better light than without the glass, just as all lamps burn better with a shade than without one.

Olefiant Gas—Hist. and Prep.—Discovered in 1796 by some associated Dutch chemists, who gave it the name of *olefiant gas*, from its property of forming an oil-like liquid with chlorine. It is prepared by mixing, in a capacious retort, one measure of strong alcohol with three measures of concentrated sulphuric acid, and heating the mixture as soon as it is made. The acid soon acts upon the alcohol, effervescence ensues, and olefiant gas passes over. The chemical changes which take place are of a complicated nature, and the products numerous. At the commencement of the process, the olefiant gas is mixed only with a little ether; but in a short time the solution becomes dark, the formation of ether declines, and the odour of sulphurous acid begins to be perceptible: towards the close of the operation, though olefiant gas is still the chief product, sulphurous acid is freely disengaged, some carbonic acid is formed, and charcoal in large quantity deposited. The olefiant gas may be collected either over water or mercury. The greater part of the ether condenses spontaneously; and the sulphurous and carbonic acids may be separated by washing the gas with lime water, or a solution of pure potassa. The olefiant gas in this process is derived solely from the alcohol; the theory of its formation, as well as that of the accompanying products, will be given under the head of Ether in the third part of this work.

Prop.—Colourless, tasteless, inodorous; hitherto only known in a gaseous state. Water absorbs about one-eighth of its volume. Like the preceding compound, it extinguishes flame, is unable to support the respiration of animals, and is set on fire when a lighted candle is presented to it, burning slowly with the emission of a dense white light. With a proper quantity of oxygen gas, it forms a mixture which may be kindled by flame or the electric spark, and which explodes with great violence. To burn it completely, it should be detonated with four or five times its volume of oxygen. On conducting this experiment with the requisite care, Henry finds that for each measure of olefiant gas, precisely three of oxygen disappear, deposition of water takes place, and two measures of carbonic acid are produced. From these data the proportion of its

constituents may easily be deduced in the following manner:—Two measures of carbonic acid contain two measures of the vapour of carbon, which must have been present in the olefiant gas, and two measures of oxygen. Two-thirds of the oxygen which disappeared are thus accounted for; and the other third must have combined with hydrogen. But one measure of oxygen requires for forming water precisely two measures of hydrogen, which must likewise have been contained in the olefiant gas. Hence, as

	Grains.
200 cubic inches of the vapour of carbon, weigh - - -	26·1428
200 do. hydrogen gas, weigh - - - -	4·2734
100 cubic inches of olefiant gas must weigh - - - -	30·4162

These weights are in the ratio 12·24 or two equivalents of carbon to 2 or two eq. of hydrogen, as in the table. The sp. gr. of a gas so constituted should be 0·9808; whereas the density found experimentally by Saussure is 0·9852, by Henry 0·967, and by Thomson 0·97.

By a succession of electric sparks it is resolved into charcoal and hydrogen; and the latter of course occupies twice as much space as the gas from which it was derived. It is also decomposed by transmission through red-hot tubes of porcelain. The nature of the products varies with the temperature. By employing a very low degree of heat, it may probably be converted solely into carbon and light carburetted hydrogen; and in this case no increase of volume can occur, because these two gases, for equal bulks, contain the same quantity of hydrogen. But if the temperature is high, then a great increase of volume takes place; a circumstance which indicates the evolution of free hydrogen, and consequently the total decomposition of some of the olefiant gas.

Its eq. is 14·24; *eq. vol.* = 100; *symb.* 2H + 2C, or $H_4C_4 = 28·48$.

Chlorine acts powerfully on olefiant gas. When these gases are mixed together in the ratio of two measures of the former to one of the latter, they form a mixture which takes fire on the approach of flame, and which burns rapidly with formation of hydrochloric acid gas, and deposition of a large quantity of charcoal. But if the gases are allowed to remain at rest after being mixed together, a very different action ensues. The chlorine, instead of decomposing the olefiant gas, enters into direct combination with it, and a yellow liquid like oil is generated. Wöhler has remarked its production by the contact of olefiant gas with certain metallic chlorides, especially the perchloride of antimony.

The other compounds of carbon and hydrogen are described in the organic chemistry. They belong to this department not only as being products of the organic kingdom, but also on account of their atomic constitution; for whenever they are acted on by chlorine or any other dehydrodizing agents, one part of the hydrogen, which enters into their composition, is shown to be in a state of combination different from the rest. Thus evidence is obtained that these compounds, although composed of nothing but hydrogen and carbon, are not formed by the direct union of these elements, but that a portion of the hydrogen with the carbon forms a compound radical, which acts the part of an element and combines as such with the remainder of the hydrogen.

SECTION III.

COMPOUNDS OF HYDROGEN AND SULPHUR.

SULPHUR unites with hydrogen in at least two proportions, and the resulting compounds are thus constituted :—

	Hydrogen.	Sulphur.	Equiv.	Formulæ.
Hydrosulphuric acid - -	1	1 eq. + 16·1	1 eq. = 17·1	HS.
Persulphuret of hydrogen	1	1 eq. + 32·2	2 eq. = 33·2	HS_2.

Hydrosulphuric Acid, Sulphydric Acid.—Hist. and Prep.—Commonly known under the name of sulphuretted hydrogen. It is best prepared by heating sesquisulphuret of antimony in a retort, or other convenient glass vessel, with four or five times its weight of strong hydrochloric acid; when, by an interchange of elements, sesquichloride of antimony and hydrosulphuric acid are generated, the latter of which escapes with effervescence. The elements concerned before and after the change, are

1 eq. Sesquisulphuret of antimony and 3 eq. Hydrochloric acid
Sb_2S_3 3HCl.

which yield

3 eq. Hydrosulphuric acid and 1 eq. Sesquichloride of antimony.
3Hs Sb_2Cl_3

It may also be formed by the action of sulphuric acid diluted with 3 or 4 parts of water on protosulphuret of iron: this sulphuret and water interchange elements, hydrosulphuric acid and protoxide of iron are generated, and the latter unites with sulphuric acid, while the former in the state of gas is rapidly disengaged. Hydrochloric acid may be substituted for the sulphuric. A sulphuret of iron may be procured for the purpose, either by igniting common iron pyrites, by which means nearly half of its sulphur is expelled, or by exposing to a low red heat a mixture of two parts of iron filings and rather more than one part of sulphur. The materials should be placed in a common earthen or cast-iron crucible, and be protected as much as possible from the air during the process. The sulphuret procured from iron filings and sulphur always contains some uncombined iron, and therefore the gas obtained from it is never quite pure, being mixed with a little free hydrogen. This, however, for many purposes, is immaterial.

Prop.—Colourless gas, which reddens moist litmus paper feebly, and is distinguished from all other gaseous substances by its offensive taste and odour, which is similar to that of putrefying eggs, or the water of sulphurous springs. Under a pressure of 17 atmospheres, at 50°, it is compressed into a limpid liquid, which resumes the gaseous state as soon as the pressure is removed. [At a much lower temperature obtained as a transparent crystalline solid (page 53).] To animal life it is very injurious. According to Dupuytren and Thenard, the

presence of 1-1500th of this gas in air is instantly fatal to a small bird; 1-1000th killed a middle-sized dog; and a horse died in an atmosphere which contained 1-250th of its volume.

It extinguishes all burning bodies; but the gas takes fire when a lighted candle is immersed in it, and burns with a pale blue flame. Water and sulphurous acid are the products of its combustion, and sulphur is deposited. With oxygen gas it forms a mixture which detonates by the application of flame or the electric spark: if 100 measures of it are exploded with 150 of oxygen, the former is completely consumed, the oxygen disappears, water is deposited, and 100 measures of sulphurous acid gas remain (Thomson). From the results of this experiment, the composition of hydrosulphuric acid gas may be inferred; for it is clear, from the composition of sulphurous acid (page 194), that two-thirds of the oxygen must have combined with sulphur; and, therefore, that the remaining one-third contributed to the formation of water. Consequently, hydrosulphuric acid contains its own volume of hydrogen gas, and 16·66 of the vapour of sulphur; and since

	Grains.
16·66 cubic inches of the vapour of Sulphur weigh . . .	34·361
100 cubic inches of Hydrogen gas weigh	2·1318
100 cubic inches of Hydrosulp. acid gas must weigh . .	36·4928

The sp. gr. of a gas so constituted should be 1·177, which agrees with observation; and its elements are in the ratio of 1 to 16·1, as already mentioned.

The accuracy of this view is confirmed by several circumstances. Thus, according to Gay-Lussac and Thenard, the weight of 100 cubic inches of hydrosulphuric acid gas is 36·33 grains. When sulphur is heated in hydrogen gas, hydrosulphuric acid is generated without any change of volume. On igniting platinum wires in it by means of the voltaic apparatus, sulphur is deposited, and an equal volume of pure hydrogen remains; and a similar effect is produced, though more slowly, by a succession of electric sparks (Elements of Davy, p. 282.) Gay-Lussac and Thenard found that on heating tin in hydrosulphuric acid gas, sulphuret of tin is formed; and when potassium is heated in it, vivid combustion ensues, with formation of sulphuret of potassium. In both cases, pure hydrogen is left, which occupies precisely the same space as the gas from which it was derived. (Recherches Physico-Chimiques, vol. i.)

The salts of hydrosulphuric acid are called *hydrosulphates*, *sulphydrates*, and sometimes *hydrosulphurets*. This acid, however, rarely unites directly with metallic oxides; but in most cases its hydrogen combines with the oxygen of the oxide and its sulphur with the metal. All the hydrosulphates which do exist are decomposed by sulphuric or hydrochloric acids, and hydrosulphuric acid gas is disengaged with effervescence.

Recently boiled water absorbs its own volume of hydrosulphuric acid, becomes thereby feebly acid, and acquires the peculiar odour and taste of sulphurous springs. The gas is expelled without change by boiling the water.

The elements of hydrosulphuric acid may easily be separated from one another. A solution of the gas cannot be preserved in an open vessel, because its hydrogen unites with the oxygen of the atmosphere, and sulphur is deposited. When mixed with sulphurous acid, both compounds are decomposed, water is

generated, and sulphur set free. On pouring into a bottle of the gas a little fuming nitric acid, mutual decomposition ensues, a bluish-white flame frequently appears, sulphur and nitrous acid fumes come into view, and water is generated. Chlorine, iodine, and bromine decompose it, with separation of sulphur, and formation of hydrochloric, hydriodic, and hydrobromic acids. An atmosphere charged with hydrosulphuric acid gas may be purified by means of chlorine in the space of a few minutes.

Hydrosulphuric acid gas is readily distinguished from other gases by its odour, by tarnishing silver with which it forms a sulphuret, and by the character of the precipitate which it produces with solutions of arsenious acid, tartar emetic, and salts of lead. The most delicate test of its presence, when diffused in the air, is moist carbonate of oxide of lead spread on white paper.

Its eq. is 17·1; *eq. vol.* = 100; *symb.* HS.

Persulphuret of Hydrogen.—Hist. and Prep.—Discovered by Scheele, but first specially described by Berthollet (An. de Chimie, xxv.) When protosulphuret of potassium (or of any metal of the alkalies and alkaline earths) is mixed in solution with sulphuric acid, the oxygen of water unites with potassium and its hydrogen with sulphur, just as when protosulphuret of iron is employed, hydrosulphuric acid and sulphate of potassa being generated: the elements K + S and H + O mutually interchange, and yield K + O and H + S. If the potassium be combined with two or more equivalents of sulphur as in the so called *liver of sulphur* made by fusing carbonate of potassa with half of its weight of sulphur, then one of two events will happen: the hydrogen of the decomposed water will either unite with 1 eq. of sulphur and form hydrosulphuric acid, the superfluous sulphur subsiding in the form of a grey hydrate, or with 2 eqs. of sulphur, and give rise to persulphuret of hydrogen. Now, the former of these changes always occurs when the acid is added to the persulphuret of potassium; and the latter takes place when a concentrated solution of that sulphuret is added by little and little to the acid, provided the acid is in considerable excess, and the mixture well stirred after each addition. The same phenomena ensue when hydrochloric instead of sulphuric acid is employed; but then there are two sources from which hydrogen may be supplied. It may be derived, as above, from decomposed water, hydrochlorate of potassa being generated; or hydrochloric acid itself may be decomposed, its hydrogen uniting with sulphur and its chlorine with potassium. On all such occasions I adopt the latter view, and will give reasons for doing so in the section introductory to the study of the metals.

Such are the principles to be attended to in preparing persulphuret of hydrogen. In practice it is conveniently made by boiling equal parts of recently slaked lime and flowers of sulphur with 5 or 6 parts of water for half an hour, when a deep orange-yellow solution is formed, which contains persulphuret of calcium. Let this liquid be filtered, and gradually added cold to an excess of hydrochloric acid diluted with about twice its weight of water, briskly stirring. A copious deposit of sulphur falls (the sulphur præcipitatum of the London Pharmacopœia,) and persulphuret of hydrogen gradually subsides in the form of a yellowish semi-fluid matter like oil. The change which ensues in the formation of the yellow solution may be theoretically represented thus:—

2 eq. lime and 6 eq. sulphur $2CaO + S_6$ yield 1 eq. hyposulph. acid and 2 eq. bisulphuret calcium. $S_2O_2 + 2CaS_2$.

The hyposulphurous acid exists in solution united with lime, and is decomposed when hydrochloric acid is added, resolving itself into sulphurous acid and sulphur; a change not essentially connected with the production of persulphuret of hydrogen, but resulting from the mode of preparing the persulphuret of calcium. It is probable that the calcium is combined with more than 2 eqs. of sulphur, and that the deposited sulphur is derived from that source as well as from decomposed hyposulphurous acid.

Prop.—From the facility with which this substance resolves itself into sulphur and hydrosulphuric acid, its history is imperfect; we are indebted to an essay by Thenard for the principal facts which are known (An. de Ch. et Ph. xlviii. 79.) At common temperatures it is a viscid liquid, of a yellow colour, with a density of about 1·769, and a consistence varying between that of a volatile and fixed oil. It has the peculiar odour and taste of hydrosulphuric acid, though in a less degree. Its elements are so feebly united, that in the cold it gradually resolves itself into sulphur and hydrosulphuric acid, and suffers the same change instantly by a heat considerably short of 212° F. Decomposition is also produced by the contact of most substances, especially of metals, metallic oxides, even the alkalies, and metallic sulphurets. Thus effervescence from the escape of hydrosulphuric acid gas is produced by peroxide of manganese, silica, the alkaline earths in powder, and solutions of potassa or soda; and the oxides of gold and silver are reduced by it with such energy, that they are rendered incandescent. It is remarkable that the substance which causes the decomposition often undergoes no chemical change whatever. In these respects persulphuret of hydrogen bears a close analogy to peroxide of hydrogen; and Thenard has traced other points of resemblance. They are both, for instance, rendered more stable by the presence of acids; they both whiten the tongue and skin when applied to them, and they are both possessed of bleaching properties.

The composition of persulphuret of hydrogen has been variously stated. According to Dalton it is a bisulphuret, consisting of two equivalents of sulphur and one of hydrogen; and this view of its composition is corroborated by Sir John Herschel's analysis of persulphuret of calcium (Eden. Phil. Journal, i. 13.) But Thenard found its constituents to vary; whence it is probable that hydrogen is capable of uniting with sulphur in several proportions.

Persulphuret of hydrogen is sometimes regarded as an acid; and on this supposition it may be termed *hydropersulphuric acid*, and its salts *hydropersulphates*. This view is founded on the hypothesis, that the solutions formed by boiling lime or an alkali with sulphur contain hyposulphite and hydropersulphate of lime, the hydrogen in the one acid and oxygen in the other being attributed to decomposed water, and not hyposulphite of lime and persulphuret of calcium, as I have supposed. The latter view is more consistent with the fact that persulphuret of hydrogen in its free state has no acidity, and exhibits no tendency to unite with alkalies.

Its eq. is = 33·2; *symb.* H. S_2.

SECTION IV.

HYDROGEN AND SELENIUM.—HYDROSELENIC ACID.

Selenium, like sulphur, forms a gaseous compound with hydrogen, which has distinct acid properties, and is termed *seleniuretted hydrogen, hydroselenic or selenhydric acid.* It is disengaged by the action of dilute sulphuric or hydrochloric acid on a protoseleniuret of any of the more oxidable metals, such as potassium, calcium, manganese, or iron, the explanation being the same as in the formation of hydrosulphuric acid from protosulphuret of iron.

Hydroselenic acid gas is colourless. Its odour is at first similar to that of hydrosulphuric acid; but it afterwards irritates the lining membrane of the nose powerfully, excites catarrhal symptoms, and destroys for some hours the sense of smelling. It is absorbed freely by water, forming a colourless solution, which reddens litmus paper, and gives a brown stain to the skin. The acid is soon decomposed by exposure to the atmosphere; for the oxygen of the air unites with the hydrogen of the hydroselenic acid, and selenium, in the form of a red powder, subsides. It is decomposed by nitric acid and chlorine in the same manner as hydrosulphuric acid; and, like that gas, it decomposes many metallic salts, the hydrogen of the acid combining with the oxygen of the oxide, while an insoluble seleniuret of the metal is generated.

According to the analysis of Berzelius, hydroselenic acid consists of 39·6 parts or 1 eq. of selenium, and 1 part or 1 eq. of hydrogen; so that *its eq.* is 40·6; *its symb.* HSe.

SECTION V.

COMPOUNDS OF HYDROGEN AND PHOSPHORUS.

The existence of two compounds of phosphorus and hydrogen, the phosphuretted and perphosphuretted hydrogen, have, until lately, been generally admitted by chemists. Their composition and properties have been closely studied by Dumas, Buff, Rose, and Graham (An. de Ch. et Ph. xxxi. 113; xli. 220; and xli. 5 Phil. Mag. v. 401). The investigations of these chemists concurred in proving that phosphuretted hydrogen consists of 31·4 parts or 2 eqs. of phosphorus, and 3 parts or 3 eqs. of hydrogen; while the discordancy in their analyses of perphosphuretted hydrogen caused great uncertainty respecting its constitution. Thus, although Dumas and Rose agree that 100 measures of perphosphuretted hydrogen contain 150 measures of hydrogen, the former states that 1

part of hydrogen is united with 15·9 of phosphorus, the latter with 10·52, while Thomson estimates the quantity at 12. The result of Rose would indicate that the two compounds of phosphorus and hydrogen are isomeric, being identical in composition, and differing in character only by the one being spontaneously inflammable, and the other not so. The accuracy of the analytical results of Rose have been recently established by the discoveries of Leverrier (An. de Ch. et Ph. lx. 174), who has proved that perphosphuretted hydrogen is a mixture of phosphuretted hydrogen with about $\frac{1}{30}$ of its volume of a spontaneously inflammable compound, which he considers to be composed of 31·4 parts or 2 eqs. of phosphorus, and 2 parts or 2 eqs. of hydrogen. In the same paper he establishes the existence of a compound formed of 31·4 parts or 2 eqs. of phosphorus, and 1 part or 1 eq. of hydrogen. The compounds of phosphorus and hydrogen are therefore,

	Phos.		Hyd.	Equiv.	Formulæ.
Solid Phosphuretted Hydrogen	31·4 2 eq.	+	1 1 eq.	= 32·4	P_2H.
Inflammable ditto.	31·4 2 eq.	+	2 2 eq.	= 33·4	P_2H_2.
Gaseous ditto.	31·4 2 eq.	+	3 3 eq.	= 34·4	P_2H_3.

Solid Phosphuretted Hydrogen.—When phosphuretted hydrogen gas, recently prepared by the action of quick-lime and phosphorus, is exposed in the moist state to a strong diffused light, or to the direct rays of the sun, the solid phosphuretted hydrogen is deposited on the sides of the glass vessel. It is also left as an insoluble powder when phosphuret of potassium is dissolved in water. As obtained by the former process, it is a canary yellow flocculent matter, is insoluble in water and alcohol; but with the former, a slow oxidation takes place, and hydrogen is evolved. It is not altered by a temperature of 234°, but heated beyond that point it is decomposed. When brought into contact with chlorine and nitric acid, it suffers instantaneous decomposition. According to the analysis of Leverrier, it is composed of 1 part or 1 eq. of hydrogen, and 31·4 parts or 2 eqs. of phosphorus. Hence *its eq.* is 32·4; *symb.* HP_2.

PHOSPHURETTED HYDROGEN.

Hist. and Prep.—Discovered by Davy in 1812. It may be prepared by several methods. Davy prepared it by heating hydrated phosphorous acid in a retort (page 204); and it is evolved from hydrous hypophosphorous acid by similar treatment, and by the action of strong hydrochloric acid on phosphuret of calcium according to Dumas. It may also be obtained, but in an impure state, by boiling phosphorus with a solution of potassa or milk of lime. Its production is in these cases dependent on the decomposition of water, the oxygen and hydrogen of which unite with different portions of phosphorus, and phosphoric acid, hypophosphorus acid and phosphuretted hydrogen are generated.

Prop.—A transparent colourless gas of an exceedingly offensive odour and bitter taste. It has no action on test paper. It is absorbed in small quantity by water, but freely by solutions of chloride of calcium or sulphate of the oxide of copper, by which means its purity may be ascertained. Like sulphuretted hydrogen, it frequently decomposes metallic salts, giving rise to the formation of water and a phosphuret of the metal. But if the metal have a feeble affinity for oxygen, it is thrown down in the metallic state, and water and phosphoric acid are generated. This is the case, according to Rose, with solutions of gold and silver.

It is a non-supporter of combustion, and is very destructive to animal life. When pure, it may be mixed with air or oxygen gas at common temperatures without danger; but the mixture detonates with the electric spark or at a temperature of 300°. Even diminished pressure causes an explosion; an effect which, in operating with a mercurial trough, is produced simply by raising the tube, so that the level of the mercury within may be a few inches higher than at the outside. Such is the property of the pure gas, as obtained from the hydrated phosphorous or hypophosphorous acids; but if it be procured from the action of phosphorus on potassa or hydrate of lime, it is remarkable for being spontaneously inflammable when mixed with air or oxygen gas. If the beak of the retort from which it issues is plunged under water, so that successive bubbles of the gas may arise through the liquid, a very beautiful appearance takes place. Each bubble, on reaching the surface of the water, bursts into flame, and forms a ring of dense white smoke which enlarges as it ascends, and retains its shape, if the air is tranquil, until it disappears. The wreath is formed by the products of the combustion—metaphosphoric acid and water. If received in a vessel of oxygen gas, the entrance of each bubble is instantly followed by a strong concussion, and a flash of white light of extreme intensity. It is remarkable that whatever may be the excess of oxygen, traces of phosphorus always escape combustion; but that if the gas be previously mixed with three times its volume of carbonic acid, and be then mixed with oxygen, the combustion is perfect. Dalton observed that it may be mixed with pure oxygen in a tube three-tenths of an inch in diameter without taking fire; but that the mixture detonates when an electric spark is transmitted through it.

In consequence of the combustibility of phosphuretted hydrogen, it would be hazardous to mix it in any quantity with air or oxygen gas in close vessels. For the same reason care is necessary in the formation of this gas, lest, in mixing with the air of the apparatus, an explosion ensue, and the vessel burst. The risk of such an accident is avoided, when phosphuret of calcium is used, by filling the flask or retort entirely with dilute acid; and in either of the other processes, by causing the phosphuretted hydrogen to be formed slowly at first, in order that the oxygen gas within the apparatus may be gradually consumed. A very simple method of averting all danger has been mentioned by Graham. It consists in moistening the interior of the retort with one or two drops of ether, the vapour of which, when mixed with atmospheric air even in small proportion, effectually prevents the combustion of phosphuretted hydrogen. The same effect may be produced by the addition of several other bodies. He also finds that a gas, which is not spontaneously inflammable, acquires this property on being mixed with from $\frac{1}{1000}$ to $\frac{1}{10000}$ of its volume of nitrous acid. According to Leverrier, it is very probable that there exists a compound of phosphorus and hydrogen composed of 2 eqs. of each of its elements, and that this compound being spontaneously inflammable communicates that property to phosphuretted hydrogen gas. This opinion is grounded on the fact that when spontaneously inflammable phosphuretted hydrogen is kept for any length of time in a dark place it suffers no change, but if brought into a strong light solid phosphuretted hydrogen is deposited, and the residual gas is no longer spontaneously inflammable. Thus it appears that by the action of light P_2H_2 is decomposed, and P_2H and P_2H_3 are formed. The result of his analysis supports this view.

[According to the still more recent observations of H. Rose, perfectly *dry* phosphuretted hydrogen undergoes no change when kept either in the dark or

exposed to sunlight. He therefore rejects the opinion of Leverrier, that the self-inflammability of the gas in question arises from its containing another compound of phosphorus and hydrogen. From the researches of Graham this property would seem to be due to the presence, in minute quantity, of some unknown compound, perhaps, of phosphorus and oxygen, which in its action corresponds to that of nitrous acid. The gas examined by Leverrier was not dry.]

Dumas ascertained the composition of phosphuretted hydrogen by introducing into a tube containing the gas a fragment of bichloride of mercury, and applying heat so as to convert it into vapour. Mutual decomposition instantly took place: phosphuret of mercury and hydrochloric acid were generated; and 100 measures of gas, thus decomposed, yielded 300 measures of hydrochloric acid gas, corresponding to 150 of hydrogen. The quantity of hydrogen contained in any given volume of phosphuretted hydrogen is thus found; and the weight of the former deducted from that of the latter gives the quantity of combined phosphorus. This inference is conformable to the quantity of oxygen required for the combustion of phosphuretted hydrogen. Thomson affirms that when this gas is detonated with 1·5 of its volume of oxygen gas, the only products are water and phosphorous acid; but that when the oxygen is in considerable excess, two volumes disappear for one of the compound, and water and phosphoric acid are generated. Now the hydrogen contained in one volume of phosphuretted hydrogen is equal to 1·5, and it unites with 0·75 of oxygen. Hence if 0·75, or $\frac{3}{4}$, be deducted from 1·5 and from 2, the remainders, $\frac{3}{4}$ and $\frac{5}{4}$, represent the relative quantity of oxygen which is required to convert the same weight of phosphorus into phosphorous and phosphoric acid. These numbers are obviously in the ratio of 3 to 5, as already stated on the authority of Berzelius (page 203). The elements of the calculation have been confirmed both by Dumas and Buff.

Agreeably to these views, and to the combining volume of phosphorus (page 140), 100 measures of phosphuretted hydrogen gas contain 150 of hydrogen gas and 25 of the vapour of phosphorus; and hence, as

			Grains.
150	cubic inches of	Hydrogen gas weigh	3·1977
25	do.	Phosphorous vapour weigh	33·5425
100	do.	Phosphuretted Hydrogen gas should weigh	36·7402.

The calculated density of a gas so constituted should be 1·1853, which is nearly a mean of the observations of Dumas and Rose.

If the equivalent of phosphorus were 31·4 instead of 15·7, as is very far from improbable, then the combining volume of phosphorous vapour would be 50 instead of 25 (page 140); and phosphuretted hydrogen would consist of 50 measures of phosphorous vapour and 300 of hydrogen gas condensed into 200 measures.

Phosphuretted hydrogen has neither an acid nor alkaline reaction; but in its chemical relations it inclines to alkalinity. Thus it unites with hydrobromic and hydriodic acids, forming definite compounds which crystallize in cubes; and Rose finds that it unites with metallic chlorides, forming compounds analogous to those which ammonia forms with metallic chlorides.

Its eq. is 34·4; *eq. vol.* = 100; *symb.* P_2H_3, or PH_3.

SECTION VI.

COMPOUNDS OF NITROGEN AND CARBON.

BICARBURET OF NITROGEN, OR CYANOGEN GAS.

Hist. and Prep.—Discovered in 1815 by Gay-Lussac (An. de Ch. xcv.). It is prepared by heating carefully dried bicyanide of mercury in a small glass retort by means of a spirit lamp. This cyanide, which was formerly considered a compound of oxide of mercury and prussic acid, and was then called *prussiate of mercury*, is composed of metallic mercury and cyanogen. On exposure to a low red heat it is resolved into its elements; the cyanogen passes over in the form of gas, and the metallic mercury is sublimed. The retort, at the close of the process, contains a small residue of a dark brown matter like charcoal, but which Johnston has shown to consist of the same ingredients as the gas itself.

Prop.—A colourless gas possessing a strong pungent and very peculiar odour. At the temperature of 45° and under a pressure of 3·6 atmospheres, it is a limpid liquid, which Kemp finds to be a non-conductor of electricity, and which resumes the gaseous form when the pressure is resumed. It extinguishes burning bodies; but it is inflammable, and burns with a beautiful and characteristic purple flame. It can support a strong heat without decomposition. Water at the temperature of 60° absorbs 4·5 times, and alcohol 23 times its volume of the gas. The aqueous solution reddens litmus paper; but this effect is not to be ascribed to the gas itself, but to the presence of acids which are generated by the mutual decomposition of cyanogen and water. It appears from the observations of Wöhler that two of the products are cyanic acid and ammonia; which, uniting together, generate urea (An. de Ch. et Ph. xliii. 73).

The composition of cyanogen may be determined by mixing that gas with a due proportion of oxygen, and inflaming the mixture by electricity. Gay-Lussac ascertained in this way that 100 measures of cyanogen require 200 of oxygen for complete combustion, that no water is formed, and that the products are 200 measures of carbonic acid gas and 100 of nitrogen. Hence it follows that cyanogen contains its own bulk of nitrogen, and twice its volume of the vapour of carbon. Consequently, since

		Grains.
100 cubic inches of	Nitrogen gas weigh . . .	30·166
200 do.	the vapour of Carbon weigh . .	26·306
100 cubic inches of	Cyanogen gas must weigh . .	56·472

The ratio of its elements by weight is,

Nitrogen	30·166	0·9727	14·15	1 eq.
Carbon	26·306	0·8430 (2 + 0·4215)	12·24	2 eq.

The sp. gr. of a gas so constituted is 0·9727 + 0·843 = 1·8157, which is near 1·8064, the number found experimentally by Gay-Lussac.

Cyanogen is a *bicarburet of nitrogen*, the formula of which is N + 2C, or NC_2; but its most convenient name is *cyanogen*, proposed by its discoverer,* which may be expressed shortly by Cy. *Its eq. is* 26·39.

Paracyanogen.—An examination of the brown matter, left in the retort after the preparation of cyanogen gas, has been made by Johnston, who by burning it with chlorate of potassa found it to contain carbon and nitrogen united in the same ratio as in cyanogen gas. It is, in fact, a solid bicarburet of nitrogen, isomeric with cyanogen, but differing from it essentially in its physical and chemical relations. On heating this solid bicarburet in the open air, several definie compounds of carbon and nitrogen may be successively obtained. After considerable heating, the ratio of carbon to nitrogen is as 3 to 2; again heated, the proportion becomes as 7 to 6; and finally, after a still longer heat, the ratio of the equivalents is as 1 to 1. Thus the carbon is gradually burned away, leaving the nitrogen fixed, until a protocarburet of nitrogen is formed. On continuing the heat after this period, both elements fly off together, and the whole is dissipated. The solid bicarburet of cyanogen is also generated, when a saturated solution of cyanogen in alcohol is kept in contact with mercury; and Johnston suggests that the carbonaceous residue after the charring of animal substances by heat, is probably in many cases a carburet of nitrogen, and not pure charcoal as is commonly thought. (Brewster's Journ. N. S. i. 75.) Paracyanogen is soluble in sulphuric and nitric acids, and forms a compound with oxygen in which 1 eq. of oxygen is combined with 4 eqs. of nitrogen and 8 eqs. of carbon. Hence the eq. of paracyanogen is probably 105·56, and its symb. N_4C_8.

Mellon—Is obtained when sulphuret of cyanogen, melame, melamine, ammeline, or ammelide, is exposed to a red heat. It is a lemon yellow powder, is insoluble in water and alcohol, but is dissolved and decomposed by acids and alkalies. Exposed to a strong red heat, it is decomposed and forms 1 vol. of nitrogen and 3 vols. of cyanogen gas. It is one of the compound radicals. *Its eq. is* 93·32; *symb.* N_4C_6. (*Lieb. An.* ix. 5.)

Cyanogen, though a compound body, has a remarkable tendency to combine with elementary substances. Thus it is capable of uniting with the simple non-metallic bodies, and evinces a strong attraction for metals. When potassium, for instance, is heated in cyanogen gas, such energetic action ensues, that the metal becomes incandescent, and cyanide of potassium is generated. The affinity of cyanogen for metallic oxides, on the contrary, is comparatively feeble. It enters into direct combination with a few alkaline bases only, and these compounds are by no means permanent. From these remarks it is apparent that cyanogen has no claim to be regarded as an acid, as it has none of the properties of a compound. It is, in fact, a compound radical of organic chemistry, and therefore its various combinations will be described in that part of the work.

* From κυανος, *blue*, and γενναω, *I generate*; because it is an essential ingredient of Prussian blue.

SECTION VII.

COMPOUND OF PHOSPHORUS AND NITROGEN.

Phosphuret of Nitrogen.—First described by Rose (Pogg. An. xxviii. 529). On saturating either of the chlorides of phosphorus with dry ammoniacal gas, a white solid mass is obtained, which on exposure to a strong red heat gives rise to the formation of phosphuret of nitrogen, hydrochloric acid gas being at the same time evolved. It is also formed when the vapour of either chlorides of phosphorus are brought into contact with sal-ammonia heated nearly to its point of sublimation.

It is a light snow-white powder; is insoluble in water, and in dilute acid, or alkaline solutions. It is not changed by a red heat in close vessels, or in an atmosphere of chlorine, or the vapour of sulphur; but in hydrogen it is decomposed with the formation of ammoniacal gas. It is composed of 31·4 parts or 2 eqs. of phosphorus, and 14·15 parts or 1 eq. of nitrogen.

Its eq. is 45·55; *symb.* N + 2P, or NP_2.

SECTION VIII.

COMPOUND OF SULPHUR, CARBON, ETC.

The compounds described in this section are thus constituted:—

Bisulph. of Carbon	Carb. 6·12 + Sulp. 32·2 = 38·32.	C + 2S CS_2.
Sulph. of Phosphorus	Composition uncertain.	
Bisulph. of Selenium	Selen. 39·6 + Sulp. 32·2 = 71·8	Se + 2S SeS_2.
Seleni. of Phosphorus	Composition uncertain.	

Bisulphuret of Carbon.—Hist.—This substance was discovered accidentally in the year 1796 by Professor Lampadius, who regarded it as a compound of sulphur and hydrogen, and termed it *alcohol of sulphur*. Clément and Desormes first declared it to be a sulphuret of carbon, and their statement was fully confirmed by the joint researches of Berzelius and the late Dr. Marcet (Phil. Trans. 1813).

Prep.—Bisulphuret of carbon may be obtained by heating in close vessels native bisulphuret of iron (iron pyrites) with one-fifth of its weight of well-dried charcoal; or by transmitting the vapour of sulphur over fragments of charcoal heated to redness in a tube of porcelain. The compound, as it is formed, should be conducted by means of a glass tube into cold water, at the bottom of which it is collected. To free it from moisture and adhering sulphur, it should be distilled at a low temperature in contact with chloride of calcium.

Prop.—It is a transparent colourless liquid, which is remarkable for its high refractive power. Its sp. gr. is 1·272; of its vapour, 2·668. It has an acid, pungent, and somewhat aromatic taste, and a very fetid odour. It is exceedingly volatile; its vapour at 63·5° supports a column of mercury 7·36 inches long; and at 110° it enters into brisk ebullition. From its great volatility it may be employed for producing intense cold. It is very inflammable, and kindles in the open air at a temperature scarcely exceeding that at which mercury boils. It burns with a pale blue flame. Admitted into a vessel of oxygen gas, so much vapour rises as to form an explosive mixture; and when mixed in like manner with binoxide of nitrogen, it forms a combustible mixture, which is kindled on the approach of a lighted taper, and burns rapidly, with a large greenish-white flame of dazzling brilliancy. It dissolves readily in alcohol and ether, and is precipitated from the solution by water. It dissolves sulphur, phosphorus, and iodine, and the solution of the latter has a beautiful pink colour. Chlorine decomposes it, with formation of chloride of sulphur. The pure acids have little action upon it. By nitro-hydrochloric acid it is changed into a white crystalline substance like camphor, which Berzelius regards as a compound of the hydrochloric, carbonic, and sulphurous acids.

Bisulphuret of carbon is a sulphur-acid, that is, unites with *sulphur-bases* to constitute compounds analogous to ordinary salts, and hence called *sulphur-salts*. Thus bisulphuret of carbon unites with sulphuret of potassium, forming a sulphur-salt, in which the former acts as an acid and the latter as a base. The same compound is formed by the action of bisulphuret of carbon on a solution of pure potassa: but in this case sulphuret of potassium is first generated by an interchange of elements with a portion of bisulphuret of carbon, carbonic acid being produced at the same time. Thus—

2 eq. potassa & 1 eq. bisulph. carbon yield 2 eq. sulphuret potassium and 1 eq. carb. acid.

$$2KO + CS_2 \quad \text{yield} \quad 2KS + CO_2.$$

If the bisulphuret of carbon is in sufficient quantity, carbonic acid gas is disengaged, and a neutral compound results. Such is inferred to be the nature of the change, agreeably to the researches of Berzelius on the sulphur-salts.

Its eq. is 38·32; *eq. vol.* = 100; *symb.* CS_2.

Sulphuret of Phosphorus.—When sulphur and fused phosphorus are brought into contact they unite readily, but in proportions which have not been precisely determined; and they frequently react on each other with such violence as to cause an explosion. For this reason the experiment should be made with a quantity of phosphorus not exceeding 30 or 40 grains. The phosphorus is placed in a glass tube, 5 or 6 inches long, and about half an inch wide; and when by a gentle heat it is liquefied, the sulphur is added in successive small portions. Heat is evolved at the moment of combination, and hydrosulphuric and phosphoric acids, owing to the presence of moisture, are generated. This compound may also be made by agitating flowers of sulphur with fused phosphorus under water. The temperature should not exceed 160°; for otherwise hydrosulphuric and phosphoric acids would be evolved so freely as to prove dangerous, or at least to interfere with the success of the process.

Sulphuret of phosphorus, from the nature of its elements, is highly combustible. It is much more fusible than phosphorus. A compound made by Faraday with about 5 parts of sulphur and 7 of phosphorus, was quite fluid at 32°, and did not solidify at 20° (Quarterly Journal, iv.).

Bisulphuret of Selenium.—Sulphur and selenium mix together in all proportions by fusion, and therefore by such means it is difficult to procure a definite compound; but the bisulphuret of an orange colour was formed by Berzelius by precipitating a solution of selenious acid with hydrosulphuric acid. The sulphuret found by Stromeyer among the volcanic products of the Lipari isles is probably similar in composition. Bisulphuret of selenium fuses at a heat a little above 212°, and at a higher temperature may be sublimed without change. In the open air it takes fire when heated, and sulphurous, selenious, and selenic acids are the products of its combustion. The alkalies and soluble metallic sulphurets dissolve it. Nitric acid acts upon it with difficulty; but the nitro-hydrochloric converts it into sulphuric and selenious acids. (An. of Phil. xiv.)

Seleniuret of Phosphorus.—This compound may be prepared in the same manner as the sulphuret of phosphorus; but as selenium is capable of uniting with phosphorus in several proportions, the compound formed by fusing them together can hardly be supposed to be of a definite nature. This seleniuret is very fusible, sublimes without change in close vessels, and is inflammable. It decomposes water gradually when digested in it, giving rise to seleniuretted hydrogen, and one of the acids of phosphorus.

Sulphuret of Nitrogen.—This compound is formed, according to Soubeiran, by the action of water on a compound of chloride of sulphur and ammonia, $SCl + 2NH_3$. The sulphuret of nitrogen is a yellow or green solid, the colour of which varies according to the mode of preparation. It is converted, by digestion with water, entirely into hyposulphurous acid and ammonia; hence its composition is NS_3 and $2NS_3 + 6HO = 2NH_3 + 3S_2O_2$.

When aqua ammoniæ acts on chloride of sulphur a red solid compound is formed which is composed of chloride of sulphur, sulphuret of nitrogen, and ammonia. This body undergoes spontaneous decomposition, and is converted into a yellow pulverulent mass (Soubeiran). When this mass, which consists chiefly of sulphur, is boiled with alcohol, or exhausted by percolation with cold alcohol, the alcohol dissolves a substance in small quantity, which may be had in white needles or cubical crystals, and which contains 92 — 93 p. c. sulphur and 5 — 6 p. c. nitrogen. Gregory, who discovered this compound, thought that it might be a sulphuret of nitrogen. But in its analysis he always obtained a little hydrogen, and the nature of this substance was left unsettled. Soubeiran is of opinion that it contains sulphur, nitrogen, and ammonia. The quantity of sulphur, however, is so large, that its constitution must be unusual; and it merits a careful examination. Gregory showed that its solution in alcohol, when mixed with an alcoholic solution of caustic potash, acquires a deep amethyst colour, which soon disappears, while ammonia is set free, pure hyposulphate of potash is deposited, and traces of a volatile compound, probably formed at the expense of the alcohol, are observed.

METALS.

GENERAL PROPERTIES OF METALS.

METALS are distinguished from other substances by the following properties. They are all conductors of electricity and heat. When the compounds which they form with oxygen, chlorine, iodine, sulphur, and similar substances, are submitted to the action of galvanism, the metals always appear at the negative side of the battery, and are hence said to be positive electrics. They are quite opaque, refusing a passage to light, though reduced to very thin leaves. They are in general good reflectors of light, and possess a peculiar lustre, which is termed the metallic lustre. Every substance in which these characters reside may be regarded as a metal.

The number of metals, the existence of which is admitted by chemists, amounts to forty-two. The following table contains the names of those that have been procured in a state of purity, together with the date at which they were discovered, and the names of the chemists by whom the discovery was made.

Table of the Discovery of Metals.

Names of Metals.	Authors of the Discovery.	Dates of the Discovery.
Gold, Silver, Iron, Copper, Mercury, Lead, Tin	Known to the Ancients.	
Antimony	Described by Basil Valentine	1490
Bismuth	Described by Agricola in	1530
Zinc	First mentioned by Paracelsus	16th century
Arsenic, Cobalt	Brandt, in	1733
Platinum	Wood, assay-master, Jamaica	1741
Nickel	Cronstedt	1751
Manganese	Gahn and Scheele	1774
Tungsten	D'Elhuyart	1781
Tellurium	Müller	1782
Molybdenum	Hielm	1782
Uranium	Klaproth	1789
Titanium	Gregor	1791
Chromium	Vauquelin	1797

Table of the Discovery of Metals—(continued).

Names of Metals.	Authors of the Discovery.	Dates of the Discovery.
Columbium	Hatchett	1802
Palladium, Rhodium	Wollaston	1803
Iridium	Descotils and Smithson Tennant	1803
Osmium	Smithson Tennant	1803
Cerium	Hisinger and Berzelius	1804
Potassium, Sodium, Barium, Strontium, Calcium	Davy	1807
Cadmium	Stromeyer	1818
Lithium	Arfwedson	1818
Zirconium	Berzelius	1824
Aluminium, Glucinium, Yttrium	Wöhler	1828
Thorium	Berzelius	1829
Magnesium	Bussy	1829
Vanadium	Sefström	1830
Lantanium	Mosander	1839

Most of the metals are remarkable for their great specific gravity; some of them, such as gold or platinum, which are the densest bodies known in nature, being more than 19 times heavier than an equal bulk of water. Great density was once supposed to be an essential characteristic of metals; but the discovery of potassium and sodium, which are so light as to float on the surface of water, has shown that this supposition is erroneous. Some metals experience an increase of density to a certain extent when hammered, their particles being permanently approximated by the operation. On this account, the density of some of the metals contained in the following table is represented as varying between two extremes.

Table of the Specific Gravity of Metals at 60° Fahr. compared to Water as Unity.

Platinum	20·98	Brisson.
Gold	19·257	Do.
Tungsten	17·6	D'Elhuyart.
Mercury	13·568	Brisson.
Palladium	11·3 to 11·8	Wollaston.
Lead	11·352	Brisson.
Silver	10·474	Do.
Bismuth	9·822	Do.
Uranium	9·000	Bucholz.
Copper	8·895	Hatchett.
Cadmium	8·604	Stromeyer.
Cobalt	8·538	Haüy.
Arsenic	5·8843	Turner.
Nickel	8·279	Richter.
Iron	7·788	Brisson.
Molybdenum	7·400	Hielm.
Tin	7·291	Brisson.
Zinc	6·861 to 7·1	Do.

Manganese	6·850	Bergmann.
Antimony	6·702	Brisson.
Tellurium	6·115	Klaproth.
Titanium	5·3	Wollaston.
Sodium	0·972	Gay-Lussac and Thenard.
Potassium	0·865	

Some metals possess the property of *malleability*, that is, admit of being beaten into thin plates or leaves by hammering. The malleable metals are gold, silver, copper, tin, platinum, palladium, cadmium, lead, zinc, iron, nickel, potassium, sodium, and frozen mercury. The other metals are either malleable in a very small degree only, or, like antimony, arsenic and bismuth, are actually brittle. Gold surpasses all metals in malleability: one grain of it may be extended so as to cover about 52 square inches of surface, and to have a thickness not exceeding $\frac{1}{282020}$th of an inch.

Nearly all malleable metals may be drawn out into wires, a property which is expressed by the term *ductility*. The only metals which are remarkable in this respect are gold, silver, platinum, iron, and copper. Wollaston devised a method by which gold wire may be obtained so fine that its diameter shall be only $\frac{1}{5000}$th of an inch, and that 550 feet of it are required to weigh one grain. He obtained a platinum wire so small, that its diameter did not exceed $\frac{1}{30000}$th of an inch (Phil. Trans. 1813). It is singular that the ductility and malleability of the same metal are not always in proportion to each other. Iron, for example, cannot be made into fine leaves, but it may be drawn into very small wires.

The tenacity of metals is measured by ascertaining the greatest weight which a wire of a certain thickness can support without breaking. According to the experiments of Guyton-Morveau, whose results are comprised in the following table, iron, in point of tenacity, surpasses all other metals.

The diameter of each wire was 0·787th of a line.

	Pounds.
Iron wire supports	549·25
Copper	302·278
Platinum	274·32
Silver	187·137
Gold	150·753
Zinc	109·54
Tin	34·63
Lead	27·621

According to some recent observations of Baudrimont, the process of annealing destroys the tenacity of metals to a considerable extent. Thus he found that a wire of soft iron which supported a weight of 26 lbs., on being annealed could only bear 12 lbs.; and a copper wire which could support 22 lbs. was broken, when annealed, by 9 lbs. Numerous experiments with different specimens of brass wire confirm the generality of the result (An. de Ch. et Ph. lx. 78).

Metals differ also in hardness; but I am not aware that their exact relation to each other, under this point of view, has been determined by experiment. In the list of hard metals may be placed titanium, manganese, iron, nickel, copper, zinc, and palladium. Gold, silver, and platinum are softer than these; lead is softer still, and potassium and sodium yield to the pressure of the fingers. The properties of elasticity and sonorousness are allied to that of hardness. Iron and copper are in these respects the most conspicuous.

Many of the metals have a distinctly crystalline texture. Iron, for example, is fibrous; and zinc, bismuth, and antimony are lamellated. Metals are sometimes obtained also in crystals; and most of them in crystallizing assume the figure of a cube, the regular octohedron, or some form allied to it. Gold, silver, and copper occur naturally in crystals; while others crystallize when they pass gradually from the liquid to the solid condition. Crystals are most readily procured from those metals which fuse at a low temperature; and bismuth, from conducting heat less perfectly than other metals, and therefore cooling more slowly, is best fitted for the purpose. The process should be conducted in the way already described for forming crystals of sulphur.

Metals, with the exception of mercury, are solid at common temperatures; but they may all be liquefied by heat. The degree at which they *fuse*, or their *point* of *fusion*, is very different for different metals, as appears from the following table:—

Table of the fusibility of different Metals.

		Fahr.	
Fusible below a red heat	Mercury	—39°	Different chemists.
	Potassium	136	Gay-Lussac and Thenard.
	Sodium	190	
	Tin	442	Crichton.
	Bismuth	497	
	Lead	612	
	Tellurium—rather less fusible than lead		Klaproth.
	Arsenic—undetermined.		
	Zinc	773	Daniell.
	Antimony—a little below a red heat.		
	Cadmium	about 442	Stromeyer.
Infusible below a red heat.	Silver	1873	Daniell.
	Copper	1996	
	Gold	2016	
	Cobalt—rather less fusible than iron.		
	Iron, cast	2786	Daniell.
	Iron, malleable		Requiring the highest heat of a smith's forge.
	Manganese		
	Nickel—nearly the same as cobalt.		
	Palladium.		
	Molybdenum, Uranium, Tungsten, Chromium		Almost infusible, and not to be procured in buttons by the heat of a smith's forge. Fusible before the oxy-hydrogen blowpipe.
	Titanium, Cerium, Lantanium, Osmium, Iridium, Rhodium, Platinum, Columbium		Infusible in the heat of a smith's forge, but fusible before the oxy-hydrogen blowpipe.

Metals differ also in volatility. Some are readily volatilized by heat, while others are of so fixed a nature that they may be exposed to the most intense heat of a wind furnace without being dissipated in vapour. There are seven metals, the volatility of which has been ascertained with certainty; namely, cadmium, mercury, arsenic, tellurium, potassium, sodium, and zinc.

Metals cannot be resolved into more simple parts; and therefore, in the present state of chemistry, they must be regarded as elementary bodies. It was formerly

conceived that they might be converted into each other; and this notion led to the vain attempts of the alchemists to convert the baser metals into gold. The chemist has now learned that his art solely consists in resolving compound bodies into their elements, and causing substances to unite which were previously uncombined. One elementary principle cannot assume the properties peculiar to another.

Metals have an extensive range of affinity, and on this account few of them are found in the earth *native*, that is, in an uncombined form. They commonly occur in combination with other bodies, especially with oxygen and sulphur, in which state they are said to be *mineralized*. It is a singular fact in the chemical history of the metals, that they are little disposed to combine in the metallic state with compound bodies, such as an oxide or an acid. They unite readily, on the contrary, with elementary substances. Thus they often combine with each other, yielding compounds termed *alloys*, which possess all the characteristic physical properties of pure metals. They unite likewise with the simple non-metallic substances, such as oxygen, chlorine, and sulphur, giving rise to new bodies in which the metallic character is wholly wanting. In all these combinations the same tendency to unite in a few definite proportions, is equally conspicuous as in that department of the science of which I have just completed the description. The chemical changes are regulated by the same general laws, and in describing them the same nomenclature is applicable.

The order which it is proposed to follow in describing the metals has already been explained in the introduction; but before treating of each separately, some general observations may be premised, by which the study of this subject will be much facilitated.

Metals are of a combustible nature, that is, they are not only susceptible of slow oxidation, but, under favourable circumstances, they unite rapidly with oxygen, giving rise to all the phenomena of real combustion. Zinc burns with a brilliant flame when heated to full redness in the open air; iron emits vivid scintillations on being inflamed in an atmosphere of oxygen gas; and the least oxidable metals, such as gold and platinum, scintillate in a similar manner when heated by the oxy-hydrogen blowpipe.

The product either of the slow or rapid oxidation of a metal, when heated in the air, has an earthy aspect, and was called a *calx* by the older chemists, the process of forming it being expressed by the term *calcination*. Another method of oxidizing metals is by *deflagration*; that is, by mixing them with nitrate or chlorate of potassa, and projecting the mixture into a red-hot crucible. Most metals may be oxidized by digestion in nitric acid; and nitro-hydrochloric acid is an oxidizing agent of still greater power.

Some metals unite with oxygen in one proportion only, but most of them have two or three degrees of oxidation. Metals differ remarkably in their relative forces of attraction for oxygen. Potassium and sodium, for example, are oxidized by mere exposure to the air; and they decompose water at all temperatures the instant they come in contact with it. Iron and copper may be preserved in dry air without change, nor can they decompose water at common temperatures; but they are both slowly oxidized by exposure to a moist atmosphere, and combine rapidly with oxygen when heated to redness in the open air. Iron has a stronger affinity for oxygen than copper; for the former decomposes water at a red heat, whereas the latter cannot produce that effect. Mercury is less inclined than copper to unite with oxygen. Thus it may be exposed without change to the

influence of a moist atmosphere. At a temperature of 650° or 700° it is oxidized; but at a red heat it is reduced to the metallic state, while oxide of copper can sustain the strongest heat of a blast furnace without losing its oxygen. The affinity of gold for oxygen is still weaker than that of mercury; for it will bear the most intense heat of our furnaces without oxidation.

Metallic oxides suffer *reduction*, or may be reduced to the metallic state in several ways:

1. By heat alone. By this method the oxides of gold, silver, mercury, and platinum, may be decomposed.

2. By the united agency of heat and combustible matter. Thus, by transmitting a current of hydrogen gas over the oxides of copper or iron heated to redness in a tube of porcelain, water is generated, and the metals are obtained in a pure form. Carbonaceous matters are likewise used for the purpose with great success. Potassa and soda, for example, may be decomposed by exposing them to a white heat after being intimately mixed with charcoal in fine powder. A similar process is employed in metallurgy for extracting metals from their ores, the inflammable materials being wood, charcoal, coke, or coal. In the more delicate operations of the laboratory, charcoal, *black flux*, and formiate of soda are preferred.

3. By the galvanic battery. This is a still more powerful agent than the preceding; since some oxides, such as baryta and strontia, which resist the united influence of heat and charcoal, are reduced by the agency of galvanism.

4. By the action of deoxidizing agents on metallic solutions. Phosphorous acid, for example, when added to a liquid containing oxide of mercury, deprives the oxide of its oxygen, metallic mercury subsides, and phosphoric acid is generated. Formic acid and formiate of soda, when boiled with the solutions of the oxides of gold, platinum, silver, mercury, &c. reduces the metals. In like manner, one metal may be precipitated by another, provided the affinity of the latter for oxygen exceeds that of the former. Thus, when mercury is added to a solution of nitrate of the oxide of silver, metallic silver is thrown down, and oxide of mercury is dissolved by the nitric acid. On placing metallic copper in the liquid, pure mercury subsides, and a nitrate of the oxide of copper is formed; and from this solution metallic copper may be precipitated by means of iron.

Metals, like the simple non-metallic bodies, may give rise to oxides or acids by combining with oxygen. The former are the most frequent products. Many metals which are not acidified by oxygen may be formed into oxides; whereas one metal only, arsenic, is capable of forming an acid and not an oxide. All the other metals which are convertible into acids by oxygen, such as chromium, tungsten, and molybdenum, are also susceptible of yielding one or more oxides. In these instances, the acids always contain a larger quantity of oxygen than the oxides of the same metal.

Many of the metallic oxides have the property of combining with acids. In some instances all the oxides of a metal are capable of forming salts with acids, as is exemplified by the oxides of iron; but, generally, the protoxide is the sole *alkaline* or *salifiable base*. Most of the metallic oxides are insoluble in water; but all those that are soluble have the property of giving a brown stain to yellow turmeric paper, and of restoring the blue colour of reddened litmus.

Oxides sometimes unite with each other, and form definite compounds. The most abundant ore of chromium, commonly called chromate of iron, is an instance

of this kind; and the red oxide of manganese, the magnetic oxide of iron, and the red oxide of lead, appear to belong to the same class of bodies.

Chlorine has a powerful affinity for metallic substances. It combines readily with most metals at common temperatures, and the action is in many instances so violent as to be accompanied with the evolution of light. For example, when powdered zinc, arsenic, or antimony is thrown into a jar of chlorine gas, the metal is instantly inflamed. The attraction of chlorine for metals even surpasses that of oxygen. Thus, when chlorine is brought into contact at a red heat with pure lime, magnesia, baryta, strontia, potassa or soda, oxygen is emitted, and a chloride of the metal is generated, the elements of which are so strongly united that no temperature hitherto tried can separate them. All other metallic oxides are, with few exceptions, acted on in the same manner by chlorine, and in some cases the change takes place below the temperature of ignition.

Most of the metallic chlorides are solid at common temperatures. They are fusible by heat, assume a crystalline texture in cooling, and under favourable circumstances crystallize with regularity. Several of them, such as the chlorides of tin, arsenic, antimony, and mercury, are volatile, and may be sublimed without change. They are for the most part colourless, do not possess the metallic lustre, and have the aspect of a salt. Two of the chlorides are insoluble in water, namely, chloride of silver and protochloride of mercury; several, such as the chlorides of antimony, arsenic and titanium, are decomposed by that liquid; but most of them are more or less soluble.

Some of the metallic chlorides, those especially of gold and platinum, are decomposable by heat. All the chlorides of the common metals are decomposed at a red heat by hydrogen gas, hydrochloric acid being disengaged while the metal is set free. Pure charcoal does not affect their decomposition; but if moisture be present at the same time, hydrochloric and carbonic acid gases are formed, and the metal remains. They resist the action of anhydrous sulphuric acid; but all the chlorides, excepting those of silver and mercury, are readily decomposed by hydrated sulphuric acid, with disengagement of hydrochloric acid gas. The change is accompanied with decomposition of water, the hydrogen of which combines with chlorine, and its oxygen with the metal. When in solution, they may be recognized by yielding with nitrate of oxide of silver a white precipitate, which is chloride of silver.

Metallic chlorides may in most cases be formed by direct action of chlorine on the pure metals. They are also frequently procured by dissolving metallic oxides in hydrochloric acid, evaporating to dryness, and applying heat so long as any water is expelled. Metallic chlorides are often deposited from such solutions by crystallization.

Iodine has a strong attraction for metals; and most of the compounds which it forms with them sustain a red heat in close vessels without decomposition. But in the degree of its affinity for metallic substances it is inferior to chlorine and oxygen. We have seen that chlorine has a stronger affinity than oxygen for metals, since it decomposes nearly all oxides at high temperatures; and it separates iodine also from metals under the same circumstances. If the vapour of iodine is brought into contact with potassa, soda, protoxide of lead, or oxide of bismuth, heated to redness, oxygen gas is evolved, and the metals of those oxides will unite with iodine. But iodine, so far as is known, cannot separate oxygen from any other metal; nay, all the iodides, except those just mentioned,

are decomposed by exposure to oxygen gas at the temperature of ignition. All the iodides are decomposed by chlorine, bromine, and concentrated sulphuric and nitric acids; and the iodine which is set free may be recognized either by the colour of its vapour, or by its action on starch. The metallic iodides are generated under circumstances analogous to those above mentioned for procuring the chlorides.

The action of iodine on metallic oxides, when dissolved or suspended in water, is precisely analogous to that of chlorine. On adding iodine to a solution of the pure alkalies or alkaline earths, an iodide and iodate are generated.

Bromine in its affinity for metallic substances is intermediate between chlorine and iodine; for while chlorine disengages bromine from its combination with metals, metallic iodides are decomposed by bromine. The same phenomena attend the union of bromine with metals, as accompany the formation of metallic chlorides. Thus, antimony and tin take fire by contact with bromine, and its action with potassium is attended with a flash of light, and intense heat. These compounds have as yet been but partially examined. They may be formed by the action of bromine on the pure metals, and often by dissolving metallic oxides in hydrobromic acid, and evaporating the solution to dryness. Bromine unites with potassa, soda, and some other oxides, constituting bleaching compounds similar to the chlorides above described. Bromide of lime is obtained by the action of bromine on milk of lime, a yellowish solution being formed with water, which bleaches powerfully.

As fluorine has not hitherto been obtained in a separate state, the nature of its action on the metals is unknown; but the chief difficulty of procuring it in an insulated form appears to arise from its extremely powerful affinity for metallic substances, in consequence of which, at the moment of becoming free, it attacks the vessels and instruments employed in its preparation. The best mode of preparing the soluble fluorides, such as those of potassium and sodium, is by dissolving the carbonate of these alkalies in hydrofluoric acid, and evaporating the solution to perfect dryness. The insoluble fluorides are easily formed by precipitation from the soluble fluorides. They are without exception decomposed by concentrated sulphuric acid with the aid of heat; and the hydrofluoric acid, in escaping, may easily be detected by its action on glass.

Sulphur, like the preceding elementary substances, has a strong tendency to unite with metals, and the combination may be effected in several ways:

1. By heating the metal directly with sulphur. The metal, in the form of powder or filings, is mixed with a due proportion of sulphur, and the mixture heated in an earthen crucible, which is covered to prevent the access of air; or if the metal can sustain a red heat without fusing, the vapour of sulphur may be passed over it while heated to redness in a tube of porcelain. The act of combination, which frequently ensues below the temperature of ignition, is attended by free disengagement of heat, which in several instances is so great, that the whole mass becomes luminous, and shines with a vivid light. This appearance of combustion, which occurs quite independently of the presence of oxygen, is exemplified by the sulphurets of potassium, sodium, copper, iron, lead, and bismuth.

2. By igniting a mixture of a metallic oxide and sulphur.

3. By depriving the sulphate of an oxide of its oxygen by means of heat and combustible matter. Charcoal or hydrogen gas may be employed for the purpose, as will be described immediately.

4. By hydrosulphuric acid, or a soluble metallic sulphuret. Nearly all the salts of the second class of metals are decomposed when a current of hydrosulphuric acid gas is conducted into their solutions. The salts of uranium, iron, manganese, cobalt, and nickel are exceptions; but these are precipitated by sulphuret of potassium.

The sulphurets are opaque brittle solids, many of which, such as the sulphurets of lead, antimony, and iron, have a metallic lustre. They are all fusible by heat, and commonly assume a crystalline texture in cooling. Most of them are fixed in the fire; but the sulphurets of mercury and arsenic are remarkable for their volatility. All the sulphurets, excepting those of the first class of metals, are insoluble in water.

Most of the protosulphurets support an intense heat without decomposition; but, in general, those which contain more than one equivalent of sulphur, lose part of it when strongly heated. They are all decomposed without exception by exposure to the combined agency of air or oxygen gas and heat; and the products depend entirely on the degree of heat and the nature of the metal. The sulphuret is more or less converted into the sulphate of an oxide, provided the sulphate is able to support the temperature employed in the operation. If this is not the case, the sulphur is evolved under the form of sulphurous acid, and a metallic oxide is left; or if the oxide itself is decomposed by heat, the pure metal remains. The action of heat and air in decomposing metallic sulphurets is the basis of several metallurgic processes. A few sulphurets are decomposed by the actiou of hydrogen gas at a red heat, the pure metal being set free and hydrosulphuric acid evolved. Rose finds that the only sulphurets which admit of being easily reduced to the metallic state in this way are those of antimony, bismuth, and silver. The sulphuret of tin is decomposed with difficulty, and requires a very high temperature. All the other sulphurets which he subjected to this treatment were either deprived of a part only of their sulphur, such as bisulphuret of iron, or were not attacked at all, as happened with the sulphurets of zinc, lead, and copper. (Poggendorff's Annalen, iv. 109.)

Many of the metallic sulphurets were formerly thought to be compounds of sulphur and a metallic oxide; an error first pointed out by Proust, who demonstrated that protosulphuret of iron, as well as the bisulphuret, are compounds of sulphur and metallic iron without any oxygen. (Journal de Physique, liii.) He proved the same of the sulphurets of other metals, such as mercury and copper. He was of opinion, however, that in some instances sulphur does unite with a metallic oxide. Thus, when sulphur and peroxide of tin are heated together, sulphurous acid is disengaged, and the residue according to Proust is a sulphuret of the protoxide, but in this he was in error.

In 1817 Vauquelin extended these views to the compounds formed by heating an alkali or an alkaline earth with sulphur, which were previously regarded as sulphurets of a metallic oxide. He explained that the elements of the alkali unite with separate portions of sulphur, forming a metallic sulphuret and sulphuric acid, the latter of which unites with undecomposed alkali. Thus, in preparing the so-called *liver of sulphur*, made by fusing carbonate of potassa with sulphur, one portion of the alkali is completely decomposed, its elements unite separately with sulphur, giving rise to sulphuret of potassium and sulphuric acid,

the latter of which combines with undecomposed potassa. Those views were at the same time supported by Gay-Lussac. (An. de Ch. et Ph. vi.)

One of the chief arguments adduced by Vauquelin in support of his opinion was drawn from the action of charcoal on sulphate of potassa. When a mixture of this salt with powdered charcoal is ignited without exposure to the air, carbonic oxide and carbonic acid gases are formed, and a sulphuret is left, analogous both in appearance and properties to that which may be made by igniting carbonate of potassa directly with sulphur. They are both essentially the same substance, and Vauquelin conceived from the strong attraction of carbon for oxygen, that both the sulphuric acid and potassa would be decomposed by charcoal at a high temperature; and that, consequently, the product must be a sulphuret of potassium.

Berthier has proved that these changes do actually occur. (An. de Ch. et de Ph. xxii.) He put a known weight of sulphate of baryta into a crucible lined with a mixture of clay and charcoal, defended it from contact with the air, and exposed it to a white heat for the space of two hours. By this treatment it suffered complete decomposition, and it was found that in passing into a sulphuret, it had suffered a loss in weight precisely equal to the quantity of oxygen originally contained in the acid and earth. This circumstance, coupled with the fact that there had been no loss of sulphur, is decisive evidence that the baryta as well as the acid had lost its oxygen, and that a sulphuret of barium had been formed. He obtained the same results also with the sulphates of strontia, lime, potassa, and soda; but from the easy fusibility of the sulphurets of potassium and sodium, their loss of weight could not be determined with such precision as in the other instances.

The experiments of Berzelius, performed about the same time, are exceedingly elegant, and still more satisfactory than the foregoing. (An. de Ch. et Ph. xx.) He transmitted a current of dry hydrogen gas over a known quantity of sulphate of potassa, heated to redness. It was expected from the strong affinity of hydrogen for oxygen, that the sulphate would be decomposed; and, accordingly, a considerable quantity of water was formed, which was carefully collected and weighed. The loss of weight which the salt had experienced was precisely equivalent to the oxygen of the acid and alkali; and the oxygen of the water was exactly equal to the loss in weight. A similar result was obtained with the sulphates of soda, baryta, strontia, and lime.

It is demonstrated, therefore, that the metallic bases of the alkalies and alkaline earths agree with the common metals in their disposition to unite with sulphur. It is now certain that, whether a sulphate be decomposed by hydrogen or charcoal, or sulphur ignited with an alkali or an alkaline earth, a metallic sulphuret is always the product. Direct combination between sulphur and a metallic oxide is a very rare occurrence, nor has the existence of such a compound been clearly established. Gay-Lussac indeed states that, when an alkali or an alkaline earth is heated with sulphur in such a manner that the temperature is never so high as a low red heat, the product is really the sulphuret of an oxide. But the facts adduced in favour of this opinion are not altogether satisfactory, so that the real nature of the product must be decided by future observation.

Several of the metallic sulphurets occur abundantly in nature. Those that are most frequently met with are the sulphurets of lead, antimony, copper, iron, zinc, molybdenum, and silver.

The metallic seleniurets have so close a resemblance in their chemical rela-

tions to the sulphurets, that it is unnecessary to give a separate description of them. They may be prepared either by bringing selenium in contact with the metals at a high temperature, or by the action of hydroselenic acid on metallic solutions.

Respecting the preceding compounds there remains one subject, the consideration of which, as applying equally to all, has been purposely delayed. The non-metallic ingredient of each is the radical of a hydracid, that is, has the property of forming with hydrogen an acid, which, like other acids, is unable to unite with metals, but appears to combine readily with many metallic oxides. Owing to this circumstance, a difficulty arises in explaining the action of such substances on water. Thus, when chloride of potassium is put into water, it may dissolve without suffering any other chemical change, and the liquid accordingly contain chloride of potassium in solution. But it is also possible that the elements of this compound may react on those of water, its potassium uniting with oxygen, and its chlorine with hydrogen; and as the resulting potassa and hydrochloric acid have a strong affinity for each other, the solution would of course contain hydrochlorate of potassa. A similar uncertainty attends the action of water on other metallic chlorides, and on the compounds of metals with iodine, bromine, sulphur, and similar substances; so that when iodide, sulphuret, and cyanuret of potassium are put into water, it may be doubted whether they dissolve as such, or whether they may not be converted, by decomposition of water, into hydriodate, hydrosulphate, and hydrocyanate of potassa. This question would at once be decided, could it be ascertained whether water is or is not decomposed during the process of solution; but this is the precise point of difficulty, since, from the operation of the laws of chemical union, no disengagement of gas does or can take place by which the occurrence of such a change may be indicated. Chemists, accordingly, being guided by probabilities, are divided in opinion, and I shall therefore give a brief statement of both views, with the arguments in favour of each.

According to one view, then, chloride of potassium and all similar compounds dissolve in water without undergoing any other change, and are deposited in their original state by crystallization. When any hydracid, such as hydrochloric or hydriodic acid, is mixed with potassa or any similar metallic oxide, the acid and salifiable base do not unite, but the oxygen of the oxide combines with the hydrogen of the acid, and the metal itself with the radical of the hydracid. This kind of double decomposition unquestionably takes place in some instances, as when hydrosulphuric acid acts upon acetate of oxide of lead, the insoluble sulphuret of lead being actually precipitated; but it is also thought to occur even when the transparency of the solution is undisturbed. It is argued, accordingly, that hydrochlorate of potassa, and the salts of the hydracids in general, have no existence. Thus, when nitrate of the oxide of silver is added to a solution of chloride of potassium, metallic silver is said to unite with chlorine, while the oxygen of the oxide of silver combines with potassium; so that nitrate of potassa and chloride of silver are generated. On adding sulphuric acid to a solution of chloride of potassium, hydrochloric acid and potassa, not previously existing, are instantly formed in consequence of the decomposition of water, which yields its hydrogen to chlorine, and its oxygen to potassium; exactly as happens when concentrated sulphuric acid is brought into contact with solid chloride of potassium. It is further believed that the crystallized hydrochlorate of lime, baryta, and strontia, which contain water or its elements, are metallic

chlorides combined with water of crystallization; and the same view is applied to all analogous compounds.

According to the other doctrine, chloride of potassium is converted into hydrochlorate of potassa in the act of dissolving; and when the solution is evaporated, the elements existing in the salt reunite at the moment of crystallization, and crystals of chloride of potassium are deposited. The same explanation applies in all cases, when the salt of a hydracid crystallizes without retaining the elements of water. Of those compounds which in crystallizing retain water or its elements in combination, two opinions may be formed. Thus crystallized hydrochlorate of baryta, which consists of one equivalent of chlorine, one of barium, two of oxygen, and two of hydrogen, may be regarded as a compound either of hydrochlorate of baryta with one equivalent of water of crystallization, or of chloride of barium with two equivalents of water. When exposed to heat, two equivalents of water are expelled, and chloride of barium is left. When nitrate of the oxide of silver is mixed in solution with hydrochlorate of potassa, the oxygen of the oxide of silver unites with the hydrogen of the hydrochloric acid, chloride of silver is precipitated, and nitrate of potassa remains in the liquid. On adding sulphuric acid to a hydrochlorate, hydrochloric acid is simply displaced, just as when carbonic acid in marble is separated from lime by the action of nitric acid.

On comparing these opinions it is manifest that both are consistent with well-known affinities. When a metallic chloride is dissolved in water, the attraction of chlorine for the metal, and that of oxygen for hydrogen, tend to prevent chemical change; but the affinities of the metal for oxygen, of chlorine for hydrogen, and of hydrochloric acid for metallic oxides, co-operate in determining the decomposition of water, and the production of a hydrochlorate. In favour of the latter view, the following considerations may be adduced:—1. The solution of some compounds, such as sulphuret of potassium, actually emit an odour of hydrosulphuric acid. 2. Other compounds, such as the chlorides of copper, cobalt, and nickel, instantly acquire, when put into water, the colour peculiar to the salts of the oxides of those metals. 3. The solution of protochloride of iron, like the protosulphate, absorbs oxygen from the atmosphere; an effect which seems to indicate the presence of the protoxide of iron in the liquid. 4. In some instances there is direct proof of decomposition of water. Thus when sulphuret of aluminium is put into that fluid, alumina is generated, and hydrosulphuric acid gas disengaged with effervescence. In like manner chloride and sulphuret of silicon are converted by water into silica and hydrochloric and hydrosulphuric acid. In these cases the want of affinity between the new compounds causes their separation, and thus affords direct proof that water is decomposed. But the affinities which produce this change do not appear so likely to be effective, as those which are in operation when chloride of potassium is put into water; especially when it is considered that the attraction of chlorine for hydrogen, and potassium for oxygen, is aided by that of the resulting acid and oxide for each other.

These arguments may be successively answered in the following manner:—1. That solutions of cyanide and sulphuret of potassium smell of hydrocyanic and hydrosulphuric acids, because the carbonic acid of the atmosphere gradually decomposes them. 2. That metals may yield with chlorine compounds of the same colour as the oxides of the same metals. Thus the terchloride and terfluoride of chromium have a red colour closely resembling that of chromic acid.

3. Protochloride of iron may attract oxygen from the air because of its known tendency to pass into the state of a sesquichloride, a portion of iron being at the same time converted into peroxide. 4. That while certain chlorides do really decompose water, it must be conceded that others dissolve directly without change. The bichloride of platinum and terchloride of gold are soluble in ether, forming solutions which must be regarded as chlorides and not hydrochlorates, since pure ether is anhydrous; and when aqueous solutions of these chlorides are agitated with ether, ethereal solutions of platinum and gold are formed, exactly similar to those made with ether alone. It can scarcely be doubted, then, that these chlorides exist as such in water. In favour of the same view it may with truth be alleged, that the chlorides of potassium and sodium dissolve in and crystallize out of water without evincing the least sign of any other change than mere solution and mere crystallization. Again, crystals of the so-called hydrochlorate of baryta become chloride of barium with loss of water by mere exposure to a dry air; a cause apparently inadequate to determine the hydrogen of the acid to unite with the oxygen of the oxide, but sufficient to explain the phenomena if the crystals were chloride of barium with water of crystallization.

On weighing these and other considerations of a like kind, it appears undeniable that *some* metallic chlorides, iodides, and similar compounds dissolve as such in water: that all do so is a position which cannot, I think, be maintained; and therefore the existence of such compounds as hydracids united with metallic oxides, can scarcely be denied; and in the case of chloride of aluminium, which cannot be recovered from its solution in water, but yields alumina and hydrochloric acid, the change is obvious to the senses. At the same time it is necessary, to avoid a perpetually recurring two-fold explanation, to adhere consistently to one view; and the reader may have observed that I have, in this edition, uniformly gone on the supposition that chlorides, and the same class of bodies, dissolve as such in water. The considerations which have led to this preference are principally drawn from the history of the sulphur-salts.

Chemists are acquainted with several metallic phosphurets; and it is probable that phosphorus, like sulphur, is capable of uniting with all the metals. Little attention, however, has hitherto been devoted to their compounds; and for the greater part of our knowledge concerning them we are indebted to the researches of Pelletier and Rose. (An. de Ch. i. and xiii.; and Pog. An. vi. 205.)

The metallic phosphurets may be prepared in several ways. The most direct method is by bringing phosphorus in contact with metals at a higher temperature, or by igniting metals in contact with phosphoric acid and charcoal. Several of the phosphurets may be formed by transmitting a current of phosphuretted hydrogen gas over metallic oxides heated to redness in a porcelain tube, when water is generated, and a phosphuret of the metal remains. By similar treatment the chlorides and sulphurets of many metals may be decomposed, and phosphurets formed, provided the metal is capable of retaining phosphorus at a red heat. According to Rose, the phosphurets of copper, nickel, cobalt, and iron are the only ones which admit of being advantageously prepared by this method. When chlorides are employed, hydrochloric acid, and with sulphurets hydrosulphuric acid gas, is of course generated.

Phosphorus is said to unite with metallic oxides. For example, phosphuret of lime is said to be formed by conducting the vapour of phosphorus over that earth at a low red heat; but it is probable that in this instance, as with a mix-

ture of sulphur and an alkali, part of the metallic oxide is decomposed, and that the product contains phosphuret of calcium and phosphate of lime.

The only metallic carburets of importance are those of iron, which will be described in the section on that metal.

Hydrogen unites with few metals. The only metallic hydrogurets, or hydurets, known are those of zinc, potassium, arsenic, antimony, and tellurium. No definite compound of nitrogen and a metal has hitherto been discovered.

The discoveries of modern chemistry have materially added to the number of the metals, especially by associating with them a class of bodies which was formerly believed to be of a nature entirely different. The metallic bases of the alkalies and earths, previous to the year 1807, were altogether unknown; and before that date the list of metals, with few exceptions, included those only which are commonly employed in the arts, and which are hence often called the common metals. In consequence of this increase in number, it is found convenient, for the purpose of description, to arrange them in separate groups; and as the alkalies and earths differ in several respects from the oxides of other metals, it will be convenient to describe them separately. I have accordingly divided the metals into the following classes:—

Class I. Metals which by oxidation yield alkalies and earths.
Class II. Metals, the oxides of which are neither alkalies nor earths.

Class I. This class includes 12 metals, which may properly be arranged in three orders.

Order 1. Metallic bases of the alkalies. They are three in number; namely,

Potassium, Sodium, Lithium.

These metals have such a powerful attraction for oxygen, that they decompose cold water and even ice at the moment of contact, and are oxidized with disengagement of hydrogen gas. The resulting oxides are distinguished by their causticity and solubility in water, and by possessing alkaline properties in an eminent degree.

They are called *alkalies*, and their metallic bases are sometimes termed *alkaline* or *alkaligenous* metals.

Order 2. Metallic bases of the alkaliae earths. These are four in number; namely,

Barium, Strontium, Calcium, Magnesium.

These metals, excepting magnesium, also decompose water rapidly at common temperatures. The resulting oxides are called *alkaline earths;* because, while in their appearance they resemble the earths, they are similar to the alkalies in having a strong alkaline reaction with test paper and in neutralizing acids. The three first are strongly caustic, and baryta and strontia are soluble in water to a considerable extent.

Order 3. Metallic bases of the earths. These are five in number; namely,

Aluminium, Glucinium, Yttrium.
Thorium, Zirconium,

The oxides of these metals are well known as the pure earths. They are white and of an earthy appearance, in their ordinary state are quite insoluble in

water, and do not affect the colour of turmeric or litmus paper. As salifiable bases they are inferior to the alkaline earths.

Class II. The number of the metals included in this class amounts to 30. They are all capable of uniting with oxygen, and generally in more than one proportion. Their protoxides have an earthy appearance, but with few exceptions are coloured. They are insoluble in water, and in general do not affect the colour of test paper. Most of them act as salifiable bases in uniting with acids, and forming salts; but in this respect they are much inferior to the alkalies and alkaline earths, by which they may be separated from their combinations. Several of these metals are capable of forming with oxygen compounds, which possess the characters of acids. The metals in which this property has been noticed are, manganese, arsenic, chromium, vanadium, molybdenum, tungsten, antimony, columbium, titanium, tellurium, gold, and osmium.

The metals belonging to the second class may be conveniently arranged in the three following orders:

Order 1. Metals which decompose water at a red heat. They are seven in number; namely,

Managnese,	Cadmium,	Nickel,
Iron,	Cobalt,	Tin.
Zinc,		

Order 2. Metals which do not decompose water at any temperature, and the oxides of which are not reduced to the metallic state by the sole action of heat. Of these there are fifteen in number; namely,

Copper,	Chromium,	Cerium,
Lead,	Vanadium,	Lantanium,
Bismuth,	Molybdenum,	Titanium,
Arsenic,	Tungsten,	Tellurium,
Antimony,	Uranium,	Columbium.

Order 3. Metals, the oxides of which are decomposed by a red heat. These are,

Mercury,	Platinum,	Osmium,
Siver,	Palladium,	Iridium.
Gold,	Rhodium,	

CLASS I.

METALS WHICH BY OXIDATION YIELD ALKALIES OR EARTHS.

ORDER I.

METALLIC BASES OF THE ALKALIES.

SECTION I.

POTASSIUM.

Hist. and Prep.—Discovered in the year 1807 by Davy, and the circumstances which led to the discovery have already been described. Hydrate of potassa, slightly moistened for the purpose of increasing its conducting power, was made to communicate with the opposite poles of a galvanic battery of 200 double plates; when the oxygen both of the water and the potassa passed over to the positive pole, while the hydrogen of the former, and the potassium of the latter, made their appearance at the negative pole. By this process potassium is obtained in small quantity only; but Gay-Lussac and Thenard invented a method by which a more abundant supply may be procured. (Recherches Physico-Chimiques, vol. i.) Their process consists in bringing fused hydrate of potassa in contact with turnings of iron heated to whiteness in a gun-barrel. The iron, under these circumstances, deprives the water and potassa of oxygen, hydrogen gas combined with a little potassium is evolved, and pure potassium sublimes, and may be collected in a cool part of the apparatus.

Potassium may also be prepared, as first noticed by Curaudau, by mixing dry carbonate of potassa with half its weight of powdered charcoal, and exposing the mixture, contained in a gun-barrel or spheroidal iron bottle, to a strong heat. An improvement on both processes has been made by Brunner, who decomposes potassa by means of iron and charcoal. From eight ounces of fused carbonate of potassa, six ounces of iron filings, and two ounces of charcoal, mixed intimately and heated in an iron bottle, he obtained 140 grains of potassium. (Quarterly Journal, xv. 379.) Berzelius has observed that the potassium thus made, though fit for all the usual purposes to which it is applied, contains a minute quantity of carbon; and therefore, if required to be quite pure, must be rendered so by distillation in a retort of iron or green glass. A modification of this process has been since described by Wöhler, who effects the decomposition of the potassa solely by means of charcoal. The material employed for the purpose is carbonate of potassa prepared by heating cream of tartar to redness in a covered crucible. (Poggendorff's Annalen, iv. 23.) According to Liebig, 2 eq. of charcoal and 1 eq. of carbonate of potassa react on each other, and form 1 eq. of potassium and 3 eq. of carbonic oxide; or

$$\begin{matrix} KO+CO_2 \\ \text{and } 2C \end{matrix} \quad \text{yield} \quad \begin{matrix} K \\ \text{and } 3CO. \end{matrix}$$

The whole of the potassium thus liberated is not, however, obtained in the metallic form, for 2 out of every 3 eq. combine with 7 out of the 9 eq. of carbonic oxide gas at the same time produced. The resulting compound has a dark grey colour, and is recognized by burning on water with a violent flame, and the production of croconate and oxalate of potassa. This compound is sometimes almost the sole product of the process. (Geiger's Pharmacie, 348.)

Prop.—Solid at the ordinary temperature of the atmosphere. At 70° it is somewhat fluid, though its fluidity is not perfect till it is heated to 150°. At 50° it is soft and malleable, and yields like wax to the pressure of the fingers; but it becomes brittle when cooled to 32°. It sublimes at a low red heat without undergoing any change, provided atmospheric air be completely excluded. Its texture is crystalline, as may be seen by breaking it across while brittle, and cubic crystals have been obtained by Pleischl (Pog. An. xxxi. 431.) In colour and lustre it is precisely similar to mercury. At 60° its density is 0·865, so that it is considerably lighter than water. It is quite opaque, and is a good conductor of heat and electricity.

The most prominent chemical property of potassium is its affinity for oxygen gas. It oxidizes rapidly in the air, or by contact with fluids which contain oxygen. On this account it must be preserved either in glass tubes hermetically sealed, or under the surface of liquids, such as naphtha, of which oxygen is not an element. If heated in the open air, it takes fire, and burns with a purple flame and great evolution of heat. It decomposes water on the instant of touching it; and so much heat is disengaged, that the potassium is inflamed, and burns vividly while swimming upon its surface. The hydrogen unites with a little potassium at the moment of separation; and this compound takes fire as it escapes, and thus augments the brilliancy of the combustion. When potassium is plunged under water, violent reaction ensues, but without light, and pure hydrogen gas is evolved.

The combining weight or equivalent of potassium is easily deducible from the composition of potassa and chloride of potassium, which are admitted to consist of single equivalents of their elements. Gay-Lussac, and Thenard, and Davy, inferred the composition of potassa from the hydrogen gas evolved when a known weight of potassium is oxidized under water, the volume of the oxygen which unites with the metal being equal to half the volume of the hydrogen. Berzelius analyzed chloride of potassium by means of nitrate of oxide of silver, and inferred that 39·15 is the eq. of potassium. Its symb. is K.

	Potassium.			Equiv.	Formulæ.
Protoxide	39·15	1 eq. + Oxygen	8	1 eq. = 47·15	K + O or KO.
Peroxide	39·15	1 eq. +	24	3 eq. = 63·15	K + 3O or KO_3.
Chloride	39·15	1 eq. + Chlor.	35·42	1 eq. = 74·57	K + Cl or KCl.
Iodide	39·15	1 eq. + Iodine	126·3	1 eq. = 165·45	K + I or KI.
Bromide	39·15	1 eq. + Brom.	78·4	1 eq. = 117·55	K + Br. or KBr.
Fluoride	39·15	1 eq. + Fluor.	18·68	1 eq. = 57·83	K + F or KF.
Hydurets Carburet	Composition uncertain.				
Sulphuret	39·15	1 eq. + Sulphur	16·1	1 eq. = 55·25	K + S or KS.
Bisulphuret	39·15	1 eq. + do.	32·2	2 eq. = 71·35	K + 2S or KS_2.
Tersulphuret	39·15	1 eq. + do.	48.3	3 eq. = 87·45	K + 3S or KS_3.
Quadrosulphuret	39·15	1 eq. + do.	64·4	4 eq. = 103·35	K + 4S or KS_4.
Quintosulphuret	39·15	1 eq. + do.	80·5	5 eq. = 119·65	K + 5S or KS_5.
Phosohurets Seleniurets	Composition and number uncertain.				

Protoxide of Potassium.—Hist. and Prep.—This compound, commonly called *potash* or *potassa*, and by the Germans *kali* (an Arabic word), is always formed when potassium is put into water, or when it is exposed at common temperatures to dry air or oxygen gas. By the former method the protoxide is obtained in combination with water; and in the latter it is anhydrous. In porforming the last-mentioned process, the potassium should be cut into very thin slices; for otherwise the oxidation is incomplete. The product, when partially oxidized, is regarded by Berzelius as a distinct oxide; but most chemists admit it to be a mere mixture of potassa and potassium.

Prop.—Anhydrous potassa is a white solid substance, highly caustic, which fuses at a temperature somewhat above that of redness, and bears the strongest heat of a wind furnace without being decomposed or volatilized. It has a powerful affinity for water, and intense heat is disengaged during the act of combination. Three compounds are known; they are composed of 47·15, or 1 eq. of potassa united with 9, 27, and 45 parts, or 1, 3, and 5 eq. of water respectively. In the last compound a portion of the water probably exists as water of crystallization.

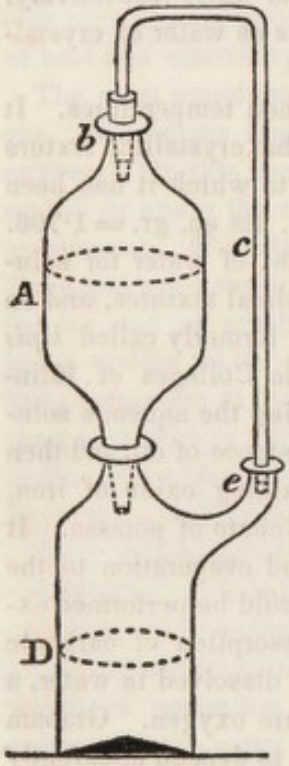
The *protohydrate of potassa*, KO, HO, is solid at common temperatures. It fuses at a heat rather below redness, and assumes a somewhat crystalline texture in cooling. It is not decomposed by any degree of heat to which it has been exposed, and hence was long considered to be pure potassa. Its sp. gr. = 1·706. It is highly deliquescent, and requires about half its weight of water for solution. It is soluble, likewise, in alcohol. It destroys all animal textures, and on this account is employed in surgery as a caustic. It was formerly called *lapis causticus*, but is now termed *potassa* and *potassa fusa* by the Colleges of Edinburgh and London. This preparation is made by evaporating the aqueous solution of potassa in a silver or clean iron capsule to the consistence of oil, and then pouring it into moulds. In this state it is impure, containing oxide of iron, together with chloride of potassium, and carbonate and sulphate of potassa. It is purified from these substances by solution in alcohol, and evaporation to the same extent as before in a silver vessel. The operation should be performed expeditiously, in order to prevent, as far as possible, the absorption of carbonic acid. When common caustic potassa of the druggists is dissolved in water, a number of small bubbles of gas is disengaged, which is pure oxygen. Graham finds its quantity to be variable in different specimens, and to depend apparently on the impurity of the specimen.

If the protohydrate be exposed to the air, it rapidly becomes moist, but after absorbing a certain portion of water, a perfectly dry substance is again obtained, which is the *terhydrate of potassa*, KO, 3HO. It is very similar in all its characters to the protohydrate, but is much whiter and more crystalline in its texture. The *quintohydrate*, KO, 5HO, is obtained by exposing a very concentrated solution of potassa to an intense cold. It is then deposited in four-sided prisms terminated by a four-sided pyramid, and sometimes in four-sided tables and octohedrons.

The aqueous solution of potassa, *aqua potassæ* of the Pharmacopœia, is prepared by decomposing carbonate of potassa by lime. The best proportions are 1 part of dry lime to 2 of carbonate of potassa. The lime is to be slaked by being covered with boiling water, when it forms a very minutely divided hydrate, in the form of a cream, every particle of which acts, which is not the case in dry slaking (Mohr). The carbonate is now dissolved in not less than 10 parts

of hot water, and the cream of lime is added by small portions to the solution, and the mixture boiled after each addition in a clean iron vessel. The lime takes the carbonic acid, forming insoluble carbonate of lime. When the whole lime has been added, and the mixture has been boiled for some time, it is allowed to subside in the covered vessel, and the solution of caustic potassa may be decanted perfectly clear. If the carbonate have been pure, the solution yields by rapid evaporation pure hydrate of potassa. But if pearlash be employed, the sulphate of potash contained in it may be got rid of by evaporating till crystals appear; on cooling, the sulphate is so completely deposited that its presence can no longer be detected in the liquid (Liebig). The same chemist finds that a strong solution of caustic potassa actually deprives carbonate of lime of its acid, and that, from this circumstance, carbonate of potassa cannot be rendered quite caustic by lime, unless diluted with about ten times its weight of water.

As pure potassa absorbs carbonic acid rapidly when freely exposed to the atmosphere, it is desirable to filter its solution in vessels containing as small a quantity of air as possible. This is easily effected by means of the filtering apparatus devised by Donovan. It consists of two vessels A and D, of equal capacity, and connected with each other as represented in the annexed wood-cut. The neck *b* of the upper vessel contains a tight cork, perforated to admit one end of the glass tube *c*; and the lower extremity of the same vessel terminates in a funnel pipe, which fits into one of the necks of the under vessel D by grinding, luting, or a tight cork. The vessel D is furnished with another neck *e*, which receives the lower end of the tube *c*, the junction being secured by means of a perforated cork, or luting. The throat of the funnel pipe is obstructed by a piece of coarse linen loosely rolled up, and not pressed down into the pipe itself. The solution is then poured in through the mouth at *b*, the cork and tube having been removed; and the first droppings, which are turbid, are not received in the lower vessel. The parts of the apparatus are next joined together, and the filtration may proceed at the slowest rate, without exposure to more air than was contained in the vessels at the beginning of the process. This apparatus should be made of green in preference to white glass, as the pure alkalies act on the former much less than on the latter. (Annals of Philosophy, xxvi. 115.)



The mode by which this apparatus acts scarcely needs explanation. In order that the liquid should descend freely, two conditions are required:—first, that the air above the liquid should have the same elastic force, and therefore exert the same pressure, as that below; and secondly, as one means of securing the first condition, that the air should have free egress from the lower vessel. Both objects, it is manifest, are accomplished in the filtering apparatus of Donovan; since for every drop of liquid which descends from the upper to the lower vessel, a corresponding portion of air passes along the tube *c* from the lower vessel to the upper. This apparatus is applicable to any other case where it is wished to exclude the atmosphere. Other similar contrivances will be found in the scientific journals, for which there is no space in this work.

Solution of potassa is highly caustic, and its taste intensely acrid. It pos-

sesses alkaline properties in an eminent degree, converting the vegetable blue colours to green, and neutralizing the strongest acids. It absorbs carbonic acid gas rapidly, and is consequently employed for withdrawing that substance from gaseous mixtures. When of the sp. gr. 1·25, it is used in the analysis of organic bodies, to absorb the carbonic acid formed, the weight of which is equal to the increase in the weight of the potash apparatus. The solution made from pearlash, which has deposited the sulphate of potash, is exactly of the proper strength for this purpose (Gregory). For the same reason it should be preserved in well-closed bottles, that it may not absorb carbonic acid from the atmosphere.

Potassa is employed as a reagent in detecting the presence of bodies, and in separating them from each other. The solid hydrate, owing to its strong affinity for water, is used for depriving gases of hygrometric moisture, and is admirably fitted for forming frigorific mixtures (page 40).

Potassa may be distinguished from all other substances by the following characters:—1. If tartaric acid be added in excess to a salt of potassa dissolved in cold water, and the solution be stirred with a glass rod, a white precipitate, bitartrate of potassa, soon appears, which forms peculiar white streaks upon the glass by the pressure of the rod in stirring. 2. It is precipitated by perchloric acid in the cold, the perchlorate of potassa having nearly the same degree of solubility as the bitartrate. 3. A solution of chloride of platinum causes a yellow precipitate, the double chloride of platinum and potassium. A drop or two of hydrochloric acid should be added at the same time as the test, the mixture be evaporated to dryness at 212°, and a little cold water be afterwards added, when the double chloride is left in the form of small shining yellow crystals. Chloride of platinum dissolved in alcohol often gives an immediate precipitate, which falls of a pale yellow colour. 4. The alcoholic solution of carbazotic acid throws down potassa in deep yellow crystals of carbazotate of potassa, which is very sparingly soluble. 5. It yields a light gelatinous precipitate, the double fluoride of potassium and silicon with silicated hydrofluoric acid. Of these tests carbazotic acid is the most delicate in a solution of pure potassa; but when the alkali is combined with a strong acid, the chloride of platinum is preferable.

The following test has been recommended by Harkort for distinguishing between potassa and soda in minerals:—Oxide of nickel, when fused by the blowpipe flame with borax, gives a brown glass; and this glass if melted with a mineral containing potassa, becomes blue, an effect which is not produced by the presence of soda.

Its eq. is 47·15; *symb.* K + O, K, or KO.

Peroxide.—When potassium burns in the open air or in oxygen gas, it is converted into an orange-coloured substance, which is peroxide of potassium. It may likewise be formed by conducting oxygen gas over potash at a red heat; and it is produced in small quantity when potash is heated in the open air. It is the residue of the decomposition of nitre by heat in metallic vessels, provided the temperature be kept up for a sufficient time. When the peroxide is put into water, it is resolved into oxygen and potash, the former of which escapes with effervescence, and the latter is dissolved. *Its eq. is* 63·15; *symb.* K + 3O, $\dddot{K}$, or KO_3.

Chloride of Potassium.—Potassium takes fire spontaneously in an atmosphere of chlorine, and burns with greater brilliancy than in oxygen gas. This chloride is

generated with evolution of hydrogen when potassium is heated in hydrochloric acid gas; and it is the residue after the decomposition of chlorate of potassa by heat. It is formed when potassa is dissolved in a solution of hydrochloric acid, and is deposited by slow evaporation in anhydrous colourless cubic crystals. It has a saline and rather bitter taste, is insoluble in alcohol, and requires for solution 3 parts of water at 60°, and still less of hot water. *Its eq. is* 74·57; *symb.* K + Cl, or K Cl.

Iodide of Potassium.—Prep.—This compound is formed with evolution of heat and light, when potassium is heated in contact with iodine; it is the sole residue after decomposing iodate of potassa by heat; and by neutralizing potassa with hydriodic acid it is obtained in solution. The simplest process for preparing it in quantity is to add iodine to a hot solution of pure potassa until the alkali is neutralized, when iodide of potassium and iodate of potassa are generated, evaporate to dryness, and expose the dry mass in a platinum crucible to a gentle red heat in order to decompose the iodate. The fused mass is then dissolved out by water and crystallized. (Gregory, Edin. Med. and Surg. Jour. 1830.) Another process is to digest iodine with zinc or iron filings in water, and then decompose the resulting iodide of zinc or iron by a quantity of potassa just sufficient to precipitate the oxide.

Prop.—Iodide of potassium fuses readily when heated, and rises in vapour at a heat below full redness, especially in an open vessel. It is very soluble in water, requiring only two-thirds of its weight at 60° for solution, and in a moist atmosphere deliquesces. It dissolves also in strong alcohol, even in the cold; and the solution, when evaporated, yields colourless cubic crystals of iodide of potassium.

The commercial iodide is frequently impure, often containing chloride of potassium or sodium, and sulphate or carbonate of potassa, the last sometimes in very large quantity. It is well to purchase it in crystals, which ought not to deliquesce in a moderately dry air, but when in powder are completely soluble in the strongest alcohol.

Iodine is freely soluble in water which contains iodide of potassium, a brown solution resulting, which has been thought to arise from potassium uniting with two or more equivalents of iodine. No solid compound of the kind, however, has been obtained.

Its eq. is 165·45; *symb.* K + I, or KI.

Bromide of Potassium.—This compound is formed by processes similar to those for preparing the iodide, and is analogous to it in most of its properties. It is very soluble in water, and crystallizes by evaporation in anhydrous cubic crystals, which fuse readily, and decrepitate when heated like sea-salt. It is but slightly soluble in alcohol. *Its eq. is* 117·55; *symb.* K + Br, or KBr.

Fluoride of Potassium.—This compound is best formed by nearly saturating hydrofluoric acid with carbonate of potassa, evaporating to dryness in platinum, and igniting to expel any excess of acid. The resulting fluoride has a sharp saline taste, is alkaline to test paper, deliquesces in the air, and dissolves freely in water. On evaporating its solution at a temperature of 100° it may be obtained in tubes or rectangular four-sided prisms, which deliquesce rapidly. The solution acts on glass in which it is kept or evaporated. Heated with silicic acid it forms a fusible limpid glass, which when cold is opaque and deliquescent. Water dissolves fluoride of potassium, and the silicic acid is left.

Its eq. is 57·83; *symb.* K + F, or KF.

Hydrogen and Potassium.—These substances unite in two proportions, forming in one case a solid, and in the other a gaseous compound. The latter is produced when hydrate of potash is decomposed by iron at a white heat, and it appears also to be generated when potassium burns on the surface of water. It inflames spontaneously in air or oxygen gas; but on standing for some hours over mercury, the greater part, if not the whole of the potassium, is deposited.

The solid hyduret of potassium was made by Gay-Lussac and Thenard, by heating potassium in hydrogen gas. It is a grey, solid substance, which is readily decomposed by heat or contact with water. It does not inflame spontaneously in oxygen gas.

Carburet of Potassium.—This compound has not been obtained in a pure state; but it is thought to form part of the residue in the preparation of potassium from charcoal; for on pouring that matter into water, effervescence ensues, owing to the escape of carburetted hydrogen gas, and carbonate of potassa is found in solution.

Sulphurets of Potassium.—Potassium unites readily with sulphur by the aid of gentle heat, emitting so much heat that the mass becomes incandescent. The nature of the product depends on the proportions which are employed. The protosulphuret is readily prepared by decomposing sulphate of potassa by charcoal or hydrogen gas at a red heat. It may be prepared in the moist way by a process which will be mentioned in describing the sulphur-salts.

The protosulphuret of potassium fuses below a red heat, and acquires on cooling a crystalline texture. It has a red colour, its taste is at first strongly alkaline and then sulphurous, has an alkaline reaction with test paper, deliquesces on exposure to the air, and is soluble in water and alcohol. Most of the acids decompose it with evolution of hydrosulphuric acid gas, and without any deposite of sulphur. It takes fire when heated before the blowpipe, and quickly acquires a coating of sulphate of potassa, which stops the combustion; but when mixed in fine division with charcoal, it kindles spontaneously, forming a good pyrophorus.

Its eq. is 55·25; *symb.* K + S, or KS.

The *bisulphuret* is formed by exposing a saturated solution in alcohol of hydrosulphate or sulphuret of potassium (KS + HS), until a pellicle begins to form upon its surface, and then evaporating to dryness without further exposure. The first change consists in oxygen of the air uniting with hydrogen of hydrosulphuric acid, the sulphur of which unites with potassium. Then the formation of hyposulphurous acid begins; and as the hyposulphite of potassa is insoluble in alcohol, it gives a pellicle on its surface. It may also be obtained from an aqueous solution of the protosulphuret. This compound, when pure, dissolves in water without colour; but exposed to the air, oxygen is rapidly absorbed, and the solution becomes yellow. The change is effected by one half of the potassium combining with oxygen and yielding its sulphur to the remainder by which the bisulphuret of potassium and potassa are formed. Thus 2KS yield KS_2, and KO. If the solution continues to be exposed, it again becomes colourless, owing to the conversion of the bisulphuret into hyposulphite of potassa.

Its eq. is 71·35; *symb.* K + 2S, or KS_2.

The *tersulphuret* is prepared pure by transmitting the vapour of bisulphuret of carbon over carbonate of potassa at red heat, as long as carbonic acid or carbonic oxide gases are disengaged. It is also formed when carbonate of potassa is heated to low redness with half its weight of sulphur, until the mass appears in tranquil fusion: the oxygen of 3-4ths of the potassa unites with sulphur to form sulphuric

acid, which exactly suffices to neutralize 1-4th of the alkali, and all the carbonic acid is evolved as gas.—Thus

4 eq. Potassa and 10 eq. Sulphur			3 eq. Tersulphuret and 1 eq. Sulphate.
4KO	S_{10}	yield	$3KS_3$ KO, SO_3.

This is known under the name of *liver of sulphur* (p. 284).

Its eq. is 87·45; *symb.* K + 3S, or KS_3.

The *quadrosulphuret* is prepared by transmitting the vapour of bisulphuret of carbon over sulphate of potassa at a red heat until carbonic acid gas ceases to be disengaged; or by conducting the same process with the tersulphuret prepared by the second method, until its sulphuric acid and potassa are decomposed.

Its eq. is 103·55; *symb.* K + 4S, or KS_4.

The *quintosulphuret* is formed by fusing carbonate of potassa with its own weight of sulphur, the residue containing sulphate of potassa as in preparing the tersulphuret. Each equivalent of potassium with five of sulphur, being the highest degree of sulphuration which can be formed by fusion.

Its eq. is 119·65; *symb.* K + 5S, or KS_5.

These four last sulphurets are deliquescent in the air, have a sulphurous odour, and are soluble in water; and those who consider them to decompose water in dissolving, suppose the formation of corresponding compounds of hydrogen and sulphur. On decomposing the solutions with hydrochloric or sulphuric acid, the changes ensue which have already been explained (page 264). As the solution of the quintosulphuret dissolves sulphur, a still higher degree of sulphuration must probably exist.

Two other compounds of sulphur and potassium, the composition of which are K_2S, and K_2S_9, have been described. The first of these is produced when sulphate of potassa is heated in a stream of sulphuretted hydrogen; and the latter, when the quadrosulphuret of potassium is heated in a similar manner. The definite nature of these compounds may be considered doubtful.

Phosphurets of Potassium.—When potassium is heated in phosphuretted hydrogen gas, it takes fire, phosphuret of potassium is formed, and hydrogen set free; and combination is also effected by gently heating phosphorus with potassium. The number and proportion of these compounds have not yet been determined. They decompose water with formation of phosphuretted hydrogen, potassa, and some acid of phosphorus.

Seleniurets of Potassium.—These elements unite when fused together, sometimes with explosive violence, forming a crystalline fusible compound of an iron grey colour and metallic lustre. It dissolves completely in water, yielding a deep red solution, very similar in taste and odour to solutions of sulphuret of potassium. On adding an acid, hydroselenic acid gas is evolved, and selenium deposited. Solution of potassa dissolves selenium, and gives rise to a seleniuret of potassium and selenite of potassa; and the same compounds are formed when selenium is heated with carbonate of potassa.

SECTION II.

SODIUM.

Hist. and Prep.—The *Natrium* of the Germans, was discovered in 1807, a few days after the discovery of potassium. The first portions of it were obtained by means of galvanism; but it may be procured in much larger quantity by chemical processes, precisely similar to those described in the last section. As sodium may be obtained in much larger quantity than potassium, owing to the fact that it does not combine, like the former, with carbonic acid, the method of preparing sodium as described by Schœdler (Liebig's Annalen, vol. xx. p. 2) is here briefly noticed. Three pounds of commercial acetate of soda are ignited, and the residue, which weighs 1 lb. consisting of carbonate mixed with charcoal, is further mixed with $\frac{1}{4}$ lb. of finely-powdered charcoal and $\frac{1}{2}$ lb. of charcoal in coarser particles, to prevent fusion of the mass. It is then heated in the usual manner in an iron bottle, such as is used for holding mercury in commerce. This process is so productive that in one operation with the above quantities Schœdler obtained $4\frac{1}{2}$ oz. of pure sodium. As a quantity half larger may be heated in such a bottle, it is possible to obtain in one operation upwards of 6 oz. of sodium; and this from the cheapest materials. Sodium thus prepared has been sold at three or four shillings per ounce. It might be made much cheaper even than this, and as it oxidizes less rapidly than potassium, it is much better adapted for experiments of research.

Prop.—It has a strong metallic lustre, and in colour is very analogous to silver. It is so soft at common temperatures, that it may be formed into leaves by the pressure of the fingers. It fuses at 200°, and rises in vapour at a red heat. Its sp. gr. is 0·972. It soon tarnishes on exposure to the air, though less rapidly than potassium. Like that metal, it is instantly oxidized by water, hydrogen gas in temporary union with a little sodium being disengaged. When thrown on cold water, it swims on its surface, and is rapidly oxidized, though in general without inflaming; but with hot water it scintillates, or even takes fire. Ducatel finds that the heat rises high enough for inflammation with cold water, if the sodium be confined to one spot, and the water rest on a non-conducting substance, such as charcoal. (Silliman's Journal, xxv. 90.) In each case, soda is generated, and the water acquires an alkaline reaction.

The composition of soda was determined by the same methods as that of potassa, and agreeably to the observations of Berzelius 23·3 may be taken as the *eq.* of sodium. *Its symb. is* Na. The composition of the compounds of sodium described in this section is as follows.—

	Sodium.		Equiv.		Formulæ.
Protoxide .	23·3	1 eq. + Oxygen	8	1 eq. = 31·3	Na + O or $\dot{N}a$.
Peroxide .	46·6	2 eq. + do.	24	3 eq. = 70·6	2Na + 3O or $\ddot{N}a$.
Chloride .	23·3	1 eq. + Chlorine	35·42	1 eq. = 58·72	Na + Cl or $N\overline{Cl}$.
Iodide .	23·3	1 eq. + Iodine	126·3	1 eq. = 149·6	Na + I or Na I.

	Sodium.			Equiv.	Formulæ.
Bromide .	23·3	1 eq. + Bromine	78·4	1 eq. = 101·7	Na + Br. or NaBr.
Fluoride .	23·3	1 eq. + Fluorine	18·68	1 eq. = 41·98	Na + F or Na F.
Sulphuret .	23·3	1 eq. + Sulphur	16·1	1 eq. = 39·4	Na + S or Na S.

Soda.—Prep.—The protoxide of sodium, commonly called *soda*, and by the Germans *natron*, is formed by the oxidation of sodium in air or water, as potassa is from potassium. In its anhydrous state it is a grey solid, difficult of fusion, and very similar in all its characters to potassa. With water it forms a solid hydrate, easily fusible by heat, which is very caustic, soluble in water and alcohol, has powerful alkaline properties, and in all its chemical relations is exceedingly analogous to potassa. It is prepared from the solution of pure soda, exactly in the same manner as the corresponding preparations of potassa. The solid hydrate (NaO, HO) is composed of 31·3 parts or 1 eq. of soda, and 9 parts or 1 eq. of water.

Prop.—Soda is readily distinguished from other alkaline bases by the following characters. 1. It yields, with sulphuric acid, a salt which, by its taste and form, is easily recognized as Glauber's salt, or sulphate of soda. 2. All its salts are soluble in water, and are not precipitated by any reagent. 3. On exposing its salts by means of platinum wire to the blowpipe flame, they communicate to it a rich yellow colour.

Its eq. is 31·3; *symb.* Na + O, Na, or NaO.

Peroxide of Sodium.—This compound is formed when sodium is heated to redness in an excess of oxygen gas. It has an orange colour, has neither acid nor alkaline properties, and is resolved by water into soda and oxygen.

Its eq. is 70·6; *symb.* 2Na + 3O, $\ddot{\underline{\mathrm{Na}}}$, or Na_2O_3.

Chloride of Sodium.—Hist. and Prep.—This compound may be formed directly by burning sodium in chlorine, by heating sodium in hydrochloric acid gas, and by neutralizing soda with hydrochloric acid. It exists as a mineral under the name of *rock salt*, is the chief ingredient of sea-water, and is contained in many saline springs. From these sources are derived the different varieties of common salt, such as rock, bay, fishery, and stoved salt, which differ from each other only in degrees of purity and mode of preparation. The rock and bay salt are the purest, but always contain small quantities of sulphate of magnesia and lime, and chloride of magnesium. These earths may be precipitated as carbonate by boiling a solution of salt for a few minutes with a slight excess of carbonate of soda, filtering the liquid, and neutralizing with hydrochloric acid. On evaporating this solution rapidly, chloride of sodium crystallizes in hollow four-sided pyramids; but it occurs in regular cubic crystals when the solution is allowed to evaporate spontaneously. These crystals contain no water of crystallization, but decrepitate remarkably when heated, owing to the expansion of water mechanically confined within them.

Prop.—Pure chloride of sodium has an agreeably saline taste. It fuses at a red heat, and becomes a transparent brittle mass on cooling. It deliquesces slightly in a moist atmosphere, but undergoes no change when the air is dry. In pure alcohol it is insoluble. It requires twice and a half its weight of water at 60° for solution, and its solubility is not increased by heat. Hydrous sulphuric acid decomposes it with evolution of hydrochloric acid gas, and formation of sulphate of soda.

The uses of chloride of sodium are well known. Besides its employment in

seasoning food, and in preserving meat from putrefaction, a property which, when pure, it possesses in a high degree, it is used for various purposes in the arts, especially in the formation of hydrochloric acid and hypochlorite of lime.

Its eq. is 58·72; *symb.* Na + Cl, or NaCl.

Iodide of Sodium.—It is obtained pure by processes similar to those for preparing iodide of potassium; but it is contained in sea-water, in many salt springs, and in the residual liquor from kelp. It is a neutral compound, deliquescent in the air, soluble in water and alcohol, fuses readily by heat, and is volatile, though in a less degree than iodide of potassium. Evaporated at 123° it crystallizes from its aqueous solution in cubes, which Berzelius found to contain 20·23 per cent. of water.

Its eq. is 149·6; *symb.* Na + I, or NaI.

Bromide of Sodium.—This compound is very analogous to sea-salt, and is associated with it in sea-salt and most salt springs. At 86° it crystallizes from its aqueous solution in anhydrous cubes; but at lower temperatures it separates in hexagonal tables, which Mitscherlich found to contain 26·37 per cent. of water, or 4 eq. to 1 eq. of the bromide.

Its eq. is 101·7; *symb.* Na + Br, or NaBr.

Fluoride of Sodium.—This compound is formed by neutralizing hydrofluoric acid by soda, and by igniting the double fluoride of sodium and silicon, when the fluoride of silicon is expelled. When obtained by the second process, it crystallizes from its aqueous solution in rhomboidal crystals, but is obtained in cubes, its proper form, by a second crystallization: when carbonate of soda is present, it crystallizes in octohedrons.

Fluoride of sodium in crystals is anhydrous, is almost insoluble in alcohol, and requires 25 times its weight both of hot and cold water for solution. It attacks glass vessels when evaporated in them, and by fusion unites with silicic acid, forming a glass which is more fusible than the pure fluoride; but water dissolves out the fluoride, and leaves the silicic acid.

Its eq. is 41·98; *symb.* Na + F, or NaF.

Sulphuret of Sodium.—The protosulphuret is obtained by processes similar to those for protosulphuret of potassium, to which in its taste and chemical relations it is very similar. A concentrated solution of it yields hydrated, square, four-sided prisms, which, when heated, fuse in their water of crystallization, and then leave a white anhydrous mass. It deliquesces in the air, is very soluble in water, and is also dissolved, though in a smaller degree, by alcohol. In solution it absorbs oxygen very rapidly from the air, and passes into hyposulphate of soda.

Its eq. is 39·4; *symb.* Na + S, or NaS.

Sodium unites with sulphur in other proportions; but the resulting compounds have not been studied.

According to Gmelin of Tübingen, sulphuret of sodium is the colouring principle of *lapis lazuli*, to which the colour of ultramarine is owing; and he has succeeded in preparing artificial ultramarine by heating sulphuret of sodium with a mixture of silicic acid and alumina. (An. de Ch. et Ph. xxxvii. 409.) Artificial ultramarine, thus prepared, is sold in Paris at a moderate price. The finer specimens are quite equal to the native ultramarine, and much less expensive.

SECTION III.

LITHIUM.

Davy succeeded by means of galvanism in obtaining from lithia a white-coloured metal like sodium; but it was oxidized, and thus reconverted into lithia, with such rapidity that its properties could not be farther examined. Its eq. inferred from the composition of sulphate of lithia by Stromeyer and Thomson, is 10; but the accuracy of this estimate is rendered doubtful by the experiments of M. Herrman, according to which 6 is a nearer estimate. Its symb. is L. The compounds of lithium described in this section are thus constituted:—

	Lithium.			Equiv.	Formulæ.
Lithia.	6	1 eq. + Oxygen	8	1 eq. = 14	L + O or LO.
Chloride	6	1 eq. + Chlorine	35·42	1 eq. = 41·42	L + Cl or LCl.
Fluoride	6	1 eq. + Fluorine	18·68	1 eq. = 24·68	L + F or LF.

Lithia.—Hist.—This, the only known oxide of lithium, was discovered in 1818 by M. Arfwedson (An. de Ch. et Ph. x.) in a mineral called *petalite*; and its presence has since been detected in spodumene, lepidolite, and in several varieties of mica. Berzelius has found it also in the waters of Carlsbad in Bohemia. From the circumstance of its having been first obtained from an earthy mineral, Arfwedson gave it the name of *lithion*, (from λιθειος, *lapideus*,) a term since changed in this country to *lithia*. It has hitherto been procured in small quantity only, because spodumene and petalite are rare, and do not contain more than 6 or 8 per cent. of the alkali. It is combined in these two minerals with silicic acid and alumina, whereas potassa is likewise present in lepidolite and lithion-mica, and therefore lithia should be prepared solely from the former.

Prep.—The best process for preparing lithia is that which was suggested by Berzelius. One part of petalite or spodumene, in fine powder, is mixed intimately with two parts of fluor-spar, and the mixture is heated with three or four times its weight of sulphuric acid, as long as any acid vapours are disengaged. The silicic acid of the mineral is attacked by hydrofluoric acid, and dissipated in the form of fluosilicic acid gas, while the alumina and lithia unite with sulphuric acid. After dissolving these salts in water, the solution is boiled with pure ammonia to precipitate the alumina: it is then filtered and evaporated to dryness, and the dry mass heated to redness to expel the sulphate of ammonia. The residue is pure sulphate of lithia.

Prop.—Lithia, in its alkalinity, in forming a hydrate with water, and in its chemical relations, is closely allied to potassa and soda. It is distinguished from them by its greater neutralizing power, by forming sparingly soluble compounds with carbonic and phosphoric acids, and by its salts, when heated on platinum wire before the blowpipe, tinging the flame of a red colour. Also, when fused on platinum foil, it attacks that metal and leaves a dull yellow trace round the spot where it lay. It is distinguished from baryta, strontia, and lime, by form-

ing soluble salts with sulphuric and oxalic acids, and from magnesia by its carbonate, though sparingly soluble in water, forming with it a solution which has an alkaline reaction. *Its eq. is* 14; *symb.* L + O, L, or LO.

Chloride of Lithium.—It is readily obtained by dissolving lithia or its carbonate in hydrochloric acid. Like the chlorides of sodium and potassium, it yields by evaporation in a warm place colourless, anhydrous, cubic crystals, which differ from those chlorides in being very deliquescent, dissolving freely in alcohol as well as water, and in its alcoholic solution burning with a red flame.

Its eq. is 41·42; *symb.* L + Cl, or LCl.

The iodide and bromide of lithium have not been examined.

Fluoride of Lithium.—This is a fusible compound, prepared by dissolving lithia in hydrofluoric acid, and possesses about the same solubility in water as the carbonate.

CLASS I.

ORDER II.

METALLIC BASES OF THE ALKALINE EARTHS.

SECTION IV.

BARIUM.

Hist. and Prep.—Davy discovered *barium*, the metallic base of baryta, in the year 1808, by a process suggested by Berzelius and Pontin. It consists in forming carbonate of baryta into a paste with water, placing a globule of mercury in a little hollow made in its surface, and laying the paste on a platinum tray which communicated with the positive pole of a galvanic battery of 100 double plates, while the negative wire was in contact with the mercury. The baryta was decomposed, and its barium combined with mercury. This amalgam was then heated in a vessel free from air, by which means the mercury was expelled, and barium obtained in a pure form.

Prop.—A dark grey coloured metal, with a lustre inferior to cast iron. It is far denser than water, for it sinks rapidly in strong sulphuric acid. It attracts oxygen with avidity from the air, and in doing so yields a white powder, which is baryta. It effervesces strongly from the escape of hydrogen gas when thrown into water, and a solution of baryta is produced. It has hitherto been obtained in very minute quantities, and consequently its properties have not been determined with precision.

The eq. of barium, deduced from an analysis of the chloride by Berzelius and

myself, is 68·7. Its symb. is Ba. The composition of its compounds described in this section is as follows :—

	Barium.			Equiv.	Formulæ.
Protoxide	68·7	1 eq. + Oxygen	8	1 eq. = 76·7	Ba + O or BaO.
Peroxide	68·7	1 eq. + Ditto	16	2 eq. = 84·7	Ba + 2O or BaO_2.
Chloride	68·7	1 eq. + Chlorine	35·42	1 eq. = 104·12	Ba + Cl or BaCl.
Iodide	68·7	1 eq. + Iodine	126·3	1 eq. = 195·0	Ba + I or BaI.
Bromide	68·7	1 eq. + Bromine	78·4	1 eq. = 147·1	Ba + Br or BaBr.
Fluoride	68·7	1 eq. + Fluorine	18·68	1 eq. = 87·38	Ba + F or BaF.
Sulphuret	68·7	1 eq. + Sulphur	16·1	1 eq. = 84·8	Ba + S or BaS.

Protoxide of Barium.—Hist. and Prep.—Barytes or *Baryta*, so called from the great density of its compounds, (from βαρυς, heavy,) was discovered in the year 1774 by Scheele. It is the sole product of the oxidation of barium in air or water. It may be prepared by decomposing either the nitrate or iodate of baryta at a red heat; or by exposing carbonate of baryta contained in a black-lead crucible to an intense white heat, a process which succeeds much better when the carbonate is intimately mixed with charcoal.

Prop.—A grey powder, the sp. gr. of which is about 4. It requires a very high temperature for fusion; its solution in water has a sharp caustic alkaline taste, converts vegetable blue colours to green, and neutralizes the strongest acids. Its alkalinity, therefore, is equally distinct as that of potassa or soda; but it is much less caustic than those alkalies. In pure alcohol it is insoluble. It has an exceedingly strong affinity for water. When mixed with that liquid it slakes in the same manner as quicklime, but with the evolution of a more intense heat, which, according to Döbereiner, sometimes amounts to incandescence. The result is a white bulky hydrate, fusible at a red heat, and which bears the highest temperature of a smith's forge without parting with its water. It is composed of 76·7 parts or 1 eq. of baryta, and 9 parts or 1 eq. of water. HO, BaO.

Hydrate of baryta dissolves in three times its weight of boiling water, and in twenty parts of water at the temperature of 60° F. (Davy.) It is therefore less soluble than potassa or soda. A saturated solution of baryta in boiling water deposits, in cooling, transparent, flattened prismatic crystals, which are composed, according to Phillips, of 76·7 parts or 1 eq. of baryta, and 90 parts or 10 eq. of water. Smith states, however, that the quantity of water amounts only to 81 parts or 9 eq. He has also pointed out the existence of a hydrate containing only 2 eq. of water; it is a white powder which is formed by exposing the crystallized hydrate to the temperature of a sand bath. (Phil. Mag. and An. vi. 53, and ix. 87.)

The aqueous solution of baryta is an excellent test of the presence of carbonic acid in the atmosphere or in other gaseous mixtures. The carbonic acid unites with the baryta, and a white insoluble precipitate, carbonate of baryta, subsides.

Baryta is distinguished from all other substances by the following characters. 1. By dissolving in water and forming an alkaline solution. 2. By all its soluble salts being precipitated as white carbonate of baryta by alkaline carbonates, and as sulphate of baryta, which is insoluble both in acid and alkaline solutions, by sulphuric acid or any soluble sulphate. 3. By the characters of chloride of barium, formed by the action of hydrochloric acid on baryta.

The readiest method of preparing the soluble salts of baryta is by dissolving the carbonate in dilute acid. All of its soluble salts are poisonous; and the car-

bonate, from being dissolved by the juices of the stomach, likewise acts as a poison. The sulphate, from its insolubility, is inert.

Its eq. is 76·7 ; *symb.* Ba + O, Ba, or BaO.

Peroxide of Barium.—This oxide, which is used by Thenard in preparing peroxide of hydrogen, may be formed by conducting dry oxygen gas over pure baryta at a low red heat. A still easier process, given by Wöhler and Liebig, is to heat pure baryta to low redness in a platinum crucible, and then gradually to add chlorate of potassa in the ratio of about one part of the latter to four of the former. The oxygen of the chlorate goes over to the baryta, and chloride of potassium is generated. Cold water afterwards removes the chloride, and the peroxide of barium is left as a hydrate with 6 eq. of water, its formula being $BaO_2 + 6$ aq.

Chloride of Barium.—It is generated when chlorine gas is conducted over baryta at a red heat, oxygen gas being disengaged; but it is most conveniently prepared by dissolving carbonate of baryta in hydrochloric acid diluted with about three times its weight of water, or by decomposing a solution of sulphuret of barium with hydrochloric acid. On concentrating its solution, the chloride crystallizes on cooling in flat four-sided tables bevelled at the edges, very like crystals of heavy spar. These crystals consist of 104·12 parts or 1 eq. of chloride of barium, and 18 parts or 2 eq. of water, its formula being BaCl + 2 aq. They do not change in ordinary states of the air; but in a very dry atmosphere at 60° they lose all their water, and recover it again in a moist air. They are still more rapidly rendered anhydrous at 212°, and fusion ensues at a full red heat. They are insoluble in strong alcohol : 100 parts of water dissolve 43·5 at 60° and 78 at 222°, which is the boiling point of the solution. *Its eq. is* 104·12; *symb.* Ba + Cl, or BaCl.

Iodide of Barium.—This compound may be formed in the same way as iodide of potassium. It is very soluble in water, and crystallizes in small colourless needles, which deliquesce slightly. On exposure to the air a portion of carbonate of baryta is formed, and iodine set free, which probably forms a periodide of barium.

Its eq. is 159 ; *symb.* Ba + I, or BaI.

Bromide of Barium.—It was prepared by M. Henry, jun. who has examined it, by boiling protobromide of iron with moist carbonate of baryta in excess, evaporating the filtered solution, and heating the residue to redness. The product crystallizes by careful evaporation in white rhombic prisms, which have a bitter taste, are slightly deliquescent, and are soluble in water and alcohol.

Its eq. is 147·1 ; *symb.* Ba + Br, or Ba Br.

Fluoride of Barium.—On digesting recently precipitated and moist carbonate of baryta in hydrofluoric acid, carbonic acid is expelled, and fluoride of barium collects in the form of a white powder, which bears a red heat without decomposition. It is sparingly soluble in water, and by evaporation separates in crystalline grains. It is soluble in nitric and hydrochloric acids.

Its eq. is 87·38 ; *symb.* Ba + F, or BaF.

Sulphuret of Barium.—Prep.—This compound may be formed by transmitting dry hydrosulphuric acid gas over pure baryta at a red heat; and by the action of hydrogen gas or charcoal on sulphate of baryta. The easiest process is to mix sulphate of baryta in fine powder into a paste with an equal volume of flour, one-third its weight of finely powdered charcoal, place it in a hessian crucible on

which a cover is luted, and expose it to a white heat for an hour or two, raising the temperature slowly. On pouring hot water on the ignited mass, the sulphuret of barium is dissolved, and may be separated from undecomposed sulphate and excess of charcoal by filtration.

Protosulphuret of barium is very soluble in hot water, and the solution if saturated deposits colourless crystals on cooling, which are sulphuret of barium with water of crystallization. The solution has a sulphurous odour, and absorbs oxygen and carbonic acid from the air, yielding carbonate and hyposulphite of baryta. Boiled with sulphur it yields a yellow solution, and contains a persulphuret of barium.

Sulphuret of barium supplies a ready mode of obtaining pure baryta and its salts, when the carbonate cannot be obtained. Thus its solution boiled with black oxide of copper until it ceases to precipitate a salt of lead black, yields pure baryta, which should be filtered while hot to separate the sulphuret of copper: it is apt to retain traces of oxide of copper. With a solution of carbonate of potassa, carbonate of baryta falls, and sulphuret of potassium remains in solution; and with hydrochloric acid it interchanges elements, by which hydrosulphuric acid and chloride of barium are formed. The sulphuret of barium is now much used in organic researches, particularly in purifying vegetable acids, such as malic acid (Liebig). *Its eq. is* 84·8; *symb.* Ba + S, or BaS.

SECTION V.

STRONTIUM.

Davy discovered the metallic base of strontia, called *strontium*, by a process analogous to that described in the last section. All that is known respecting its properties is, that it is a heavy metal, similar in appearance to barium, that it decomposes water with evolution of hydrogen gas, and oxidizes quickly in the air, being converted in both cases into strontia, which is the protoxide of the metal.

The eq. of strontium, deduced from the experiments of Stromeyer, is 43·8; its symb. Sr. The composition of its several compounds described in this section is as follows:—

	Strontium.			Equiv.	Formulæ.
Protoxide .	43·8	1 eq. + Oxygen	8	1 eq. = 51·8	Sr + O or SO.
Peroxide .	43·8	1 eq. + Do.	16	2 eq. = 59·8	Sr + 2O or SO_2.
Chloride .	43·8	1 eq. + Chlorine	35·42	1 eq. = 79·22	Sr + Cl or SrCl.
Iodide .	43·8	1 eq. + Iodine	126·3	1 eq. = 170·1	Sr + I or SrI.
Fluoride .	43·8	1 eq. + Fluorine	18·68	1 eq. = 62·48	Sr + F or Srf.
Sulphuret .	43·8	2 eq. + Sulphur	16·1	1 eq. = 59·9	Sr + S or SrS.

Protoxide of Strontium.—Hist.—From the close resemblance between baryta and strontia, these substances were once supposed to be identical. Crawford, however, and Sulzer noticed a difference between them; but the existence of

strontia was first established with certainty in the year 1792 by Hope,* and the discovery was made about the same time by Klaproth.† It was originally extracted from strontianite, native carbonate of strontia, a mineral found at Strontian in Scotland; and hence the origin of the term *Strontites*, or *Strontia*, by which the earth itself is designated.

Prep. and Prop.—Pure strontia may be prepared from nitrate and carbonate of strontia, in the same manner as baryta. It resembles this earth in appearance, in infusibility, and in possessing distinct alkaline properties. It slakes when mixed with water, causing intense heat, and forming a white solid hydrate, which consists of 51·8 parts or 1 eq. of strontia, and 9 parts or 1 eq. of water. Hydrate of strontia fuses readily at a red heat. It is insoluble in alcohol. Boiling water dissolves it freely, and a hot saturated solution, on cooling, deposits transparent crystals in the form of thin quadrangular tables, which consist of 1 eq. of strontia and 10 eq. of water according to Phillips. Smith gives its composition to be SrO + 9HO. He also states that dried at 212° it becomes SrO + HO, and is anhydrous on exposure to a red heat. It requires 50 times its weight of water at 60° degrees for solution, and twice its weight at 212° F. (Dalton.)

The solution of strontia has a caustic taste and alkaline reaction. Like the solution of baryta, it is a delicate test of the presence of carbonic acid in air or other gaseous mixtures, forming with it the insoluble carbonate of strontia.

The salts of strontia are best prepared from the native carbonate. Like those of baryta, they are precipitated by alkaline carbonates, and by sulphuric acid or soluble sulphates. But sulphate of strontia is less insoluble than sulphate of baryta: on adding sulphate of soda in excess to a barytic solution, baryta cannot afterwards be found in the liquid by any precipitant; but when strontia is thus treated, so much sulphate of strontia remains in solution, that the filtered liquid yields a white precipitate with carbonate of soda. [The hyposulphite of strontia is quite soluble, while that of baryta is insoluble. These earths may therefore be separated by means of hyposulphite of soda.] The salts of strontia are not poisonous; and most of them, when heated on platinum wire before the blowpipe, communicate to the flame a red tint.

Its eq. is 51·8; *symb.* Sr + O, Sr, or SO.

Peroxide of Strontium is prepared in the same way as peroxide of barium, and, like it, is resolved by dilute acids into strontia and oxygen, the latter of which forms peroxide of hydrogen with the water.

Chloride of Strontium.—This compound is formed by processes similar to those for preparing chloride of barium, and crystallizes from its solution in colourless prismatic crystals, which deliquesce in a moist atmosphere, require only twice their weight of water at 60° for solution, and still less of boiling water, and are soluble in alcohol. The alcoholic solution, when set on fire, burns with a red flame. These characters afford a certain mode of distinguishing strontia from baryta. The crystals consist of 79·22 parts or 1 eq. of chloride of strontium, and 81 parts or 9 eq. of water, which are expelled by heat. The anhydrous chloride fuses at a red heat, and yields a white crystalline brittle mass on cooling.

Its eq. is 79·22; *symb.* Sr + Cl, or SrCl.

Iodide of Strontium may be prepared in the same manner as that of barium. It is very soluble in water, and fuses without decomposition in close vessels; but when heated to redness in the open air, iodine escapes, and strontia is generated.

* Edin. Philos. Trans. iv. 3. † Klaproth's Contributions, i.

Fluoride of Strontium is obtained in the same way as fluoride of barium, and is a white powder of sparing solubility.

Protosulphuret of Strontium is similar in its properties and mode of preparation to sulphuret of barium, and may be applied to similar uses. Strontium also combines with more than one equivalent of sulphur; but these compounds have not been examined.

SECTION VI.

CALCIUM.

The existence of calcium, the metallic base of lime, was demonstrated by Davy by a process similar to that described in the section on barium. It is of a whiter colour than barium or strontium, and is converted into lime by being oxidized. Its other properties are unknown.

According to the analysis of chloride of calcium by Berzelius, the eq. of calcium is 20·5; its symb. is Ca. Its compounds described in this section are composed as follows:—

	Calcium.		Equiv.	Formulæ.
Protoxide .	20·5 1 eq. + Oxygen	8	1 eq. = 28·5	Ca + O or CaO.
Peroxide .	20·5 1 eq. +	16·0	2 eq. = 36·5	Ca + 2O or CaO_2.
Chloride .	20·5 1 eq. + Chlorine	35·42	1 eq. = 55·92	Ca + Cl or CaCl.
Iodide .	20·5 1 eq. + Iodine	126·3	1 eq. = 146·8	Ca + I or CaI.
Bromide .	20·5 1 eq. + Bromine	78·4	1 eq. = 98·9	Ca + Br or CaBr.
Fluoride .	20·5 1 eq. + Fluorine	18·68	1 eq. = 39·18	Ca + F or CaF.
Sulphuret .	20·5 1 eq. + Sulphur	16·1	1 eq. = 36·6	Ca + S or CaS.
Bisulphuret .	20·5 1 eq. +	32·2	2 eq. = 52·7	Ca + 2S or CaS_2.
Quintosulphuret	20·5 1 eq. +	80·5	5 eq. = 101	Ca + 5S or CaS_5.
Phosphuret .	20·5 1 eq. + Phosph.	15·7	1 eq. = 36·2	Ca + P or CaP.

Protoxide of Calcium.—Prep.—This compound, commonly known by the name of *lime* and *quicklime*, is obtained by exposing carbonate of lime to a strong red heat, so as to expel its carbonic acid. If lime of great purity is required, it should be prepared from pure carbonate of lime, such as Iceland spar or Carrara marble; but in burning lime in lime-kilns for making mortar, common limestone is employed. The expulsion of carbonic acid is facilitated by mixing the carbonate with combustible substances, in which case carbonic oxide is generated. A current of air also greatly facilitates the burning of lime; for in close vessels it is hardly possible to expel the whole carbonic acid. The effect of a current of air is partly due to the diffusion of one gas in another.

Prop.—It is a brittle white earthy solid, the sp. gr. of which is about 2·3. It phosphoresces powerfully when heated to full redness, a property which it possesses in common with strontia and baryta. It is one of the most infusible bodies known; fusing with difficulty, even by the heat of the oxy-hydrogen blowpipe. It has a powerful affinity for water, and the combination is attended with great increase of temperature, and formation of a white bulky hydrate, which is com-

posed of 28·5 parts or 1 eq. of lime, and 9 parts or 1 eq. of water. The process of *slaking* lime consists in forming this hydrate, and the hydrate itself is called *slaked* lime. It differs from the hydrate of baryta in parting with its water at a red heat.

Hydrate of lime is dissolved very sparingly by water, and it is a singular fact, first noticed, I believe, by Dalton, that it is more soluble in cold than in hot water. Thus he found that one grain of lime requires for solution

778 grains	of water	at 60° F.
972	"	130°
1270	"	212°

And, consequently, on heating a solution of *lime water*, which has been prepared in the cold, deposition of lime ensues. This fact was determined experimentally by Phillips, who has likewise observed that water at 32° is capable of dissolving twice as much lime as at 212° F. Owing to this circumstance pure lime cannot be made to crystallize in the same manner as baryta or strontia; but Gay-Lussac succeeded in obtaining crystals of lime by evaporating lime water under the exhausted receiver of an air-pump by means of sulphuric acid. Small transparent crystals, in the form of regular hexahedrons, were deposited, which consist of water and lime in the same proportion as in the hydrate above mentioned.

Lime water is prepared by mixing hydrate of lime with water, agitating the mixture repeatedly, and then setting it aside in a well-stopped bottle until the undissolved parts shall have subsided. The substance called *milk* or *cream* of lime is made by mixing hydrate of lime with a sufficient quantity of water to give it the liquid form;—it is merely lime water in which hydrate of lime is mechanically suspended.

Lime water has a harsh acrid taste, and converts vegetable blue colours to green.—It agrees, therefore, with baryta and strontia in possessing distinct alkaline properties. Like the solutions of these earths, it has a strong affinity for carbonic acid, and forms with it an insoluble carbonate. On this account lime water should be carefully protected from the air. For the same reason, lime water is rendered turbid by a solution of carbonic acid; but on adding a large quantity of the acid, the transparency of the solution is completely restored, because carbonate of lime is soluble in an excess of carbonic acid. The action of this acid on the solutions of baryta and strontia is precisely similar.

The salts of lime which are easily prepared by the action of acids on pure marble, are in many respects similarly affected by reagents, as those of baryta and strontia. They are precipitated, for example, by alkaline carbonates. Sulphuric acid and soluble sulphates likewise precipitate lime from a moderately strong solution. But sulphate of lime has a considerable degree of solubility. Thus, a dilute solution of a salt of lime is not precipitated at all by sulphuric acid; and when the sulphate of lime is separated, it may be redissolved by the addition of nitric acid.

The most delicate test of the presence of lime in neutral solutions is oxalate of ammonia or potassa; for of all the salts of lime, the oxalate is the most insoluble in water. This serves to distinguish lime from most substances, though not from baryta and strontia; because the oxalates of baryta and strontia, especially the latter, are likewise sparingly soluble.—All these oxalates dissolve readily in water acidulated with nitric or hydrochloric acid. It is distinguished from baryta and strontia by the fact, that nitrate of lime yields prismatic crystals

by evaporation, is deliquescent in a high decree, and very soluble in alcohol; while the nitrates of baryta and strontia crystallize in regular octohedrons, or segments of the octohedron, undergo no change on exposure to the air, except when it is very moist, and do not dissolve in pure alcohol.

The salts of lime, when heated before the blowpipe, or when their solutions in alcohol are set on fire, communicate to the flame a dull brownish-red colour.

Its eq. is 28·5; *symb.* Ca + O, Ca, or CaO.

Peroxide of Calcium.—This oxide is prepared in the same way as peroxide of barium, and is similar to it in its properties.

Chloride of Calcium.—This compound exists in sea-water and in many saline springs, is the residue of the process for preparing ammonia, and is readily formed by dissolving marble or chalk in hydrochloric acid. On evaporating its solution to the consistence of a syrup, the chloride crystallizes on cooling in irregular, colourless prismatic crystals, which consist of 55·92 parts or 1 eq. of chloride of calcium and 54 parts or 6 eq. of water. By heat it loses its water, and at a gentle red heat fuses; but on exposure to the air it rapidly recovers its water of crystallization and then deliquesces. Owing to its strong affinity for water, it is much used for frigorific mixtures with snow; but for this purpose the hydrous chloride is preferable, as prepared by evaporating its solution so far, that the whole becomes a solid mass on removal from the fire, reducing it when cold quickly to powder, and preserving it in bottles closed with great care. It is also used for drying gases, and ethereal and oily liquids, and, in organic analysis, to absorb the water formed, and thus determine the amount of hydrogen. Chloride of calcium is very soluble in alcohol, and forms with it a definite compound.

Its eq. is 55·92; *symb.* Ca + Cl, or CaCl.

Iodide of Calcium.—This compound may be prepared by digesting hydrate of lime with protiodide of iron. It is deliquescent and very soluble in water, sustains a red heat unchanged in close vessels, but when heated in the open air its iodine is replaced by oxygen, and lime remains. The solution of iodide of calcium dissolves a large quantity of iodine, and on evaporating the brown solution in vacuo above a vessel with dry carbonate of potassa, a periodide of calcium crystallizes in large black prisms of a metallic lustre.

Its eq. is 46·8; *symb.* Ca + I, or CaI.

Bromide of Calcium.—It was prepared by Henry by digesting hydrate of lime with a solution of protobromide of iron, and crystallizes in acicular crystals which are very deliquescent, and extremely soluble in alcohol and water. It is very analogous in taste and properties to chloride of calcium, fuses by heat, but in open vessels suffers partial decomposition.

Its eq. is 98·9; *symb.* Ca + Br, or CaBr.

Fluoride of Calcium.—Hist. and Prep.—This is a natural product, which frequently accompanies metallic ores, especially those of lead and tin, often occurs in cubic crystals, and is well known under the name of *fluor* or *Derbyshire spar*. The crystals found in the lead mines of Derbyshire are remarkable for the largeness of their size, the regularity of their form, and the variety and beauty of their colours. It may be prepared artificially by digesting moist, recently precipitated, carbonate of lime in an excess of hydrofluoric acid; or by mixing a solution of chloride of calcium with fluoride of potassium or sodium. As prepared in the latter mode, it is a bulky gelatinous mass, which it is very difficult to wash;

whereas the former method gives it in the state of a granular white powder, which may be washed with ease.

Prep.—Fluoride of calcium fuses at a red heat without farther change. It is insoluble in water, slightly soluble in hot diluted hydrochloric acid, and is decomposed by sulphuric acid aided by gentle heat. It is in a small degree decomposed by boiling nitric acid. Fused with carbonate of potassa, carbonate of lime and fluoride of potassium are generated.

Fluor-spar is much used in forming vases, as a flux in metallurgic processes, and in the preparation of hydrofluoric acid.

Its eq. is 39·18; *symb.* Ca + F, or CaF.

Protosulphuret of Calcium.—Prep.—By reduction from the sulphate by hydrogen or charcoal, and when pure is white with a reddish tint, and is very sparingly soluble in water. It has the property, in common with sulphuret of barium, of being phosphorescent after exposure to light, and appears to be the essential ingredient of Canton's Phosphorus.

When 3 parts of slaked lime, 1 of sulphur, and 20 of water are boiled together for an hour, and the solution, without separation from the sediment, is set aside in a corked flask for a few days, a copious deposite of orange-coloured crystals are deposited, which, when slowly formed, are flat quadrilateral prisms. These, from the analysis of Herschel, appear to be bisulphuret of calcium with 3 eq. of water. They are decomposed by exposure to the air, and are of sparing solubility in water. *Symb.* CaS.

When either of the foregoing sulphurets is boiled in water along with sulphur, a yellow solution is formed containing calcium combined with 5 eq. of sulphur. *Symb.* CaS_5.

Phosphuret of Calcium.—It is formed by passing the vapour of phosphorus over fragments of quicklime at a low red heat, or by heating to redness small pieces of quicklime in the bottom of a tall crucible or matrass, and dropping into a hollow made in the centre of the ignited lime, small fragments of phosphorus, when a brown matter is formed, consisting of phosphate of lime and phosphuret of calcium. When put into water, mutual decomposition ensues, and phosphuretted hydrogen, hypophosphorous acid, and phosphoric acid are generated.

SECTION VII.

MAGNESIUM.

Hist. and Prep.—The galvanic researches of Davy demonstrated the existence of magnesium, though he obtained it in a quantity too minute for determining its properties. It was prepared by Bussy, in the year 1830, by the action of potassium on chloride of magnesium. For this purpose five or six pieces of potassium, of the size of peas, were introduced into a glass tube, the sealed extremity of which was bent into the form of a retort, and upon the potassium were laid fragments of chloride of magnesium. The latter being then heated to near its

point of fusion, a lamp was applied to the potassium, and its vapour transmitted through the mass of heated chloride. Vivid incandescence immediately took place, and on putting the mass, after cooling, into water, the chloride of potassium with undecomposed chloride of magnesium was dissolved, and metallic magnesium subsided. These results have been since confirmed by Liebig. (An. de Ch. et Ph. xlvi. 435.)

Prop.—Magnesium has a brilliant metallic lustre, and a white colour like silver, is very malleable, and fuses at a red heat. Moist air oxidizes it superficially; but it undergoes no change in a dry air, and may be boiled in water without oxidation. Heated to redness in air or oxygen gas, it burns with brilliancy, yielding magnesia; and it inflames spontaneously in chlorine gas. It is readily dissolved by dilute acids with disengagement of hydrogen, and the solution is found to contain a pure salt of magnesia. In these and other respects it is more strikingly analogous to zinc than any of the metals thus far treated of.

The eq. of magnesium, inferred by Berzelius from the quantity of sulphate obtained from a known weight of pure magnesia, is 12·7; its symb. is Mg. Its compounds described in this section are composed as follows:—

	Magnesium.		Equiv.		Formulæ.
Protoxide .	12·7	1 eq. + Oxygen 8	1 eq. =	20·7	Mg + O or MgO.
Chloride .	12·7	1 eq. + Chlorine 35·42	1 eq. =	48·12	Mg + Cl or MgCl.
Iodide . .	12·7	1 eq. + Iodine 126·3	1 eq. =	139	Mg + I or MgI.
Bromide .	12·7	1 eq. + Bromine 78·4	1 eq. =	91·1	Mg + Br or MgBr.
Fluoride .	12·7	1 eq. + Fluorine 18·68	1 eq. =	31·38	Mg + F or MgF.

Protoxide of Magnesium.—Prep.—This, the only known oxide of magnesium, commonly known by the name of *magnesia*, is best obtained by exposing carbonate of magnesia to a very strong red heat, by which its carbonic acid is expelled. It is a white friable powder, of an earthy appearance; and when pure it has neither taste nor odour. Its sp. gr. is about 2·3, and it is exceedingly infusible. It has a weaker affinity than lime for water; for though it forms a hydrate when moistened, the combination is effected with hardly any disengagement of heat, and the product is readily decomposed by a red heat. According to the analysis of Stromeyer, the native hydrate contains 1 eq. of each of its constituents; and the results of the analyses of Berzelius and Fyfe accord very nearly with this proportion. It has generally been thought that magnesia formed several hydrates; but the recent observations of Rees indicate that the artificial hydrates have the same composition as the native (Phil. Mag. and An. x. 454).

Prop.—Very sparingly soluble in water. According to Fyfe, it requires 5142 times its weight of water at 60°, and 36,000 of boiling water for solution. The resulting liquid does not change the colour of violets; but when pure magnesia is put upon moistened turmeric paper, it causes a brown stain. From this there is no doubt that the inaction of magnesia with respect to vegetable colours, when tried in the ordinary mode, is owing to its insolubility.—It possesses the still more essential character of alkalinity, that, namely, of forming neutral salts with acids, in an eminent degree. It absorbs both water and carbonic acid when exposed to the atmosphere, and therefore should be kept in well-closed phials.

Magnesia is characterized by the following properties. With nitric and hydrochloric acids it forms salts which are soluble in alcohol, and exceedingly deliquescent. The sulphate of magnesia is very soluble in water, a circumstance by which it is distinguished from the other alkaline earths. Magnesia is precipi-

tated from its salts as a bulky hydrate by the pure alkalies. It is precipitated as carbonate of magnesia, by the carbonates of potassa and soda; but the bicarbonates, and the common carbonate of ammonia, do not precipitate it in the cold. If moderately diluted, the salts of magnesia are not precipitated by oxalate of ammonia. By means of this reagent magnesia may be both distinguished and separated from lime. [The most delicate test for magnesia, even in very dilute solutions, is the common phosphate of soda, with the addition of ammonia. A white crystalline precipitate of basic phosphate of magnesia and ammonia is formed, the separation of which is much promoted by brisk stirring with a glass rod.]

Its eq. is 20·7; *symb.* Mg + O, Mg, or MgO.

Chloride.—This compound may be prepared by transmitting dry chlorine gas over a mixture of magnesia and charcoal at a red heat; but Liebig has given an easier process, which consists in dissolving magnesia in hydrochloric acid, evaporating to dryness, mixing the residue with its own weight of hydrochlorate of ammonia, and projecting the mixture in successive portions into a platinum crucible at a red heat. As soon as the ammoniacal salt is wholly expelled, the fused chloride of magnesium is left in a state of tranquil fusion, and on cooling becomes a transparent colourless mass, perfectly anhydrous, highly deliquescent, and is very soluble in alcohol and water.

[When carbonate of magnesia is neutralized by hydrochloric acid, a chloride of magnesium is formed which contains 6 eq. of water. This, however, suffers decomposition when heated, hydrochloric acid escapes and pure magnesia remains; so that it cannot be obtained in an anhydrous condition. The chloride, prepared by Leibig's method, is that which is employed in obtaining the metal.]

Its eq. is 48·12; *symb.* MgCl.

Iodide of magnesium is obtained by dissolving magnesia in hydriodic acid, is very soluble in water, and is only known in solution.

Bromide of magnesium, obtained by dissolving magnesia in hydrobromic acid, crystallizes in small acicular prisms, which have a sharp taste, are deliquescent, and very soluble in water and alcohol. It is decomposed by a strong heat.

Fluoride of magnesium is prepared by digesting magnesia in hydrofluoric acid in excess. It is insoluble in water and in excess of hydrofluoric acid, and bears a red heat without decomposition.

CLASS I.

ORDER III.

METALLIC BASES OF THE EARTHS.

SECTION VIII.

ALUMINIUM.

Hist.—That alumina is an oxidized body was proved by Davy, who found that potassa is generated when the vapour of potassium is brought into contact with pure alumina heated to whiteness; and it was inferred, chiefly by analogical reasoning, to be a metallic oxide. The propriety of this inference has been demonstrated by Wöhler, who has procured *aluminium*, the metallic base of alumina, in a pure state (Edinburgh Journal of Science, No. xvii. 178).

Prep.—Depends on the property which potassium possesses, of decomposing the chloride of aluminium. Decomposition is effected by aid of a moderate increase of temperature; but the action is so violent, and accompanied with such intense heat, that the process cannot be safely conducted in glass vessels. Wöhler succeeded with a platinum crucible, retaining the cover in its place by a piece of wire. The heat developed during the action was so great, that the crucible, though but gently heated externally, suddenly became red hot. The platinum is scarcely attacked during the process; but to prevent the possibility of error from this source, the decomposition was also effected in a crucible of porcelain. The potassium employed for the purpose should be quite free from carbon, and the quantity operated on at one time not exceed the size of ten peas. The heat was applied by means of a spirit lamp, and continued until the action was completed. The proportion of the materials requires to be carefully adjusted; for the potassium should be in such quantity as to prevent any chloride of aluminium from subliming during the process, but not so much as to yield an alkaline solution when the product is put into water. The matter contained in the crucible at the close of the operation is in general completely fused, and of a dark grey colour. When *quite cold*, the crucible is put into a large glass full of water, in which the saline matter is dissolved, with slight disengagement of hydrogen of an offensive odour; and a grey powder separates, which on close inspection, especially in sunshine, is found to consist solely of minute scales of metal. These scales, after being well washed with *cold* water, are pure aluminium. The saline matter removed by water is chloride of potassium, and a considerable quantity of chloride of aluminium.

Prop.—As thus formed, it is a grey powder, very similar to that of platinum. It is generally in small scales or spangles of a metallic lustre; and sometimes small, slightly coherent, spongy masses are observed, which in some places have the lustre and white colour of tin. The same appearance is rendered per-

fectly distinct by pressure on steel, or in an agate mortar; so that the lustre of aluminium is decidedly metallic. In this fused state it is a conductor of electricity, though it does not possess this property when in the form of powder. This remark, of a metal conducting the electric fluid in one state and not in another, is very instructive; and Wöhler observed an instance of the same kind in iron, which in the state of fine powder is a non-conductor of electricity.

Aluminium requires for fusion a temperature higher than that at which cast iron is liquefied. When heated to redness in the open air, it takes fire and burns with vivid light, yielding aluminous earth of a white colour, and of considerable hardness. Sprinkled in powder in the flame of a candle, brilliant sparks are emitted, like those given off during the combustion of iron in oxygen gas. When heated to redness in a vessel of pure oxygen gas, it burns with an exceedingly vivid light, and emission of intense heat. The resulting alumina is partially vitrified, of a yellowish colour, and equal in hardness to the native crystallized aluminous earth, corundum. Heated to near redness in an atmosphere of chlorine, it takes fire, and chloride of aluminium is sublimed.

Aluminium is not oxidized by water at common temperatures, nor is its lustre tarnished by lying in water during its evaporation. On heating the water to near its boiling point, oxidation of the metal commences, with feeble disengagement of hydrogen gas, the evolution of which continues even long after cooling, but at length wholly ceases. The oxidation, however, is very slight; and even after continued ebullition, the smallest particles of aluminium appear to have suffered scarcely any change.

It is not attacked by concentrated sulphuric or nitric acid at common temperatures. In the former, with the aid of heat, it is rapidly dissolved with disengagement of sulphurous acid gas. In dilute hydrochloric and sulphuric acid, and also in a dilute solution of potassa, it dissolves with evolution of hydrogen gas. Ammonia produces a similar effect, and dissolves a large quantity of alumina. The hydrogen gas which makes its appearance is of course derived from water, the oxygen of which combines with the metal so as to constitute alumina.

From the composition of the sulphates of alumina, ascertained by Berzelius, Stromeyer, and Philips, the equivalent of alumina may be estimated either at 25·7, or at 51·4, twice that number. Now chemists have no direct means of discovering the atomic constitution of alumina, inasmuch as aluminium combines with oxygen and most other elements in one proportion only. Thomson assumes alumina to consist of single atoms of its elements: but most chemists, seeing that alumina has little analogy to protoxides in its modes of combining, but that in its crystalline form and all its chemical relations it closely resembles peroxide of iron, have inferred that the simplest molecule of alumina contains 2 atoms of aluminium and 3 atoms of oxygen. On this supposition 51·4 must be the *eq.* of alumina, and 13·7 that of aluminium; its *symb.* Al. The composition of its compounds described in this section is the following:—

2 eq. Aluminium.			Equiv.	Formulæ.
Sesquioxide	26·4 + oxygen	24	3 eq. = 51·4	2Al + 3O or Al_2O_3.
Sesquichloride	26·4 + chlorine	106·26	3 eq. = 132·66	2Al + 3Cl or Al_2Cl_3.
Sesquisulphuret	26·4 + sulphur	48·3	3 eq. = 74·7	2Al + 3S or Al_2S_3.
Sesquiphosphuret	26·4 + phosphs.	47·1	3 eq. = 73·5	2Al + 3P or Al_2P_3.
Sesquiseleniuret	26·4 + selenium	118·2	3 eq. = 144·6	2Al + 3Se or Al_2Se_3.

The composition of the four last compounds is matter of inference from the change which they respectively undergo by the action of water.

Sesquioxide of Aluminium.—Hist. and Prep.—The only known oxide of this metal, and is commonly called *alumina* or *aluminous earth*. It is one of the most abundant productions of nature. It is found in every region of the globe, and in rocks of all ages, being a constituent of the oldest primary mountains, of the secondary strata, and of the most recent alluvial depositions. The different kinds of clay of which bricks, pipes, and earthenware are made, consist principally of silicate of alumina in a greater or less degree of purity. Though this earth commonly appears in rude amorphous masses, it is sometimes found beautifully crystallized.—The ruby and the sapphire, two of the most beautiful gems with which we are acquainted, are composed almost solely of alumina.

Pure alumina is prepared from alum, sulphate of alumina and potassa. This salt, as purchased in the shops, is frequently contaminated with peroxide of iron, and consequently unfit for many chemical purposes; but it may be separated from this impurity by repeated crystallization. Its absence is proved by the alum being soluble without residue in a solution of pure potassa; whereas when peroxide of iron is present, it is either left undissolved in the first instance, or deposited after a few hours in yellowish brown flocks. Any quantity of purified alum is dissolved in four or five times its weight of boiling water, a slight excess of carbonate of potassa added, and after digesting for a few minutes, the bulky hydrate of alumina is collected on a filter, and well washed with hot water. It is necessary in this operation to digest and employ an excess of alkali; since otherwise the precipitate would retain some sulphuric acid in the form of a subsulphate. But the alumina, as thus prepared, is not yet quite pure; for it retains some of the alkali with such force, that it cannot be separated by the action of water. For this reason the precipitate must be re-dissolved in dilute hydrochloric acid, and thrown down by means of pure ammonia or its carbonate. This precipitate, after being well washed and exposed to a white heat, yields pure anhydrous alumina. Ammonia cannot be employed for precipitating aluminous earth directly from alum, because sulphate of alumina is not completely decomposed by this alkali (Berzelius). Liebig precipitates alum with an excess of chloride of barium, evaporates the filtered liquid to dryness, and ignites the residue. Water now dissolves the chlorides of potassium and barium, and leaves alumina as a white powder, very easily washed. The washing of the hydrate, in the process first described, is a most tedious operation. An easier process, proposed by Gay-Lussac, is to expose sulphate of alumina and ammonia to a strong heat, so as to expel the ammonia and sulphuric acid.

Prop.—Alumina has neither taste nor smell, and is quite insoluble in water. It is very infusible, though less so than lime or magnesia. It has a powerful affinity for water, attracting moisture from the atmosphere with avidity; and for a like reason, it adheres tenaciously to the tongue when applied to it. Mixed with a due proportion of water, it yields a soft cohesive mass, susceptible of being moulded into regular forms, a property upon which depends its employment in the art of pottery. When once moistened, it cannot be rendered anhydrous, except by exposure to a full white heat; and in proportion as it parts with water, its volume diminishes. Owing to its insolubility, it does not affect the blue colour of plants. It appears to possess the properties both of an acid and of an alkali:—of an acid, by uniting with alkaline bases, such as potassa, lime, and baryta;—and of an alkali, by forming salts with acids. In neither case, however, are its soluble compounds neutral with respect to test paper.

Alumina most probably forms several different hydrates with water, and two have been described by Thomson. One of these, apparently composed of 6 eq.

of water to one of alumina, so that its formula is Al_2O_3 + 6 aq. was procured by exposing precipitated alumina for the space of two months to a dry air, the temperature of which did not exceed 60°. The other is a terhydrate prepared by drying the preceding at a heat of about 100°, and its formula is therefore Al_2O_3 + 3 aq. The mineral called Gibbsite has a similar composition. [The mineral called *diaspor*, from crumbling to pieces when heated, is said to be also a hydrate with 2 eq. of water; its formula is Al_2O_3 + aq.]

Alumina is easily recognized by the following characters. 1. It is separated from acids, as a hydrate, by all the alkaline carbonates and by pure ammonia. 2. It is precipitated by pure potassa or soda, but the precipitate is completely re-dissolved by an excess of the alkali. [Hydrate of alumina has a remarkable attraction for organic colouring matters. On this account it is extensively used in the preparation of lakes and pigments. When added to coloured solutions it precipitates with it the colouring matters. The fibres of various fabrics when impregnated with it, seize hold of the same colouring matters, and fix them permanently.—Hence the aluminous salts are largely used in dying and calico printing.]

Its eq. is 51·4; *symb.* 2 Al + 3O, $\dddot{\underline{Al}}$, or Al_2O_3.

Sesquichloride of Aluminium.—Hist.—Oersted discovered this compound by transmitting dry chlorine gas over a mixture of alumina and charcoal heated to redness. By acting on this substance with an amalgam of potassium and expelling the mercury by heat, he obtained metallic matter, which he believed to be aluminium; but not having leisure to pursue the inquiry himself, he requested Wöhler to investigate the subject. Wöhler did not arrive at any satisfactory conclusion by the method suggested by Oersted; but met with complete success by means of pure potassium, as already described.

Prep—To procure chloride of aluminium, Wöhler precipitated aluminous earth from a hot solution of alum by means of potassa, and mixed the hydrate, when dry, with pulverized charcoal, sugar, and oil, so as to form a thick paste, which was heated in a covered crucible until all the organic matter was destroyed. By this means the alumina was brought into a state of intimate mixture with finely divided charcoal, and while yet hot, was introduced into a tube of porcelain, fixed in a convenient furnace. After expelling atmospheric air from the interior of the apparatus by a current of dry chlorine gas, the tube was brought to a red heat. The formation of chloride of aluminium then commenced, and continued, with disengagement of carbonic oxide gas, during an hour and a half, when the tube became impervious from sublimed chloride of aluminium collected within it. The process was then necessarily discontinued.

Prop.—As thus formed, chloride of aluminium is of a pale greenish yellow colour, partially translucent, and of a highly crystalline lamellated texture, somewhat like talc, but without regular crystals. On exposure to the air, it fumes slightly, emits an odour of hydrochloric acid gas, and, deliquescing, yields a clear liquid. When thrown into water, it is speedily dissolved with a hissing noise; and so much heat is evolved, that the water, if in small quantity, is brought into a state of brisk ebullition. The solution is a true hydrochlorate of alumina, formed by decomposition of water; for when gently evaporated, hydrochloric acid escapes, and alumina is gradually deposited. According to Oersted it is volatile at a temperature a little higher than 212°, and fuses nearly at the same degree.

Sesquisulphuret of Aluminium.—Sulphur may be distilled from aluminium without combining with it; but if a piece of sulphur is dropped on aluminium when

strongly incandescent, so that it may be enveloped in an atmosphere of the vapour of sulphur, the union is effected with a vivid emission of light. The resulting sulphuret is a partially vitrified, semi-metallic mass, which acquires an iron-black metallic lustre when burnished. Applied to the tongue, it excites a pricking warm taste of hydrosulphuric acid. When put into pure water, or on exposure to the air, it is resolved, by an interchange of elements, into alumina and hydrosulphuric acid, the latter escaping as gas. It is to be presumed that

1 eq. Sulphuret	and 3 eq. Water	yield	1 eq. Alumina	and 3 eq. Hydrosulph. Acid.
Al_2S_3	3HO		Al_2O_3	3HS

Wöhler finds that sulphuret of aluminium cannot be generated by the action of hydrogen gas on sulphate of alumina at a red heat; for in that case all the acid is expelled, without the aluminous earth being reduced.

Sesquiphosphuret of Aluminium.—When aluminium is heated to redness in contact with the vapour of phosphorus, it takes fire, and emits a brilliant light. The product is described by Wöhler as a blackish grey pulverulent mass, which by friction acquires a dark grey metallic lustre, and in the air smells instantly of phosphuretted hydrogen. By the action of water alumina and phosphuretted hydrogen gas are generated, but the latter is not spontaneously inflammable. The effervescence is less rapid than with the sulphuret, but is increased by heat.

Sesquiseleniuret of Aluminium.—This compound is formed, with disengagement of heat and light, by heating to redness a mixture of selenium and aluminium. The product is black and pulverulent, and assumes a dark metallic lustre when rubbed. In the air it emits a strong odour of hydroselenic acid; and this gas is rapidly disengaged by the action of water, which is speedily reddened by the separation of selenium.

SECTION IX.

GLUCINIUM, YTTRIUM, THORIUM, ZIRCONIUM.

GLUCINIUM.

Glucina, which was discovered by Vauquelin in the year 1798, has hitherto been found only in three rare minerals, the euclase, beryl, and emerald. It is the only oxide of a metal which Wöhler succeeded in preparing in the year 1828 by a process exactly similar to that described in the last section. Chloride of glucinium is readily attacked by potassium when heated with the flame of a spirit-lamp, and the decomposition is attended with intense heat. After removing the resulting chloride of potassium by cold water, the glucinium appears in the form of a greyish black powder, which acquires a dark metallic lustre by burnishing. It may be exposed to air and moisture, or be even boiled in water, without oxidation. When heated in the open air, it takes fire and burns with a most vivid light; and in oxygen gas the combustion is attended with extraordinary splendour. The product in both cases is glucina, which is not at all fused by the intense heat that accompanied its formation. The metal is readily oxidized and

dissolved in sulphuric, nitric, or hydrochloric acid with the aid of heat; and the same ensues, with disengagement of hydrogen gas, in solution of potassa. It is not attacked, however, by pure ammonia. When moderately heated in chlorine gas, it burns with great splendour, and a crystallized chloride sublimes. Similar phenomena ensue in the vapour of bromine and iodine; and it unites readily with sulphur, selenium, phosphorus, and arsenic. (Phil. Mag. and Annals, v. 392.)

According to the experiments of Berzelius, glucina contains 31·154 per cent. of oxygen, and consequently its eq. is 26·5 on the supposition that its constitution is similar to that of alumina, with which it is closely associated both in nature and in many of its properties. *Its symb.* is G.

Oxide of Glucinium or Glucina.—Prep.—This oxide is commonly prepared from beryl, in which it exists to the extent of about 14 per cent. combined with silicic acid and alumina. In order to procure it in a separate state, the mineral is reduced to an exceedingly fine powder, mixed with three times its weight of carbonate of potassa, and exposed to a strong red heat for half an hour, so that the mixture may be fused. The mass is then dissolved in dilute hydrochloric acid, and the solution evaporated to perfect dryness; by which means the silicic acid is rendered quite insoluble. The alumina and glucina are then redissolved in water acidulated with hydrochloric acid, and thrown down together by pure ammonia. The precipitate, after being well washed, is macerated with a large excess of carbonate of ammonia, by which glucina is dissolved; and on boiling the filtered liquid, carbonate of glucina subsides. By means of a red heat its carbonic acid is entirely expelled.

Another process has been recommended by Berthier, who directs the beryl to be mixed in fine powder with its own weight of marble, and the mixture to be exposed in a crucible to a strong heat. In this manner a glass is obtained, which when in fine powder is attached freely by hydrochloric or sulphuric acid. From this solution the glucina may be obtained as before.

Prop.—Glucina is a white powder, which has neither taste nor odour, and is quite insoluble in water. Its sp. gr. is 3. Vegetable colours are not affected by it. The salts which it forms with acids have a sweetish taste, a circumstance which distinguishes glucina from other earths, and from which its name is derived (from γλυκυς, sweet.)

Glucina may be known chemically by the following characters. 1. Pure potassa or soda precipitates glucina from its salts, but an excess of the alkali redissolves it. 2. It is precipitated permanently by pure ammonia as a hydrate, and by fixed alkaline carbonates as a carbonate of glucina. 3. It is dissolved completely by a cold solution of carbonate of ammonia, and is precipitated from it by boiling. By means of this property, glucina may be both distinguished and separated from alumina.

Its eq. is 77; *symb.* 2G + 3O, $\dddot{\underline{G}}$, or G_2O_3.

YTTRIUM.

Yttrium is the metallic base of an earth which was discovered in the year 1794 by Professor Gadolin, in a mineral found at Ytterby in Sweden, from which it received the name of *Yttria*. The metal itself was prepared by Wöhler in 1828 by a process similar to that above described. Its texture, by which it is distinguished from glucinium and aluminium, is scaly, its colour greyish-black, and its lustre perfectly metallic. In colour and lustre it is inferior to aluminium,

bearing in these respects nearly the same relation to that metal, that iron does to tin. It is a brittle metal, while aluminium is ductile. It is not oxidized either in air or water; but when heated to redness, it burns with splendour even in atmospheric air, and with far greater brilliancy in oxygen gas. The product, yttria, is white, and shows unequivocal marks of fusion. It dissolves in sulphuric acid, and also, though less readily, in solution of potassa, but it is not attacked by ammonia. It combines with sulphur, selenium, and phosphorus. (Phil. Mag. and Annals, v. 393.)

The salts of yttria have in general a sweet taste, and the sulphate and several others have an amethyst colour. It is precipitated as a hydrate by the pure alkalies, and is not redissolved by an excess of the precipitant; but alkaline carbonates, especially that of ammonia, dissolve in the cold, though less freely than glucina, and carbonate of yttria is precipitated by boiling. Of all the earths it bears the closest resemblance to glucina; but it is readily distinguished from it by the colour of its sulphate, by its insolubility in pure potassa, and by yielding a precipitate with ferrocyanuret of potassium (Berzelius). The *eq.* of yttrium, as deduced by Berzelius, is 32·2; and that of yttria, which is probably a protoxide, is 40·2.

The *symb.* of the metal is Y; of its oxide Y + O, Y, or YO.*

THORIUM.

The earthy substance formerly called *thorina* was found by Berzelius to be phosphate of yttria; but in 1828 he discovered a new earth, so similar in some respects to what was formerly called thorina, that he applied this term to the new substance. The metallic base of thorina (thorium) was procured by the action of potassium on chloride of thorium, the decomposition being accompanied with a slight detonation. On washing the mass, thorium is left in the form of a heavy metallic powder, of a deep leaden-grey colour; and when pressed in an agate mortar, it acquires metallic lustre and an iron-grey tint. Thorium is not oxidized either by hot or cold water; but when gently heated in the open air it burns with great brilliancy, comparable to that of phosphorus burning in oxygen. The resulting thorina is as white as snow, and does not exhibit the least trace of fusion. It is not attacked by caustic alkalies at a boiling heat; is scarcely at all acted on by nitric acid, and very slowly by the sulphuric, but it is readily dissolved with disengagement of hydrogen gas by hydrochloric acid.

Thorina.—Hist. and Prep.—Procured from a rare Norwegian mineral, now called *thorite*, which was sent to Berzelius by Esmark. It constitutes 57·91 per cent. of the mineral, and occurs in the form of a hydrated silicate of thorina. In order to prepare thorina, the mineral is reduced to powder, and digested in hydrochloric acid; when a gelatinous mass is formed, from which silicic acid is separated by evaporating to dryness, and dissolving the soluble parts in dilute acid. The solution is then freed from lead and tin, which occur in thorina along with several impurities, by hydrosulphuric acid, and the earths are thrown down by pure ammonia. The precipitate, after being well washed, is dissolved in dilute sulphuric acid, and the solution evaporated at a high temperature till only a small

* The recent researches of Mosander show that the substance hitherto looked upon as pure yttria is in reality a mixture containing besides, the oxides of two different metals, possessing different properties. Upon these new metals he has conferred the names of *Erbium* and *Terbium*. (Phil. Mag. Oct. 1843.) (R.)

quantity of fluid remains. During the evaporation the greater part of the thorina is deposited as a sulphate; and on decanting the remaining fluid, washing the residue, and heating it to redness, pure thorina remains. (An. de Ch. et Ph. xliii. 5.)

Prop.—Thorina, when formed by the oxidation of thorium, or after being strongly heated, is a white earthy substance, of sp. gr. 9·402, and insoluble in all the acids except the sulphuric; and it dissolves even in that with difficulty. It is precipitated from its solutions by the caustic alkalies as a hydrate, and in this state absorbs carbonic acid from the atmosphere, and dissolves readily in acids. All the alkaline carbonates dissolve the hydrate, carbonate, and sub-salts of thorina. Its exact composition is not known; but its eq. is about 67·6.

Thorina is distinguished from alumina and glucina by its insolubility in pure potassa; from yttria by forming with sulphate of potassa a double salt which is quite insoluble in a cold saturated solution of sulphate of potassa; and from zirconia by the circumstance that this earth, after being precipitated from a hot solution of sulphate of potassa, is almost insoluble in water and the acids. Thorina is precipitated, also, by ferrocyanide of potassium, which does not separate zirconia from its solutions. Berzelius has remarked that sulphate of thorina is much more soluble in cold than in hot water, so that a cold saturated solution becomes turbid when heated, and in cooling recovers its transparency.

Chloride of thorium is readily prepared by carbonizing an intimate mixture of thorina and sugar in a covered platinum crucible, and then exposing the residue at a red heat in a porcelain tube to a current of dry chlorine. The chloride, possessing but little volatility, collects in the tube just beyond the ignited part in the form of a partially fused, crystalline, white mass. It is soluble in water with considerable rise of temperature.

When thorium is heated in the vapour of sulphur, the phenomena of combustion ensue with the same brilliancy as in air, and a sulphuret results. A phosphuret may be formed by a similar process.

ZIRCONIUM.

Hist. and Prep.—The experiments of Davy proved zirconia to be an oxidized body, and afforded a presumption that its base, *zirconium*, is of a metallic nature; but Berzelius first obtained the metal in 1824 by heating with a spirit-lamp a mixture of potassium and the double fluoride of zirconium and potassium, carefully dried in a tube of glass or iron. The reduction takes place at a temperature below redness, without emission of light; and the mass is washed with boiling water, and afterwards digested for some time in dilute hydrochloric acid. The residue is pure zirconium.

Prop.—Zirconium, thus obtained, is in the form of a black powder, which may be boiled in water without being oxidized, and is attacked with difficulty by sulphuric, hydrochloric, or nitro-hydrochloric acids; but it is dissolved readily, and with disengagement of hydrogen gas, by hydrofluoric acid. Heated in the open air, it takes fire at a temperature far below incandescence, burns brightly, and is converted into zirconia. Its metallic nature seems somewhat questionable. It may indeed be pressed out into thin shining scales of a dark grey colour, and of a lustre which may be called metallic; but its particles cohere together very feebly, and it has not been procured in a state capable of conducting electricity.

These points, however, require further investigation before a decisive opinion on the subject can be adopted. (Pog. Annalen, iv.)

Oxide of Zirconium was discovered in the year 1789 by Klaproth in the Jargon or Zircon of Ceylon, and has since been found in the Hyacinth from Expailly in France. Berthier prepares it by fusing zircon in fine powder with litharge in the ratio of 17 to 21, when a glass is obtained which is soluble in acids. It is an earthy substance, resembling alumina in appearance, of sp. gr. 4·3, having neither taste nor odour, and quite insoluble in water. It is so hard that it will scratch glass. Its colour, when pure, is white; but it has frequently a tinge of yellow, owing to the presence of iron, from which it is separated with difficulty. It phosphoresces vividly when heated strongly before the blowpipe. Its salts are distinguished from those of alumina or glucina by being precipitated by all the pure alkalies, in an excess of which it is insoluble. The alkaline carbonates precipitate it as carbonate of zirconia, and a small portion of it is redissolved by an excess of the precipitant, especially when a bicarbonate is employed. It differs from all the earths, except thorina, in being precipitated when any of its neutral salts are boiled with a saturated solution of sulphate of potassa, the zirconia subsiding as a subsalt, and the potassa remaining in solution as a bisulphate. Zirconia is precipitated from its salts by pure ammonia as a bulky hydrate, which is readily soluble in acids; but if this hydrate is ignited, dried, or even washed with boiling water, it afterwards resists the action of the acids, and is dissolved by them with great difficulty. Strong sulphuric acid is then its best solvent (Berzelius). When hydrated zirconia is heated to commencing redness, it parts with its water, and soon after emits a very vivid glow for a short time. This phenomenon appears to depend upon the particles of the zirconia suddenly approaching each other, and thus acquiring much greater density than it previously possessed. Oxide of chromium, titanic acid, and several other compounds afford instances of the same appearance; and whenever it takes place the susceptibility of the substance to be attacked by fluid reagents is greatly diminished (Berzelius).

The composition of zirconia has not yet been satisfactorily determined. From some analyses by Berzelius, described in the Essay above referred to, it is probable that the *eq.* of this earth is about 33·7; *its symb.* $2Zr + 3O$, $\dddot{Z}r$, or $Zr_2 O_3$.

Sulphuret of Zirconium.—This compound may be prepared, according to Berzelius, by heating zirconium with sulphur in an atmosphere of hydrogen gas; and the union is effected with feeble emission of light. The product is pulverulent, a non-conductor of electricity, of a dark chestnut-brown colour, and without lustre. It is insoluble in sulphuric, nitric, and hydrochloric acid; and it is slowly attacked by nitro-hydrochloric acid, even with the aid of heat. It is readily dissolved by hydrofluoric acid, with disengagement of hydrogen gas.

CLASS II.

METALS, THE OXIDES OF WHICH ARE NEITHER ALKALIES NOR EARTHS.

ORDER I.

METALS WHICH DECOMPOSE WATER AT A RED HEAT.

SECTION X.

MANGANESE.

Hist. and Prep.—The black oxide of manganese was described in the year 1774 by Scheele, as a peculiar earth, and Gahn subsequently showed that it contains a new metal, to which he gave the name of *magnesium*; a term since applied to the metallic base of magnesia, and for which the words *manganesium* and *manganium* have been substituted. This metal, owing doubtless to its strong affinity for oxygen, has never been found in an uncombined state in the earth; but its oxides are very abundant. The metal may be obtained by forming finely powdered oxide of manganese into a paste with oil, laying the mass in a hessian crucible lined with charcoal, luting down a cover carefully, and exposing it during an hour and a half, or two hours, to the strongest heat of a smith's forge.

Prop.—A hard brittle metal, of a greyish-white colour, and granular texture. Its sp. gr. according to John, is 8·013. When pure it is not attracted by the magnet, but Berthier has lately stated that it possesses this property at very low temperatures. It is exceedingly infusible, requiring the highest heat of a wind furnace for fusion. It soon tarnishes on exposure to the air, and absorbs oxygen with rapidity when heated to redness in open vessels. It slowly decomposes water at common temperatures with disengagement of hydrogen gas; but at a red heat decomposition is rapid, and protoxide of manganese is generated. Decomposition of water is likewise occasioned by dilute sulphuric acid, and sulphate of protoxide of manganese is the product.

Berzelius, from an analysis of chloride of manganese, found 27·7 as the eq. of manganese, a number which agrees closely with my own experiments on the same chloride. Its symb. is Mn. The composition of the compounds of manganese described in this section is as follows:—

	Manganese.			Equiv.		Formulæ.
Protoxide	27·7	1 eq. +	Oxygen 8	1 eq. =	35·7	Mn + O.
Sesquioxide	55·4	2 eq. +	do. 24	3 eq. =	79·4	2Mn + 3O.
Peroxide	27·7	1 eq. +	do. 16	2 eq. =	43·7	Mn + 2O.
Red Oxide	83·1	3 eq. +	do. 32	4 eq. =	115·1	3Mn + 4O.

	Manganese.			Equiv.	Formulæ.
Varvicite	110·8	4 eq. +	do. 56	7 eq. = 166·8	4Mn + 7O.
Manganic Acid	27·7	1 eq. +	do. 24	3 eq. = 51·7	Mn + 3O.
Permang. Acid	55·4	2 eq. +	do. 56	7 eq. = 111·4	2Mn + 7O.
Protochloride	27·7	1 eq. +	Chlor. 35·42	1 eq. = 63·12	Mn + Cl.
Perchloride	55·4	2 eq. +	do. 247·94	7 eq. = 303·34	2Mn + 7Cl.
Perfluoride	55·4	2 eq. +	Fluor. 130·76	7 eq. = 186·16	2Mn + 7F.
Protosulphuret	27·7	1 eq. +	Sulphur. 16·1	1 eq. = 43·8	Mn + S.

OXIDES OF MANGANESE.

In studying metallic oxides, it is necessary to distinguish oxides formed by the direct union of oxygen and a metal, from those that consist of two other oxides united with each other, and which therefore, in composition, partake of the nature of a salt rather than of an oxide. An instance of this kind of combination is supplied by the black oxide of iron; and it is probable that two of the five compounds enumerated as oxides of manganese have a similar constitution. Their composition has been particularly investigated by Berzelius, Thomson (First Principles, i.), Arfwedson,* Berthier,† and myself.‡

Protoxide.—Prep.—By this term is meant that oxide of manganese which is a strong salifiable base, is contained in all the ordinary salts of this metal, and which appears to be its lowest degree of oxidation. This oxide may be formed by exposing the peroxide, sesquioxide, or red oxide of manganese, to the combined agency of charcoal and a white heat; or by exposing either of the oxides of manganese contained in a tube of glass, porcelain, or iron, to a current of hydrogen gas at an elevated temperature. The best material for this purpose is the red oxide prepared from nitrate of oxide of manganese; since the native oxides, especially the peroxide, are fully reduced to the state of protoxide by hydrogen with difficulty. The reduction commences at a low red heat; but to decompose all the red oxide, a full red heat is required. The same compound is formed by the action of hydrogen gas at an intense white heat. Wöhler and Liebig have shown that the protoxide is also obtained by fusing chloride of manganese in a platinum crucible with about twice its weight of carbonate of soda, and its own weight of sal-ammoniac, and afterwards dissolving the chloride of sodium by water.

Prop.—Protoxide of manganese, when pure, is of a light green colour, very near the mountain green. According to Forchammer it attracts oxygen rapidly from the air; but in my experiments it was very permanent, undergoing no change either in weight or appearance during the space of nineteen days. At 600° it is oxidized with considerable rapidity, and at a low red heat is converted in an instant into red oxide. It sometimes takes fire when thus heated, especially when the mass is considerable. It unites readily with acids without effervescence, producing the same salts as when the same acids act on carbonate of oxide of manganese. When it comes in contact with concentrated sulphuric acid, intense heat is instantly evolved; and the same phenomenon is produced, though in a less degree, by strong hydrochloric acid. The resulting salt is the same as when these acids are heated with either of the other oxides of manganese. If quite pure, the protoxide should readily and completely dissolve in cold dilute sulphuric acid, and yield a colourless solution.

* Letter from Berzelius in the An. de Ch. et Ph. vi. † Ibid. xx.

‡ Philos. Trans. of Edin. for 1828; or Phil. Mag. and Annals, iv.

In order to prepare a pure salt of manganese from the common peroxide of commerce, the following process may be employed :—The solution which remains when chlorine is made by the action of muriatic acid on peroxide of manganese is rendered neutral by gently evaporating it to dryness. A portion, which varies with the proportion of iron present, and is easily ascertained by trial on a small scale, is then precipitated by an excess of carbonate of soda; and the mixed precipitate of carbonate of manganese and peroxide of iron, well washed, is digested with the remainder of the liquid. The protoxide of manganese enters the liquid, expelling the peroxide of iron, and at last a liquid is obtained quite free from iron. It ought to give a bright flesh-coloured precipitate with hydrosulphuret of ammonia, and a white with ferrocyanide of potassium. Should the first drop of the former test cause a dark precipitate, this is owing to the presence, not of iron, but of cobalt and nickel, which, according to Gregory, are almost uniformly present in small quantity in the oxide of manganese. They are easily removed by adding the hydrosulphuret till it gives a pure flesh-coloured precipitate. If the oxide, before being dissolved in muriatic acid, has been digested in very diluted muriatic acid, and washed, no lime can be present in the solution. The iron can only escape complete precipitation if it be partly in the state of protoxide ; but in preparing chlorine the iron is fully oxidized. If, however, protoxide should be present, it is readily peroxidized by boiling with a little nitric acid. This process, suggested by Everitt, is founded on the fact, that all carbonates of protoxides, when digested with solutions of peroxide of iron, precipitate the latter ; and the manganese contained in the mixed solution is thus ingeniously made use of to effect its own purification. (Phil. Mag. and An. vi. 193.) Other less convenient methods, which, however, yield a pure product, have been suggested, particularly one by Faraday. (Quart. Journ. vi.)

The salts of the protoxide of manganese are in general colourless if quite pure ; but more frequently they have a shade of pink, owing to the presence of a little red oxide or permanganic acid. [They are strictly isomorphous with the salts of magnesia and zinc.] The protoxide is precipitated from their solutions as a white hydrate by ammonia, or the pure fixed alkalies ; as white carbonate of protoxide of manganese by alkaline carbonates and bicarbonates ; and as white ferrocyanide of manganese by ferrocyanide of potassium, a character by which the absence of iron may be demonstrated. These white precipitates, with the exception of that obtained by means of a bicarbonate, very soon become brown from the absorption of oxygen. None of the salts of manganese which contain a strong acid, such as the nitric, or sulphuric, are precipitated by hydrosulphuric acid. With an alkaline hydrosulphate, on the contrary, a flesh-coloured precipitate is formed, which is a hydrated protosulphuret of manganese: when heated in close vessels, it yields a dark-coloured sulphuret, and water is evolved.

Its eq. is 35·7 ; *symb.* Mn + O, Mn, or MO.

Sesquioxide.—Hist. and Prep.—This oxide occurs nearly pure in nature, constituting the mineral *braunite*, and as a hydrate it is found abundantly, often in large prismatic crystals, at Jhlefeld in the Hartz. It may be formed artificially by exposing peroxide of manganese for a considerable time to a moderate red heat, and therefore is the chief residue of the usual process for procuring a supply of oxygen gas ; but it is difficult so to regulate the degree and duration of the heat, that the resulting oxide shall be quite pure.

Prop.—The colour of the sesquioxide of manganese varies with the source

from which it is derived. That which is procured by means of heat from the native peroxide or hydrated sesquioxide, has a brown tint; but when prepared from nitrate of oxide of manganese, it is nearly as black as the peroxide, and the native sesquioxide is of the same colour. With sulphuric and hydrochloric acids it gives rise to the same phenomenon as the peroxide, but of course yields a smaller proportional quantity of oxygen and chlorine gases. It is more easily attacked than the peroxide by cold sulphuric acid. With strong nitric acid it yields a soluble protonitrate and the peroxide, and when boiled with dilute sulphuric acid, it undergoes a similar change. From the proportion of oxygen and manganese in this oxide, it has sometimes been regarded as a compound of 43·7 parts or 1 eq. of peroxide, and 35·7 parts or 1 eq. of protoxide of manganese. In that case the sesquioxide would be constituted like a salt, and should have the properties of that class of compounds; but Mitscherlich has succeeded in combining it with sulphuric acid, and has obtained with it an alum similar in form and constitution to those of peroxide of iron and alumina. It must therefore be considered as a direct compound of 2 eq. of manganese and 3 eq. of oxygen.

Its eq. is 79·4; *symb.* 2M + 3O, M, or M_2O_3.

Peroxide.—Hist. and Prep.—The well-known ore commonly called, from its colour, black oxide of manganese. It generally occurs massive, of an earthy appearance, and mixed with other substances, such as siliceous and aluminous earths, oxide of iron, and carbonate of lime. It is sometimes found, on the contrary, in the form of minute prisms grouped together, and radiating from a common centre, forming the mineral *pyrosulite*. In these states it is anhydrous; but the essential ingredient of one variety of the earthy mineral called *wad* is hydrated peroxide of manganese, consisting of 1 eq. of water and 2 of the oxide. The peroxide may be made artificially by exposing nitrate of oxide of manganese to a commencing red heat, until the whole of the nitric acid is expelled; but I have never succeeded in procuring it quite pure by this process, because the heat required to drive off the last traces of acid likewise expels some oxygen from the peroxide. The hydrated peroxide, containing 1 eq. of water and 1 of oxide, is formed by precipitating the protochloride of manganese by chloride of lime; and the same compound results from the decomposition of the acids of manganese, either in water or by dilute acid.

Prop.—Not changed by exposure to the air, is insoluble in water, and does not unite either with acids or alkalies. When boiled with sulphuric acid, it yields oxygen gas, and a sulphate of the protoxide is formed. With hydrochloric acid, chloride of manganese is generated, and chlorine is evolved. The solution in both cases is of a deep-red colour, provided undissolved oxide is present; but if separated from the undissolved portions, it is readily rendered colourless by heat. The colour is commonly attributed to a small quantity of the sesquioxide or red oxide of manganese dissolved by the free acid; but Mr. Pearsall, of Hull, has gone far to prove that it is owing to the presence of permanganic acid. (R. Inst. Journal, N. S. No. iv. 49.) The action of sulphuric acid in the cold is exceedingly tardy and feeble, a minute quantity of oxygen gas is slowly disengaged, and the acid acquires an amethyst-red tint On exposure to a red heat, it is converted, with evolution of oxygen gas, into the sesquioxide of manganese.

Peroxide of manganese is employed in the arts, in the manufacture of glass, and in preparing chlorine for bleaching. In the laboratory it is used for pro-

curing chlorine and oxygen gases, and in the preparation of the salts of manganese.

Red Oxide.—The substance called red oxide of manganese, *Oxidum Manganoso-Manganicum* of Arfwedson, occurs as a natural production, and may be formed artificially by exposing the peroxide of sesquioxide to a white heat either in close or open vessels. It is also produced by absorption of oxygen from the atmosphere when the protoxide is precipitated from its salts by pure alkalies, or when the anhydrous protoxide or carbonate is heated to redness. It is very permanent in the air, not passing to a higher stage of oxidation at any temperature. Its colour when rubbed to the same degree of fineness is brownish-red when cold, and nearly black while warm. Fused with borax or glass it communicates a beautiful violet tint, a character by which manganese may be easily detected before the blowpipe; and it is the cause of the rich colour of the amethyst. It is acted on by strong sulphuric and hydrochloric acids, with the aid of heat, in the same manner as the peroxide and sesquioxide, but of course yields proportionally a smaller quantity of oxygen and chlorine gases. By cold concentrated sulphuric acid it is dissolved in small quantity, without appreciable disengagement of oxygen gas, and the solution is promoted by a slight increase of temperature. The liquid has an amethyst tint, which disappears when heat is applied, or by the action of deoxidizing substances, such as protochloride of tin, or sulphurous and phosphorous acids, sulphate of protoxide of manganese being generated. By strong nitric acid, or when boiled with dilute sulphuric acid, it undergoes the same kind of change as the sesquioxide.

It may be doubted whether the red oxide is not rather a kind of salt composed of two other oxides, than a direct compound of manganese and oxygen. From the ratio of its elements it may consist either of

Sesquioxide	79·4 or 1 equiv.	or	Peroxide	43·7 or 1 equiv.
Protoxide	35·7 or 1 equiv.		Protoxide	71·4 or 2 equiv.
	115·1			115·1

It contains 27·586 per cent. of oxygen, and loses 6·896 per cent. when converted into the green oxide. *Its eq. is* 115·1; *its symb.* either $MnO + Mn_2O_3$, or $2MnO + MnO_2$.

Varvicite.—This compound is known only as a natural production, having been first noticed a few years ago by Mr. Phillips among some ores of manganese found at Hartshill, in Warwickshire. The locality of the mineral suggested its name; but I have also detected it as the constituent of an ore of manganese from Jhlefeld, sent me by Professor Stromeyer. Varvicite was at first mistaken for peroxide of manganese, to which in the colour of its powder it bears considerable resemblance; but it is readily distinguished from that ore by its stronger lustre, greater hardness, more lamellated texture, which is very similar to that of manganite, and by yielding water freely when heated to redness. Its sp. gr. is 4·531. It has not been found regularly crystallized; but my specimen from Jhlefeld is in *pseudo-crystals*, possessing the form of the six-sided pyramid of calcareous spar. When strongly heated it is converted into red oxide, losing 5·725 per cent. of water, and 7·385 of oxygen. It is probably, like the red oxide, a compound of two other oxides; and the proportions just stated justify the supposition that it consists of 2 eq. of peroxide and 1 of sesquioxide of manga-

nese, united in the mineral with an eq. of water. (Phil. Mag. and Annals, v. 209, vi. 281, and vii. 284.)

It has been inferred from some experiments of Berzelius and John, that there are two other oxides of manganese, which contain less oxygen than the green or protoxide. We have no proof, however, of the existence of such compounds.

Its eq. is 166·8; *symb.* probably $M_2O_3 + 2MO_2$.

Manganic Acid.—Hist. and Prep.—Manganese is one of those metals which is capable of forming an acid with oxygen. Manganate of potassa is generated when hydrate or carbonate of potassa is heated to redness with peroxide of manganese; and nitre may be used successfully, provided the heat be high enough to decompose the nitrate of potassa. The materials absorb oxygen from the air when fused in open vessels; but manganate of potassa is equally well formed in close vessels, one portion of oxide of manganese then supplying oxygen to another. The product has been long known under the name of *mineral chameleon*, from the property of its solution to pass rapidly through several shades of colour: on the first addition of cold water a green solution is formed, which soon becomes blue, purple, and red; and ultimately a brown flocculent matter, hydrated peroxide of manganese, subsides, and the liquid becomes colourless. These changes, which are more rapid by dilution with hot water, have been successively elucidated by Chevillot and Edwards, Forchammer, and Mitscherlich. (An. de Ch. et Ph. viii., and xlix. 113; and An. of Phil. xvi.)

Prop.—The phenomena above mentioned are owing to the formation of manganate of potassa of a green colour, and to its ready conversion into the red permanganate of potassa, the blue and purple tints being due to a mixture of these compounds. Manganic acid itself cannot be obtained in an uncombined state, because it is then resolved into the hydrated peroxide and oxygen, a property which Mitscherlich availed himself of in analyzing this acid; but Mitscherlich has proved that it is analogous in composition to sulphuric acid, and its salts isomorphous with the sulphates. Manganate of potassa is obtained in crystals by forming a concentrated solution of mineral chameleon in cold water, very pure and free from carbonic acid, allowing it to subside in a stoppered bottle, and evaporating the clear green solution in vacuo with the aid of sulphuric acid. All contact of paper and other organic matter must be carefully avoided, since they deoxidize the acid, and the process be conducted in a cool apartment. The crystals are anhydrous, and permanent in the dry state; but in solution the carbonic acid of the air suffices to decompose the acid, or even simple dilution with cold water. Mixed with a solution of potassa the manganate may be crystallized a second time in vacuo without change.

Its eq. is 51·7; *symb.* $Mn + 3O$, $\dot{M}n$, or MnO_3.

Permanganic Acid.—Prep.—Permanganate of potassa is obtained by heating a solution of mineral chameleon, however prepared. A better process has been indicated by Wöhler (Pog. An. xxvii. 626); it consists in fusing chlorate of potassa in a platinum crucible, and then adding peroxide of manganese in fine powder. An improvement on this has been proposed by Gregory (Lieb. An. xv. 237): he recommends 4 parts of peroxide of manganese to be mixed in fine powder with $3\frac{1}{2}$ parts of chlorate of potassa, and then added to 5 parts of hydrate of potassa dissolved in a small quantity of water. The whole is evaporated to perfect dryness, powdered, and exposed in a platinum crucible to a low red heat.

The mass, which has not been fused, is again powdered, and added to a large quantity of boiling water, which when clear is decanted from the sediment of peroxide of manganese, rapidly concentrated and allowed to crystallize. The crystals are at first small and almost black; but by washing with a little cold water, and resolution in the smallest possible quantity of boiling water, they are obtained in very fine crystals. The acid may be obtained by adding to a solution of permanganate of baryta a quantity of dilute sulphuric acid exactly sufficient for precipitating the baryta.

[Permanganic acid may be obtained in a much more permanent state, according to M. Huenefeld, by washing the manganate of baryta with hot water, by which it is resolved into peroxide of manganese and permanganic of baryta, and then treating the latter with phosphoric acid, in quantity sufficient to neutralize the baryta. The free permanganic acid is separated by solution, evaporated to dryness, and by resolution and evaporation is obtained as a reddish brown crystalline mass, having in parts the lustre of indigo. It is completely soluble in water. (Berzelius's Traité, i. 522.)]

Prop.—Has a rich red colour; is more stable than the manganic acid, though still very prone to decomposition. Contact with paper or linen as in filtering, particles of cork, organic particles floating in the atmosphere, decompose it rapidly, for which reason Gregory recommends that all solutions containing it should be filtered through a pledget of asbestus, placed in the throat of the funnel. Colouring matters are bleached by it; and in pure water its decomposition begins at 86° and is complete at 212°. On these occasions oxygen gas is abstracted or given out, and hydrated peroxide of manganese subsides. Its salts are more permanent than the free acid, so that most of them may be boiled in solution, especially if concentrated. When heated they give out oxygen gas, and are reconverted into manganates. They deflagrate like nitre with burning charcoal, and detonate powerfully with phosphorus. Their colour in solution is a rich purple, and a small quantity of the salt imparts this colour to a very large quantity of water. When mixed with dilute nitric acid and boiled, oxygen gas is evolved, and hydrated peroxide of manganese subsides, from the respective quantities of which Mitscherlich ascertained the composition of the acid. In addition to the remarkable analogy which its constitution bears to perchloric acid, Mitscherlich finds that permanganate and perchlorate of potassa are isomorphous, an observation confirmed by Miller.

Its eq. is 111·4; *symb.* 2 Mn + 7O, $\dot{\dot{\dot{\dot{\underline{\text{Mn}}}}}}$, or Mn_2O_7.

Protochloride of Manganese.—This compound is best prepared by evaporating a solution of the chloride to dryness by a gentle heat, and heating the residue to redness in a glass tube, while a current of hydrochloric acid gas is transmitted through it. The heat of a spirit-lamp is sufficient for the purpose. It fuses readily at a red heat, and forms a pink-coloured lamellated mass on cooling. It is deliquescent, and of course very soluble in water.

Its eq. is 63·12; *symb.* Mn + Cl, or MnCl.

Perchloride of Manganese.—Hist. and Prep.—Dumas discovered this compound, which is readily formed by putting a solution of permanganic into strong sulphuric acid, and then adding fused sea-salt. The hydrochloric and permanganic acids mutually decompose each other; water and perchloride of manganese are generated, and the latter escapes in the form of vapour. The best mode of preparation is to form the green mineral chameleon, and acidulate with sulphuric

acid: the solution, when evaporated, leaves a residue of sulphate and permanganate of potassa. This mixture, treated by strong sulphuric acid, yields a solution of permanganic acid, into which are added small fragments of sea-salt, as long as coloured vapour continues to be evolved. (Edin. Journ. of Science, viii. 179.)

Prop.—The perchloride, when first formed, appears as a vapour of a copper or greenish colour; but on traversing a glass tube cooled to — 4°, it is condensed into a greenish-brown coloured liquid. When generated in a capacious tube, its vapour gradually displaces the air, and soon fills the tube. If it is then poured into a large flask, the sides of which are moist, the colour of the vapour changes instantly on coming into contact with the moisture, a dense smoke of a pretty rose-tint appears, and hydrochloric and permanganic acids are generated. It is hence analogous in composition to permanganic acid, its elements being in such a ratio that

1 eq. perchloride and 7 eq. water		yield	1 eq. permang. acid and 7 eq. hydrochloric acid.	
Mn_2Cl_7	7HO		Mn_2O_7	7HCl.

Hence *its eq. is* 303·34; *symb.* 2Mn + 7Cl, or Mn_2Cl_7.

Perfluoride of Manganese.—This gaseous compound, discovered by Dumas and Wöhler (Edin. Journ. of Science, ix.), is best formed by mixing common mineral chameleon with half its weight of fluor-spar, and decomposing the mixture in a platinum vessel by fuming sulphuric acid. The fluoride is then disengaged in the form of a greenish-yellow gas or vapour, of a more intensely yellow tint than chlorine. When mixed with atmospheric air, it instantly acquires a beautiful purple-red colour; and it is freely absorbed by water, yielding a solution of the same red tint. It acts instantly on glass, with formation of fluosilicic acid gas, a brown matter being at the same time deposited, which becomes of a deep purple-red tint on the addition of water.

It may be inferred from the experiments of Wöhler that this yellow gas is a fluoride of manganese; that when mixed with water both compounds are decomposed, and hydrofluoric and permanganic acids generated, which are dissolved; that a similar formation of the two acids ensues from the admixture of the yellow gas with atmospheric air, owing to the moisture contained in the latter; and that by contact with glass, fluosilicic acid gas is produced, and anhydrous permanganic acid deposited. In consequence of its acting so powerfully on glass, its other properties have not been ascertained; but from those above mentioned, its composition is obviously similar to that of the gaseous chloride of manganese.

Its eq. is 186·16; *symb.* 2Mn + 7F, or Mn_2F_7.

The *protosulphuret* of *manganese* may be procured by igniting the sulphate with one-sixth of its weight of charcoal in powder. (Berthier.) It is also formed by the action of hydrosulphuric acid gas on the protosulphate at a red heat. (Arfwedson in An. of Phil. vol. vii. N. S.) It occurs native in Cornwall and at Nagyag in Transylvania. It dissolves completely in dilute sulphuric or hydrochloric acid, with disengagement of very pure hydrosulphuric acid gas. *Its eq. is* 43·8; *symb.* Mn + S, or MnS.

SECTION XI.

IRON.

Hist.—Known from the remotest antiquity. The occurrence of native iron, except that of meteoric origin, which always contains nickel and cobalt, is exceedingly rare; and few of the specimens said to be such have been well attested.* In combination, however, especially with oxygen and sulphur, it is abundant; being contained in animals and plants, and being diffused so universally in the earth that there are few mineral substances in which its presence may not be detected. Minerals which contain iron in such form, and in such quantity, as to be employed in the preparation of the metal, are called *ores of iron*; and of these the principal are the following. The red oxides of iron included under the name of red hæmatite; the brown hæmatite of mineralogists, consisting of hydrated peroxide of iron; the black oxide, or magnetic iron ore; and carbonate of protoxide of iron, either pure, or in the form of clay iron ore, when it is mixed with siliceous, aluminous, and other foreign substances. The two former occur abundantly, both in primary and secondary districts; the latter is most abundant in primary formations, and is the source of the finest kind of iron made in Sweden and India; while clay-iron stone, from which most of the English iron is extracted, occurs in secondary deposites, and chiefly in the coal formation.

Prep.—The exaction of iron from its ores is effected by exposing the ore, previously roasted and reduced to a coarse powder, to the action of charcoal, or coke, and lime at a high temperature. The action of carbonaceous matter in depriving the ore of its oxygen is obvious; and the lime plays a part equally important. It acts as a flux by combining with all the impurities of the ore, and forming a fusible compound called a *slag*. The whole mass being thus in a fused state, the particles of reduced metal descend by reason of their greater density, and collect at the bottom; while the slag forms a stratum above, protecting the melted metal from the action of the air. The latter, as it collects, runs out at an aperture in the side of the furnace: and the fused iron is let off by a hole in the bottom, which was previously filled with sand. The process is never successful unless the flux, together with the impurities of the ore, are in such proportion as to constitute a fusible compound. The mode of accomplishing this object is learned only by experience; and as different ores commonly differ in the nature or quantity of their impurities, the workman is obliged to vary his flux according to the composition of the ore with which he operates. Thus if the ore is deficient in siliceous matter, sand must be added; and if it contain a large quantity of lime,

* It is said to be found native associated with the platinum of the Uralian mountains, and it exists of undoubted terrestrial origin as a thin vein of about two inches thick, attached to a mass of mica slate, at Canaan, in Connecticut. It contains grophite between its plates, and exhibits no obvious crystalline structure, nor is any developed by etching with nitric acid, as in most iron of meteoric origin.—(Dana's Mineralogy, p. 457.) (R.)

proportionally less of that earth will be required. Much is often accomplished by the admixture of different ores with each other. The slag consists of a compound of earthy salts, similar to some siliceous minerals, in which silicic acid is combined with lime, alumina, magnesia, protoxide of manganese, and sometimes oxide of iron. The most usual combination, according to Mitscherlich, is bisilicate of lime and magnesia, sometimes with a little protoxide of iron; a compound which he has obtained in crystals, having the precise form and composition of Augite. Artificial minerals may in fact by such processes be procured, similar in form and composition to those which occur in the earth. We are indebted to Mitscherlich for some valuable facts on this subject (An. de Ch. et Ph. xxiv. 355).

The iron obtained by this process is the cast iron of commerce, and contains a considerable quantity of carbon, unreduced ore, and earthy substances. It is converted into a soft or malleable iron by exposure to a strong heat while a current of air plays upon its surface. By this means any undecomposed ore is reduced, earthy impurities rise to the surface as slag, and carbonaceous matter is burned. The exposed iron is also more or less oxidized at its surface, and the resulting oxide, being stirred with the fused metal below, facilitates the oxidation of the carbon. As the purity of the iron increases, its fusibility diminishes, until at length, though the temperature continue the same, the iron becomes solid. It is then subjected, while still hot, to the operation of rolling or hammering, by which its particles are approximated, and its tenacity greatly increased. It is then the malleable iron of commerce. It is not, however, absolutely pure; for Berzelius has detected in it about one-half per cent. of carbon, and it likewise contains traces of silicon. The carbonaceous matter may be removed by mixing iron filings with a quarter of its weight of black oxide of iron, and fusing the mixture, confined in a covered hessian crucible, by means of a blast furnace. A little powdered green glass should be laid on the mixture, in order that the iron may be completely protected from the air by a covering of melted glass, and any unreduced oxide dissolved. But the best and readiest mode of procuring iron in a state of perfect purity, is by transmitting hydrogen gas over the pure oxide heated to redness in a tube of porcelain. The oxygen of the oxide unites with hydrogen, and the metal is left in the form of a porous spongy mass.

Prop.—Iron has a peculiar grey colour, and strong metallic lustre, which is susceptible of being heightened by polishing. In ductility and malleability it is inferior to several metals, but exceeds them all in tenacity. At common temperatures it is very hard and unyielding, and its hardness may be increased by being heated and then suddenly cooled; but it is at the same time rendered brittle. When heated to redness it is remarkably soft and pliable, so that it may be beaten into any form, or be intimately incorporated or *welded* with another piece of red-hot iron by hammering. Its texture is fibrous. Its sp. gr. may be estimated at 7·7; but it varies slightly according to the degree with which it has been rolled, hammered, or drawn, and it is increased by fusion. In its pure state it is exceedingly infusible, requiring for fusion the highest temperature of a wind furnace. It is attracted by the magnet, and may itself be rendered permanently magnetic by several processes;—a property of great interest and importance, and which is possessed by no other metal excepting nickel. It retains this quality, however, only within certain temperatures: thus iron of an orange-red heat ceases to be attracted, and a steel magnet loses its polarity at the boiling point of almond oil—a loadstone just below visible ignition (Faraday).

Iron, in its ordinary state, has a strong affinity for oxygen. In a perfectly dry atmosphere it undergoes no change; but when moisture is present, its oxidation, or *rusting*, is rapid. In the first part of the change carbonate of protoxide of iron is generated; but the protoxide gradually passes into hydrated peroxide, and the carbonic acid at the same time is evolved. Rust of iron always contains ammonia, a circumstance which indicates that the oxidation is probably accompanied by decomposition of water; and Chevalier has observed that ammonia is also present in the native oxides of iron. Heated to redness in the open air, iron absorbs oxygen rapidly, and is converted into black scales, called the *black oxide* of iron; and in an atmosphere of oxygen gas it burns with vivid scintillations. The same effect was observed by Bierley on exposing a bar of iron at a full white heat to the blast of a powerful pair of bellows. This has been confirmed by D'Arcet, who also obtained the combustion by causing the heated iron to revolve rapidly through the air: for this purpose he attached one extremity of the bar by means of wire to a string, and then whirled it rapidly round. Magnus has observed that the spongy mass obtained by reducing the oxide of iron with hydrogen may be obtained at a heat considerably below that of redness; and that when the iron, thus reduced, is exposed to the air, it takes fire spontaneously, and the oxide is instantly reproduced. This singular property, which Magnus has also remarked in nickel and cobalt prepared in a similar manner, appears to depend on the extremely divided and expanded state of the metallic mass; for when the reduction is effected at a red heat, which enables the metal to acquire its natural degree of compactness, the phenomenon is not observed. If the oxide be mixed with a little alumina, and then reduced at a red heat, the presence of the earth prevents that contraction which would otherwise ensue: the metal is in the same mechanical condition as when it is deoxidized at a low temperature, and its spontaneous combustibility is preserved.

Iron decomposes the vapour of water, by uniting with its oxygen, at all temperatures, from a dull red to a white heat; a singular fact when it is considered, that at the very same temperatures the oxides of iron are reduced to the metallic state by hydrogen gas. (Gay-Lussac in An. de Ch. et de Physique, i. 36.) These opposite effects, various instances of which are known to chemists, are accounted for by a mode of reasoning similar to that explained on a former occasion (page 123). It is rapidly oxidized by sulphuric and nitric acids: in the former case the oxidation occurs at the sole expense of water, the hydrogen of which is at the same time evolved, while in the latter the nitric acid itself yields a part of its oxygen. The action of nitric acid on iron is attended by a series of very remarkable phenomena, which have recently been observed by Professor Schönbein. He first observed that nitric acid of sp. gr. 1·35, though capable of acting with great violence on ordinary iron, was perfectly inert on a portion of iron wire one extremity of which had been made red hot previously to its introduction into the acid. He found, too, that this indifference to nitric acid may be communicated by mere contact from one iron wire to another, by submersion for a few moments into strong nitric acid, or by making it the positive electrode of a galvanic current, the negative electrode having been previously introduced into the acid. It is remarkable that under these circumstances the iron wire possesses the properties of one of gold or platinum, and does not combine with the oxygen liberated at its surface. Faraday, who has examined this voltaic condition of iron with his usual success, has remarked that the same property is communicated to iron by contact with platinum, and that the effect is not limited to nitric

acid, but extends to various saline solutions which are usually acted on by iron. For the particulars on this interesting subject the reader may consult the original papers of Schönbein and Faraday in the Phil. Mag. and An. ix. 53; x. 133, 172, 175, 267, 428.

The equivalent of iron has not yet been determined with accuracy. From the analysis of its oxides by Berzelius, Stromeyer, and Gay-Lussac, it may be estimated at 27·16, 27·8, and 28·3. In the uncertainty as to which of these numbers is the most accurate, I shall continue to use 28, the number generally adopted in this country. *Its symb.* is Fe. The composition of the compounds of iron described in this section is as follows:—

	Iron				Equiv.	Formulæ.
Protoxide	28	1 eq.+Oxyg.	8	1 eq.	= 36	Fe+O or FeO.
Peroxide	56	2 eq.+do.	24	3 eq.	= 80	2 Fe+3O or Fe_2O_3.
Black Oxide	Protoxide		36	1 eq.	=116	FeO+Fe_2O_3.
	Peroxide		80	1 eq.		
Ferric acid	28	1 eq.+do.	16	2 eq.	= 44	Fe + 2O or FeO_2.
Protochloride	28	1 eq.+Chlor.	35·42	1 eq.	=63.42	Fe +Cl or FeCl.
Perchloride	56	2 eq.+do.	106·26	3 eq.	=162·26	2 F+3Cl or Fe_2Cl_3.
Protiodide	28	1 eq.+Iodine	126·3	1 eq.	=154·3	Fe+I or FeI.
Periodide	56	2 eq.+do.	378·9	3 eq.	=434·9	2Fe+3I or F_2I_3.
Protobromide	28	1 eq.+Brom.	78·4	1 eq.	=106·4	Fe+Br or FeBr.
Perbromide	56	2 eq.+do.	235·2	3 eq.	=291·2	2 Fe+3Br or Fe_2Br_3.
Protofluoride	28	1 eq.+Fluor.	18·68	1 eq.	= 46·68	Fe+F or FeF.
Perfluoride	56	2 eq.+Fluor.	56·04	3 eq.	=112·04	2 Fe+3F or Fe^2F^3.
Tetrasulphuret	112	4 eq.+Sulph.	16·1	1 eq.	=128·1	4Fe+S or Fe_4S.
Disulphuret	56	2 eq.+do.	16·1	1 eq.	= 72·1	2 Fe+S or Fe_2S.
Protosulphuret	28	1 eq.+do.	16·1	1 eq.	= 44·1	Fe+S or FeS.
Sesquisulphuret	55	2 eq.+do.	48·4	3 eq.	=104·3	2 Fe+3S or Fe_2S^3.
Bisulphuret	28	1 eq.+do.	32·2	2 eq.	= 60·2	Fe+2S or FeS_2.
Magnetic Pyrites	Bisulph. of iron		60·2	1 eq.	=280·7	5FeS+FeS_2.
	Protosulph. of iron		220·5	5 eq.		
Diphosphuret	56	2 eq.+Phosp.	15·7	1 eq.	= 71·7	2Fe+P or Fe_2P.
Perphosphuret	84	3 eq.+do.	62·8	4 eq.	=146·8	3F+4P or Fe_3P_4
Carburets. Constitution not determined.						

OXIDES OF IRON.

Protoxide.—This oxide is the base of the native carbonate of iron, and of the green vitriol of commerce. Its existence was inferred some years ago by Gay-Lussac (An. de Ch. vol. lxxx.); but it is doubtful if it has ever been obtained in an insulated form. Its salts, particularly when in solution, absorb oxygen from the atmosphere with such rapidity that they may even be employed in eudiometry. This protoxide is always formed with evolution of hydrogen gas when metallic iron is put into dilute sulphuric acid; and its composition may be determined by collecting and measuring the gas which is disengaged.

Protoxide of iron is precipitated from its salts as a white hydrate by pure alkalies, as a white carbonate by alkaline carbonates, and as a white ferrocyanide by ferrocyanide of potassium. The two former precipitates become first green and then red, and the latter green and blue, by exposure to the air. The solution of gall-nuts produces no change of colour. Hydrosulphuric acid does not act if

the protoxide is united with any of the stronger acids; but alkaline hydrosulphates cause a black precipitate, protosulphuret of iron.

Its eq. is 36; *symb.* Fe + O, Fe, or FeO.

Peroxide.—Sesquioxide.—Hist. and Prep.—The red or peroxide is a natural product, known to mineralogists under the name of *red hæmatite*. It sometimes occurs massive, at other times fibrous, and occasionally in the form of beautiful rhomboidal crystals. It may be made chemically by dissolving iron in nitro-hydrochloric acid, and adding an alkali. The hydrate of the red oxide of a brownish-red colour subsides, which is identical in composition with the mineral called *brown hæmatite*, and consists of 80 parts or 1 eq. of the peroxide, and 18 parts or 2 eq. of water.

Prop.—Is not attracted by the magnet. Fused with vitreous substances it communicates to them a red or yellow colour. It combines with most of the acids, forming salts, the greater number of which are red. Its presence may be detected by very decisive tests. The pure alkalies, fixed or volatile, precipitate it as the hydrate. Alkaline carbonates have a similar effect, peroxide of iron not forming a permanent salt with carbonic acid. With ferrocyanide of potassium it forms Prussian blue. Sulphocyanide of potassium causes a deep blood-red, and infusion of gall-nuts a black colour. Hydrosulphuric acid converts the peroxide into protoxide of iron, with deposition of sulphur. These reagents, and especially ferrocyanide and sulphocyanide of potassium, afford an unerring test of the presence of minute quantities of peroxide of iron. On this account it is customary, in testing for iron, to convert it into the peroxide, an object which is easily accomplished by boiling the solution with a small quantity of nitric acid. [The sesquioxide of iron and its compounds are strictly isomorphous with alumina and the compounds of that earth, and very analogous to them in properties.]

Its eq. is 80; *symb.* 2Fe + 3O, $\dddot{\text{Fe}}$, or Fe_2O_3.

Black or Magnetic Oxide.—Hist. and Prep.—This substance, the *oxidum ferroso-ferricum* of Berzelius, long supposed to be protoxide of iron, contains more oxygen than the protoxide, and less than the red-oxide. It cannot be regarded as a definite compound of iron and oxygen; but it is composed of the two real oxides. It occurs native, frequently crystallized in the form of a regular octohedron and dodecahedron; and it is not only attracted by the magnet, but is itself sometimes magnetic. It is always formed when iron is heated to redness in the open air; and is likewise generated by the contact of watery vapour with iron at elevated temperatures. The composition of the product, however, varies with the duration of the process and the temperature which is employed. Thus, according to Bucholz, Berzelius, and Thomson, 100 parts of iron, when oxidized by steam, unite with nearly 30 of oxygen; whereas in a similar experiment performed by Gay-Lussac, 37·8 parts of oxygen were absorbed. The oxide of Gay-Lussac has the composition stated in the table; and Berzelius thinks that of magnetic iron ore to be similar. This has been satisfactorily confirmed by Abich, by precipitating a mixture of the two oxides from their solution in sulphuric acid, in which they were contained in their equivalent proportions. The green precipitate which falls he found to be as highly magnetic as the native magnetic iron ore, and to suffer no change on exposure to the atmosphere. But if the protoxide were contained in the solution in greater quantity, its presence in the precipitate as such was indicated by the production of the hydrated per-

oxide on exposure to the air. An excess of the peroxide diminished the magnetic effects. (An. de Ch. et Ph. lx. 369.) Gregory has observed, that when a solution of protosulphate of iron is divided into two equal parts, one of which is peroxidized, then mixed with the other, and precipitated by ammonia at a boiling heat, a black oxide is obtained, which does not attract oxygen in drying, and is highly magnetic. Its composition must be $2FeO + Fe_2O_3$; as the two solutions contain equal quantities of iron; and Gregory suggests that it may occur native as a variety of magnetic iron ore. Wöhler (Liebig's Annalen, xxii. 56) erroneously gives the above proportions for forming the common magnetic oxide, $FeO, + Fe_2O_3$; to obtain which 1 part of protosulphate should be mixed with 2 of the same salt peroxidized by nitric acid. M. Mosander states, that on heating a bar of iron in the open air, the outer layer of the scales contains a greater quantity of peroxide than the inner layer. The former consists of 1 eq. of peroxide to 4 of the protoxide, and in the latter are contained 1 eq. of peroxide to 6 eq. of protoxide. The inner layer seems uniform in composition; but the outer is variable, its more exposed parts being richer in oxygen.

The nature of the black oxide is farther elucidated by the action of acids. On digesting the black oxide in sulphuric acid, an olive-coloured solution is formed, containing two salts, sulphate of the peroxide and protoxide, which may be separated from each other by means of alcohol. (Proust and Gay-Lussac.) The solution of these mixed salts gives green precipitates with alkalies, and a very deep blue ink with infusion of gall-nuts. The black oxide of iron is the cause of the dull green colour of bottle glass.

Its eq. is 116; *symb.* $FeO + Fe_2O_3$.

[*Ferric Acid.—Hist. and Prep.*—This remarkable compound, recently discovered by M. Fremy, has not yet been obtained isolated, but only in combination with potassa and some other bases. The ferrate of potassa is most easily procured in solution, by exposing one part of the sesquioxide of iron and four parts of dry nitrate of potassa to a full red heat in a covered crucible for an hour. The resulting reddish violet coloured mass when dissolved in water forms a deep amethystine red solution of ferrate of potassa. It is likewise obtained, according to Fremy, by passing a current of chlorine through a solution of potassa in which is suspended hydrated sesquioxide of iron; the liquid assumes a fine purplish colour, and the sesquioxide of iron is dissolved. When the potassa is in excess the ferrate of potassa is precipitated as an insoluble black powder. This powder is very soluble in water and imparts to it a reddish violet tint. This solution gradually decomposes, evolves oxygen and precipitates the sesquioxide of iron. By heat the decomposition is hastened, and at a boiling temperature it is instantaneous. Its decomposition is likewise promoted by the presence of finely divided substances, and by several metallic oxides as those of silver and manganese; in other respects it resembles the peroxide of hydrogen. It is decomposed by all the acids, and the liberated ferric acid is immediately resolved into oxygen and the sesquioxide of iron, the solution at the same time becoming colourless; a property which serves to distinguish the ferrate from the manganate of potassa. It is likewise decomposed by most organic bodies, even by the contact of paper, and hence cannot be filtered. It precipitates the salts of baryta, giving rise to an insoluble ferrate of baryta of a deep crimson colour; but the salts of lime, magnesia, or strontia, are not precipitated by it. From all its properties it is seen to be strikingly analogous to the manganate of potassa, and its constitution is correctly inferred to be similar in containing an acid repre-

sented by the formula Fe + 3O or Fe O_3. (Berzelius, Rapport, 1842, and An. de Chim., 1844.)]

Protochloride of Iron.—Prep.—This compound is formed by transmitting dry hydrochloric acid gas over iron at a red heat, when hydrogen gas is evolved, and the surface of the iron is covered with a white crystalline protochloride, which at a stronger heat is sublimed. Also, on acting with hydrochloric acid on iron, which is dissolved with evolution of hydrogen gas, evaporating to dryness, and heating to redness in a tube without exposure to the air, a grey crystalline protochloride is left; but it contains some protoxide formed by an interchange of elements between the last portions of water and the chloride, hydrochloric acid being also generated.

Prop.—It dissolves freely in water, yielding a pale green solution, from which rhomboidal prisms of the same colour are obtained by evaporation. The crystals contain four equivalents of water of crystallization, deliquesce by exposure to the air, owing to the formation of perchloride, and are soluble in alcohol as well as water. The aqueous solution absorbs oxygen from the air, and becomes yellow from the formation of perchloride of iron: one portion of iron takes oxygen from the air, and yields its chlorine to another portion of iron, whereby perchloride and peroxide of iron are generated, and the latter falls as an ochreous sediment combined with some of the perchloride. A solution of the protochloride of iron dissolves binoxide of nitrogen with the same phenomena as the protosulphate, a circumstance favourable to the view entertained by many that protochloride of iron is converted by water into hydrochlorate of the protoxide.

Its eq. is 63·42; *symb.* Fe + Cl, or FeCl.

Perchloride or Sesquichloride of Iron.—It is formed by the combustion of iron wire in dry chlorine gas, and by transmitting that gas over iron moderately heated, when it is obtained in small iridescent plates of a red colour, which are volatile at a heat a little above 212°, deliquesce readily, and dissolve in water, alcohol, and ether. On agitating ether with a strong aqueous solution of the perchloride, the ether abstracts a part of it, and acquires a gold-yellow colour. The readiest mode of obtaining a solution of the perchloride is to dissolve peroxide of iron in hydrochloric acid. On concentrating to the consistence of syrup and cooling, it separates as red crystals, which by distillation yield at first water and hydrochloric acid, and then anhydrous perchloride of iron, leaving a compound of peroxide and perchloride of iron in crystalline laminæ. The formation of peroxide appears due to an interchange of elements between it and water. The same kind of interchange ensues between the vapours of water and the perchloride at a high temperature; and this is probably the source, as Mitscherlich suggests, of the crystals of peroxide of iron found in volcanic products.

Its eq. is 162·26; *symb.* 2Fe + 3Cl, or Fe_2Cl_3.

Protiodide of Iron.—It exists as a pale green solution when iodine is digested with water and iron wire, the latter being in excess; and on evaporating the solution, without exposure to the air, to dryness and heating moderately, the protiodide is fused, and on cooling becomes an opaque crystalline mass of an iron-grey colour and metallic lustre. It is deliquescent and very soluble in water and alcohol. Its aqueous solution attracts oxygen rapidly from the air, undergoing the same kind of change as the protochloride: to preserve a solution of protiodide as such a long piece of iron wire should be kept permanently in the liquid. [The presence of honey, or other saccharine substance, in the proportion of one part to three of the solution, is said to protect it from the action of

oxygen.] This compound has been very successfully employed in medical practice by my colleague Dr. A. T. Thomson.

Its eq. is 154·3 ; *symb.* Fe + I, or FeI.

The *periodide*, of a yellow or orange colour according to the strength of the solution, is obtained by freely exposing a solution of the protiodide to the air, or digesting iron wire with excess of iodine, gently evaporating, and subliming the periodide. It is a volatile red compound, deliquescent, and soluble in water and alcohol. *Its eq. is* 434·9 ; *symb.* 2Fe + 3I, or Fe_2I_3.

The *bromides* of iron are formed under similar conditions to the chlorides and iodides, and are very analogous to them in their properties.

Protofluoride of Iron is best prepared by dissolving iron in a solution of hydrofluoric acid, out of which it crystallizes as the acid becomes saturated, in small white square tables, which are sparingly soluble in water, and become pale yellow by the action of the air. By heat they part with their water of crystallization, and afterwards bear a red heat without decomposition. (Berzelius.)

Its eq. is 46·68 ; *symb.* Fe + F, or FeF.

The *perfluoride* is formed by dissolving peroxide of iron in hydrofluoric acid, and yields a colourless solution even when saturated. By evaporation it is left as a crystalline mass of a pale flesh-colour, and of a mild astringent taste. It is sparingly soluble in water. *Its eq. is* 112·04; *symb.* 2Fe + 3F, or Fe_2F_3.

Sulphurets of Iron.—These elements have for each other a remarkably strong affinity, and unite under various circumstances and in several proportions. The two lowest degrees of sulphuration, the *tetrasulphuret* and *disulphuret*, were prepared by Arfwedson by transmitting a current of hydrogen gas at a red heat over the anhydrous disulphate of peroxide of iron to procure the tetrasulphuret, and over anhydrous sulphate of protoxide of iron for the disulphuret. In both cases sulphurous acid and water are evolved, and the resulting sulphurets are left as greyish black powders susceptible of a metallic lustre by friction. They both dissolve in dilute sulphuric acid with evolution of hydrogen and hydrosulphuric acid gases.

Protosulphuret of Iron is prepared by heating thin laminæ of iron to redness with sulphur in a covered hessian crucible, and continuing the heat until any excess of sulphur is expelled. The iron is found with a crust of protosulphuret, which is brittle, of a yellowish-grey colour and metallic lustre, and is attracted by the magnet. When pure it is completely dissolved by dilute sulphuric acid, yielding pure hydrosulphuric acid. The protosulphuret of iron exists in nature as an ingredient in variegated copper pyrites ; and it falls on mixing hydrosulphate of ammonia with sulphate of protoxide of iron as a black precipitate, which oxidizes rapidly by absorbing oxygen from the air as soon as the excess of hydrosulphate of ammonia is removed by washing.

Its eq. is 44·1 ; *symb.* Fe + S, or FeS.

The *sesquisulphuret* is formed in the moist way by adding perchloride of iron drop by drop to hydrosulphate of ammonia or sulphuret of potassium in excess, and falls as a black precipitate, which is oxidized readily by the air. In the dry way it is slowly produced by the action of hydrosulphuric acid gas on peroxide of iron at a heat not exceeding 212°, water being also formed ; and by the action of the same gas on the hydrated peroxide at common temperatures. This sulphuret, when anhydrous, has a yellowish grey colour, is not attracted by the magnet, and dissolves in dilute sulphuric or hydrochloric acid, yielding hydrosulphuric acid and a residue of bisulphuret of iron (Berzelius).

Its eq. is 104·3; *symb.* 2Fe +3S, or Fe_2S_3.

Bisulphuret of iron, iron pyrites of mineralogists, exists abundantly in the earth. It occurs in cubes or some allied form, has a yellow colour, metallic lustre, a density of 4·981, and is so hard that it strikes fire with steel. Some varieties have a white colour; but these usually contain arsenic. Others occur in rounded nodules, have a radiated structure divergent from a common centre, are often found in beds of clay, and are much disposed by the influence of air and moisture to yield sulphate of oxide of iron: these are suspected by Berzelius to be compounds of protosulphuret and bisulphuret of iron.

Bisulphuret of iron is not attacked by any of the acids except the nitric, and its best solvent is the nitro-hydrochloric acid. Heated in close vessels it gives off nearly half its sulphur, and is converted into magnetic iron pyrites. By heat and air together it yields peroxide of iron. *Its eq. is.* 60·2; *symb.* Fe + 2S, or FS_2.

Magnetic iron pyrites.—This is a natural product, termed magnetic pyrites, from being attracted by the magnet, and was formerly regarded as protosulphuret of iron; but Stromeyer has shown that its elements are in such a ratio, that it may be regarded as a compound of bisulphuret and protosulphuret. It is formed by heating the bisulphuret to redness in close vessels, by fusing iron filings with half their weight of sulphur, or by rubbing sulphur upon a rod of iron heated to whiteness. It is soluble in dilute sulphuric acid, yielding hydrosulphuric acid gas and a residue of sulphur. It is much more oxidable by air and moisture than the pure bisulphuret. *Its eq. is* 280·7; *symb.* 5FeS + FeS_5.

Diphosphuret of Iron.—It is prepared by exposing the phosphate of protoxide of iron to a strong heat in a covered crucible lined with charcoal, the excess of phosphorus being dissipated in vapour. It is a fused granular mass, of the colour and lustre of iron, but very brittle, and is not attacked by hydrochloric acid. It is sometimes contained in metallic iron, to the properties of which it is very injurious by rendering it brittle at common temperatures. *Its eq. is* 71·7; *symb.* 2Fe + P, or Fe_2P.

The *perphosphuret* has been obtained by Rose by the action of phosphuretted hydrogen gas on sulphuret of iron at a moderate temperature, and resembles the former in its properties.

Its eq. is 146·8; *symb.* 3Fe + 4P, or Fe_3P_4.

Carburets of Iron.—Carbon and iron unite in very various proportions; but there are three compounds very distinct from each other—namely, graphite, cast or pig iron, and steel.

Graphite, also known under the names of *plumbago* and *black lead*, occurs not unfrequently as a mineral production, and is found in great purity at Borrowdale in Cumberland. It may be made artificially by exposing iron with excess of charcoal to a violent and long-continued heat; and it is commonly generated in small quantity during the preparation of cast iron. Pure specimens contain about four or five per cent. of iron, but sometimes its quantity amounts to 10 per cent. Most chemists believe the iron to be chemically united with the charcoal; but according to the researches of Karsten of Berlin, native graphite is only a mechanical mixture of charcoal and iron, while artificial graphite is a real carburet.

Graphite is exceedingly unchangeable in the air, and, like charcoal, is attacked with difficulty by chemical reagents. It may be heated to any extent in close vessels without change; but if exposed at the same time to the air, its carbon is

entirely consumed, and oxide of iron remains. It has an iron grey colour, metallic lustre, and granular texture; and it is soft and unctuous to the touch. Its chief use is in the manufacture of pencils and crucibles, and in burnishing iron to protect it from rust.

Cast iron is the product of the process for extracting iron from its ores, and is commonly regarded as a real compound of iron and charcoal. It always contains impurities, such as charcoal, undecomposed ore, and earthy matters, which are often visible by mere inspection; and sometimes traces of chromium, manganese, sulphur, phosphorus, and arsenic are present. It fuses readily at 2786° (Daniell,) which is a full red heat, and in cooling it acquires a crystalline granular texture. The quantity of different specimens is by no means uniform; and two kinds, white and grey cast iron, are in particular distinguished from each other. The former is exceedingly hard and brittle, sometimes breaking like glass from sudden change of temperature; while the latter is softer and much more tenacious. This difference appears owing to the mode of combination, rather than to a difference in the proportion of carbon; for the white variety may be converted into the grey by exposure to a strong heat and cooling slowly, and the grey may be changed into the white by being heated and rapidly cooled. According to Karsten the carbon of the latter is combined with the whole mass of iron, and amounts as a maximum to 5·25 per cent.; but in some specimens its proportion is considerably less. The former, on the contrary, contains from 3·15 to 4·65 per cent. of carbon, of which about three-fourths are in the state of graphite, and are left as such after the iron is dissolved by acids; while the remaining fourth is in combination with the whole mass of metal, constituting a carburet which is very similar to steel. Grey cast iron may hence be regarded as a kind of steel, in which graphite is mechanically mixed.

Steel is commonly prepared in this country by the process of cementation, which consists in filling a large furnace with alternate strata of bars of the purest malleable iron and powdered charcoal, closing every aperture so as perfectly to exclude atmospheric air, and keeping the whole during several days at a red heat. By this treatment the iron gradually combines with from 1·3 to 1·75 per cent. of carbon, its texture is greatly changed, and its surface is blistered. It is subsequently hammered at a red heat into small bars, and may be welded either with other bars of steel or with malleable iron. Mackintosh, of Glasgow, has introduced an elegant process of forming steel by exposing heated iron to a current of coal gas, when carburretted hydrogen is decomposed, its carbon enters into combination with iron, and hydrogen gas is evolved.

In ductility and malleability it is far inferior to iron; but exceeds it greatly in hardness, sonorousness, and elasticity. Its texture is also more compact, and it is susceptible of a higher polish. It sustains a full read heat without fusing, and is therefore less fusible than cast iron; but it is much more so than malleable iron. By fusion it forms cast steel, which is more uniform in composition and texture, and possesses a closer grain, than ordinary steel.

SECTION XII.

ZINC.—CADMIUM.

ZINC.

Hist. and Prep.—This metal was first mentioned under the term *zinetum* in the sixteenth century by Paracelsus; but it was probably known at a much earlier period. In commerce it is often called *spelter*, and is obtained either from *calamine*, native crabonate of zinc, or from the native sulphuret, *zinc blende* of mineralogists. It is procured from the former by heat and carbonaceous matters; and from the latter by a similar process after the ore has been previously oxidized by *roasting*, that is, by exposure to the air at a low red heat. Its preparation affords an instance of what is called *distillation by descent*. The furnace or crucible for reducing the ore is closed above, and in its bottom is fixed an iron tube, the upper aperture of which is in the interior of the crucible, and its lower terminates just above a vessel of water. The vapour of zinc, together with all the gaseous products, passes through this tube, and the zinc is condensed. The first portions are commonly very impure, containing cadmium and arsenic, the period of their disengagement being indicated by what the workmen call the *brown blaze*; but when the *blue blaze* begins, that is, when the metallic vapour burns with a bluish white flame, the zinc is collected. As thus obtained, it is never quite pure: it frequently contains traces of charcoal, sulphur, cadmium, arsenic, lead, and copper; and iron is always present. It may be freed from these impurities by distillation,—by exposing it to a white heat in an earthen retort, to which a receiver full of water is adapted; but the first portions, as liable to contain arsenic and cadmium, should be rejected.

Prop.—It has a strong metallic lustre, and a bluish white colour. Its texture is lamellated, and its sp. gr. about 7. It is a hard metal, being acted on by the file with difficulty. At low or high degrees of heat it is brittle; but at temperatures between 210° and 300°, it is both malleable and ductile, a property which enables zinc to be rolled or hammered into sheets of considerable thinness. Its malleability is considerably diminished by the impurities which the zinc of commerce contains. It fuses at 773° (Daniell), and when slowly cooled crystallizes in four or six-sided prisms. Exposed in close vessels to a white heat, it sublimes unchanged.

Zinc undergoes a slight change by the action of air and moisture, becoming coated with a thin grey film of suboxide which seems to protect the metal beneath. When fused in open vessels it absorbs oxygen, and forms the white oxide, called flowers of zinc. Heated to full redness in a covered crucible, it bursts into flame as soon as the cover is removed, and burns with a brilliant white light. The combustion ensues with such violence, that the oxide as it is formed is mechanically carried up into the air. The heat at which it begins to burn is estimated by Daniell at 941° F. Zinc is readily dissolved by dilute sul-

phuric or hydrochloric acid, by the substitution for hydrogen which is evolved, and which often contains a small quantity of metallic zinc in combination.

Gay-Lussac and Berzelius found that the protoxide of zinc consists of 100 parts of metallic zinc and 24·8 of oxygen, being a ratio of 32·3 to 8. Its other combinations justify the adoption of 32·3 as the eq. of zinc; its symb. is Zn. The composition of its compounds described in this section is as follows:—

	Zinc.			Equiv.	Formulæ.
Protoxide .	32·3	1 eq. + Oxygen	8	1 eq. = 40·3	Zn + O or ZnO.
Peroxide .	Composition uncertain.				
Chloride .	32·3	1 eq. + Chlorine	35·42	1 eq. = 67·72	Zn + Cl or ZnCl.
Iodide .	32·3	1 eq. + Iodine	126·3	1 eq. = 158·6	Zn + I or ZnI.
Bromine .	32·3	1 eq. + Bromine	78·4	1 eq. = 110·7	Zn + Br or ZnBr.
Fluoride .	32·3	1 eq. + Fluorine	18·68	1 eq. = 50·98	Zn + F or ZnF.
Sulphuret .	32·3	1 eq. + Sulphur	16·1	1 eq. = 48·4	Zn + S or ZnS.

Protoxide of Zinc.—This is the only oxide of zinc which acts as a salifiable base, and the only one of known composition. It is generated during the solution of zinc in dilute sulphuric acid, and may be obtained in a dry state by collecting the flakes which rise during the combustion of zinc, or by heating the carbonate to redness. At common temperatures it is white; but when heated to low redness it assumes a yellow colour, which gradually disappears on cooling. It is quite fixed in the fire. It is insoluble in water, and therefore does not affect the blue colour of plants; but it is a strong salifiable base, forming regular salts with acids, most of which are colourless. It combines also with some of the alkalies.

The presence of zinc is easily recognized by the following characters:—The oxide is precipitated from its solutions as a white hydrate by pure potassa or ammonia, and as carbonate by carbonate of ammonia, but is completely redissolved by an excess of the precipitant. The fixed alkaline carbonates precipitate it permanently as white carbonate of oxide of zinc. Hydrosulphate of ammonia causes a white precipitate, a hydrated sulphuret of zinc. Hydrosulphuric acid acts in a similar manner, if the solution is quite neutral; but it has no effect if an excess of any strong acid is present.

Its eq. is 40·3; *symb.* Zn + O, Zn, or ZnO.

When metallic zinc is exposed for some time to air and moisture, or is kept under water, it acquires a superficial coating of a grey matter, which Berzelius describes as a sub-oxide. It is probably a mixture of metallic zinc and the white oxide, into which it is resolved by the action of acids. The peroxide is prepared, according to Thenard, by acting on hydrated white oxide of zinc with peroxide of hydrogen diluted with water. It resolves itself so readily into oxygen and the oxide already described, that it cannot be preserved even under the surface of water; and its composition is quite unknown.

Chloride of Zinc.—This compound is formed, with evolution of heat and light, when zinc filings are introduced into chlorine gas; and it is readily prepared by dissolving zinc in hydrochloric acid, evaporating to dryness, and heating the residue in a tube through which dry hydrochloric acid gas is transmitted. It is colourless, fusible at a heat a little above 212°, has a soft consistence at common temperatures, hence called *butter of zinc*, sublimes at a red heat, and deliquesces in the air.

Its eq. is 67·72; *symb.* Zn + Cl, or ZnCl.

Iodide of Zinc is prepared by digesting iodine in water with zinc filings in excess. A colourless solution results, which by evaporation yields a deliquescent iodide. By heat in close vessels it may be sublimed, and then crystallizes in brilliant needles; but if heated in the open air, oxide of zinc is formed, and iodine expelled. If zinc is digested in water with an excess of iodine, a brown solution results, which probably contains a biniodide.

Its eq. is 158·6; *symb.* Zn + I, or ZnI.

Bromide of Zinc may be formed by a process similar to that for the iodide, but its properties have not been studied.

Its eq. is 110·7; *symb.* Zn + Br, or ZnBr.

Fluoride of Zinc is obtained by acting directly on oxide of zinc with hydrofluoric acid, and is a white compound of sparing solubility.

Its eq. is 50·98; *symb.* Zn + F, or ZnF.

Sulphuret of Zinc.—This compound is well known to mineralogists under the name of *zinc blende*, and occurs in dodecahedral crystals or some allied form. Its structure is lamellated, lustre adamantine, and colour variable, being sometimes, yellow, red, brown, or black. It may be formed artificially by igniting in a closed crucible a mixture of oxide of zinc and sulphur, or sulphate of oxide of zinc and charcoal, or by drying the hydrated sulphuret of zinc. *Its eq. is* 48·4; *symb.* Zn + S, or ZnS.

CADMIUM.

Hist.—Cadmium, so called (from καδμεια, a term applied to calamine, and to the volatile matters which rise from the furnace in preparing brass) because it is associated with zinc, was discovered in the year 1817, by Stromeyer, in an oxide of zinc which had been prepared for medical use; and he has since found it in several of the ores of that metal, especially in a radiated blende from Bohemia, which contains about five per cent. of cadmium. The late Dr. Clarke detected its existence in some of the zinc ores of Derbyshire, and in the common zinc of commerce. Herapath has found it in considerable quantity in the zinc works near Bristol. During the reduction of calamine by coal, the cadmium, which is very volatile, flies off in vapour mixed with soot and some oxide of zinc, and collects in the roof of the vault, just above the tube leading from the crucible. Some portions of this substance yielded from 12 to 20 per cent. of cadmium. (An. of Phil. xiv. and xvii.)

Prep.—The process by which Stromeyer separates cadmium from zinc or other metals is the following. The ore of cadmium is dissolved in dilute sulphuric or hydrochloric acid, and after adding a portion of free acid, a current of hydrosulphuric acid gas is transmitted through the liquid, by which means the cadmium is precipitated as a sulphuret, while the zinc continues in solution. The sulphuret of cadmium is then decomposed by nitric acid, and the solution evaporated to dryness. The dry nitrate is dissolved in water, and an excess of carbonate of ammonia added. The white carbonate of oxide of cadmium subsides, which, when heated to redness, yields a pure oxide. By mixing this oxide with charcoal, and exposing the mixture to a red heat, metallic cadmium is sublimed.

A very elegant process for separating zinc from cadmium was proposed by Wollaston. The solution of the mixed metals is put into a platinum capsule, and a piece of metallic zinc is placed in it. If cadmium is present, it is reduced,

and adheres so tenaciously to the capsule, that it may be washed with water without danger of being lost. It may then be dissolved either by nitric or dilute hydrochloric acid.

Prop.—Cadmium, in colour and lustre, has a strong resemblance to tin, but is somewhat harder and more tenacious. It is very ductile and malleable. Its sp. gr. is 8·604 before being hammered, and 8.694 afterwards. It melts at about the same temperature as tin, and is nearly as volatile as mercury, condensing like it into globules which have a metallic lustre. Its vapour has no odour. When heated in the open air, it absorbs oxygen, and is converted into an oxide. Cadmium is readily oxidized and dissolved by nitric acid, which is its proper solvent. Sulphuric and hydrochloric acids act upon it less easily, and the oxygen is then derived from water.

The eq. of cadmium, deduced from Stromeyer's analysis of its oxide, is 55·8. *Its symb.* is Cd. The composition of its compounds described in this section is as follows:—

	Cadmium.			Equiv.	Formulæ.
Oxide of Cadm.	55·8	1 eq.+Oxygen	8	1 eq.= 63·8	Cd+O or CdO.
Chloride . .	55·8	1 eq.+Chlorine	35·42	1 eq.= 91·22	Cd+Cl or CdCl.
Iodide . .	55·8	1 eq.+Iodine	126·3	1 eq.=182·1	Cd+I or CdI.
Sulphuret .	55·8	1 eq.+Sulphur	16·1	1 eq.= 71·9	Cd+S or CdS.

Oxide of Cadmium.—This, the only known, oxide of cadmium is prepared by igniting its carbonate, has an orange colour, is fixed in the fire, and is insoluble in water. It has no action on test paper, but is a strong alkaline base, forming neutral salts with acids. It is precipitated as a white hydrate by pure ammonia, but is redissolved by excess of that alkali. It is precipitated permanently by pure potassa or soda as a hydrate, and by all the alkaline carbonates as carbonate of oxide of cadmium.

Its eq. is 63·8; *symb.* Cd + O, Cd, or CdO.

Chloride of Cadmium.—By dissolving oxide of cadmium in hydrochloric acid and concentrating duly, the chloride with water of crystallization crystallizes in transparent four-sided rectangular prisms, which lose their water by heat and even in a dry air, fuse at a heat short of redness, and acquire a lamellated texture in cooling. At a high temperature it is sublimed.

Its eq. is 91·22; *symb.* Cd + Cl, or CdCl.

Iodide of Cadmium may be formed in the same manner as iodide of zinc, is soluble in water and alcohol, and crystallizes by evaporation in large, colourless, transparent, hexagonal tables, which do not change in the air, and have a pearly lustre. By heat they lose water, and then fuse. *Its eq. is* 182·1; *symb.* Cd + I, or CdI.

Sulphuret of Cadmium occurs in mixture or combination in some kinds of zinc blende, and is easily prepared by the action of hydrosulphuric acid on a salt of cadmium. It has a yellowish-orange colour, and is distinguished from the sulphurets of arsenic by being insoluble in pure potassa, and by sustaining a white heat without subliming (Stromeyer).

Its eq. is 71·9; *symb* Cd + S, or CdS.

SECTION XIII.

COBALT.—NICKEL.

COBALT.

Hist.—This metal is met with in the earth chiefly in combination with arsenic, constituting an ore from which all the cobalt of commerce is derived. It is a constant ingredient of meteoric iron, though in very small quantity. (Stromeyer.) Gregory has detected it also in many specimens of native peroxide of manganese. Its name is derived from the term *Kobold, an evil spirit*, applied to it by the German miners at a time when they were ignorant of its value, and considered it unfavourable to the presence of valuable metals.

Prep.—When native arseniuret of cobalt is broken into small pieces, and exposed in a reverberatory furnace to the united action of heat and air, its elements are oxidized, most of the arsenious acid is expelled in the form of vapour, and an impure oxide of cobalt, called *zaffre*, remains. This is dissolved in hydrochloric acid, and a current of hydrosulphuric acid gas is transmitted through the solution until the arsenious acid is completely separated in the form of orpiment. The filtered liquid is then boiled with a little nitric acid, in order to convert the protoxide into peroxide of iron, and an excess of carbonate of potassa is added. The precipitate consisting of peroxide of iron and carbonate of protoxide of cobalt, after being well washed with water, is digested in a solution of oxalic acid, which dissolves the oxide of iron and leaves the oxide of cobalt in the form of an insoluble oxalate. (Laugier.) On heating this oxalate in a retort from which atmospheric air is excluded, a large quantity of carbonic acid is evolved, and a black powder, metallic cobalt, is left. (Thomson in Annals of Philosophy, N. S. i.) The pure metal is easily procured also by passing a current of dry hydrogen gas over oxide of cobalt heated to redness in a tube of porcelain. In this state it is porous, and if formed at a low temperature it inflames spontaneously, as stated in the section on iron.

Prop.—A brittle metal, of a reddish-grey colour, and weak metallic lustre. Its density, according to my observation, is 7·834. It fuses at a heat rather lower than iron, and when slowly cooled it crystallizes. It has long been considered to be attracted by the magnet, but Faraday denies that it possesses this property when pure. It undergoes little change in the air, but absorbs oxygen when heated in open vessels. It is attacked with difficulty by sulphuric or hydrochloric acid, but is readily oxidized by means of nitric acid. Like iron and the other metals of this order, it decomposes water at a red heat with disengagement of hydrogen gas. (Despretz.)

According to the analyses by Rothoff of the oxides of cobalt, its equivalent is inferred to be 29·5 (An. of Phil. iii. 356). Its symb. is Co. The composition of its compounds described in this section is as follows:—

	Cobalt.		Equiv.	Formulæ.
Protoxide .	29·5 1 eq.	+ Oxygen 8	1 eq. = 37·5	Co + O or CoO.
$\frac{4}{3}$ Oxide .	88·5 3 eq.	+ · 32	4 eq. = 120·5	$3Co + 4O$ or Co^3O^4.

	Cobalt.			Equiv.	Formulæ.
Peroxide .	59·0	2 eq.+ .	24	3 eq.= 83·0	2Co+3O or Co_2O_3.
Chloride .	29·5	1 eq.+Chlorine	35·42	1 eq.= 64·92	Co+Cl or ClCo.
Protosulphuret	29·5	1 eq.+Sulphur	16·1	1 eq.= 45·6	Co+S or CoS.
Sesquisulphuret	59	2 eq.+ ·	48·3	3 eq.=107·3	2Co+3S or Co_2S_3.
Bisulphuret .	29·5	1 eq.+ .	32·2	2 eq.= 61·7	Co+2S or CoS_2.
Subphosphuret	88·5	3 eq.+Phosph.	31·4	2 eq.=119·9	3Co+2 P or Co_3P_2.

Protoxide of Cobalt.—Prepared by decomposing carbonate of the protoxide by heat in a vessel from which atmospheric air is excluded. It is of an ash-grey colour, and is the basis of the salts of cobalt, most of which are of a pink hue. When heated to redness in open vessels it absorbs oxygen, and is converted into the peroxide. It is easily recognized by giving a blue tint to borax when melted with it; and is employed in the arts, in the form of smalt, for communicating a similar colour to glass, earthenware, and porcelain. It is precipitated from its salts by pure potassa as a blue hydrate, which absorbs oxygen from the air, and gradually acquires a dirty green tint. Pure ammonia likewise causes a blue precipitate, which is redissolved by the alkali if in excess. It is thrown down as a pale pink carbonate by carbonate of potassa, soda, or ammonia; but an excess of the last redissolves it with facility. Hydrosulphuric acid produces no change, unless the solution is quite neutral, or the oxide is combined with a weak acid. Alkaline hydrosulphates always precipitate it as black protosulphuret of cobalt.

Its eq. is 37·5; *symb.* $\dot{Co}$ + O, Co, or CoO.

$\frac{4}{3}$ *Oxide of Cobalt.*—It is said that when protoxide of cobalt, or the nitrate, carbonate, or oxalate of that oxide, is gently ignited in an open fire, peroxide of cobalt results; but M. Hess has lately shown that the oxide then obtained is analogous in composition to the red oxide of manganese. The peroxide of cobalt is converted into it, with loss of oxygen, by a full red heat, whether exposed to the air or not; so that of the oxides of cobalt it is the most stable. The same compound is obtained as a dirty green hydrate by the action of the air on the hydrated protoxide. It is probably a compound of peroxide and protoxide of cobalt, since 3Co + 4O obviously contain the elements $CoO + Co_2O_3$. This intermediate oxide is of a dark brown colour, and does not unite with acids or alkalies (Pog. Annalen, xxvi. 542).

Its eq. is 120·5; *symb.* $CoO + Co_2O_3$.

Peroxide.—Is obtained as a black hydrate containing 2 eq. of water, Co_2O_3 + 2HO, when chloride of cobalt in solution is decomposed by hypochlorite of lime, or chlorine is transmitted into water in which hydrated protoxide of cobalt is suspended. In this case

3 eq. Protoxide & 1 eq. Chlorine			1 eq. Peroxide & 1 eq. Chloride
3 CoO	Cl	yield	Co_2O_3 CoCl

This hydrate has a black colour and yields the black anhydrous peroxide by exposure to a heat of 600° or 700°; but it is difficult to drive off all the water, without also losing oxygen. It combines with none of the acids, and when digested with hydrochloric acid it emits chlorine gas, and chloride of cobalt is generated.

Its eq is 83·0; *symb.* 2Co + 3O, $\ddot{\underline{Co}}$, or Co_2O_3.

When a salt of cobalt is treated with pure ammonia in close vessels, part of the cobalt is dissolved, and part subsides in form of a blue powder. On admitting atmospheric air, this substance passes to a higher state of oxidation, and is gra-

dually dissolved. If nitrate of cobalt is used, a double salt may be obtained in crystals, which M. Gmelin, to whom we are indebted for these remarks, believes to consist of nitrate and *cobaltate* of ammonia. Of the existence of this acid, however, Winkelblech, who has examined the subject, could obtain no evidence (Lieb. An. xiii. 253).

Chloride of Cobalt.—It is obtained in solution on dissolving metallic cobalt, its protoxide or either of the other oxides in hydrochloric acid, with evolution of hydrogen gas with the first and of chlorine with the latter. It yields a pink-coloured solution, and by evaporation small crystals of the same colour containing water of crystallization. When deprived of water its colour is blue, a character on which is founded its use as a sympathetic ink: when letters are written with a dilute solution of the chloride, the colour is so pale that it is invisible in the cold; but on heating gently the letters appear of a blue colour, and disappear as soon as the chloride has recovered its moisture from the atmosphere. When iron or nickel is present the dry chloride of cobalt is green instead of blue.

Its eq. is 64·92; *symb.* Co + Cl, or CoCl.

Sulphurets.—Cobalt appears to unite with sulphur in three proportions; the first being a protosulphuret, the second a sesquisulphuret, and the third a bisulphuret. The protosulphuret may be formed in the dry way either by throwing fragments of sulphur on red-hot cobalt, or by igniting protoxide of cobalt with sulphur; and it is thrown down as a black precipitate from the salts of cobalt by alkaline hydrosulphates, or even by hydrosulphuric acid gas if the salt is quite neutral, or the oxide united with any of the feebler acids. It has a grey colour, a metallic lustre, and a crystalline texture.

Its eq. 45·6; *symb.* Co + S, or CoS.

Arfwedson has observed that when hydrogen gas is transmitted over sulphate of oxide of cobalt heated to redness, water and sulphurous acid are evolved, and a compound remains, called an *oxysulphuret*, consisting of oxide of cobalt united with sulphuret of cobalt. When this substance is exposed to hydrosulphuric acid gas at a red heat, the oxide is decomposed, and the sesquisulphuret is formed.

Its eq. is 107·3; *symb.* 2Co + 3S, or Co_2S_3.

The bisulphuret is prepared, according to Setterberg, by heating 2 parts of carbonate of oxide of cobalt intimately mixed with 3 parts of sulphur. The process is conducted in a glass retort, and the heat continued as long as sulphur is expelled; but the temperature should not be suffered to reach that of redness.

Its eq. 61·7; *symb.* Co + 2S, or CoS_2.

Subphosphuret of Cobalt.—Rose obtained this phosphuret by the action of hydrogen gas on subphosphate of oxide of cobalt heated in a tube, water being also generated. In this case

1 eq. Phosphate and 8 eq. Hydrogen		yield	1 eq. Phosphuret and 8 eq. water	
3(Co + O) + (2P + 5O)	8H		3Co + 2P	8(H + O).

This phosphuret is pulverulent and of a grey colour, and is also obtained by the action of phosphuretted hydrogen gas on chloride of cobalt.

Its eq. is 119·9; *symb.* 3Co + 2P, or Co_3P_2.

NICKEL.

Hist. and Prep.—Nickel is a constituent of meteoric iron, and, according to Gregory, of native peroxide of manganese; but its principal ore is the copper-

coloured mineral of Westphalia, termed *kupfernickel, copper-nickel; nickel* being an epithet of detraction, applied by the older German miners, because the mineral looked like an ore of copper, and yet they could extract none from it. The preparations of nickel may either be prepared from copper-nickel, which is an arseniuret of nickel containing small quantities of sulphur, copper, cobalt, and iron, or from the artificial arseniuret called *speiss*, a metallurgic production obtained in forming smalt from the roasted ores of cobalt. Various processes have been devised for procuring a pure salt of nickel, but the following appears to me as simple and perhaps as successful as any. After reducing speiss to fine powder, it is digested in sulphuric acid, to which a fourth part of nitric acid is added; and when the solution is saturated with nickel, it is set aside for several hours in order that arsenious acid may separate, and is then filtered. The clear liquid is subsequently mixed with a solution of sulphate of potassa, and set aside to crystallize spontaneously; when a double salt, sulphate of oxide of nickel and potassa, is deposited. Thomson, who proposed this process, states that the crystals thus obtained are quite free from arsenic and iron, and contain no impurities except copper and cobalt. The former is precipitated as sulphuret by a current of hydrosulphuric acid gas, a little free sulphuric acid being previously added; and at the same time any traces of arsenic, if present, would likewise subside as orpiment. The filtered liquid is then heated to expel free hydrosulphuric acid, and the oxides of nickel and cobalt precipitated by carbonate of potassa. The separation of these oxides may then be effected by the method suggested by Berthier; namely, by precipitating them together by pure potassa, and, after washing the mixed hydrates, suspending them in water through which chlorine gas is transmitted to saturation. All the cobalt and generally some nickel is converted into peroxide and thus rendered insoluble; while the greater part of the nickel is dissolved in the form of chloride, and may be removed from the insoluble peroxides by filtration. The metal may be prepared either by heating the oxalate in close vessels, or by the combined action of heat and charcoal or hydrogen on oxide of nickel.

Prop.—It is of a white colour, intermediate between that of tin and silver. It has a strong metallic lustre, and is both ductile and malleable. It is attracted by the magnet, and like iron may be rendered magnetic at common temperatures, but loses this power at 630° (Faraday). Its sp. gr. after fusion is about 8·279, and is increased to near 9·0 by hammering.

Nickel is very infusible, but less so than pure iron. It suffers no change at common temperatures by exposure to air and moisture; but it absorbs oxygen at a red heat, though not rapidly, and is partially oxidized. It decomposes water at the same temperature. Hydrochloric and sulphuric acids act upon it with difficulty; but by nitric acid it is readily oxidized, and forms a nitrate of the protoxide of nickel.

From the analyses of the oxides of nickel by Rothoff and Tupputi the eq. of nickel may be estimated at 29·5. Its symb. is Ni. The composition of its compounds described in this section is as follows:—

	Nickel.			Equiv.	Formulæ.
Protoxide	29·5	1 eq. + Oxygen	8	1 eq. = 37·5	Ni + O or NiO.
Peroxide	59·0	2 eq. + do.	24	3 eq. = 83·0	2Ni + 3O or Ni_2O_3.
Chloride	29·5	1 eq. + Chlorine	35·42	1 eq. = 64·92	Ni + Cl or NiCl.
Disulphuret	59	2 eq. + Sulphur	16·1	1 eq. = 75·1	2Ni + S or Ni_2S.
Protosulphuret	29·5	1 eq. + do.	16·1	1 eq. = 45·6	Ni + S or NiS.
Subphosphuret	88·5	3 eq. + Phosphorus	31·4	2 eq. = 119·9	3Ni + 2P or Ni_3P_2.

Protoxide of Nickel.—This oxide may be formed by heating the carbonate, oxalate, or nitrate to redness in an open vessel, and is then of an ash-grey colour; but after exposure to a white heat, its colour is a dull olive-green. It is not reducible by heat unaided by combustibles. It is not attracted by the magnet. It is a strong alkaline base, and nearly all its salts have a green tint. It is precipitated as a hydrate of a pale-green colour by the pure alkalies, but is redissolved by ammonia in excess; as a pale green carbonate by alkaline carbonates, but is dissolved by an excess of carbonate of ammonia; and as a black sulphuret by alkaline hydrosulphates. Hydrosulphuric acid occasions no precipitate, unless the solution is quite neutral, or the oxide combined with a weak acid. *Its eq. is* 37·5; *symb.* Ni + O, $\dot{N}i$, or NiO.

Peroxide.—It is formed by transmitting chlorine gas through water in which the hydrate of the protoxide is suspended. It has a black colour, does not unite with acids, is decomposed by a red heat, and with hot hydrochloric acid forms the chloride with disengagement of chlorine gas.

Its eq. is 83·0; *symb.* 2 Ni + 3O, $\ddot{\underline{N}}i$, or Ni_2O_3.

Thenard succeeded in preparing a peroxide by the action of peroxide of hydrogen on hydrated protoxide of nickel; but it is uncertain whether the composition of this peroxide is identical with that above described, or different. Two suboxides have likewise been enumerated; but their existence is exceedingly problematical.

Chloride of Nickel.—This compound is formed by acting with hydrochloric acid on metallic nickel, its protoxide, or peroxide, hydrogen gas being evolved with the former, and chlorine with the latter. It forms an emerald green solution, and by evaporating yields crystals of the same tint, which lose water or deliquesce according as the air is dry or moist. In its anhydrous state it is yellow; but a small admixture with cobalt causes a green tint. At a low red heat it sublimes and condenses in brilliant scales of a gold-yellow colour.

Its eq. is 64·92; *symb.* Ni + Cl, or NiCl.

Protosulphuret of nickel is formed by processes similar to those described for preparing protosulphuret of cobalt. The precipitated sulphuret is dark brown or nearly black, and is dissolved by hydrochloric acid with evolution of hydrosulphuric; while that procured in the dry way is of a greyish yellow colour, and requires for solution nitric or nitro-hydrochloric acid. It occurs as a natural production in very delicate acicular crystals, the *haarkies* of the Germans. *Its eq. is* 45·6; *symb.* Ni + S, or NiS.

Arfwedson obtained the disulphuret by transmitting hydrogen gas over sulphate of oxide of nickel at a red heat. It is of a lighter yellow and more fusible than the other.

Its eq. is 75·1; *symb.* 2Ni + S, or Ni S.

Subphosphuret of Nickel.—Rose obtained it by the action of hydrogen gas on subphosphate of oxide of nickel, the same change ensuing as with cobalt; and it is generated by the action of phosphuretted hydrogen gas on chloride of nickel. It has a black colour, is insoluble in hydrochloric acid, but dissolves in nitric acid. Heated by the blowpipe it burns with flame.

Its eq. is 119·9; *symb.* 3 Ni + 2P, or Ni^3P_2.

SECTION XIV.

TIN.

Hist. and Prep.—Tin was known to the ancients, who obtained it principally, if not solely, from Cornwall. The tin of commerce is distinguished into two varieties, called *block* and *grain tin*, both of which are procured from the native oxide by means of heat and charcoal. In Cornwall, which has been celebrated for its tin mines during many centuries, the ore is both extracted from veins, and found in the form of rounded grains, among beds of rolled materials, which have been deposited by the action of water. These grains, commonly called *stream tin*, contain a very pure oxide, and yield the purest kind of grain tin. An inferior sort is prepared by heating bars of tin, extracted from the common ore, to very near their point of fusion, when the more fusible parts, which are the purest, flow out; and the less fusible portions constitute block tin. The usual impurities are iron, copper and arsenic.

Prop.—It has a white colour, and a lustre resembling that of silver. The brilliancy of its surface is but very slowly impaired by exposure to the atmosphere, nor is it oxidized even by the combined agency of air and moisture. Its malleability is very considerable; for the thickness of common tin-foil does not exceed 1-1000th of an inch. In ductility and tenacity it is inferior to several metals. It is soft and inelastic, and when bent backwards and forwards emits a peculiar crackling noise. Its sp. gr. is about 7·291. At 442° it fuses, and if exposed at the same time to the air, its surface tarnishes, and a grey powder is formed. When heated to whiteness, it takes fire and burns with a white flame, being converted into peroxide of tin.

The eq. of tin deduced by Berzelius from his analysis of its oxides is 57·9; its symb. is Sn. The composition of the compounds of tin described in this section is as follows:—

	Tin.			Equiv.	Formulæ.
Protoxide	57·9	1 eq. + Oxygen	8	1 eq. = 65·9	Sn + O or SnO.
Sesquioxide	105·8	2 eq. + . .	24	3 eq. = 129·8	2Sn + 3O or Sn_2O_3.
Binoxide	57·9	1 eq. + . .	16	2 eq. = 73·9	Sn + 2O or SnO_2.
Protochloride	57·9	1 eq. + Chlorine	35·72	1 eq. = 93·32	Sn + Cl or SnCl.
Bichloride	57·9	1 eq. + . .	70·84	2 eq. = 128·74	Sn + 2Cl or $SnCl_2$.
Protiodide	57·9	1 eq. + Iodine	126·3	1 eq. = 184·2	Sn + I or SnI.
Biniodide	57·9	1 eq. + . .	252·6	2 eq. = 310·5	Sn + 2I or SnI_2.
Protosulphuret	57·9	1 eq. + Sulphur	16·1	1 eq. = 74·0	Sn + S or SnS.
Sesquisulph.	115·8	2 eq. + . .	48·3	3 eq. = 164·1	2Sn + 3S or Sn_2S_3.
Bisulphuret	57·9	1 eq. + . .	32·2	2 eq. = 90·1	Sn + 2S or SnS_2.
Tersulphuret	57·9	1 eq. + Phosph.	47.1	3 eq. = 105·0	Sn + 3P or SnP_3.

Protoxide of Tin.—Prep.—When chloride of tin in solution is mixed with an alkaline carbonate, hydrated oxide of tin falls, which may be obtained as such in a dry form by washing with warm water, and drying at a heat not above 196°,

with the least possible exposure to the air. The best mode of obtaining the anhydrous oxide is by heating the hydrate to redness in a tube from which air is excluded by a current of carbonic acid gas. The same oxide is formed when tin is kept for some time fused in an open vessel.

Prop.—Its sp. gr. is 6·666. At common temperatures it is permanent in the air; but if touched by a red-hot body it takes fire, and is converted into the peroxide. It is dissolved by the sulphuric and hydrochloric acids, as also by dilute nitric acid; and the pure fixed alkalies likewise dissolve it. From the alkaline solution metallic tin is gradually deposited, and peroxide of tin remains in solution. Its salts are remarkably prone to absorb oxygen, both from the air and from compounds which yield oxygen readily. Thus it converts peroxide of iron into protoxide, and throws down mercury, silver, and platinum in the metallic state from their salts. With a solution of gold it causes a purple precipitate, the *purple of Cassius*, which appears to be a compound of peroxide of tin and protoxide of gold. By this character protoxide of tin is recognized with certainty. It is thrown down by hydrosulphuric acid as black protosulphuret of tin.

Its eq. is 65·9; *symb.* Sn + O, Ṡn, or SnO.

Sesquioxide of Tin.—Fuchs has lately succeeded in preparing this oxide by mixing recently precipitated and moist hydrated peroxide of iron with a solution of protochloride of tin as free as possible from hydrochloric acid; when, by an interchange of elements

1 eq. perox. iron & 2 eq. chloride of tin		yield	1 eq. sesquiox. tin & 2 eq. chlo. iron.	
Fe_2O_3	2SnCl		Sn_2O_3	2FeCl

The sesquioxide falls as a slimy grey matter, and in general rather yellow from adhering oxide of iron. Berzelius obtained it purer by using a solution made by saturating hydrochloric acid as far as possible with hydrated peroxide of iron. The sesquioxide of tin, while moist, is soluble in hydrochloric acid, and the solution strikes the purple of Cassius with gold; and it is readily soluble in a solution of ammonia, which distinguishes it from the protoxide of tin, just as its action on gold does from the binoxide (Pog. Annalen, xxviii. 443.)

Its eq. is 129·8; *symb.* 2Sn + 3O, S̈n, or Sn_2O_3.

Peroxide of Tin.—*Prep.*—Most conveniently by the action of nitric acid on metallic tin. The acid in its most concentrated state, does not act easily upon tin; but when a small quantity of water is added, violent effervescence takes place owing to the evolution of nitrous acid and binoxide of nitrogen, and a white powder, the hydrated peroxide, is produced. On edulcorating this substance, and heating it to redness, watery vapour is expelled, and the pure peroxide, of a straw yellow colour, remains. In this process ammonia is generated, a circumstance which proves water as well as nitric acid to be decomposed. Peroxide of tin may likewise be obtained by precipitation from a solution of perchloride of tin by potassa, ammonia, or the alkaline carbonates; but in this case it falls as a very bulky hydrate, different from the other hydrate both in appearance and several of its chemical properties. Thus the latter dissolves readily in sulphuric, nitric, and hydrochloric acid, even when diluted; while the former is completely insoluble in the same acids, even when concentrated. It unites, indeed, with hydrochloric acid, and the compound is soluble in pure water.

Prop.—It has very little disposition in any state to unite with acids, and when dissolved by them is very apt to separate itself spontaneously as a gelatinous

hydrate. It acts the part of a feeble acid: it reddens litmus when its hydrate moistened is laid upon it, and it unites with the pure alkalies, forming soluble compounds which are called *stannates*.

Peroxide of tin is recognized by its insolubility in acids in its anhydrous state; by separating from its solution by means of hydrochloric acid as a bulky hydrate by any of the alkalies or alkaline carbonates, which is easily and completely dissolved by pure potassa or soda in excess; and by yielding with hydrosulphuric acid the yellow bisulphuret of tin, which is also soluble in pure potassa. Peroxide of tin, when melted with glass, forms a white enamel.

Its eq. 73·9; *symb.* Sn + 2O, $\ddot{\text{S}}\text{n}$, or SO_2.

Protochloride of Tin.—This compound is obtained by transmitting hydrochloric acid gas over metallic tin heated in a glass tube, when hydrogen gas is evolved; or by distilling a mixture either of granulated tin with an equal weight of bichloride of mercury, of an amalgam of tin with calomel, urging the heat till the mercury is expelled. In this state it is a grey solid, of a resinous lustre, which fuses below redness, and at a high temperature sublimes. It is obtained by crystallization from a concentrated solution of the chloride in crystals, which are sometimes in small white needles, and at others in large transparent prisms, and consist of 93·32 parts or 1 eq. of protochloride of tin and 27 parts or 3 eq. of water. On heating these crystals, they not only lose water, but reaction ensues between the elements of water and the chloride, hydrochloric acid gas is evolved, and protoxide of tin remains combined with the chloride. The same kind of compound is formed when a large quantity of the water is poured upon the crystals: the solution contains protochloride of tin and hydrochloric acid, and a white powder subsides which consists of 1 eq. of the protochloride, 1 eq. of protoxide, and 2 eqs. of water (Berzelius).

A solution of protochloride of tin is obtained by heating granulated tin in strong hydrochloric acid as long as hydrogen gas continues to be evolved. This solution is much employed as a deoxidizing agent, being more powerful than the sulphate or nitrate of the protoxide; owing apparently to the tendency of the protochloride of tin to resolve itself into bichloride and metallic tin, the latter taking oxygen or chlorine from any metallic solutions which yield them readily. *Its eq. is* 93·32; *symb.* Sn + Cl, or SnCl.

Bichloride of Tin.—When protochloride of tin is heated in chlorine gas, or on distilling a mixture of 8 parts of granulated tin with 24 of bichloride of mercury, a very volatile colourless liquid passes over, which is bichloride of tin. In an open vessel it emits dense white fumes, caused by the moisture of the air, and hence it was formerly called the *fuming liquor* of Libavius, who discovered it. At 248° it boils and the sp. gr. of its vapour was found by Dumas to be 9·1997. With one-third of its weight of water it forms a solid hydrate, and in a larger quantity of water dissolves.

The solution of bichloride of tin, commonly called *permuriate of tin*, is much used in dyeing, and is prepared by dissolving tin in nitro-hydrochloric acid. The process requires care; for if the action be very rapid, as is sure to happen if strong acid be employed and much tin added at once, the peroxide will be spontaneously deposited as a bulky hydrate, and be subsequently redissolved with great difficulty. But the operation will rarely fail, if the acid is made with two measures of hydrochloric acid, one of nitric acid, and one of water, and if the tin

is gradually dissolved, one portion disappearing before another is added. The most certain mode of preparation, however, is to prepare a solution of the protochloride, and convert it into the bichloride either by chlorine, or by gentle heat and nitric acid.

Its eq. is 128·74; *symb.* Sn + 2Cl, or $SnCl_2$.

Iodides of Tin.—The protiodide is formed by heating granulated tin with about 2½ times its weight of iodine, and is a brownish red, translucid substance, very fusible, volatile at a high temperature, and soluble in water.

Its eq. is 184·2; *symb.* Sn + I, or SnI.

The periodide is prepared by dissolving in hydriodic acid the hydrate of the peroxide precipitated by alkalies from the bichloride. It crystallizes in yellow crystals of a silky lustre, which are resolved by boiling water into hydriodic acid and peroxide of tin.

Its eq. is 310·5; *symb.* Sn + 2I, or SnI_2.

Protosulphuret of Tin.—This compound is prepared by pouring melted tin upon its own weight of sulphur, and stirring rapidly with a stick during the action; as some tin usually escapes the sulphur from the latter being rapidly expelled, the product should be pulverized, mixed with its weight of sulphur, and projected in successive portions into a hot hessian crucible, and then heated to redness. It is a brittle compound, of bluish grey, nearly black, colour and metallic lustre, which fuses at a red heat, and acquires a lamellated texture in cooling. It is dissolved by hydrochloric acid with evolution of hydrosulphuric acid. The same sulphuret is obtained in the moist way by adding hydrosulphuric acid to a solution of protochloride of tin.

Its eq. is 74·0; *symb.* Sn + S, or SnS.

The *Sesquisulphuret* is formed by mixing the protosulphuret in fine powder with a third of its weight of sulphur, and heating the mixture to low redness until sulphur ceases to escape. Its colour is of a deep greyish yellow, it is reconverted by a strong heat into the protosulphuret, and dissolves in hydrochloric acid gas, yielding hydrosulphuric acid gas and a residue of bisulphuret of tin.

Its eq. is 164·1; *symb.* 2Sn + SS, or Sn_2S_3.

Bisulphuret of Tin, formerly called *mosaic gold*, is prepared by heating in a glass or earthen retort a mixture of 2 parts of peroxide of tin, 2 of sulphur, and 1 part of sal-ammoniac, and maintaining a low red heat until sulphurous acid ceases to be evolved. These materials are sometimes employed without sal-ammoniac, but Berzelius says that the latter is essential for obtaining the bisulphuret. The product, when successfully prepared, is in crystalline scales, and sometimes even in regular six-sided tables, of a golden yellow colour and metallic lustre. It is soluble in pure potassa and in its carbonate by boiling; but its only solvent among the acids is the nitro-hydrochloric. The bisulphuret is obtained as a bulky hydrate of a dirty yellow colour by the action of hydrosulphuric acid or hydrosulphate of ammonia on bichloride of tin in solution.

Its eq. is 90.1; *symb.* Sn + 2S, or SnS_2.

Terphosphuret of Tin.—Rose formed this compound by acting on a solution of protochloride of tin by phosphuretted hydrogen. It is readily oxidized by the action of the air.

Its eq. is 105·0; *symb.* Sn + 3P, or SnP_2.

CLASS II.

ORDER II.

METALS WHICH DO NOT DECOMPOSE WATER AT ANY TEMPERATURE, AND THE OXIDES OF WHICH ARE NOT REDUCED TO THE METALLIC STATE BY THE SOLE ACTION OF HEAT.

SECTION XV.

COPPER.

Hist. and Prep.—One of the most abundant of the metals, and was well known to the ancients. Native copper is by no means uncommon, being found more or less in most copper mines: it occurs in large amorphous masses in some parts of America, and is sometimes met with in octohedral crystals, or in some of the forms allied to the octohedron. Stromeyer has lately discovered it in several specimens of meteoric iron, but in a quantity not exceeding 2-1000ths of the mass. The copper of commerce is extracted chiefly from the native sulphuret; especially from copper pyrites, a double sulphuret of iron and copper. The first part of the process consists in roasting the ore, so as to burn off some of the sulphur, and leave the remainder as a subsulphate of the oxides of iron and copper. The mass is next heated with some unroasted ore and siliceous substances, by which means much of the iron unites in the state of black oxide with silicic acid, and rises as a fusible slag to the surface; while most of the copper returns to the state of sulphuret. It is then subjected to long-continued roasting, when the greater part of the sulphur escapes as sulphurous acid, and the metal is oxidized; after which it is reduced by charcoal, and more of the iron separated as a silicate by the addition of sand. Lastly, the metal is strongly heated while a current of air plays upon its surface: the impurities, chiefly sulphur and iron, being more oxidable than copper, combine with oxygen by preference, and the copper is at length left in a state of purity sufficient for the purposes of commerce.

Prop.—Distinguished from all other metals, titanium excepted, by having a red colour. It receives a considerable lustre by polishing. Its density, when fused, is 8·667, and it is increased by hammering. It is both ductile and malleable, and in tenacity is inferior only to iron. It is hard and elastic, and consequently sonorous. Its point of fusion is 1996° F. according to Daniell, being less fusible than silver and more so than gold.

It undergoes little change in a perfectly dry atmosphere, but is rusted in a short time by exposure to air and moisture, being converted into a green substance, subcarbonate of the black oxide of copper. At a red heat it absorbs oxygen, and is converted into black scales of oxide. It is attacked with difficulty by hydrochloric and sulphuric acids, and not at all by solutions of the

vegetable acids, if atmospheric air be excluded; but if air have free access, the metal absorbs oxygen with rapidity, the attraction of the acid for the oxide of copper co-operating with that of the copper for oxygen. Nitric acid acts with violence on copper, forming a nitrate of the black oxide.

The most trustworthy experiments for determining the eq. of copper are those of Berzelius on the reduction of the black oxide by means of hydrogen gas at a red heat. According to the best of his analyses, 8 parts of oxygen unite with 31·6 parts of copper to constitute the black oxide; and, therefore, if this oxide be formed of an atom of oxygen united with an atom of copper, the eq. of this metal will be 31·6. This opinion, which I have adopted, is maintained by Thomson, Berzelius, and many Continental chemists. Others consider it as a binoxide, regarding red oxide of copper as the real protoxide; and these take twice 31·6 or 63·2 as an eq. of copper. The principal arguments in favour of the former view are these:—1, the red oxide has very much the character of a *suboxide*, a term frequently used to designate an oxide which has little or no tendency to unite with acids, and which contains less than one atom of oxygen to one atom of metal; 2, the product of the eq. and specific heat of most metals is a constant quantity, and copper coincides with the law, provided the black oxide contain an atom of each element; 3, the salts of the black oxide are isomorphous with the salts of protoxide of iron, which gives a strong presumption that these oxides possess the same atomic constitution.

Its symb. is Cu.

The composition of the compounds described in this section is as follows:—

	Copper.		Equiv.	Formulæ.
Red or Dioxide	63·2	2 eq.+Oxygen 8	1 eq.= 71·2	2Cu+O.
Black or Protoxide	31·6	1 eq.+do. 8	1 eq.= 39·6	Cu+O.
Superoxide .	31·6	1 eq.+do. 16	2 eq.= 47·6	Cu+2O.
Dichloride .	63·2	2 eq.+Chlorine 35·42	1 eq.= 98·62	2Cu+Cl.
Chloride . .	31·6	1 eq.+do. 35·42	1 eq.= 66·02	Cu+Cl.
Diniodide . .	63·2	2 eq.+Iodine 126·3	1 eq.=189·5	2Cu+I.
Disulphuret . .	63·2	2 eq.+Sulphur 16·1	1 eq.= 79·3	2Cu+S.
Sulphuret . .	31·6	1 eq.+Sulphur 16·1	1 eq.= 47·7	Cu+S.
Triphosphuret .	94·8	3 eq.+Phosphorus 15·7	1 eq.=110.5	3Cu+P.
Subsesquiphosph. .	94·8	3 eq.+do. 31·4	2 eq.=126·2	3Cu+2P.

Red Oxide or Dioxide.—Hist. and Prep.—This compound occurs native in the form of octohedral crystals, and is found of peculiar beauty in the mines of Cornwall. It may be prepared artificially by heating in a covered crucible a mixture of 31·6 parts of copper filings with 39·6 of the black oxide; or still better by arranging thin copper plates one above the other with interposed strata of the black oxide, and exposing them to a red heat carefully protected from the air. Another method is by boiling a solution of acetate of protoxide of copper with sugar, when the suboxide subsides as a red powder; and another is to fuse at a low red heat the dichloride of copper with about an equal weight of carbonate or bicarbonate of soda, subsequently dissolving the sea-salt by water, and drying the red powder.

In this case, by an interchange of elements,

1 eq. Dichloride of Copper	Cu_2Cl	yield	1 eq. Red Oxide	Cu_2O
and 1 eq. Soda	NaO		and 1 eq. Chloride of Sodium .	NaCl.

Malaguti recommends the following process :—100 parts of sulphate of copper and 57 of carbonate of soda, both in crystals, are fused at a gentle heat; and the mass left when all water is expelled, is pulverized and mixed with 25 parts of copper filings. The mixture is pressed into a crucible and exposed for 20 minutes to a white heat. The result is again pulverized and carefully washed (An. de Ch. et Ph. liv. 216).

Prop.—The red oxide of copper has a sp. gr. of 6·093, and in colour is very similar to copper. It may be preserved in a dry atmosphere; but at a red heat it absorbs oxygen and is converted into the protoxide. Dilute acids act on it very slowly; and the resulting solution, as is indicated by its tint, does not arise from the union of the red oxide itself with the acid, but from its being resolved, like other sub-oxides, into metal and a protoxide. With strong nitric acid it is oxidized, binoxide of nitrogen escapes, and a nitrate of the black oxide is formed. Strong hydrochloric acid forms with it a colourless solution, from which alkalies throw it down as a hydrate of an orange tint. In this state it readily absorbs oxygen from the air. The red oxide of copper is soluble in ammonia, and the solution is quite colourless; but it becomes blue with surprising rapidity by free exposure to air, owing to the formation of the black oxide.

Its eq. is 71·2; *symb.* 2Cu + O, or Cu_2O.

Black Oxide or Protoxide.—Hist and Prep.—This compound, the *copper black* of mineralogists, is sometimes found native, being formed by the spontaneous oxidation of other ores of copper. It may be prepared artificially by calcining metallic copper, by precipitation from the salts of copper by means of pure potassa, and by heating nitrate of copper to redness.

Prop.—It varies in colour from a dark brown to a bluish-black, according to the mode of formation: its sp. gr. is 6·401. It undergoes no change by heat alone, but is readily reduced to the metallic state by heat and combustible matter; and is hence much employed as an oxidizing agent in the analysis of organic substances. It is insoluble in water, and does not affect the vegetable blue colours; it combines with nearly all the acids, forming salts which have a green or blue tint. It is soluble likewise in ammonia, forming with it a deep blue solution, a property by which protoxide of copper is distinguished from all other substances. Its salts are distinguished from most substances by their colour, and are easily recognized by reagents. When pure soda or potassa is mixed with a solution of sulphate of the protoxide, a greenish-blue disulphate at first subsides; but as soon as the alkali is added in excess, a blue bulky hydrate of the oxide is formed, which is decomposed by boiling, and consequently becomes black. Pure ammonia also throws down the disulphate when carefully added; but an excess of the alkali instantly redissolves the precipitate, and forms a deep blue solution. Alkaline carbonates cause a bluish-green precipitate, carbonate of the protoxide, which is redissolved by an excess of carbonate of ammonia. It is precipitated as a dark brown sulphuret by hydrosulphuric acid, and as a reddish-brown ferrocyanide by ferrocyanide of potassium. It is thrown down of a yellowish-white colour by albumen, and M. Orfila has proved that this compound is inert, so that albumen is an antidote to poisoning by copper.

Copper is separated in the metallic state by a rod of iron or zinc. The copper thus obtained, after being digested in a dilute solution of hydrochloric acid, is almost chemically pure.

The best mode of detecting copper, when supposed to be present in mixed

fluids, is by hydrosulphuric acid. The sulphuret, after being collected, and heated to redness in order to char organic matter, should be placed on a piece of porcelain, and be digested in a few drops of nitric acid. Sulphate of protoxide of copper is formed, which, when evaporated to dryness, strikes the characteristic deep blue tint on the addition of ammonia; but the most delicate test of black oxide of copper in solution is ferrocyanide of potassium.

Its eq. is 39·6; *symb.* Cu + O, $\dot{Cu}$, or CuO.

Superoxide.—This oxide was prepared by Thenard by the action of peroxide of hydrogen diluted with water on the hydrated black oxide. It suffers spontaneous decomposition under water; but it may be dried *in vacuo* by means of sulphuric acid.

Its eq. is 47·6; *symb.* Cu + 2O, $\ddot{Cu}$, or CuO_2.

Dichloride.—Prep.—When copper filings are introduced into an atmosphere of chlorine gas, the metal takes fire spontaneously, and both the chlorides are generated. The *dichloride* may be conveniently prepared by heating copper filings with twice their weight of corrosive sublimate. In this way it was originally made by Boyle, who termed it *resin of copper*, from its resemblance to common resin. Proust, who called it *white muriate of copper*, procured it by the action of protochloride of tin on chloride of copper; and also by decomposing the chloride by heat, air being excluded. It is slowly deposited in crystalline grains when the green solution of chloride of copper is kept in a corked bottle in contact with metallic copper.

Prop.—The dichloride of copper is fusible at a heat just below redness, and bears a red heat in close vessels without subliming. It is insoluble in water, but dissolves in hydrochloric acid, and is precipitated unchanged by water as a white powder. Its colour varies with the mode of preparation, being white, yellow, or dark brown. It is apt to absorb oxygen from the atmosphere, forming a green-coloured compound of oxide and chloride of copper; a change to which the dichloride prepared in the moist way is peculiarly prone.

Its eq. is 98·62; *symb.* 2Cu + Cl, or Cu_2Cl.

Chloride.—The chloride of copper is obtained in solution of a green colour by dissolving protoxide of copper in hydrochloric acid, and crystallizes by due concentration in blue prismatic needles, containing two eq. of water; Cu Cl + 2 HO, which are deliquescent and very soluble in alcohol. When heated they fuse, lose water, and the anhydrous chloride in form of a yellow powder is left; but the heat must not exceed 400°, as beyond that degree the chloride loses half its chlorine, and is converted into the dichloride. *Its eq. is* 66·02; *symb.* Cu + Cl, or CuCl.

Diniodide of Copper.—This substance is obtained by adding iodide of potassium to a solution made of the sulphates of the protoxides of copper and iron, both in crystals, in the ratio of 1 to $2\frac{1}{4}$, when the protoxide of iron takes the oxygen of the oxide of copper and the iodine the metallic copper, forming a white precipitate, the diniodide. It may be dried, and will bear a high temperature in close vessels, without change; but if heated with the oxides of iron, manganese, or copper, iodine is expelled and the copper oxidized.

Its eq. is 189·5; *symb.* 2Cu + I, or Cu_2I.

Iodide of Copper is scarcely known. For on mixing a salt of oxide of copper with iodide of potassium, iodine is set free and the diniodide of copper falls. A small quantity of iodide of copper remains in solution.

Sulphurets of Copper.—The *disulphuret* is a natural production, well known to mineralogists under the name of *copper glance;* and in combination with protosulphuret of iron, it is a constituent of variegated copper ore. It is formed artificially by heating copper filings with a third of their weight of sulphur, the combination being attended with such free disengagement of heat, that the mass becomes vividly luminous.

Its eq. is 79·3; *symb.* 2Cu + S, or Cu_2S.

Sulphuret of Copper is formed by the action of hydrosulphuric acid on a salt of copper. When ignited without exposure to the air, it loses half of its sulphur, and is converted into the disulphuret.

Its eq. is 47·7; *symb.* Cu + S, or CuS.

Phosphurets of Copper.—Rose states that the triphosphuret is generated by the action of phosphuretted hydrogen gas on dichloride of copper, the mutual interchange of elements being such that

3 eq. Dichloride of Copper	$3Cu_2Cl$	yield	2 eq. Triphosphuret	$2Cu_3P$.
and 1 eq. Phosphuretted Hyd.	P_2H_3		and 3 eq. Hydrochl. Acid	3 HCl.

The subsesquiphosphuret is formed by a similar interchange between chloride of copper and phosphuretted hydrogen, so that

3 eq. Chloride of Copper	3CuCl	yield	1 eq. Subsesquiphosphuret	Cu_2P_3
and 1 eq. Phosp. Hyd.	P_2H_3		and 3 eq. Hydrochl. Acid	3HCl.

Rose obtained the protosulphuret by the action of hydrogen gas on phosphate of protoxide of copper at a red heat. All these phosphurets resemble each other, being pulverulent, of a grey colour, insoluble in hydrochloric acid, oxidized and dissolved by nitric acid, and burn with a phosphorous flame before the blowpipe. A phosphuret of copper is also obtained by transmitting phosphuretted hydrogen gas through a solution of sulphate of oxide of copper; but the dark precipitate which falls seems to be a variable mixture of different phosphurets, phosphoric acid being generated at the same time. (An. de Ch. et Ph. li. 47.)

SECTION XVI.

LEAD.

Hist. and Prep.—This metal was well known to the ancients. As a native production it is very rare; but in combination with sulphur it occurs in great quantity. All the lead of commerce is extracted from the native sulphuret, the *galena* of mineralogists. This ore, in the state of a coarse powder, is heated in a reverberatory furnace; when part of it is oxidized, yielding sulphate of protoxide of lead, sulphuric acid, which is evolved, and free oxide of lead. These oxidized portions then react on sulphuret of lead: by the reaction of two eq. of

oxide of lead and one of the sulphuret, three eq. of metallic lead and one of sulphurous acid result; while one equivalent of the sulphuret and one of sulphate mutually decompose each other, giving rise to two eq. of sulphurous acid and two of metallic lead. The slag which collects on the surface of the fused lead contains a large quantity of sulphate of protoxide of lead, and is decomposed by the addition of quicklime, the oxide so separated reacting as before on sulphuret of lead. The lead of commerce commonly contains silver, iron, and copper.

Prop.—It has a bluish-grey colour, and when recently cut, a strong metallic lustre; but soon tarnishes by exposure to the air, acquiring a superficial coating of carbonate of protoxide of lead. (Christison.) Its sp. gr. is 11·381. It is soft, flexible, and inelastic. It is both malleable and ductile, possessing the former property in particular to a considerable extent. In tenacity, it is inferior to all ductile metals. It fuses at about 612°, and when slowly cooled forms octohedral crystals. It may be heated to whiteness in close vessels without subliming.

Lead absorbs oxygen quickly at high temperatures. When fused in open vessels, a grey film is formed upon its surface, which is a mixture of metallic lead and protoxide; and when strongly heated, it is dissipated in fumes of the protoxide. In distilled water, previously boiled and preserved in close vessels, it undergoes no change; but in open vessels it is oxidized with considerable rapidity, yielding minute, shining, brilliantly white, crystalline scales of carbonate of the protoxide, the oxygen and carbonic acid being derived from the air. The presence of saline matter in water retards the oxidation of the lead; and some salts, even in very minute quantity, prevent it altogether. The protecting influence, exerted by certain substances, was first noticed by Guyton Morveau; but it has been minutely investigated by Christison of Edinburgh, who has discussed the subject in his excellent Treatise on Poisons. He finds that the preservative power of neutral salts is materially connected with the insolubility of the compound which their acid is capable of forming with lead. Thus, phosphates and sulphates, as well as chlorides and iodides, are highly preservative; so small a quantity as 1-30,000th part of phosphate of soda or iodide of potassium in distilled water preventing the corrosion of lead. In a preservative solution the metal gains weight during some weeks, in consequence of its surface gradually acquiring a superficial coating of carbonate, which is slowly decomposed by the saline matter of the solution. The metallic surface being thus covered with an insoluble film, which adheres tenaciously, all further change ceases. Many kinds of spring water, owing to the salts which they contain, do not corrode lead; and hence, though intended for drinking, it may be safely collected in leaden cisterns. Of this, the water of Edinburgh is a remarkable instance.

Lead is not attacked by the hydrochloric or the vegetable acids, though their presence, at least in some instances, accelerates the absorption of oxygen from the atmosphere in the same manner as with copper. Cold sulphuric acid does not act upon it; but when boiled in that liquid, the lead is slowly oxidized at the expense of the acid. The only proper solvent for lead is nitric acid. This reagent oxidizes it rapidly, and forms with its oxide a salt which crystallizes in opaque octohedrons by evaporation.

From my experiments on the composition of the protoxide of lead, and of the nitrate and sulphate of that oxide, I have deduced 103·6 as the eq. a number which agrees very closely with the researches of Berzelius on the same subject.

(Phil. Trans. 1833, part ii.) Its symb. is Pb. The composition of its compounds described in this section is as follows :—

	Lead.			Equiv.	Formulæ.
Dinoxide	207·2	2 eq. + Oxygen	8	1 eq. = 215·2	2Pb + O or Pb_2O.
Protoxide	103·6	1 eq. + ...	8	1 eq. = 111·6	Pb + O or PbO.
Sesquioxide	207·2	2 eq. + ...	24	3 eq. = 231·2	2Pb + 3O or Pb_2O_3.
Peroxide	103·6	1 eq. + ...	16	2 eq. = 119·6	Pb + 2O or PbO_2.
Red Oxide	310·8 or Protox. 223·2	3 eq. + ... or 2 eq. + Perox. 119·6	32	4 eq. = 342·8 1 eq.	3Pb + 4O. 2PbO + PbO_2.
Chloride	103·6	1 eq. + Chlorine	35·42	1 eq. = 139·02	Pb + Cl.
Iodide	103·6	1 eq. + Iodine	126·3	1 eq. = 229·9	Pb + I.
Bromide	103·6	1 eq. + Bromine	78·4	1 eq. = 182	Pb + Br.
Fluoride	103·6	1 eq. + Fluorine	18·68	1 eq. = 122·28	Pb + F.
Sulphuret	103·6	1 eq. + Sulphur	16·1	1 eq. = 119·7	Pb + S.
Phosphuret, Carburet	Composition uncertain.				

Dinoxide of Lead.—Dulong observed that on heating dry oxalate of protoxide of lead in a glass tube to low redness, air being excluded, a mixture of carbonic acid and carbonic oxide gases is evolved, and a suboxide remains of a dark grey, nearly black, colour. Boussingault has lately proved that it is a dinoxide. It does not unite with acids, but is resolved by them into a salt of the protoxide with separation of metallic lead. (An. de Ch. et Ph. liv. 263.) *Its eq. is* 215·2; *symb.* 2Pb + O, or Pb O.

Protoxide.—Prep.—This oxide is prepared on a large scale by collecting the grey film which forms on the surface of melted lead, and exposing it to heat and air until it acquires a uniform yellow colour. In this state it is the *massicot* of commerce; and when partially fused by heat the term *litharge* is applied to it. As thus procured it is always mixed with the red oxide. It may be obtained pure by adding ammonia to a cold solution of nitrate of protoxide of lead until it is faintly alkaline, washing the precipitated subnitrate with cold water, and when dry, heating it to moderate redness for an hour in a platinum crucible. An open fire should be used, and great care taken to prevent combustible matter in any form from contact with the oxide.

Prop.—It is red while hot, but has a rich lemon-yellow colour when cold, is insoluble in water, fuses at a bright red heat, and is fixed and unchangeable in the fire. Its sp. gr. is 9·4214. The fused protoxide has a highly foliated texture, and is very tough, so as to be pulverized with difficulty. By transmitted light it is yellow; but by reflected light it appears green in some parts and yellow in others. Heated with combustible matters it parts with oxygen, and is reduced. From its insolubility it does not change the vegetable colours under common circumstances; but when rendered soluble by a small quantity of acetic acid, it has a distinct alkaline reaction. It unites with acids, and is the base of all the salts of lead, most of which are of a white colour, and isomorphous with the salts of baryta and strontia. From its solutions it is precipitated by pure alkalies as a white hydrate, which is redissolved by potassa in excess; as a white carbonate, which is the well-known pigment *white lead*, by alkaline carbonates; as a white sulphate by soluble sulphates; as a dark brown sulphuret by hydrosulphuric acid; and as yellow iodide of lead by hydriodic acid or iodide of potassium.

With regard to the poisonous property of the salts of lead, a remarkable fact has been observed by my colleague Dr. A. T. Thomson, who has proved that of all the ordinary preparations of lead, the carbonate is by far the most virulent poison. Any salt of lead which is easily convertible into the carbonate, as for instance the subacetate, is also poisonous; but he has given large doses of the nitrate of the protoxide and chloride of lead to rabbits without producing perceptible inconvenience. He finds that acetate of protoxide of lead, mixed with vinegar to prevent the formation of any carbonate, may be freely and safely administered in medical practice.

The best method of detecting the presence of lead in wine or other suspected mixed fluids is by means of hydrosulphuric acid. The sulphuret of lead, after being collected on a filter and washed, is to be digested in nitric acid diluted with twice its weight of water, until the dark colour of the sulphuret disappears. The solution of the nitrate should then be brought to perfect dryness on a watch-glass, in order to expel the excess of nitric acid, and the residue be redissolved in a small quantity of cold water. On dropping a particle of iodide of potassium into a portion of this liquid, yellow iodide of lead will instantly appear.

Protoxide of lead unites readily with earthy substances, forming with them a transparent colourless glass. Owing to this property it is much employed for glazing earthenware and porcelain. It enters in large quantity into the composition of flint glass, which it renders more fusible, transparent, and uniform.

Lead is separated from its salts in the metallic state by iron or zinc. The best way of demonstrating this fact is by dissolving one part of acetate of protoxide of lead in 24 of water, and suspending a piece of zinc in the solution by means of a thread. The lead is deposited upon the zinc in a peculiar arborescent form, giving rise to the appearance called *arbor saturni*.

Its eq. is 111·6; *symb.* Pb + O, Ṗb, or PbO.

Red Oxide.—Prep.—This compound, the *minium* of commerce, is employed as a pigment, and in the manufacture of flint glass. It is formed by oxidizing lead by heat and air without allowing it to fuse, and then exposing it in open vessels to a temperature of 600° or 700°, while a current of air plays upon its surface. It slowly absorbs oxygen and is converted into minium.

Prop.—This oxide does not unite with acids. When heated to redness, it gives off pure oxygen gas, and is reconverted into the protoxide. When digested in nitric acid it is resolved into protoxide and peroxide of lead, the former of which unites with the acid, while the latter remains as an insoluble powder. From the facility with which this change is effected even by acetic acid, most chemists consider red lead, not so much as a definite compound of lead and oxygen, but as a salt composed of the protoxide and peroxide, as stated at page 360. This oxide has been long considered as a sesquioxide, an error first corrected by Dalton (New System of Chemistry, ii. 41), whose observation has been confirmed by Dumas and Phillips. (An. de Ch. et Ph. xlix. 398, and Phil. Mag. N. S. iii. 125.) Dumas shows that the minium is not uniform in composition, but consists of variable mixtures of the protoxide with real red lead. The former may be oxidized by continued exposure to air and heat, and may be dissolved by acetic acid very much diluted with cold water.

Its eq. is 342·8; *symb.* 2 PbO + PbO_2.

Sesquioxide.—Winkelblech (Ann. der Pharm. xxi. 29) has proved the existence of this compound. It is prepared by adding hypochlorite of soda to a solution of

protoxide of lead in caustic potash. It forms a reddish-yellow insoluble powder, which is resolved by heat and by acids into protoxide and oxygen. *Its eq. is* 231·2; *symb.* Pb_2O_3. Red lead may be a compound of 1 at. sesquioxide and 1 at. protoxide, Pb_2O_3, PbO = Pb_3O_4.

Peroxide.—Prep.—This oxide may be obtained by the action of nitric acid on minium, as just mentioned; by fusing protoxide of lead with chlorate of potassa, at a temperature short of redness, and removing the chloride of potassium by solution in water; and by transmitting a current of chlorine gas through a solution of acetate of the protoxide of lead, or the protoxide suspended in water. In the last the reaction is such, that

1 eq. Chlorine and 2 eq. Protox. Lead	yield	1 eq. Perox. Lead and 1 eq. Chloride Lead
Cl 2PbO		PbO_2 PbCl.

The chloride is removed by washing with warm water.

Prep.—It is of a puce colour, is insoluble in water, and is resolved by strong ox-acids, such as the sulphuric and nitric, into a salt of the protoxide and oxygen gas. With hydrochloric acid it yields chlorine gas and chloride of lead. At a red heat it emits oxygen gas and is converted into the protoxide.

Its eq. is 119·6; *symb.* Pb + 2O, $\ddot{P}b$, or PbO_2.

Chloride of Lead.—This compound, sometimes called *horn lead*, is slowly formed by the action of chlorine gas on thin plates of lead, and may be obtained more easily by adding hydrochloric acid or a solution of sea-salt to acetate or nitrate of oxide of lead dissolved in water. This chloride dissolves to a considerable extent in hot water, especially when acidulated with hydrochloric acid, and separates on cooling in small acicular anhydrous crystals of a white colour. It fuses at a temperature below redness, and forms as it cools a semi-transparent mass, which has a density of 5·133. It bears a full red heat in close vessels without subliming; but in open vessels it smokes from spurious evaporation, loses some of its chlorine and absorbs oxygen, yielding an oxychloride of a yellow colour. [It combines in several proportions with oxide of lead and forms a number of basic compounds—as the *bibasic chloride* PbCl + 2PbO a crystalline mineral found in Somersetshire, England. The *tribasic chloride of lead* PbCl + 3PbO + 3HO, precipitated by ammonia from a solution of chloride of lead; and the *surbasic chloride of lead* formed by digesting 1 part of common salt with 7 parts of oxide of lead, and fusing the resulting oxichloride. In this form it constitutes a beautiful yellow pigment, known as Turner's patent yellow.] *Its eq. is* 139·02; *symb.* Pb + Cl, or PbCl.

Iodide of Lead is easily formed by mixing a solution of hydriodic acid in excess with the nitrate of protoxide of lead dissolved in water; and it is of a rich yellow colour. It is dissolved by boiling water, forming a colourless solution, and is deposited on cooling in yellow crystalline scales of a brilliant lustre.

Its eq. is 229·9; *symb.* Pb + I, or PbI.

Bromide of Lead.—It falls as a white crystalline powder, of sparing solubility in water, when a soluble salt of lead is mixed with bromide of potassium in solution. Exposed to heat it fuses into a red liquid which becomes yellow when cold.

Its eq. is 182; *symb.* Pb + Br, or PbBr.

Fluoride of Lead is formed by mixing hydrofluoric acid with acetate of protoxide of lead, and falls as an uncrystalline white powder of very sparing solubi-

lity. It is soluble in nitric and hydrochloric acids, but is decomposed when the solution is evaporated.

Its eq. is 122·28; *symb.* Pb + F, or PbF.

Sulphurets of Lead.—It is probable that lead unites with sulphur in several different proportions; but the only one of these compounds well known to chemists in the native sulphuret, *galena*, which occurs in cubic crystals, or in forms allied to the cube. It may be formed artificially by fusing lead with sulphur, or by the action of hydrosulphuric acid on a salt of lead.

Its eq. is 119·7; *symb.* Pb + S, or PbS.

Phosphuret of Lead has been little examined. It may be formed by heating phosphate of oxide of lead with charcoal, by mixing a solution of phosphorus in alcohol or ether with the solution of a salt of lead, or by the action of phosphuretted hydrogen on a similar solution.

Carburet of Lead may be obtained by reducing oxide of lead in a state of fine division and intimate admixture with charcoal. It is also generated, when salts of lead, which contain a vegetable acid, are decomposed by heat in close vessels. (Berzelius.)

SECTION XVII.

ARSENIC.

Hist. and Prep.—Metallic arsenic sometimes occurs native but more frequently it is found in combination with other metals, and especially with cobalt and iron. On roasting these arsenical ores in a reverberatory furnace, the arsenic, from its volatility, is expelled, combines with oxygen as it rises, and condenses into thick cakes on the roof of the chimney. The sublimed mass, after being purified by a second sublimation, is the virulent poison known by the name of *arsenic* or *white oxide of arsenic*. From this substance the metal itself is procured by heating it with charcoal. The most convenient process is to mix the white oxide with about twice its weight of black flux, and expose the mixture to a red heat in a hessian crucible, over which is luted an empty crucible for receiving the metal. The reduction is easily effected, and metallic arsenic collects in the upper crucible, which should be kept cool for the purpose of condensing the vapour.

Prop.—An exceedingly brittle metal, of a strong metallic lustre, and white colour, running into steel grey. Its structure is crystalline, and when slowly sublimed it is said to crystallize in rhombohedrons. Its sp. gr. is 5·8843. When heated to 356° it sublimes without previously liquefying; for its point of fusion is far above that of its sublimation, and has not hitherto been determined. Its vapour has a strong odour of garlic; a property which affords a distinguishing character for metallic arsenic, as it is not possessed by any other metal, with the exception perhaps of zinc, which is said to emit a similar odour when thrown in powder on burning charcoal, an effect, however, most probably due to the presence of arsenic in the zinc. In close vessels it may be sublimed without

change; but if atmospheric air be admitted, it is rapidly converted into the white oxide. According to Hahneman it is slowly oxidized and dissolved by being boiled in water. In general it speedily tarnishes by exposure to air and moisture, acquiring upon its surface a dark film which is extremely superficial; but Berzelius remarks that he has kept some specimens in open vessels for years without loss of lustre, while others are oxidized through their whole substance, and fall into powder. It has lately been suggested (Liebig's Annalen, 1840), that this effect is owing to the presence of potassium, derived from the black flux. The arsenic sublimed from the cakes which occur in commerce is permanent in the air. The product of this spontaneous oxidation, which is known abroad under the name of *fly powder*, is supposed by Berzelius to be an oxide; but it is more generally regarded as a mixture of white oxide and metallic arsenic.

The eq. of arsenic, as inferred by Berzelius from the composition of arsenious and arsenic acids, is 37·7. Its symb. is As. The compounds of this metal described in this section are thus constituted:—

	Arsenic.			Equiv.	Formulæ.
Arsenious Acid	75·4	2 eq.+Oxygen	24	3 eq.= 99·4	2As+3O or As_2O_3.
Arsenic Acid	75·4	2 eq.+do.	40	5 eq.=115·4	2As+5O or As_2O_5.
Protochloride	37·7	1 eq.+Chlorine	35·42	1 eq.= 73·12	As+Cl or AsCl.
Sesquichloride	75·4	2 eq.+do.	106·26	3 eq.=181·66	2As+3Cl or As_2Cl_3.
Periodide	75·4	2 eq.+Iodine	631.5	5 eq.=706·9	2As+5I or As_2I_5.
Sesquibromide	75·4	2 eq.+Bromine	235·2	3 eq.=313·6	2As+3Br or As_2Br_3.
Protohyduret	37·7	1 eq.+Hydrogen	1	1 eq.= 38·7	As+H or AsH.
Arseniur. Hydro.	75·4	2 eq.+do.	3	3 eq.= 78·4	2As+3H or As_2H_3.
Protosulphuret	37·7	1 eq.+Sulphur	16·1	1 eq.= 53·8	As+S or AsS.
Sesquisulphuret	75·4	2 eq.+do.	48·3	3 eq.=123·7	2As+3S or As_2S_3.
Persulphuret	75·4	2 eq.+do.	80·5	5 eq.=155·9	2As+5S or As_2S_5.

Arsenious Acid.—Prep.—This compound, frequently called *white arsenic* and *white oxide of arsenic*, is always generated when arsenic is heated in open vessels, and may be prepared by digesting the metal in dilute nitric acid. The white arsenic of commerce is derived from the native arseniurets of cobalt, being sublimed during the roasting of these ores for the preparation of zaffre, and it is purified by a second sublimation in iron vessels.

Prop.—It is commonly sold in the state of a fine white powder; but when first sublimed, it is in the form of brittle masses, more or less transparent, colourless, of a vitreous lustre, and conchoidal fracture. This glass, which may also be obtained by fusion, gradually becomes opaque without undergoing any apparent change of constitution, either with respect to water or any other substance; but the change is certainly promoted by exposure to the atmosphere. Its sp. gr. is 3·7. At 380° it is volatilized, yielding vapours which do not possess the odour of garlic, and which condense unchanged on cold surfaces. Its point of fusion is rather higher than that at which it sublimes; and therefore, in order to be fused, it must either be heated under pressure, or its temperature be suddenly raised above 380°. Arsenious acid is *dimorphous*, that is, susceptible of assuming two crystalline forms belonging to different systems of crystallization. By slow sublimation in a glass tube it is always obtained in distinct octohedral crystals of adamantine lustre and perfectly transparent. Its unusual form is that of six-sided scales derived from a rhombic prism, and was first lately found by Wöhler among the products in a manufacture of smalt: the conditions for enabling it to

assume this form are unknown, and by subliming the crystals, they crystallized in octohedrons. (An. de Ch. et Ph. li. 201.)

The taste of arsenious acid is stated differently by different persons. It is prevalently thought to be acrid; but I am satisfied from personal observation that it may be deliberately tasted without exciting more than a very faint impression of sweetness, and perhaps of acidity. The acrid taste ascribed to it has probably been confounded with the local inflammation, by which its application, if of some continuance, is followed. (Christison on Poisons.) It reddens vegetable blue colours feebly, an effect which is best shown by placing the acid in powder on moistened litmus paper. It combines with salifiable bases, forming salts which are termed *arsenites*.

According to the experiments of Klaproth and Bucholz, 1000 parts of boiling water dissolve 77·75 of arsenious acid; and the solution, after having cooled to 60° F., contains only 30 parts. The same quantity of water at 60°, when mixed with the acid in powder, dissolves only two parts and a half. Guibourt has lately observed that the transparent and opaque varieties of arsenic differ in solubility. He found that 1000 parts of temperate water dissolve, during 36 hours, 9·6 of the transparent, and 12·5 of the opaque variety: that the same quantity of boiling water dissolves 97 parts of the transparent variety, retaining 18 when cold, but takes up 115 of the opaque variety, and retains 29 on cooling. By the presence of organic substances, such as milk or tea, its solubility is materially impaired. (Christison on Poisons.)

When metallic arsenic is sharply heated with hydrate of potassa, pure hydrogen gas is evolved, and a mass is left consisting of arseniuret of potassium and arsenite of potassa; facts, which prove that a portion of arsenic is oxidized, and derives its oxygen partly from water and partly from potassa. If the heat is raised to redness, the arsenious acid is resolved into arsenic acid and metal, the former remaining as an arseniate, while the latter is expelled. Similar phenomena ensue with the hydrates of soda, baryta, and lime; except that with the two latter no arsenic acid is produced. (Soubeiran in An. de Ch. et Ph. xliii. 410.)

Its eq. 99·4; *symb.* 2As + 3O, $\ddot{\underline{\text{As}}}$, or As_2O_3.

The frequent exhibition of arsenious acid as a poison renders the detection of this compound an object of great importance to medical practitioners as well as to the chemist. In this as in all similar inquiries, the object to be held in view is the discovery of a few decisive characters, by means of which the poison may be distinguished from all other bodies, and when present but in small quantity, either in pure water, or in any fluids likely to be met with in the stomach, may with certainty be detected. The attention should be fixed on one or two tests of admitted value, and all others be set aside. With this feeling I shall indicate the mode of applying the four principal tests, namely, the ammonio-nitrate of silver, ammonio-sulphate of copper, hydrosulphuric acid, and hydrogen gas.

1. *Ammonio-nitrate of Silver.*—Arsenious acid is not precipitated by nitrate of oxide of silver unless an alkali is present, to neutralize the nitric acid. Ammonia is commonly employed for the purpose; but as arsenite of oxide of silver is very soluble in ammonia, an excess of the alkali would retain the arsenite in solution. To remedy this inconvenience, Hume, of Long Acre, proposed to employ the ammoniacal nitrate of silver, which is made by dropping ammonia into a rather strong solution of lunar caustic till the oxide of silver at first thrown down is *nearly* all dissolved. The liquid thus prepared contains the precise quantity of

ammonia which is required; and when mixed with arsenious acid, two neutral salts result, the soluble nitrate of ammonia, and the insoluble yellow arsenite of oxide of silver. Ammoniacal nitrate of silver likewise diminishes the risk of fallacy that might arise from the presence of phosphoric acid. Phosphate of oxide of silver is so very soluble in ammonia, that when a neutral phosphate is mixed with the ammoniacal nitrate of silver, the resulting phosphate is held almost entirely in solution by the free ammonia.

This test, however, even in its improved state, is still liable to objection. For when arsenious acid in small proportion is mixed with sea salt, or animal and vegetable infusions, the arsenite of oxide of silver either does not subside at all, or is precipitated in so impure a state that its characteristic colour cannot be distinguished. Several methods have been proposed for obviating this source of fallacy; but Christison has shown, that this test, taken singly, cannot be relied on in practice.

2. *Ammonio-sulphate of copper*, which is made by adding ammonia to a solution of sulphate of oxide of copper until the precipitate at first thrown down is nearly all redissolved, occasions with arsenious acid a green precipitate, which has been long used as a pigment under the name of *Scheele's green*. This test, though well adapted for detecting arsenious acid dissolved in pure water, is very fallacious when applied to mixed fluids. Christison has proved that ammoniacal sulphate of copper produces in some animal and vegetable infusions, containing no arsenic, a greenish precipitate, which may be mistaken for Scheele's green: whereas in other mixed fluids, such as tea and porter, to which arsenic has been previously added, it occasions none at all, if the arsenious acid is in small quantity. In some of these liquids, a free vegetable acid is doubtless the solvent; for arsenite of oxide of copper is also dissolved by tannic acid, and perhaps by other vegetable as well as some animal principles.

3. When a current of *hydrosulphuric acid gas* is conducted through a solution of arsenious acid, the fluid immediately acquires a yellow colour, and in a short time becomes turbid, owing to the formation of orpiment, the sesquisulphuret of arsenic. The precipitate is at first partially suspended in the liquid; but as soon as free hydrosulphuric acid is expelled by heating the solution, it subsides perfectly, and may easily be collected on a filter. One condition, however, must be observed in order to ensure success, namely, that the liquid does not contain a free alkali; for sulphuret of arsenic is dissolved with remarkable facility by pure potassa or ammonia. To avoid this fallacy, it is necessary to acidulate the solution with a little acetic or hydrochloric acid. Hydrosulphuric acid likewise acts on arsenic in all vegetable and animal fluids if previously boiled, filtered, and acidulated.

But it does not necessarily follow, because hydrosulphuric acid causes a yellow precipitate, that arsenic is present; since there are not less than four other substances, namely, selenium, cadmium, tin, and antimony, the sulphurets of which, judging from their colour alone, might possibly be mistaken for orpiment. From these and all other substances whatever, the sulphuret of arsenic may be thus distinguished.—On drying the sulphuret, mixing it with black flux, and heating the mixture contained in a glass tube to redness by means of a spirit-lamp, decomposition ensues, and a metallic crust of an iron-grey colour externally, and crystalline on its inner surface, is deposited on the cool part of the tube. This character alone is quite satifactory; but it is easy to procure additional evidence, by reconverting the metal into arsenious acid, so as to

obtain it in the form of resplendent octohedral crystals. This is done by holding that part of the tube to which the arsenic adheres about three-fourths of an inch above a very small spirit-lamp flame, so that the metal may be slowly sublimed. As it rises in vapour, it combines with oxygen, and is deposited in crystals within the tube. The character of these crystals with respect to volatility, lustre, transparency, and form, is so exceedingly well marked, that a practised eye may safely identify them, though their weight should not exceed the 100th part of a grain. This experiment does not succeed unless the tube be quite clean and dry.

The only circumstance which occasions a difficulty in the preceding process, is the presence of organic substances, which cause the precipitate to subside imperfectly, render filtration tedious, and froth up inconveniently during the reduction. Hence, if so abundant as materially to impede filtration and prevent the liquid from becoming clear, they should be removed before hydrosulphuric acid is employed. This is often sufficiently effected by acidulating with acetic acid, by which caseous and albuminous substances are coagulated; but a more complete separation is accomplished by evaporating the solution at a moderate heat to dryness, redissolving anew by boiling successive portions of distilled water on the residue, and then filtering the solution after it has cooled. Most of the organic matters are thus rendered insoluble. It is of course necessary towards the close of the desiccation to guard against too high a temperature, since otherwise the arsenic itself might be expelled. (Christison on Poisons, 2nd edition, 252).

The black flux employed in the processes for reducing arsenic, is prepared by deflagrating a mixture of bitartrate of potassa with rather less than half its weight of nitre. The nitric and tartaric acids undergo decomposition, and the solid product is charcoal derived from tartaric acid, and pure carbonate of potassa. As it contains a deliquescent salt, it should be kept in well-stopped bottles. When this substance is employed in the reduction of arsenious acid or its salts, the charcoal is of course the decomposing agent; but the alkali is of use in retaining the arsenious acid until the temperature is sufficiently high for its decomposition. With sulphuret of arsenic, on the contrary, the alkali is the active principle, the potassium of which unites with sulphur and liberates the arsenic; but the charcoal operates usefully by facilitating the decomposition of the alkaline carbonate. The whole of the arsenic, however, is not sublimed; but part of it enters into union with potassium, and remains with the flux.

4. For the application of hydrogen in testing for arsenic we are indebted to the ingenuity of Marsh (Edinburgh New Phil. Journ. October, 1836). Its employment is dependent on the fact, that whenever hydrogen in the nascent state is brought into contact with any compound of oxygen and arsenic, the latter is instantly decomposed, and water and a gaseous compound of arsenic and hydrogen, the arseniuretted hydrogen, are generated. If the gas be inflamed as it escapes into the air through a fine tube, it burns with the production of the vapour of water, while metallic arsenic or arsenious acid is deposited, according as the supply of oxygen be more or less abundant. Hence if a piece of cold window-glass be held in the flame, its surface is instantly covered with a thin coating of metallic arsenic; but if the flame be made to burn in the centre of a glass tube open at both extremities, the inner surface of the latter is covered in the course of half a minute with arsenious acid. If the tube be held obliquely against it, both depositions take place, and on bringing the tube, while still warm, to the nose a peculiar odour of arsenic is readily perceived.

The experiment is made in the following manner. The suspected substances, if in the solid form, such as bread, must first be boiled with a few ounces of distilled water, and the clear solution while still hot is to be separated from the solid parts by filtration. The same process must be adopted with very thick soups, or the contents of the stomach; while thin soups, wine, beer, coffee, tea, and similar fluids require no previous preparation. The liquid is then mixed with a few ounces of dilute sulphuric acid, and introduced into the apparatus represented by the accompanying woodcut. This consists of two parts, a cylindrical glass vessel *a*, and a capped bell jar furnished with a stop-cock and small gas-burner; to the stop-cock is suspended a string, to which a fragment of zinc *c*, reaching nearly to the bottom of the bell jar, is attached. The stop-cock *b* being open, when the liquid to be examined is poured into *a* it rises in the bell jar, and so much must be used that the latter is almost full. By the action of the dilute acid on the zinc hydrogen is rapidly evolved, and after permitting a small quantity to escape in order to ensure the removal of atmospheric air from the vessel, the stop-cock is turned, and the gas allowed to accumulate in the bell jar. On burning it the presence of arsenic is readily recognized by the characters above stated, and by the light blue tint it communicates to the flame. The extreme delicacy of this method has been recently amply attested by Liebig and Mohr in their valuable journal (Lieb. Annal. xxiii. 217). To avoid every source of fallacy, however, several precautions are necessary: the most important are—to ensure the perfect purity of the reagents used, as arsenic is commonly contained both in the zinc and sulphuric acid of commerce; to employ a fresh piece of zinc with each experiment, as a portion of the arsenic in the solution is deposited as a metallic crust on the zinc, which is thus rendered impure; and to prove experimentally the purity of the apparatus before each experiment. Liebig recommends that a fragment of porcelain be held in the flame instead of the window-glass, as a very thin film of metallic arsenic is better seen on the white opaque ground than on the transparent glass. He observes, too, that owing to the rapid evolution of the gas, other metals, as for example iron, which may be contained in the solution, being carried up by the hydrogen and deposited on the porcelain, may prove a source of error to the inexperienced. For this reason he recommends that the gas, instead of being burnt by the jet, be transmitted through a fine tube of difficultly fusible glass; on bringing a part of the glass to a red-heat by a spirit-lamp flame, the arseniuretted hydrogen is decomposed as it passes, and the metallic arsenic is deposited just beyond the heated part of the glass, while other metals are deposited in the hot parts themselves.



It was hoped that this test might prove infallible even in the hands of inexperienced chemists; but according to a recent discovery of Mr. L. Thompson, antimony combines with hydrogen, forming with it a gaseous compound which is similar to arseniuretted hydrogen in the mode of its production, in the colour of its flame when burnt, and in the deposition of a metallic crust on a cold surface. The two gases may nevertheless be readily distinguished by decomposing them by means of heat while passing through a fine tube, as was proposed by Liebig for arseniuretted hydrogen; for although the metallic crusts are very similar, yet by attention to the directions of page 366, the crust of arsenic cannot be mistaken for that of antimony. For by bringing the spirit-lamp flame under

the crust when the stream of hydrogen has ceased to pass along the tube, if it be arsenic it rapidly volatilizes and condenses again on the neighbouring cool parts of the tube; the antimonial crust, on the contrary, when thus heated, fuses, runs into small globules, and assumes the appearance of mercury. If the tube be now detached from the vessel in which the hydrogen is generated, and the flame of the spirit-lamp cautiously applied to the metal, the arsenic volatilizes without fumes, and distinct octohedral crystals of arsenious acid are formed on the upper parts of the tube; with antimony, on the contrary, dense white fumes are produced and an amorphous white powder is deposited. The different characters of the two substances may be carried still further; if the tube be boiled in a small quantity of pure water, the arsenious acid is dissolved, and the first two tests may be successfully employed; the antimony, on the contrary, is insoluble.

Arsenic Acid.—This compound is made by dissolving arsenious acid in concentrated nitric, mixed with a little hydrochloric acid, distilling in glass till it acquires the consistence of syrup, and then exposing it in a platinum crucible for some time to a heat somewhat short of low redness to expel the nitric acid. The acid thus prepared has a sour metallic taste, reddens vegetable blue colours, and with alkalies forms neutral salts, which are termed *arseniates*. It is much more soluble in water than arsenious acid, dissolving in five or six times its weight of cold, and in a still smaller quantity of hot water. It forms irregular grains when its solution is evaporated, but does not crystallize. If strongly heated, it fuses into a glass which is deliquescent. When urged by a very strong red heat, it is resolved into oxygen and arsenious acid. It is an active poison.

Arsenic acid is decomposed by hydrosulphuric acid gas, and yields a sulphuret of arsenic very like orpiment in colour, but containing a greater proportional quantity of sulphur. The soluble arseniates, when mixed with the nitrates of lead and silver, form insoluble arseniates, the former of which has a white, and the latter a brick-red colour. They dissolve readily in dilute nitric acid, and when heated with charcoal yield metallic arsenic.

Its eq. is 115·4; *symb.* $2\,As + 5O$, $\underline{\overset{\cdot\cdot\cdot\cdot\cdot}{As}}$, or As_2O_5.

Protochloride of Arsenic.—It is prepared, according to Dumas, by introducing into a tubulated retort a mixture of arsenious acid with ten times its weight of concentrated sulphuric acid; and after raising its temperature to near 212°, fragments of sea-salt are thrown in by the tubular. If the salt is added in successive small portions, scarcely any hydrochloric acid gas is evolved, and the pure chloride may be collected in cooled vessels. Towards the end of the process a little water frequently passes over with the chloride; but this hydrated portion does not mix with the anhydrous chloride, but swims on its surface. The hydrate may be decomposed, and a pure chloride obtained, by distilling the mixture from a sufficient quantity of concentrated sulphuric acid. Dumas considers this compound a protochloride of arsenic, so that it is probably different from that obtained by means of corrosive sublimate. (Quarterly Journal of Science, N. S. i. 235.)

Its eq. is 73·12; *symb.* $As + Cl$, or $AsCl$.

Sesquichloride of Arsenic.—When arsenic in powder is thrown into a jar full of dry chlorine gas, it takes fire, and sesquichloride of arsenic is generated; and the same compound may be formed by distilling a mixture of six parts of corrosive sublimate with one of arsenic. It is a colourless volatile liquid, which

fumes strongly on exposure to the air, hence called *fuming liquor* of *arsenic*, and is resolved by water into hydrochloric and arsenious acids. (Davy.)

Its eq. is 181·66; *symb.* 2As + 3Cl, or As_2Cl_3.

Periodide of Arsenic is formed by bringing its elements into contact, and promoting union by gentle heat. They form a deep red compound, which is resolved into arsenic and hydriodic acids by the action of water. (Plisson in An. de Ch. et Ph. xxxix. 266.)

Its eq. is 706·9; *symb.* 2As + 5I, or As_2I_5.

Sesquibromide of Arsenic.—The elements of this compound unite at the moment of contact, with vivid evolution of heat and light. Serullas prepared it by adding dry arsenic to bromine as long as light was emitted, the former being added in successive small quantities, to prevent the temperature from rising too high. The bromide is then distilled, and then collected in a cool receiver. (An. de Ch. et Ph. xxxviii. 318.)

This compound is solid at or below 68°, liquefies between 68° and 77°, and boils at 428°. As a liquid it is transparent and slightly yellow, and yields long prisms by evaporation. By water it is resolved into arsenious and hydrobromic acids.

Its eq. is 313·6; *symb.* 2As + 3Br, or As_2Br_3.

Protohyduret of Arsenic.—This compound, which is solid and of a brown colour, was discovered by Davy as well as Gay-Lussac and Thenard. The former prepared it by attaching a piece of arsenic to the negative wire during the decomposition of water by galvanism; and the French chemists, by the action of water on an alloy of potassium and arsenic.

Its eq. is 38·7; *symb.* As + H, or AsH.

Arseniuretted Hydrogen.—This gas, which was discovered by Scheele, has been studied by Proust, Trommsdorf, and others, but especially by Stromeyer. It is generally made by digesting an alloy of tin and arsenic in hydrochloric acid; but as thus prepared it is always mixed with free hydrogen. Soubeiran generated it by fusing arsenic with its own weight of granulated zinc, and decomposing the alloy with strong hydrochloric acid. The gas thus developed, is quite free from hydrogen, being absorbed without residue by a saturated solution of sulphate of oxide of copper. Its sp. gravity, according to Dumas, is 2·695. It is colourless, and has a fetid odour like that of garlic. It extinguishes bodies in combustion, but is itself kindled by them, and burns with a blue flame. It instantly destroys small animals that are immersed in it, and is poisonous to man in a high degree, having proved fatal to a German philosopher, the late M. Gehlen, and others. Water absorbs one-fifth of its volume, and acquires the odour of the gas. It is altogether destitute of the properties of an acid.

Arseniuretted hydrogen is decomposed by various agents. It suffers gradual decomposition when mixed with atmospheric air, water being formed, and metallic arsenic, together with a little oxide, deposited. With nitric acid, water is generated, and a deposite of metal takes place, which is subsequently oxidized. Chlorine decomposes it instantly with disengagement of heat and light, hydrochloric acid being generated, and the metal set free. With iodine it yields hydriodic acid gas and iodide of arsenic, and sulphur and phosphorus produce analogous changes. By its action on salts of the easily reducible metals, such as silver and gold, the metal is revived, and its oxygen uniting with the elements of the gas constitutes arsenious acid and water. With salts of copper the pro-

ducts are water and arseniuret of copper; and with several other metallic salts its action is similar.

Soubeiran observed that arseniuretted hydrogen in a glass tube is completely decomposed by the heat of a spirit-lamp, and that its hydrogen occupies one and a half as much space as when in combination. He has also confirmed the observation of Dumas, that when mixed with oxygen, and detonated by the electric spark, each volume of the gas, in forming water and arsenious acid, requires one and a half its volume of oxygen gas. The oxygen, therefore, is equally divided between the arsenic and hydrogen; and arseniuretted hydrogen consists of one eq. of arsenic and one and a half of hydrogen. By volume, it is composed of half a volume of the vapour of arsenic, and one and a half of hydrogen, condensed into one measure. (An. de Ch. et Ph. xliii. 407.)

Its eq. is 78·4; *symb.* 2As + 3H, or $As_2 H_3$.

Sulphurets of Arsenic.—Sulphur unites with arsenic in at least three proportions, forming compounds, two of which occur in the mineral kingdom, and are well known by the names of *realgar* and *orpiment*. Realgar or the protosulphuret may be formed artificially by heating arsenious acid with about half its weight of sulphur, until the mixture is brought into a state of perfect fusion. The cooled mass is crystalline, transparent, and of a ruby-red colour; and may be sublimed in close vessels without change.

Its eq. is 53·8; *symb.* As + S, or AsS.

Orpiment, or *sesquisulphuret* of arsenic may be prepared by fusing together equal parts of arsenious acid and sulphur; but the best mode of obtaining it quite pure is by transmitting a current of hydrosulphuric acid gas through a solution of arsenious acid. Orpiment has a rich yellow colour, fuses readily when heated, and becomes crystalline on cooling, and in close vessels may be sublimed without change. It is dissolved with great facility by the pure alkalies, and yields colourless solutions.

Orpiment is employed as a pigment, and is the colouring principle of the paint called *King's yellow*. Braconnot has proposed it likewise for dyeing silk, woollen, or cotton stuffs of a yellow colour; the cloth being soaked in a solution of orpiment in ammonia, and then suspended in a warm apartment. The alkali evaporates, and leaves the orpiment permanently attached to the cloth. (An. de Ch. et Ph. xii.)

Its eq. is 123·7; *symb.* 2AS + 3S, or As_2S_3.

Persulphuret of arsenic is prepared by transmitting hydrosulphuric acid gas through a moderately strong solution of arsenic acid; or by saturating a solution of arseniate of potassa or soda with the same gas, and acidulating with hydrochloric or acetic acid. The oxygen of the acid unites with the hydrogen of the gas, and persulphuret of arsenic subsides. In colour it is very similar to orpiment, is dissolved by pure alkalies, fuses by heat, and may be sublimed in close vessels without decomposition.

Its eq. is 155·9; *symb.* 2As + 5S, or As_2S_5.

The experiments of Orfila have proved that the sulphurets of arsenic are poisonous, though in a much less degree than the arsenious acid. The precipitated sulphuret is more injurious than the native orpiment. The only antidote of arsenious acid is hydrated peroxide of iron (Bunsen), the effects of which have been amply tested in Germany, and lately elucidated by Dr. D. Maclagan. (Edin. Med. and Surg. Journal, 1840.) It acts by forming an insoluble arsenite or arseniate; and must be used in the moist state, never having been dried; and also

in large quantity. The late edition (1840) of the Edinburgh Pharmacopœia gives a process for preparing it for this object.*

SECTION XVIII.

ANTIMONY.

Hist.—First made known as a metal in the 15th century by Basil Valentine, and is said to derive its name (*anti-moine*, *anti-monk*) from having proved fatal to some monks to whom it was given as a medicine. It sometimes occurs native; but its only ore which is abundant, and from which the antimony of commerce is derived, is the sulphuret. This ore, the *stibium* of the ancients, was long regarded as the metal itself, and was called *antimony*, or *crude antimony;* while the pure metal was termed the *regulus* of *antimony*.

Prep.—Either by heating the native sulphuret in a covered crucible with half its weight of iron filings; or by mixing it with two-thirds of its weight of cream of tartar and one-third of nitre, and throwing the mixture, in small successive portions, into a red-hot crucible. By the first process the sulphur unites with iron, and in the second it is expelled in the form of sulphurous acid; while the fused antimony, which in both cases collects in the bottom of the crucible, may be drawn off and received in moulds. The antimony, thus obtained, is not absolutely pure; and therefore, for chemical purposes, should be procured by heating the oxide with an equal weight of cream of tartar.

Prop.—A brittle metal, of a white colour, running into bluish-grey, and is possessed of considerable lustre. Its sp. gr. is nearly 6·7. At 810° it fuses, and on cooling acquires a highly lamellated texture, and sometimes yields crystals: like arsenic, but unlike most other metals, its primary form is rhombohedron. It is volatile at a very intense temperature. Its surface tarnishes by exposure to the atmosphere; and by the continued action of air and moisture, a dark matter is formed, which Berzelius regards as a definite compound. It appears, however, to be merely a mixture of the sesquioxide and metallic antimony. Heated to a white or even full red heat in a covered crucible, and then suddenly exposed

* This hydrate is readily obtained by adding ammonia in excess to the neutral sulphate of the sesquioxide of iron, or indeed any red salt or tincture of iron, and washing the precipitate with water. According to the observations of Mr. Wm. Proctor, the pulpy hydrate thus formed, becomes more dense and loses somewhat of its susceptibility of reaction with arsenious acid by keeping, and should therefore be used as an antidote in a recent state. (Amer. Jour. of Phar. vol. iv. p. 29.) (R.)

According to Duflos this preparation is totally ineffectual as an antidote, when the acids of arsenic are combined with bases as in Fowler's solution, and the arseniate of potassa employed in calico printing. In such cases, and indeed when any doubt exists as to the state of combination of the arseniacal poison, he recommends the peracetate of iron, with excess of base, largely diluted with water. This liquid he states precipitates arsenious and arsenic acid from all their solutions, either free or combined with any base. (Journ. de Ch. Méd. Nov. 1844.) (R.)

to the air, it inflames, and burns with a white light. During the combustion, a white vapour rises, which condenses on cool surfaces, frequently in the form of small shining needles of silvery whiteness. These crystals were formerly called *argentine flowers of antimony*, and in chemical works are generally described as binoxide of antimony; but they are correctly considered by Berzelius, as the sesquioxide.

From the experiments of Berzelius on the composition of the oxide and acids of antimony (An. de Ch. et Ph. xvii.), the eq. of that metal may be estimated at 64·6. The composition of the compounds described in this section is as follows:

	2 eq. Antimony.			Equiv.	Formulæ.
Sesquioxide	129·2 + Oxygen	24	3 eq.	=153.2	2Sb + 3O or Sb^2O^3.
Antimonious Acid	129·2 + do.	32	4 eq.	=161·2	2Sb + 4O or Sb_2O_4.
Antimonic Acid	129·2 + do.	40	5 eq.	=169·2	2Sb + 5O or Sb_2O_5.
Sesquichloride	129·2 + Chlorine	106·26	3 eq.	=235·46	2Sb + 3Cl or Sb_2Cl_3.
Bichloride	129·2 + do.	141·68	4 eq.	=270·88	2Sb + 4Cl or Sb_2Cl_4.
Perchloride	129·2 + do.	177·1	5 eq.	=306·3	2Sb + 5 Cl or Sb_2Cl_5.
Bromide	Composition uncertain.				
Sesquisulphuret	129·2 + Sulphur	48·3	3 eq.	=177·5	2Sb + 3S or Sb_2S_3.
Bisulphuret	129·2 + do.	64·4	4 eq.	=193·6	2Sb + 4S or Sb_2S_4.
Persulphuret	129·2 + do.	80·5	5 eq.	=209·7	2Sb + 5S or Sb_2S_5.
Oxychloride of Antimony	Sesquichloride Sesquioxide	570·92 1378·8	2 eq. 9 eq.	=1949·72	$2Sb_2Cl_3 + 9Sb_2O_3$.
Oxysulphuret of Antimony	Sesquisulphuret Sesquioxide	355 153·2	2 eq. 1 eq.	=508·2	$Sb_2S^3 + Sb_2O_3$.

Sesquioxide.—When sesquichloride of antimony, made by boiling the native sulphuret in hydrochloric acid, is poured into water, a white curdy precipitate subsides, formerly called *powder of Algaroth*, which consists of sesquioxide of antimony combined with undecomposed chloride. On decomposing the latter by digestion with carbonate of potassa, and then washing with water, the sesquioxide is obtained in a state of purity. It may also be procured by adding carbonate of potassa or soda to a solution of tartar emetic, and by sublimation during the combustion of antimony. When slowly sublimed it condenses in fine needles of silvery whiteness. It occurs as a mineral, the oxide of antimony of mineralogists, the primary form of which is a right rhombic prism, isomorphous with the crystals of arsenious acid lately observed by Wöhler.

Prop.—When prepared in the moist way, it is a white powder with a somewhat dirty appearance. When heated it acquires a yellow tint, and at a dull red heat in close vessels it is fused, yielding a yellow fluid, which becomes an opaque greyish crystalline mass on cooling. Its sp. gr. is 5·566. It is very volatile, and if protected from atmospheric air may be sublimed without change. When heated in open vessels it absorbs oxygen; and when the temperature is suddenly raised, and the oxide is porous, it takes fire and burns. In both cases antimonious acid is generated. It is the only oxide of antimony which forms regular salts with acids, and is the base of the medicinal preparation, *tartar emetic*, the tartrate of antimony and potash. Most of its salts, however, are either insoluble in water, or, like chloride of antimony, are decomposed by it, owing to the affinity of that fluid for the acid being greater than that of the acid for oxide of antimony. This oxide is therefore a feeble base; and, indeed, possesses the property of uniting with alkalies. To the foregoing remark, however, tartrate of

antimony and potassa is an exception; for it dissolves readily in water without change. By excess of tartaric or hydrochloric acid, the insoluble salts of antimony may be rendered soluble in water.

The presence of antimony in solution is easily detected by hydrosulphuric acid. This gas occasions an orange-coloured precipitate, hydrated sesquisulphuret of antimony, which is soluble in pure potassa, and is dissolved with disengagement of hydrosulphuric acid gas by hot hydrochloric acid, forming a solution from which the white oxychloride is precipitated by water.

In trying the effect of reagents on solutions of oxide of antimony, it is convenient to employ tartar emetic, from its property of dissolving in pure water without decomposition. From a solution of this salt, when moderately concentrated, a little pure potassa throws down the oxide, but excess of the alkali redissolves the precipitate. The oxide is more perfectly separated by alkaline carbonates. Lime water causes a white precipitate, a mixed tartrate of lime and oxide of antimony; and earthy and metallic salts decompose tartar emetic by forming, like lime, sparingly soluble compounds with tartaric acid. Decomposition is also occasioned by most acids, which throw down a sparingly soluble salt of antimony and cream of tartar; and a recently made, pretty strong, infusion of gall-nuts, gives a yellowish white precipitate, which consists of tannic acid and oxide of antimony. But these appearances are by no means to be relied on as tests of the presence of antimony: a mixture of other substances might be similarly influenced by the same reagents; in a moderately dilute solution of tartar emetic most of them produce no effect whatever; and the too free addition of a pure alkali or of an acid, even to a strong solution, may altogether prevent that precipitate from forming, which a smaller quantity of the same reagents would have produced. The only certain method of bringing the antimony into view, even in a very weak solution, is to acidulate with tartaric acid, and then transmit through the liquid a current of hydrosulphuric acid gas. The hydrated sesquisulphuret of antimony, of a characteristic orange-red colour, is immediately formed.

The detection of antimony in mixed fluids, as when tartar emetic is mixed with articles of food, is conducted in the following manner. The substances are first digested in water acidulated with about a drachm of hydrochloric and tartaric acids, which coagulate some organic matters, and give complete solubility to the oxide of antimony. Through the filtered liquid, hydrosulphuric acid is then transmitted, when the orange-red sesquisulphuret of antimony subsides, which preserves its characteristic tint even when deposited from coloured solutions, and may be further recognized by solution in hot hydrochloric acid and precipitation by water. The metal itself may in general be obtained by placing the dry sulphuret in a glass tube, transmitting through it a current of hydrogen gas, and then, when all the atmospheric air is displaced, heating the sulpuuret by the flame of a spirit-lamp. The sulphur is carried off in the form of hydrosulphuric acid gas, and the metallic antimony, recognizable by its lustre, remains. The metal is principally found where the sulphuret lay; but if the current of gas during the reduction happen to be rapid, it causes mechanically a spurious sublimation of antimony, which lines part of the tube with a thin film of metal. When much organic matter is mixed with the sulphuret, the metal is sometimes indistinctly seen. In that case it should be dissolved in a few drops of nitro-hydrochloric acid with heat, and be precipitated by water: it may then be redissolved by tartaric acid, and again precipitated with its characteristic tint by

hydrosulphuric acid. Orfila recommends that the metal should be obtained from the sulphuret by fusion with black flux; but I have elsewhere shown this process to be very precarious, and my opinion is supported by the experience of Christison. (Treatise on Poisons, 2d Ed. 429.) It may be detected, when present even in small quantity, by decomposing the antimoniuretted hydrogen formed as described under Arsenic, where the characters by which it is distinguished from arsenic are given.

Its eq. is 153·2; *symb.* 2Sb + 3O, $\dddot{\underline{Sb}}$, or Sb_2O_3.

Antimonious Acid.—When metallic antimony is digested in strong nitric acid, the metal is oxidized at the expense of the acid, and hydrated antimonic acid is formed; and on exposing this substance to a red heat, it gives out water and oxygen gas, and is converted into antimonious acid. It is also generated when the oxide is exposed to heat in open vessels. Thus, on heating sulphuret of antimony with free exposure to the air, sulphurous acid and oxide of antimony are generated; but on continuing the roasting after all the sulphur is burned, the oxide gradually absorbs oxygen and passes into antimonious acid. Hence this acid is formed in the process of preparing the *pulvis antimonialis* of the pharmacopœia. Antimonious acid is white while cold, but acquires a yellow tint when heated, is very infusible, and fixed in the fire, two characters by which it is readily distinguished from the oxide. It is insoluble in water, and likewise in acids after being heated to redness. It combines in definite proportions with alkalies, and its salts are called *antimonites*. Antimonious acid is precipitated from these salts by acids as a hydrate, which reddens litmus paper, and is dissolved by hydrochloric and tartaric acids, though without appearing to form with them definite compounds.

Its eq. is 161·2; *symb.* 2Sb + 4O, $\dddot{\underline{Sb}}$, or Sb_2O_4.

Antimonic Acid, sometimes called *peroxide* of antimony, is obtained as a white hydrate, either by digesting the metal in strong nitric acid, or by dissolving it in nitro-hydrochloric acid, concentrating by heat to expel excess of acid, and throwing the solution into water. When recently precipitated it reddens litmus paper, and may then be dissolved in water by means of hydrochloric or tartaric acid. It does not enter into definite combination with acids, but with alkalies forms salts, which are called *antimoniates*. When the hydrated peroxide is exposed to a temperature of 500° or 600° F. the water is evolved, and the anhydrous acid of a yellow colour remains. In this state it resists the action of acids. When exposed to a red heat it parts with oxygen, and is converted into antimonious acid.

Its eq. is 169·2; *symb.* 2Sb + 5O, $\dddot{\underline{Sb}}$, or Sb_2O_5.

Chlorides of Antimony.—When antimony in powder is thrown into a jar of chlorine gas, combustion ensues, and the sesquichloride of antimony is generated. The same compound may be formed by distilling a mixture of antimony with about twice and a half its weight of corrosive sublimate, when the volatile sesquichloride of antimony passes over into the recipient, and metallic mercury remains in the retort. At common temperatures it is a soft solid, thence called *butter of antimony*, which is liquefied by gentle heat, and crystallizes on cooling. It deliquesces on exposure to the air; and when mixed with water, hydrochloric acid and sesquioxide are generated, and the latter, combined with undecomposed chloride subsides.

Its eq. is 235·46; *symb.* 2Sb + 3Cl, or Sb_2Cl_3.

The *bichloride of antimony* is formed by acting on hydrated antimonious by hydrochloric acid, when a solution is formed, which appears to be a compound of bichloride of antimony and hydrochloric acid. It possesses little permanence, and on the addition of water antimonious acid subsides, and hydrochloric acid remains in solution.

The *perchloride* is generated by passing dry chlorine gas over heated metallic antimony. It is a transparent volatile liquid, which emits fumes on exposure to the air. Mixed with water, it is converted into hydrochloric and hydrated antimonic acid, which subsides. (Rose, in the Annals of Philosophy, N. S. x.)

Bromide of Antimony.—The union of bromine and antimony is attended with disengagement of heat and light, and the compound is readily obtained by distillation, as in the process for preparing bromide of arsenic. It is solid at common temperatures, is fused at 206°, and boils at 518° F. It is colourless, and crystallizes in needles; it attracts moisture from the air, and is decomposed by water.

Sesquisulphuret of Antimony.—This is by far the most abundant ore of antimony, and is hence employed in making the preparations of antimony. Though compact or earthy, it sometimes occurs in acicular crystals and in rhombic prisms. Its sp. gr. is 4·62, colour red-grey, and its lustre metallic. When heated in close vessels, it enters into fusion without undergoing any other change. It may be formed artificially by fusing together antimony and sulphur, or by transmitting a current of hydrosulphuric acid gas through a solution of tartar emetic: in this case it falls as a hydrate of an orange-red colour, and does not acquire its dark colour till its water is expelled by heat.

Its eq. is 177·5; *symb.* 2Sb + 3S, or Sb_2S_3.

The *bisulphuret* is formed, according to Rose by transmitting hydrosulphuric acid gas through a solution of antimonious acid in dilute hydrochloric acid. (An. of Phil. N. S. x.)

Its eq. is 193·6; *symb.* 2Sb + 4S, or Sb_2S_4.

Rose formed the *persulphuret* by the action of hydrosulphuric acid on a solution of antimonic acid. The golden sulphuret, prepared by boiling sulphuret of antimony and sulphur in solution of potassa, a process which is not adopted by either of our colleges, is a persulphuret. *Its eq.* 209·7; *symb.* 2Sb + 5S, or Sb_2S_5.

Oxychloride of Antimony.—This compound has lately been studied by Malaguti and Johnston. When an acid solution of the sesquichloride of antimony is thrown into a large quantity of water, a white voluminous precipitate forms. Allowing it to subside, it contracts considerably during thirty or forty hours, and then consists of a thick bed of minute crystals. These crystals are small prismatic needles, of a white colour and brilliant lustre; they are decomposed by boiling in water, by continued washings, and by the alkaline carbonates, being thus converted into sesquioxide. They have been analyzed by Johnston, according to whom they are composed of 2 eq. of the sesquichloride united with 9 eq. of the sesquioxide; a composition which corresponds closely with the analysis of Malaguti. Hence the *eq. is* 1949·72; *symb.* $2Sb_2Cl_3 + 9Sb_2O_3$.

Oxysulphuret of Antimony.—Hist. and Prep.—Rose has shown that this compound occurs in the mineral kingdom, being the *red antimony ore* (rothspiesglanzerz) of mineralogists. The pharmaceutic preparations known by the terms *glass*, *liver*, and *crocus* of antimony, are of a similar nature, though less definite in composition. They are made by roasting the native sulphuret, so as to form sulphurous acid and oxide of antimony, and then vitrifying the oxide together

with undecomposed ore, by means of a strong heat. The product will of course differ according as more or less of the sulphuret escapes oxidation during the process.

When sulphuret of antimony is boiled in a solution of potassa or soda, a liquid is obtained, from which, on cooling, an orange-red matter called *Kermes mineral* is deposited; and on subsequently neutralizing the cold solution with an acid, an additional quantity of a similar substance, the *golden sulphuret* of the pharmacopœia, subsides. These compounds may also be obtained by igniting sulphuret of antimony with an alkali or alkaline carbonate, and treating the product with hot water; or by boiling the mineral in a solution of carbonate of soda or potassa. The finest kermes is obtained, according to M. Cluzel, from a mixture of four parts of sulphuret of antimony, 90 of crystallized carbonate of soda, and 1000 of water. These materials are boiled for half or three quarters of an hour; the hot solution is filtered into a warm vessel, in order that it may cool slowly; and after 24 hours the deposit is collected on a filter, moderately washed with cold water, and dried at a temperature of 70° or 80° F.

Prop.—Very great diversity of opinion has long existed among chemists as to the nature of kermes. Berzelius and Rose gave experiments to show that it is a hydrated sesquisulphuret, differing from the native sulphuret solely in being combined with water. Subsequently Gay-Lussac and others observed that kermes contains oxide of antimony, which may be removed by digestion with cream of tartar; and Gay-Lussac inferred from the quantity of water formed when kermes, previously rendered anhydrous, is reduced by hydrogen gas, that it is a hydrated oxysulphuret, identical, when deprived of its water, with the red ore of antimony above referred to. Still more recently Berzelius has explained, that the ordinary process for making kermes leads to the separation of a compound of oxide of antimony and potassa, which tenaciously adheres to kermes, but is not chemically united with it: he rightly argues that the question is not, whether oxide of antimony is sometimes or generally present in kermes, but whether the latter can exist *without* oxide of antimony. This question he has answered affirmatively. He fused sulphuret of antimony with black flux, boiled the residue in water, and set aside the solution to cool: a perfect kermes was deposited, which he considers, and I apprehend with good reason, to be quite free from oxide of antimony. (Pog. Annalen, xx. 364.)

The theory of the preparation of kermes, as given by Berzelius, is the following. When sesquisulphuret of antimony is fused with potassa, part of each interchanges elements with the other in such a ratio that

1 eq. Sesquisulphuret of Ant.	Sb_2S_3	yield	1 eq. Sesquioxide of Antimony	Sb_2O_3
and 3 eq. Potassa	3KO		and 3 eq. Sulphuret of Potassium	3KS.

The sulphuret of potassium unites with undecomposed sesquisulphuret of antimony, forming a sulphur-salt which will be again referred to hereafter, and sesquioxide of antimony with undecomposed potassa; and on adding hot water both compounds are dissolved, and coexist independently of each other in the solution. As the solution cools, the sesquisulphuret of antimony subsides, simply because the solvent power of sulphuret of potassium is thereby diminished; but a variable quantity of potassa and sesquioxide of antimony falls with the deposit, and cannot be entirely removed by washing with water. The cold solution still contains a double sulphuret of antimony and potassium, together with sesquioxide of antimony united with potassa: on acidulating with sulphuric acid,

the sulphuret of potassium is resolved, by decomposition of water, into potassa and hydrosulphuric acid, and the sesquioxide of antimony is deprived of its potassa; and therefore the sesquisulphuret and sesquioxide of antimony, both losing at the same instant the principles which gave them solubility, are thrown down either in combination or in mixture with each other. Berzelius believes the same change to occur when the ingredients are boiled instead of fused together. The golden sulphuret differs from kermes, in the absence of potassa, in containing more oxide of antimony, and perhaps in being or containing an oxysulphuret. It commonly contains free sulphur, derived apparently from the oxidizing influence of the air on the sulphuret of potassium. When alkaline carbonates are employed instead of pure alkalies, the same phenomena ensue, except that carbonic acid is evolved.

Its eq. is 508·2; *symb.* $2Sb_2S_3 + Sb_2O_3$.

SECTION XIX.

CHROMIUM.—VANADIUM.

CHROMIUM.

Hist.—Discovered in the year 1797 by Vauquelin in a beautiful red mineral, the native dichromate of oxide of lead. (An. de Ch. xxv. and lxx.) It has since been detected in the mineral called *chromate of iron*, a compound of the oxides of chromium and iron, which occurs abundantly in several parts of the Continent, in America, and at Unst in Shetland. (Hibbert.) It derived its name from χρωμα, *colour*, owing to its remarkable tendency to form coloured compounds.

Prep.—By exposing the oxide of chromium mixed with charcoal to the most intense heat of a smith's forge; but owing to its strong affinity for oxygen, the reduction is extremely difficult. A better process, that of Vauquelin, is to mix the dry chloride into a paste with oil, place the mass in a crucible lined with charcoal, lute on a cover, and to expose it for an hour to a very strong heat. Liebig has obtained the metal in the form of a black powder, which acquires the metallic aspect from pressure, by heating the compound of terchloride of chromium and ammonia to redness, and transmitting over it dry ammoniacal gas; the chlorine unites with the hydrogen of the ammonia, hydrochloric acid and nitrogen gases are evolved, and pulverulent chromium remains. A still more convenient process is to decompose the sesquichloride by heat and ammoniacal gas, in which case the metal has a chocolate-brown colour. In this finely divided state it takes fire when heated in the open air. (An. de Ch. et Ph. xlviii. 297.)

Prop.—As obtained by Vauquelin's process it has a white colour with a shade of yellow, and a distinct metallic lustre. It is brittle, very infusible, and with difficulty attacked by acids, even by the nitro-hydrochloric. Its sp. gr. has been stated at 5·9; but Thomson found it a little above 5. When fused with nitre it

is oxidized and converted into chromic acid. With a smaller quantity of oxygen it forms the green oxide.

From the experiments of Berzelius and Thomson the eq. of chromic acid may be estimated at 52; and as the salts of this acid are isomorphous with the sulphates and seleniates, it is inferred that chromic acid has the same atomic constitution as sulphuric and selenic acids, or consists of 1 eq. of chromium and 3 eq. of oxygen. Berzelius has moreover remarked that when the acid is converted into the green oxide of chromium, it parts with exactly half of its oxygen. Hence, 24 deducted from 52, leaves 28 as the eq. of chromium. *Its symb. is* Cr. The composition of its compounds described in this section is as follows :—

	Chromium.			Equiv.	Formulæ.
Sesquioxide	56	2 eq. + Oxygen	24	3 eq. = 80	$2Cr + 3O$ or Cr_2O_3.
Chromic Acid	28	1 eq. + . .	24	3 eq. = 52	$Cr + 3O$ or CrO_3.
Sesquichloride	56	2 eq. + Chlorine	106·26	3 eq. = 162·262	$Cr + 3Cl$ or Cr_2Cl_3.
Sesquifluoride	56	2 eq. + Fluorine	56·04	3 eq. = 112·04	$2Cr + 3F$ or Cr_2F_3.
Perfluoride	Composition unknown.				
Sesquisulphuret	56	2 eq. + Sulphur	48·3	3 eq. = 104·3	$2Cr + 3S$ or Cr_2S_3.
Protophosphuret	28	1 eq. + Phosphs.	15·7	1 eq. = 43·7	$Cr + P$ or CrP.
Oxy-chloride CrO_3	104	2 eq. + $CrCl_3$	106·26	1 eq. = 210·26	$CrCl_3 + 4CrO_3$.

Sesquioxide of Chromium.—Prep.—This, the commonly known oxide of chromium, is prepared by dissolving chromate of potassa in water, and mixing it with a solution of nitrate of protoxide of mercury, when an orange-coloured precipitate, chromate of that oxide, subsides. On heating this salt to redness in an earthen crucible, the mercury is dissipated in vapour, and the chromic acid is resolved into oxygen and oxide of chromium. It may also be obtained in small tabular crystals by exposing the bichromate of potassa to a strong red heat; one eq. of chromic acid loses oxygen, while the other forms a neutral salt with the potassa. The latter is readily removed from the insoluble oxide by boiling water. Wöhler has succeeded in obtaining this oxide in fine crystals by conducting the vapour of the oxychloride of chromium (formerly terchloride of chromium) through a red-hot glass tube, when it is decomposed, oxide of chromium is deposited in fine crystals, and a mixture of oxygen and chlorine gases is evolved.

Prep.—As obtained by either of the first processes, it is a green powder; but the crystals of Wöhler are black and possess a strong metallic lustre, and are identical in form and very similar in appearance to specular iron ore: it is as hard as corundum; and has a sp. gr. of 5·21; its powder has the common green colour of oxide of chromium. (Pog. An. xxxiii. 341.)

It is insoluble in water, and after being strongly heated, resists the action of the most powerful acids. Deflagrated with nitre, or fused with chlorate of potassa, it is oxidized to its maximum, and is thus reconverted into chromic acid. Fused with borax or vitreous substances, it communicates to them a beautiful green colour, a property which affords an excellent test of its presence, and renders it exceedingly useful in the arts. The emerald owes its colour to the presence of this oxide.

Oxide of chromium is a salifiable base, and its salts, which have a green colour, may be easily prepared in the following manner. To a boiling solution of chromate of potassa in water, equal measures of strong hydrochloric acid and alcohol are added in successive small portions, until the red tint of the chromic acid disappears entirely, and the liquid acquires a pure green colour. On pouring an

excess of pure ammonia into this solution, a pale green bulky hydrate subsides, which consists of 1 eq. of the oxide and 26 eq. of water. (Thomson.) The oxide, in this state, is readily dissolved by acids. On expelling the water by heat, the sudden approximation of the particles, which abruptly occurs at a certain temperature, causes such intense evolution of heat that the whole mass becomes vividly incandescent.

The anhydrous oxide is formed when bichromate of potassa is briskly boiled with sugar and a little hydrochloric acid. At first a brown matter falls, consisting of the acid and oxide of chromium; but subsequently the green oxide appears in the form of a finely divided powder. If the bichromate and sugar are employed without hydrochloric acid, the brown matter is the only solid product, and on boiling this compound with a little carbonate of potassa, a greenish-blue carbonate of chromium, of a very fine colour, is obtained. For this mode of preparation I am indebted to my late pupil, Mr. Thomas Thomson, of Clitheroe, near Manchester.

Its eq. is 80; *symb.* 2Cr + 3O, $\dddot{\underline{Cr}}$, or Cr O_3.

Chromic Acid.—Prep.—This acid is best prepared by transmitting the gaseous fluoride of chromium into water contained in a vessel of silver or platinum, when by mutual decomposition of the gas and the water, hydrofluoric and chromic acids are generated: the former is then expelled by evaporating the solution to dryness, and the latter in a pure state remains. If the gas is conducted into a silver vessel which is only moistened with water, and the aperture of which is closed by a piece of moist paper, the chromic acid is obtained in the form of acicular crystals of a cinnabar red colour, which are so voluminous and abundant as to fill the interior of the vessel. Another method of preparing chromic acid has been suggested by Arnold Maus, which consists in decomposing a hot concentrated solution of bichromate of potassa by silicated hydrofluoric acid. The chromic acid, after being separated from the sparingly soluble fluoride of silicon and potassium, is evaporated to dryness in a platinum capsule, and then redissolved in the smallest possible quantity of water. By this means the last portions of the double salt are rendered insoluble, and the pure chromic acid may be separated by decantation. The acid must not be filtered in this concentrated state, as it then corrodes paper like sulphuric acid, and is converted into chromate of the green oxide of chromium. Asbestus, however, might be used for filtering this acid, in the same way as the permanganic acid. (Gregory.) When it is wished to prepare a large quantity of chromic acid by this process, porcelain vessels may be safely employed in the first part of the operation, provided care is taken to add a quantity of silicated hydrofluoric acid not quite sufficient for precipitating the whole of the potassa. (Edinburgh Journal of Science, viii. 175.)

It was formerly prepared by digesting chromate of baryta or oxide of lead in dilute sulphuric acid, the quantity of the latter being regulated with the view of decomposing the chromate without being in excess. A dark ruby-red solution is thus obtained, which by evaporation yields irregular crystals, and was supposed to contain pure chromic acid; but Gay-Lussac showed that the acid when thus procured is never pure, being intimately combined with sulphuric acid. On endeavouring to expel the latter by heat, the chromic acid itself yields oxygen, and is more or less completely converted into sulphate of the green oxide.

Prop.—Pure dry chromic acid is black while warm, and of a dark red colour when cold. It is very soluble in water, rendering it red or yellow according to the degree of dilution;—when the solution is concentrated by heat and allowed

to cool, it deposits red crystals, which deliquesce readily in the air. In alcohol it is also soluble, but the action of heat or light causes its conversion into the green oxide. Its taste is sour, and with alkalies it acts as a strong acid. It is converted into the green oxide, with evolution of oxygen, by exposure to a strong heat. It yields a chloride when boiled with hydrochloric acid and alcohol, and the direct solar rays have a similar effect when hydrochloric acid is present: the mutual action sets chlorine free, and hence the solution acquires the property of dissolving gold. With sulphurous acid it forms a sulphate of the oxide; and it is more or less completely converted into the oxide by being boiled with sugar, starch, or various other organic principles. It destroys the colour of indigo, and of most vegetable and animal colouring matters; a property advantageously employed in calico-printing, and which manifestly depends on the facility with which it is deprived of oxygen.

Chromic acid is characterized by its colour, and by forming coloured salts with alkaline bases. The most important of these salts is chromate of oxide of lead, which is found native in small quantity, and is easily prepared by mixing chromate of potassa with a soluble salt of lead. It is of a rich yellow colour, and is employed in the arts of painting and dyeing to a great extent. When heated to redness, it is also much used as the oxidizing agent in the ultimate analysis of organic substances. (Liebig.)

When sulphurous acid gas is transmitted into a solution of chromate or bichromate of potassa, a brown precipitate subsides, which was long regarded as a distinct oxide of chromium; but Thomson has proved that it is the green oxide combined with a little chromic acid. The acid may in a great measure be washed away by means of water, and by ammonia it is entirely removed; but the best mode of separating it, is to dissolve the brown matter with hydrochloric acid, and then precipitate the green oxide by ammonia. The brown compound may be formed by boiling a solution of bichromate of potassa with alcohol; and it is also rapidly generated, when bichromate of potassa is gently boiled with sugar and a very little hydrochloric acid.

Its eq. is 52; *symb.* Cr + 3O, Cr, or CrO_3.

Sesquichloride of Chromium.—It is prepared by transmitting dry chlorine gas over a mixture of oxide of chromium and charcoal heated to redness in a tube of porcelain, when the sesquichloride gradually collects as a crystalline sublimate of a peach-purple colour, which in thin layers is transparent, but in thicker masses is opaque. Another method is to evaporate the green solution of this chloride gently to dryness at a temperature of 212°, when a green powder remains, consisting of 1 eq. of the sesquichloride and 3 eq. of water ($Cr_2Cl_3 + 3\ H$), these elements being exactly in the ratio to form oxide of chromium and hydrochloric acid. On raising the temperature above 212°, no water is lost until it reaches 400°; the powder then begins to swell up from the escape of water, the colour changes from green to the red of peach-blossoms, and pure sesquichloride remains. This part of the process should be conducted in a tube from which air is excluded by a current of dry carbonic acid gas. These phenomena are quoted by Liebig as favouring the notion that the green solution and powder are a hydrochlorate of an oxide, and not a chloride with water. Gregory has shown (Journ. de Pharm.) that the pink powder, first obtained by Kemp from the action of chloride of sulphur on oxychloride of chromium, is an isomeric modification of the sesquichloride above described. It is not crystalline, and quite insoluble in

water; but by long exposure to air it passes slowly into the soluble state. Being formed at a high temperature, it probably differs from the soluble variety as ignited alumina, peroxide of iron, or sesquioxide of chromium, do from the same oxides previous to ignition. The existence of this modification has lately been confirmed by Rose. (Annalen der Pharm. 1840.)

The sesquichloride of chromium dissolves slowly, forming a deep green solution. The same may be prepared by directly dissolving the hydrated oxide in hydrochloric acid; or by digesting chromate of oxide of lead in strong hydrochloric acid, adding a little alcohol from time to time to promote the deoxidation of chromic acid, and then separating the resulting chloride of chromium from that of lead by strong alcohol, which together with any excess of hydrochloric acid is ultimately expelled by evaporating to dryness. Traces of lead which may have been dissolved are easily precipitated by hydrosulphuric acid.

Its eq. is 162·26; *symb.* 2Cr + 3 Cl, or Cr_2Cl_3.

[In some recent researches on the compounds of chromium, M. Peligot announces the discovery of a protochloride ClO, which it seems had escaped the observation of chemists. He states that it is always formed in the preparation of the sesquichloride when a current of dry chlorine is passed over a mixture of the oxide of chromium and charcoal, heated to redness. In this process, it precedes the formation of the sesquichloride, and appears as a sublimate in the form of very fine sparkling white crystals which are mingled with more or less carbon and oxide of chromium. But it may be procured in a state of perfect purity by passing hydrogen over the violet sesquichloride contained in a tube of hard glass. A considerable rise of temperature attends the reaction, hydrochloric acid escapes, and the protochloride remains in the tube as a white crystalline mass, having the same form as the mass of sesquichloride originally used. The analyses of these crystals show them to be composed of single equivalents of chlorine and chromium.

The protochloride readily dissolves in water, the solution being attended by a considerable rise of temperature. The solution is at first blue in colour, but by exposure to the air, soon becomes green, oxygen, at the same time, being absorbed with great rapidity.

The solubility in water which has heretofore been attributed to the sublimed sesquichloride, M. Peligot states, is due to the presence of the protochloride which accompanies it; the former according to his observations being entirely insoluble in cold or hot water as well as remarkably indifferent to the action of most of the powerful acids. Even aqua regia does not affect it. In a solution, however, of water, containing only a minute quantity of the protochloride, it dissolves with surprising facility. The solution thus obtained possesses all the properties of that of the hydrated sesquichloride of chromium prepared in the moist way, viz. by the action of hydrochloric acid and alcohol on chromic acid or the chromate of lead.

In the same researches, M. Peligot obtained a protoxide of chromium CrO, and an intermediate oxide Cr_3O_4, or CrO + Cr_2O_3, analogous to the magnetic oxide of Iron. (Compt. Rendus, t. xix. p. 609 et 734.)]

Sesquifluoride of Chromium is formed by dissolving the oxide in hydrofluoric acid, and evaporating the solution to dryness, when the sesquifluoride remains as a green crystalline residue, which is soluble in water. *Its eq. is* 112·04; *symb.* 2Cr + 3F, or C_2F_3.

Perfluoride of Chromium.—Discovered by Unverdorben in 1825 (Ed. Journ. of

Science, iv. 129). When a mixture of 3 parts of fluor-spar and 4 of chromate of oxide of lead is distilled with 5 parts of fuming or even common sulphuric acid in a leaden or silver retort, a red-coloured gas is disengaged, which acts rapidly upon glass, with deposition of chromic acid and formation of fluosilicic acid gas. It is decomposed by water, and the solution is found to contain a mixture of hydrofluoric and chromic acids. The watery vapour of the atmosphere effects its decomposition, so that when mixed with air, red fumes appear, owing to the separation of minute crystals of chromic acid.

The red colour of terfluoride of chromium naturally excites the suspicion that the gas itself may consist, not of fluoride of chromium, but of hydrofluoric and chromic acids; and its production by means of *hydrous* sulphuric acid is consistent with this idea. But since the gas may also be formed from fluor-spar, chromate of oxide of lead, and *anhydrous* sulphuric acid, it is clear that this view is inadmissible. It was formerly considered to be composed of 1 eq. of chromium and 3 eq. of fluorine, and was hence described as the terfluoride. H. Rose has shown, however, that its elements approximate more closely to the ratio of 1 to 5 rather than 1 to 3; but its true constitution is not yet satisfactorily determined. It is perhaps CrF_5.

Sulphuret of Chromium may be formed by transmitting the vapour of bisulphuret of carbon over oxide of chromium at a white heat; by heating in close vessels an intimate mixture of sulphur and the hydrated oxide; by fusing the oxide with a persulphuret of potassium, and dissolving the soluble parts in water; or by transmitting hydrosulphuric acid gas aided by heat over the sesquichloride of chromium. It cannot be prepared in the moist way. It is of a dark grey colour, and acquires metallic lustre by friction in a mortar. It is readily oxidized when heated in the open air, and is dissolved by nitric or nitro-hydrochloric acid.

Its eq. is 104·3; *symb.* 2Cr + 3S, or Cr_2S_3.

Phosphuret of Chromium.—Rose prepared this compound by acting on the sesquichloride of chromium by phosphuretted hydrogen gas at a red heat. By mutual interchange of elements

1 eq. Sesquichloride	Cr_2Cl_3	yield	2 eq. Phosphuret	2CrP.
and 1 eq. Phosphur. Hyd.	P^2H_3		and 3 eq. Hydrochloric Acid.	3HCl.

This phosphuret is black, insoluble in hydrochloric acid, feebly attacked by nitric and nitro-hydrochloric acid, and burns before the blowpipe with a flame of phosphorus.

Its eq. is 43·7; *symb.* Cr + P, or CrP.

Another phosphuret of a grey colour may be formed by exposing the phosphate of oxide of chromium to a strong heat in a covered crucible lined with charcoal. Its composition is unknown.

Oxychloride of Chromium.—Hist.—Discovered by Unverdorben at the same time as the perfluoride of chromium: it was long considered and described as the terchloride, until Rose pointed out its real constitution. (Pog. An. xxvii. 565.)

Prep.—By the action of fuming sulphuric acid on a mixture of about equal weights of chromate of oxide of lead and chloride of sodium. Wöhler recommends the following process: 10 parts of chloride of sodium are fused in a common crucible with 16·9 parts of the neutral chromate of potassa, the fused salts are thrown upon a clean stone, and the mass when cold is broken into coarse

fragments. These are to be introduced into a capacious tubulated retort, to which a receiver kept cold by moistened paper is adapted. Twelve parts of fuming sulphuric acid are then added to the fused salts, when an energetic action commences, and in a few minutes, the oxychloride is formed and distilled over without the application of external heat. (Pog. An. xxxiii. 343.)

Prop.—It is a heavy red liquid, exceedingly volatile, yielding abundant red vapours when exposed to the air. By water it is instantly decomposed into hydrochloric and chromic acids. Its vapour is decomposed by a red heat into oxide of chromium, oxygen, and chlorine, as observed by Wöhler, who has thus confirmed the composition of the oxychloride as stated by Rose. The latter chemist found it was composed of 2 eq. of chromic acid and 1 eq. of a perchloride; and the former, that 2 eq. of the oxychloride produced 3 eq. of the oxide of chromium, 3 eq. of oxygen, and 6 eq. of chlorine. In symbols,

$$2\,(CrCl_3 + 2CrO_3) \quad \text{yield} \quad \begin{cases} 3Cr_2O_3. \\ 3O. \\ 6Cl. \end{cases}$$

Its eq. is 210·26; *symb.* $CrCl_3 + 3CrO_3$.

Millon considers it as chromic acid in which 1 eq. oxygen is replaced by chlorine, $Cr \begin{matrix} Cl \\ O_2 \end{matrix}\Big\}$. The same ingenious chemist has extended this view to the bleaching compounds of chlorine. Thus bleaching powder, commonly viewed as $CaO, ClO + CaCl$, may be viewed as an oxychloride of calcium, $Ca \begin{matrix} Cl \\ O \end{matrix}\Big\}$. For further details, I must refer to the foreign journals, as I have not been able to obtain the original memoir. (Editor).

VANADIUM.

Hist.—Vanadium, so called from *Vanadis*, the name of a Scandinavian deity, was discovered in the year 1830 by Sefström, of Fahlun, in iron prepared from the iron-ore of Taberg in Sweden. The state in which it occurs in the ore is unknown; but Sefström separated it from the iron by dissolving the latter in hydrochloric acid, when a black powder came into view containing a small quantity of vanadium, together with iron, copper, cobalt, silex, alumina, and lime. He afterwards found a more abundant source in the slag or cinder formed during the conversion of the cast-iron of Taberg into malleable iron. Soon after Sefström's discovery, the same metal was found by Johnston, of Durham, in a mineral from Wanlockhead in Scotland, where it occurs as a vanadiate of oxide of lead. A similar mineral, found at Zimapan in Mexico, was examined in the year 1801 by Professor del Rio, who, in the belief of having discovered a new metal, gave it the name of *Erythronium*, apparently from the red colour of its acid; but as Collet Descotils, on being appealed to, declared the mineral to be chromate of lead, Del Rio abandoned his own opinion in deference to a higher authority. Thus have three persons noticed the existence of vanadium, without the knowledge of each other's labours; but the merit of being the first discoverer is fairly due to Sefström.*

Prep.—From the slag above-mentioned vanadic acid may be obtained by the

* Phil. Mag. and Annals, x. 321. An. de Ch. et Ph. xlvii. 337. Brewster's Journal, v. 318, N. S. Poggendorff's Annalen, xxii. 1.

following process, contrived by Sefström and improved by Berzelius. The slag in fine powder, mixed with its own weight of nitre and twice its weight of carbonate of potassa, is strongly ignited for the space of one hour. The soluble parts are then removed by boiling water, and the solution, after being filtered and neutralized with colourless nitric acid, is precipitated by chloride of barium or acetate of lead. The precipitate, which consists of vanadiate and phosphate of baryta or oxide of lead, zirconia, alumina, and silicic acid, is decomposed, while still moist, by digestion with strong sulphuric acid; to the deep-red solution, alcohol is then added, when by continued digestion ether is disengaged, and all the vanadic acid converted into the salifiable oxide, the solutions of which are blue;—a change effected in order the more completely to remove the vanadic acid from the insoluble matters. The blue liquid is then evaporated; and when it acquires a syrupy consistence, it is mixed in a platinum crucible with a little hydrofluoric acid, and sharply heated in an open fire. By this means the silicic acid, which can only be got rid of in this way, is converted into the gaseous fluoride of silicon, the sulphuric acid expelled, and the oxide reconverted into the acid of vanadium.

The vanadic acid still contains phosphoric acid, alumina, and zirconia. For its further purification it is fused with nitre added in successive small portions, until, on cooling a small quantity, the red tint is found to have disappeared. In this process the acid of the nitre is displaced by the phosphoric and vanadic acids, the object being to cause those acids to unite with potassa without employing an excess of nitre. The vanadiate and phosphate of potassa are then taken up by as small a quantity of water as will suffice, and into the filtered liquid a piece of sal-ammoniac, larger than can be dissolved by it, is introduced: as it dissolves, vanadiate of ammonia, insoluble in a saturated solution of sal-ammoniac, subsides as a white powder, leaving the phosphoric acid in the liquid. The vanadiate of ammonia should be first washed with a solution of sal-ammoniac, and then with alcohol of sp. gr. 0·86.

By heating this salt in an open platinum crucible, vanadic acid is obtained; but the temperature ought to be kept below that of redness, and the mass be well stirred until it acquires a dark red colour. Heated in close vessels the vanadiate of ammonia is converted principally into the salifiable oxide; though some of the protoxide and acid are mixed with it. With the zirconia and alumina, left by the water after fusion with nitre, some vanadium remains: it may be extracted by fusion with sulphur and carbonate of potassa, when a double sulphuret of vanadium and potassium is generated, which is soluble in water. On adding sulphuric acid to the solution, sulphuret of vanadium is precipitated.

The preparation of vanadium from the native vanadiate of lead is much less complicated than the process above described. It suffices to dissolve the ore, as Johnston advises, in nitric acid, and to precipitate the lead by hydrosulphuric acid, which also throws down any arsenic that may be present. As vanadic acid is deoxidized by hydrosulphuric acid, a blue solution is formed; but by evaporating to dryness the acid is reproduced. The residue is then dissolved by a solution of ammonia, and the vanadiate of ammonia precipitated as before by a piece of sal-ammoniac. The vanadic acid is thus separated from arsenic, phosphoric, and hydrochloric acids, with which in the ore of Wanlockhead it is generally associated.

The attempts of Berzelius to reduce vanadic acid to the metallic state by the agency of hydrogen or charcoal at high temperatures proved unsuccessful, as the

protoxide alone was obtained. He procured the metal, however, in the form of a heavy black powder, by placing fragments of fused vanadic acid and potassium of equal size in alternate layers in a porcelain crucible, the potassium being in the largest proportion: a cover was then luted on, and heat applied by means of a spirit-lamp. The reduction took place suddenly and with violence; and when the mass had cooled, the potassa and redundant potassium were separated by water. But Berzelius succeeded better by a process similar to that of H. Rose for procuring metallic titanium. The liquid chloride of vanadium is introduced into a glass bulb blown in a barometer tube, and through it is transmitted dry ammoniacal gas until a white saline mass is produced, during the formation of which the gas is rapidly absorbed, and heat disengaged. A spirit lamp flame is then applied, which expels a quantity of hydrochlorate of ammonia, and metallic vanadium is left adhering to the interior of the bulb. The production of hydrochloric acid is obviously owing to chlorine leaving the vanadium and uniting with the hydrogen of part of the ammonia.

Prop.—The pulverulent vanadium, produced by means of potassium, has but little of the tenacity and appearance of a metal, though under strong pressure it assumes a lustre like that of graphite. Heated in the open air to commencing redness it takes fire, and is converted into the black protoxide. It conducts electricity, however, and is strongly electro-negative in relation to zinc. As procured by Rose's process the vanadium has a strong metallic lustre and a white colour considerably resembling silver, but still more like molybdenum. It is so extremely brittle that it cannot be removed from the glass bulb without falling into powder. It is not oxidized either by air or water; although by continued exposure to the air its lustre gradually grows weaker, and it acquires a reddish tint. It is not dissolved by boiling sulphuric, hydrochloric, or hydrofluoric acid; but by nitric and nitro-hydrochloric acid it is attacked, and the solution has a beautiful dark blue colour. It is not oxidized by being boiled with caustic potash, nor by carbonated alkalies at a red heat.

The eq. of vanadium, according to the analysis of its oxides by Berzelius, is 68·5; its symb is V; and its compounds described in this section are thus constituted:—

	Vanadium.			Equiv.	Formulæ.
Protoxide	68·5	1 eq. + Oxygen	8	1 eq. = 76·5	V + O or VO.
Binoxide	68·5	1 eq. + do.	16	2 eq. = 84·5	V + 2O or VO_2.
Vanadic Acid	68·5	1 eq. + do.	24	3 eq. = 92·5	V + 3O or VO_3.
Bichloride	68·5	1 eq. + Chlorine	70·84	2 eq. = 139·34	V + 2Cl or VCl_2.
Terchloride	68·5	1 eq. + do.	106·26	3 eq. = 174·76	V + 3Cl or VCl_3.
Bibromide	68·5	1 eq. + Bromine	156·8	2 eq. = 225·3	V + 2Br or VBr_2.
Bisulphuret	68·5	1 eq. + Sulphur	32·2	2 eq. = 100·7	V + 2S or VS_2.
Tersulphuret	68·5	1 eq. + do.	48·3	3 eq. = 116·8	V + 3S or VS_3.

Protoxide.—This compound is readily formed from vanadic acid by the combined agency of heat and charcoal or hydrogen gas. By means of the latter Berzelius found that the reduction is effected as perfectly at a temperature short of ignition, as at the strongest heat of a wind furnace. When prepared from fused vanadic acid, the protoxide retains the crystalline structure of the acid, and has a black colour and a semi-metallic lustre; but it is easily broken down into a fine black powder. When rendered coherent by compression it possesses

a property very unusual in oxides, that of conducting electricity, and in relation to zinc of being as strongly electro-negative as silver or copper.

It is very infusible. When heated in open vessels it takes fire and burns like tinder, being converted into the binoxide. On exposure to air and moisture it is slowly oxidized, a process which is best seen by putting it into water, when the liquid gradually acquires a green tint. In both cases the oxygen is derived from the atmosphere. A similar change occurs in acid and alkaline solutions, which, with the exception of nitric acid, do not dissolve it even at a boiling temperature. Heated in nitric acid oxidation ensues with escape of nitric oxide gas, and a blue nitrate of the binoxide of vanadium is generated. The character of an alkaline base seems wholly wanting in the protoxide, and hence Berzelius considers it as a *sub-oxide*. *Its eq. is* 76·5; *symb.* V + O, $\dot{V}$, or VO.

Binoxide.—Prep.—Best prepared, in the dry way, by heating to full redness an intimate mixture of 10 parts of the protoxide with 12 of vanadic acid in a vessel filled with carbonic acid, or from which combustible matter on one hand, and oxygen gas on the other, are carefully excluded. From the salts of the binoxide, and especially the sulphate, it is precipitated as a greyish-white hydrate by means of a very slight excess of carbonate of soda. The residual solution is colourless when the process has been properly conducted: it remains blue, from undecomposed salt, if an insufficient quantity of alkali is used; it is brown when the alkaline carbonate is too freely employed, because some of the binoxide is then dissolved by the free alkali; and if the solution contained vanadic acid, its colour after precipitation is green. The presence of the latter is avoided by transmitting hydrosulphuric acid gas into the solution, whereby vanadic acid is effectually converted into the binoxide, but the redundant gas should be expelled by gentle heat before the oxide is precipitated. As the hydrate, while moist, readily absorbs oxygen, and hence acquires a tint of brown, it must be washed and dried without exposure to the air. When thus prepared it retains its grey tint. By exposure to heat in a vessel from which the air is excluded, it gives out water, and acquires all the characters of the oxide prepared in the dry way.

Prop.—A black pulverulent substance, very infusible, insoluble in water, and free from any acid or alkaline reaction. When heated in the open air it is converted into vanadic acid, and when moist it gradually suffers the same change at ordinary temperatures. It is dissolved by acids more readily as a hydrate than after being heated to redness, and forms salts, most of which have a blue colour, and are more or less soluble in water. They may all be conveniently formed by the direct action of acids on the hydrated oxide. The nitrate may be made by acting on vanadium, or either of its oxides, by nitric acid; the salt, when diluted with water, may be boiled without change; but when evaporated even spontaneously, the blue colour passes through green into red, owing to the production of vanadic acid. The sulphate is easily prepared by dissolving vanadic acid in warm sulphuric acid diluted with an equal weight of water, decomposing the vanadic acid by hydrosulphuric acid, concentrating the solution in order that the salt may be deposited, and washing away adhering sulphuric acid by means of alcohol. The deoxidation of vanadic acid in the preceding process may also be effected by adding pure oxalic acid as long as carbonic acid gas is evolved.

The salts of the binoxide of vanadium are distinguished by their blue colour, by yielding with the alkalies or their carbonates in very slight excess the hydrated

binoxide, which becomes red by oxidation, and by forming with solution of gall-nuts a black compound, a tannate of the binoxide, very similar to ink.

The binoxide is disposed to act the part of an acid by uniting with alkaline bases, with which it forms definite, and in some cases crystalline, compounds. On digesting the hydrated binoxide in pure potassa or ammonia, combination is readily effected, and a dark brown solution is formed. These compounds, though soluble in water, are very sparingly so in strong and cold alkaline solutions, and may be precipitated by them. Most of the other salts formed by the binoxide and salifiable bases are insoluble in water, and may be formed from the preceding by way of double decomposition. ..

Its eq. is 84·5 ; *symb.* V + 2O, V, or Vo_2.

Vanadic Acid.—When vanadiate of ammonia, prepared as already mentioned, is heated in close vessels, the acid is decomposed by the hydrogen of the ammonia, and binoxide of vanadium is formed, mixed with a little protoxide and undecomposed acid. If the salt is heated in an open vessel and well stirred, the whole mass acquires a dark red colour, and pure vanadic acid is obtained : but a red heat should be avoided, since fusion would thereby be occasioned, and free exposure of every part to the atmosphere prevented. Its colour in the state of fine powder is a light rust-yellow ; but the fused acid is red with a shade of orange, and has a strong lustre. By light transmitted through thin layers it appears yellow. In the fire it is fixed, and is not decomposed by a very strong heat, provided combustible matters are excluded. It fuses at a heat lower than that of redness, and crystallizes readily as it cools. In the act of becoming solid it contracts considerably in volume, and emits so much heat of fluidity that the acid, after ceasing to be luminous, is again rendered incandescent, and remains so until the congelation is complete.

It is tasteless, insoluble in alcohol, and very slightly soluble in water, which takes up rather less than 1-100th of its weight acquiring a yellow colour and an acid reaction. Heated with combustible matter it is deoxidized, being converted into the protoxide or binoxide or mixtures of these oxides. In solutions it is deprived of oxygen by all deoxidizing agents, such as alcohol, sugar, and most organic substances, including the oxalic and several vegetable acids, by hydrosulphuric acids, and most of the other hydracids, not excepting the hydrochloric, by sulphurous and phosphorous acids, and even by nitrous acid. Like molybdic and tungstic acids it is disposed to act as a base to such of the stronger acids as do not decompose it, and to form with them definite compounds, which are soluble in water. It unites on this principle with sulphuric and phosphoric acid ; and Berzelius has remarked a compound of the phosphoric, silicic, and vanadic acids, a sort of double salt, in which the latter acid is a base to the two former, and which crystallizes in scales ; it is formed in Sefström's process for preparing vanadic acid, and its solubility opposes a great obstacle to the separation of vanadic from silicic acid.

Vanadic acid unites with salifiable bases often in two or more proportions, forming soluble salts with the alkalies, and in general sparingly soluble salts with the other metallic oxides. Those with excess of acid are commonly of a red or orange-red colour. Most of the neutral salts are yellow : but it is singular that the neutral vanadiates of the alkalies, the alkaline earths, and the oxides of lead, zinc, and cadmium may be yellow at one time and colourless at another without suffering any appreciable change in composition. Thus, on neutralizing

vanadic acid with ammonia a yellow salt is obtained, the solution of which gradually becomes colourless if kept for some hours, and suffers the same change rapidly when heated. The solution, as it is coloured or colourless, gives a yellow or white residue by evaporation, and a yellow or white precipitate with a salt of baryta or oxide of lead. These changes appear to be of the same kind as those already noticed in the description of phosphoric acid.

Vanadic acid unites in different proportions with binoxide of vanadium, and forms compounds which are soluble in pure water, but sparingly so in saline solutions, and which are purple, green, yellow, or orange, according as the acid is in a smaller or larger proportion. They are best formed by exposing the hydrated binoxide to the atmosphere, when these different colours successively appear, as a gradually increasing quantity of the acid is generated.

Vanadic acid is distinguished from all other acids except the chromic by its colour, and from this acid by the action of deoxidizing substances, which give a blue solution with the former and a green with the latter. When heated with borax in the reducing flame of the blowpipe, both of the acids yield a green glass; but in the oxidizing flame the bead becomes yellow if vanadium is present, while the green colour produced by chromium is permanent.

Its eq. is 92·5; *symb.* $V + 3O$, $\dddot{V}$, or VO_3.

Chlorides.—The bichloride is prepared by digesting a mixture of the vanadic and hydrochloric acids, deoxidizing any undecomposed vanadic acid by hydrosulphuric acid, and evaporating the solution to dryness. A brown residue is obtained, which yields a blue solution with water, part being left as an insoluble sub-salt. It may also be generated by acting directly on the ignited binoxide with strong hydrochloric acid. As thus obtained its solution is brown instead of blue, though in composition it seems identical with the preceding. *Its eq. is* 139·34; *symb.* $V + 2Cl$, or VCl_2.

The *terchloride* may be formed by transmitting a current of dry chlorine gas over a mixture of protoxide of vanadium and charcoal heated to a low redness, when the terchloride passes over in vapour, and condenses in the form of a yellow liquid, from which free chlorine may be removed by a current of dry air. It is converted by water into hydrochloric and vanadic acid, and atmospheric humidity produces the same change, which is indicated by the escape of red fumes. *Its eq. is* 174·76; *symb.* $V + 3Cl$, or VCl_3.

A *bibromide* of vanadium may be formed in the same manner as the bichloride, substituting the hydrobromic for hydrochloric acid. Similar compounds may be procured with iodine, fluorine, and cyanogen, by dissolving binoxide of vanadium in hydriodic, hydrofluoric, and hydrocyanic acid.

Sulphurets.—When the binoxide of vanadium is heated to redness in a current of hydrosulphuric acid gas, it is converted into protoxide, and both water and sulphur are obtained: on continuing the process, the protoxide is decomposed, hydrogen gas and water pass over, and bisulphuret of vanadium is generated. This compound may also be procured by mixing sulphate of ammonia with a salt of the binoxide of vanadium until the precipitate at first formed is redissolved, and then decomposing the deep purple-coloured solution by sulphuric or hydrochloric acid. The bisulphuret of a brown colour subsides, which becomes black when it is dried. It is unchanged at common temperatures by exposure to the air, but takes fire when heated. In the hydrated state it is dissolved by alkalies and alkaline sulphurets; but it is insoluble in acids, with the exception of

the nitric and nitro-hydrochloric, by which it is converted into sulphate of the binoxide.

Its eq. is 100·7; *symb.* V + 2S, or VS_2.

When hydrosulphuric acid gas is transmitted through an aqueous solution of vanadic acid, a greyish-brown precipitate is formed, consisting of hydrated binoxide of vanadium mixed mechanically with sulphur. But if a solution of vanadic acid in hydrosulphate of ammonia is acidulated by hydrochloric or sulphuric acid, the hydrated *tersulphuret* of vanadium subsides. Its colour is of a much lighter brown than the bisulphuret, becomes almost black in drying, and is resolved by a red heat in close vessels into the bisulphuret, with loss of water and sulphur. It is soluble in alkalies and alkaline sulphurets, and is oxidized by nitric acid.

Its eq. is 116·8; *symb.* V + 3S or VS_3.

The phosphuret of vanadium, of a leaden-gray colour, may be formed by exposing to a white heat phosphate of the binoxide of vanadium mixed with a small quantity of sugar.

SECTION XX.

MOLYBDENUM.—TUNGSTEN.—COLUMBIUM.

MOLYBDENUM.

Hist. and Prep.—The principal ore of molybdenum is the sulphuret, which was long mistaken for graphite, and was first distinguished from it in 1778 by Scheele; but the metal was obtained in a separate state by Hjelm. When this ore, in fine powder, is digested in nitro-hydrochloric acid until it is completely decomposed, and the residue is briskly heated in order to expel sulphuric acid, molybdic acid remains in the form of a white heavy powder. From this acid metallic molybdenum may be obtained by exposing it with charcoal to the strongest heat of a smith's forge; or by conducting over it a current of hydrogen gas while strongly heated in a tube of porcelain. (Berzelius.) Molybdenum likewise occurs in nature in the form of molybdate of oxide of lead.

Prop.—It is a brittle metal, of a white colour, and so very infusible, that hitherto it has only been obtained in a state of semifusion. In this form it has a sp. gr. varying between 8·615 and 8·636. When heated in open vessels it absorbs oxygen, and is converted into *molybdic acid*; and the same compound is generated by the action of chlorine or nitro-hydrochloric acid. It has three degrees of oxidation, forming two oxides and one acid, from the composition of which Berzelius estimates the eq. of molybdenum at 47·7. *pts symb. is* Mo. The composition of its compounds described in this section is as follows:—

	Molybdenum.		Equiv.	Formulæ.
Protoxide	47·7 1 eq. + Oxygen	8	1 eq. = 55·7	Mo + O or MoO.
Binoxide	47·7 1 eq. + do.	16	2 eq. = 63·7	Mo + 2O or MoO_2.
Molybdic Acid	47·7 1 eq. + do.	24	3 eq. = 71·7	Mo + 3O or MoO_3.
Protochloride	47·7 1 eq. + Chlorine	35·42	1 eq. = 83·12	Mo + Cl or MoCl.

	Molybdenum.			Equiv.	Formulæ.
Bichloride	47·7	1 eq. + Chlorine	70·84	2 eq. = 118·54	Mo + 2Cl or $MoCl_2$.
Bisulphuret	47·7	1 eq. + Sulphur	32·2	2 eq. = 79·9	Mo + 2S or MoS_2.
Tersulphuret	47·7	1 eq. + do.	48·3	3 eq. = 96·0	Mo + 3S or MoS_3.
Persulphuret	47·7	1 eq. + do.	64·4	4 eq. = 112·1	Mo + 4S or MoS_4.
Oxychloride$_2$ MoO_3	143.4	2 eq. + $MoCl_3$	153·96	1 eq. = 297·36	2MoO + $MoCl_3$.

Protoxide of Molybdenum.—On dissolving molybdate of potassa or soda in a small quantity of water, adding hydrochloric acid until the molybdic acid at first thrown down is redissolved, and digesting with a piece of pure metallic zinc, the latter deoxidizes the molybdic acid, the liquid changes to blue, red, and black, and then contains chloride of zinc and protochloride of molybdenum. From the black solution pure potassa throws down the protoxide of molybdenum as a black hydrate, an excess of the alkali being used in order to hold the zinc in solution. The hydrate is washed with the least possible exposure to the air, and dried in vacuo by sulphuric acid. When heated to low redness in the open air it takes fire and is converted into the binoxide; but if not exposed to the air it becomes incandescent at the moment of losing its water, like hydrated oxide of chromium. The anhydrous oxide is black and insoluble in acids; but in the state of hydrate, acids dissolve it. The recently precipitated hydrate is soluble in the cold by carbonate of ammonia, but in none of the other alkalies.

Its eq. is 55·7; *symb.* Mo + O, Mo, or MoO.

Binoxide of Molybdenum.—Prep.—Obtained as a deep brown anhydrous powder by mixing molybdate of soda with half its weight of sal-ammoniac in fine powder, projecting the mixture into a red-hot crucible, which is to be instantly covered, and the heat continued until vapours of sal-ammoniac cease to appear. In this process chloride of sodium is generated, and molybdic acid is reduced by the ammonia to the state of binoxide: by adding water to the mass when cold chloride of sodium is dissolved, and the dark brown, nearly black, binoxide left. The hydrate, of a rust-brown colour, may be formed by digesting molybdenum in powder with molybdic acid dissolved in hydrochloric acid, until the liquid acquires a deep red colour, and then adding ammonia; or by adding ammonia to a solution of the bichloride; or digesting with metallic copper a solution of molybdic in hydrochloric acid until a deep red solution is formed, and employing an excess of ammonia in order to keep oxide of copper in solution.

Prop.—The anhydrous binoxide is insoluble in acids and is changed into molybdic acid by strong nitric acid. The hydrate is very like hydrated peroxide of iron, reddens litmus paper when placed on it, is dissolved by acids with which it forms red salts, insoluble in the alkalies, but dissolves in alkaline carbonates. It is soluble, though sparingly, in pure water, so that it should be washed after precipitation by a solution of sal-ammoniac, which salt is afterwards removed by alcohol. On exposure to the air, the hydrate absorbs oxygen and becomes blue at its surface: this blue compound is more soluble in water than the hydrate, and was supposed by Bucholz to be a distinct acid, which he termed *molybdous acid*; but Berzelius has shown that it is a bimolybdate of the binoxide. (Berzelius.)

Its eq. is 63·7; *symb.* Mo + 2O, Mo, or MoO_2.

Molybdic Acid.—Prep.—When sulphuret of molybdenum is roasted in an open crucible kept at a low red heat, and constantly stirred until sulphurous acid

ceases to escape, a dirty yellow powder is left, which contains impure molybdic acid. The acid is taken up by ammonia and the filtered solution evaporated to dryness; it is again taken up by a little dilute ammonia and filtered; it is then purified by crystallization. On heating gently in an open platinum crucible, taking care to prevent fusion, the ammonia is expelled, and pure acid remains. It is also obtained by oxidizing the binoxide with nitric acid.

Prop.—As thus formed, it is a white powder, of sp. gr. 3·49, fusible by a red heat into a yellow liquid, which bears a strong red heat in closed vessels without subliming, but in an open crucible rises with the current of air, and collects on cold surfaces in colourless crystalline scales. It requires 570 times its weight of water for solution, which nevertheless has an acid reaction. It is soluble in the alkalies, forming colourless molybdates, from which molybdic acid is precipitated by the stronger acids, though an excess of the acids dissolves it; but after exposure to a red heat it is insoluble in acids.

Chlorides.—Berzelius has described three chlorides of molybdenum which he considered analogous in composition to the oxides; but his terchloride has recently been shown by Rose to be an oxychloride which has the same constitution as the oxychloride of chromium. (Pog. An. xl. 395.)

The protochloride is formed by dissolving the hydrated protoxide in hydrochloric acid, when it forms a deep nearly black coloured solution, which leaves a black viscid mass by evaporation.

Its eq. is 83·12; *symb.* Mo + Cl, or MoCl.

The *bichloride* is obtained as above mentioned, and yields a red solution. It is obtained in the anhydrous state by gently heating molybdenum in powder in dry chlorine gas, atmospheric air being excluded. The metal takes fire at its surface, but it is soon extinguished, after which the chlorine is replaced by a red vapour of such intensity that it is completely opaque in a vessel $\frac{3}{4}$ inch in diameter: this vapour condenses in the cooler parts of the apparatus brilliant black crystals just like those of iodine, which are very fusible, and sublime at a gentle heat. Exposed to dry oxygen gas it is transformed gradually into oxychloride of molybdenum and molybdic acid. With water the bichloride acts violently from the intense heat evolved, and the whole is dissolved.

Its eq. is 118·54; *symb.* Mo + 2Cl, or $MoCl_2$.

Sulphurets.—Molybdenum combines with sulphur in three proportions. The lowest grade is the *bisulphuret*, which is the most common ore of molybdenum, and is usually associated with ores of tin, has a lead-grey colour and metallic lustre resembling graphite, for which it was formerly mistaken. Its density varies from 4·138 to 4·569. It bears a strong heat in close vessels without change or fusion; but it is oxidized by nitric acid or by the joint action of heat and air. *Its eq. is* 79·9; *symb.* Mo + 2S, or MoS_2.

The *tersulphuret* is obtained by saturating molybdate of potassa, soda, or ammonia with hydrosulphuric acid gas, and adding hydrochloric acid, when the tersulphuret falls of a deep brown colour, which becomes black on drying. It is partially oxidized when dried in the air. By heat in close vessels it is changed into the bisulphuret with loss of sulphur.

Its eq. is 96; *symb.* Mo + 3S, or MoS_3.

The persulphuret is made by boiling the sulphur-salt formed of tersulphuret of molybdenum and sulphuret of potassium for a long time with the bisulphuret of molybdenum, when a precipitate collects which is to be well washed with cold

water. It is a sulphur-salt composed of persulphuret of molybdenum and sulphuret of potassium, which forms with boiling water a deep red solution, from which on the addition of hydrochloric acid the persulphuret subsides.

Its eq. is 112·1; *symb.* Mo + 4S, or MoS_4.

Oxychloride of Molybdenum.—Formerly described as a terchloride. It is obtained by heating the binoxide in a current of dry chlorine. It is white with a shade of yellow, sublimes at a heat short of redness, and condenses into crystalline scales. It dissolves in water, but the solution is slightly milky from the separation of molybdic acid. From its composition, which has been recently determined by Rose, it would appear that

3 eq. of Binoxide and	3 eq. of Chlorine	yield	1 eq. of Oxychloride
$3\,MoO_2$	$3Cl$		$MoCl_3+2MoO^3$.

Its eq. is 297·36; *symb.* $MoCl_3$ $2MoO_3$.

TUNGSTEN.

It derives its name from the Swedish words *Tung Sten, heavy stone*, from the density of its ores: and it is called Wolfram from the mineral of that name, which is a tungstate of the oxides of iron and manganese. This metal may be procured in the metallic state by exposing tungstic acid to the action of charcoal or dry hydrogen gas at a red heat; but though the reduction is easily effected, an exceedingly intense temperature is required for fusing the metal. Tungsten has a greyish-white colour, and considerable lustre. It is brittle, nearly as hard as steel, and less fusible than manganese. Its sp. gr. is near 17·4. When heated to redness in the open air it takes fire, and is converted into tungstic acid; and it undergoes the same change by the action of nitric acid. Digested with a concentrated solution of pure potash, it is dissolved with disengagement of hydrogen gas, and tungstate of potash is generated.

Chemists are acquainted with two compounds of this metal and oxygen; namely, the *dark brown oxide*, and the *yellow acid of tungsten*; and according to the analyses of Berzelius, (An. de Ch. et Ph. xvii.) the oxygen of the former is to that of the latter in the ratio of two to three. From the composition of the latter, and assuming that it contains three atoms of oxygen, the eq. of tungsten is 99·7. Its symb. is W. Its compounds described in this section are thus constituted:—

	Tungsten.			Equiv.	Formulæ.
Binoxide	99·7	1 eq.+Oxygen	16	2 eq.=115·7	W+2O or WO_2.
Blue Oxide	199·4	2 eq.+ditto	24	3 eq.=223·4	2W+3O or W_2O_3.
Tungstic Acid	99·7	1 eq.+ditto	24	3 eq.=123·7	W+3O or WO_3.
Bichloride	99·7	1 eq.+Chlorine	70·84	2 eq.=170·54	W+2Cl or WCl_2.
Bisulphuret	99·7	1 eq.+Sulphur	32·2	2 eq.=131·9	W+2S or WS_2.
Persulphuret	99·7	1 eq.+ditto	48·3	3 eq.=148·0	W+3S or WS^3.
Oxychloride $2WO_3$	257.4	2 eq.+WCl_3	205·96	1 eq.=463·36	WCl_3+2WO_3.

Binoxide.—Prep.—By the action of hydrogen gas on tungstic acid at a low red heat; but the best mode of procuring it, both pure and in quantity, is that recommended by Wöhler. (Quarterly Journal of Science, xx. 177.) This process consists in mixing Wolfram in fine powder with twice its weight of carbonate of potassa, and fusing the mixture in a platinum crucible. The resulting

tungstate of potassa is dissolved in hot water, mixed with about half its weight of hydrochlorate of ammonia in solution, evaporated to dryness, and exposed in a hessian crucible to a red heat. The mass is well washed with boiling water, and the insoluble matter digested in dilute potassa to remove any tungstic acid. The residue is oxide of tungsten. It appears that in this process the tungstate of potassa and hydrochlorate of ammonia mutually decompose each other, so that the dry mass consists of chloride of potassium and tungstate of ammonia. The elements of the latter react on each other at a red heat, giving rise to water, nitrogen gas, and oxide of tungsten; and this compound is protected from oxidation by the fused chloride of potassium with which it is enveloped. This oxide is also formed by putting tungstic acid in contact with zinc in dilute hydrochloric acid. The tungstic acid first becomes blue, and then assumes a copper colour; but the oxide in this state can with difficulty be preserved, as by exposure to the air, and even under the surface of water, it absorbs oxygen, and is reconverted into tungstic acid.

Prop.—When prepared by means of hydrogen gas, it has a brown colour, and when polished acquires the colour of copper; but when procured by Wöhler's process, it is nearly black. It does not unite, so far as is known, with acids; and when heated to near redness, it takes fire, and yields tungstic acid.

Its eq. is 115·7; *symb.* W + 2O, $\ddot{W}$, or WO_2.

Tungstic Acid.—Prep.—Conveniently by digesting native tungstate of lime, very finely levigated, in nitric acid; by which means nitrate of lime is formed, and tungstic acid separated in the form of a yellow powder. Long digestion is required before all the lime is removed; but the process is facilitated by acting upon the mineral alternately by nitric acid and ammonia. The tungstic acid is dissolved readily by that alkali, and may be obtained in a separate state by heating the tungstate of ammonia to redness. Tungstic acid may also be prepared by the action of hydrochloric acid on Wolfram. It is also obtained by heating the brown oxide to redness in open vessels.

Prop.—Tungstic acid is of a yellow colour, is insoluble in water, and has no action on litmus paper. With alkaline bases it forms salts called *tungstates*, which are decomposed by the stronger acids, the tungstic acid in general falling combined with the acid by which it is precipitated. When strongly heated in open vessels it acquires a green colour, and becomes blue when exposed to the action of hydrogen gas at a temperature of 500° or 600° F. The blue compound, according to Berzelius, is a tungstate of the oxide of tungsten; and the green colour is probably produced by an admixture of this compound with the yellow acid.

Its eq. is 123·7; *symb.* W + 3O, $\dddot{W}$, or WO_3.

Malaguti finds that the blue compound, formed in the manner stated above, is never constant in its composition; but he obtained a definite compound by heating tungstic acid by the flame of a spirit-lamp in a current of dry hydrogen. According to his analysis it contains 17·72 per cent. of oxygen; and he considers it a distinct acid, the constitution of which is represented by the *symb.* 2W + 5O, or W_2O_5. (An. de Ch. et Ph. lx. 271.)

Chlorides of Tungsten.—Tungsten and chlorine unite in two proportions. When metallic tungsten is heated in chlorine gas, it takes fire, and yields the bichloride. The compound appears in the form of delicate needles, of a deep red colour resembling wool, but more frequently as a deep-red fused mass which has

the brilliant fracture of cinnabar. When heated, it fuses, boils, and yields a red vapour. By water it is changed into hydrochloric acid and oxide of tungsten. It is entirely dissolved by solution of pure potassa, with disengagement of hydrogen gas, yielding tungstate of potassa and chloride of potassium. A similar change is produced by ammonia, except that some oxide of tungsten is left undissolved.

Its eq. is 170·54; *symb.* W + 2Cl, or WCl_2.

Another chloride has been described by Wöhler. It is formed at the same time as the first; by the action of water it is converted into hydrochloric and tungstic acids. It is the most beautiful of all these compounds, existing in long transparent crystals of a fine red colour. It is very fusible and volatile, and its vapour is red like that of nitrous acid. The difference between this compound and the chloride first described is not yet satisfactorily determined; for although the analysis of Malaguti in his paper above referred to would indicate its constitution to be similar to that of his blue oxide, and therefore W_2Cl_5, still the errors into which he fell in reference to the terchloride throw suspicion on this result. The production of tungstic acid by its decomposition with water strengthens this suspicion.

Sulphurets of Tungsten.—The protosulphuret is obtained as a black powder by transmitting hydrosulphuric acid gas, or the vapour of sulphur, over tungstic acid heated to whiteness in a tube of porcelain. The persulphuret is prepared by dissolving tungstic acid in a solution of sulphuret of potassium or hydrosulphate of ammonia, and adding an excess of hydrosulphuric acid. It falls as a brown precipitate, which becomes black in drying. It is soluble to a certain extent in water which is free from saline matter.

Oxychloride of Tungsten—Formerly described as the terchloride. It was discovered by Wöhler, and prepared by heating the binoxide of tungsten in a stream of dry chlorine gas. The action is attended with the appearance of combustion, dense fumes arise, and a thick sublimate is obtained in the form of scales, like native boracic acid. It is volatile at a low temperature without previous fusion. According to Rose, who has determined its composition, (Pog. An. xl. 395,) it is resolved when suddenly heated into tungstic acid, the bichloride of tungsten, and chlorine.

Its eq. is 463·36; *symb.* $WCl_3 + 2WO_3$; or, as in the case of the corresponding compound of chromium, $W\left\{\begin{matrix}Cl\\O_2\end{matrix}\right\}$.

COLUMBIUM.

Hist.—This metal was discovered in 1801 by Hatchett, who detected it in a black mineral belonging to the British Museum, supposed to have come from Massachusetts in North America; and from this circumstance applied to it the name of *columbium*. About two years after, M. Ekeberg, a Swedish chemist, extracted the same substance from *tantalite* and *yttro-tantalite*; and, on the supposition of its being different from columbium, described it under the name of *tantalum*. The identity of these metals, however, was established in the year 1809 by Wollaston.

Prep.—Columbic acid is with difficulty reduced to the metallic state by the action of heat and charcoal; but Berzelius succeeded in obtaining this metal by the same process which he employed in the preparation of zirconium and silicon,

namely, by heating potassium with the double fluoride of potassium and columbium. On washing the reduced mass with hot water, in order to remove the fluoride of potassium, columbium is left in the form of a black powder.

Prop.—As a powder it does not conduct electricity; but in a denser state it is a perfect conductor. By pressure it acquires a metallic lustre, and has an iron-grey colour. It is not fusible at the temperature at which glass is fused. When heated in the open air it takes fire considerably below the temperature of ignition, and glows with a vivid light, yielding columbic acid. It is scarcely at all acted on by the sulphuric, hydrochloric, or nitro-hydrochloric acid; whereas it is dissolved with heat and disengagement of hydrogen gas by hydrofluoric acid, and still more easily by a mixture of nitric and hydrofluoric acids. It is also converted into columbic acid by fusion with hydrate of potassa, the hydrogen gas of the water being evolved.

From the experiments of Berzelius on the composition of the oxide and acid of columbium, its eq. may be estimated at 185. *Its symb.* is Ta. The compounds described in this section are thus constituted:—

	Columbium.			Equiv.	Formulæ.
Binoxide .	185	1 eq.+Oxygen	16	2 eq.= 201	Ta+2O or TaO^2.
Columbic Acid	185	1 eq.+ . .	24	3 eq.= 209	Ta+3O or TaO_3.
Terchloride	185	1 eq.+Chlorine	106·26	3 eq.= 291·26	Ta+3Cl or $TaCl_3$.
Terfluoride .	185	1 eq.+Fluorine	56·04	3 eq.= 241·04	Ta+3F or TaF_3.
Sulphuret .	Composition uncertain.				

Oxide of Columbium.—It is generated by placing columbic acid in a crucible lined with charcoal, luting carefully to exclude atmospheric air, and exposing it for an hour and a half to intense heat. The acid, where in direct contact with charcoal, is entirely reduced: but the film of metal is very thin. The interior portions are pure oxide of a dark grey colour, very hard and coherent. When reduced to powder its colour is dark brown. It is not attacked by any acid, even by the nitro-hydrofluoric; but it is converted into columbic acid either by fusion with hydrate of potassa, or deflagration with nitre. When heated to low redness it takes fire and glows, yielding a light grey powder; but in this way it is never completely oxidized. Berzelius states that this oxide, in union with protoxide of iron and a little protoxide of manganese, occurs at Kimito in Finland, and may be distinguished from the other ores of columbium by yielding a chestnut-brown powder.

Its eq. is 201; *symb.* Ta + 2O, $\dot{T}a$, or TaO_2.

Columbic Acid.—Columbium exists in most of its ores as an acid, united either with the oxides of iron and manganese, as in tantalite, or with the earth yttria, as in the yttro-tantalite. This acid is obtained by fusing its ore with three or four times its weight of carbonate of potassa, when a soluble columbate of that alkali results, from which columbic acid is precipitated as a white hydrate by acids. Berzelius also prepares it by fusion with bisulphate of potassa.

Hydrated columbic acid is tasteless, and insoluble in water; but when placed on moistened litmus paper, it communicates a red tinge. It is dissolved by the sulphuric, hydrochloric, and some vegetable acids; but it does not diminish their acidity, or appear to form definite compounds with them. With alkalies it unites readily; and though it does not neutralize their properties completely, crystallized salts may be obtained by evaporation. When the hydrated acid is heated to redness, water is expelled, and the anhydrous columbic acid remains. In this state it is attacked by alkalies only.

Its eq. is 209; *symb.* Ta + 3O, $\dddot{T}a$, or TaO_3.

Perchloride of Columbium.—When columbium is heated in chlorine gas, it takes fire and burns actively, yielding a yellow vapour, which condenses in the cold parts of the apparatus in the form of a white powder with a tint of yellow. Its texture is not in the least crystalline. By contact with water, it is converted, with a hissing noise and increase of temperature, into columbic and hydrochloric acids. Hence *its eq.* is considered to be 291·26; *symb.* Ta + 3Cl, or $TaCl_3$.

Terfluoride of Columbium.—Hydrofluoric acid takes up hydrated columbic acid, and forms with it a compound of terfluoride of columbium and hydrofluoric acid, which, by evaporation at 76°, is deposited in crystals, which are soluble in water, and effervesce in the air. By gently evaporating the solution, an uncrystalline mass, white and opaque is left, which Berzelius considers to be the terfluoride of columbium. By water part of it is converted into columbic and hydrofluoric acids, the latter soluble and the former insoluble; but both of these acids retain some terfluoride in combination. *Its eq. is* 241·04; *symb.* Ta + 3F, or TaF_3.

Sulphuret of Columbium.—This compound, first prepared by Rose, is generated, with the phenomena of combustion, when columbium is heated to commencing redness in the vapour of sulphur; or by transmitting the vapour of bisulphuret of carbon over columbic acid in a porcelain tube at a white heat, carbonic oxide being also evolved.*

SECTION XXI.

URANIUM.—CERIUM.—LANTANIUM.

URANIUM.

Hist. and Prep.—This metal was discovered in 1789 by the German analyst Klaproth, who named it after the new planet Uranus, the discovery of which took place in the same year. It was obtained from a mineral of Saxony, called from its black colour *pitchblende*, which consists of protoxide of uranium and oxide of iron. From this ore the uranium may be conveniently extracted by the following process. After heating the mineral to redness, and reducing it to fine powder, it is digested in pure nitric acid diluted with three or four parts of water, taking the precaution to employ a larger quantity of the mineral than the nitric acid present can dissolve. By this mode of operating, the protoxide is converted into peroxide of uranium, which unites with the nitric acid almost to the total exclusion of the iron. A current of hydrosulphuric acid gas is then transmitted through the solution, in order to separate lead and copper, the sulphurets of which are always mixed with pitchblende. The solution is boiled to expel free hydrosulphuric acid, and after being concentrated by evaporation, is set aside to crystallize. The nitrate of peroxide of uranium is gradually deposited in flattened four-sided prisms of a beautiful lemon-yellow colour.

* Professor H. Rose has recently discovered two new metals in the Tantalite of Bavaria, which he calls *Niobium* and *Pelopium*. (Comptes Rendus, Dec. 1844.) (R.)

Prop.—The properties of metallic uranium are as yet known imperfectly. It was prepared by Arfwedson by conducting hydrogen gas over the protoxide of uranium heated in a glass tube. The substance obtained by this process was crystalline, of a metallic lustre, and of a reddish-brown colour. It suffered no change on exposure to air at common temperatures; but when heated in open vessels, it absorbed oxygen, and was reconverted into the protoxide. From its lustre it was inferred to be metallic uranium.

From the experiments of Arfwedson and Berzelius on the oxides of uranium, the eq. of the metal may be estimated at 217. (An. of Ph. N. S. vii. 258); its symb. is U. Its compounds described in this section are thus constituted:—

	Uranium.			Equiv.	Formulæ.
Protoxide	217	1 eq. + Oxygen	8	1 eq. = 225	U + O or UO.
Peroxide	434	2 eq. + do.	24	3 eq. = 458	2U + 3O or U^2O_3.
Protochloride	217	1 eq. + Chlorine	35·42	1 eq. = 252·42	U + Cl or UCl.
Perchloride	434	2 eq. + do.	106·26	3 eq. = 540·26	2U + 3Cl or U_2Cl_3.
Sulphuret	Composition unknown.				

Protoxide.—This oxide is of a very dark green colour, and is obtained by exposing nitrate of the peroxide to a strong heat. It is exceedingly infusible, and bears any temperature hitherto tried without change. It unites with acids, forming salts of a green colour. It is readily oxidized by nitric acid, yielding a nitrate of the peroxide. The protoxide is employed in the arts by giving a black colour to porcelain.

Its eq. is 225; *symb.* U + O,U̇, or UO.

Peroxide of Uranium is of a yellow or orange colour, and most of its salts have a similar tint. It not only combines with acids, but likewise unites with alkaline bases, a property which was first noticed by Arfwedson. It is precipitated from acids as a yellow hydrate of pure alkalies, fixed or volatile; but retains a portion of these bases in combination. It is thrown down as a carbonate by alkaline carbonates, but is redissolved by an excess of carbonate of soda or ammonia, a circumstance which affords an easy method of separating uranium from iron. It is not precipitated by hydrosulphuric acid, but acquires a green tint from partial deoxidation. With ferrocyanide of potassium it gives a brownish-red precipitate, very like ferrocyanuret of copper.

Peroxide of uranium is decomposed by a strong heat, and converted into the protoxide. From its affinity for alkalies, it is difficult to obtain it in a state of perfect purity. It is employed in the arts for giving an orange colour to porcelain.

Its eq. is 458; *symb.* 2U + 3O, $\ddot{\underline{U}}$, or U_2O_3.

Chlorides.—These compounds are obtained in solution by dissolving the corresponding oxides in hydrochloric acid. The protochloride is green, very soluble, and does not crystallize. The perchloride is yellow, deliquescent, soluble in alcohol, ether, and water, and yields yellow solutions.

Sulphuret of Uranium may be formed by transmitting the vapour of bisulphuret of carbon over protoxide of uranium strongly heated in a tube of porcelain. (Rose.) It is of a dark-grey or nearly black colour, is converted into protoxide of uranium when heated in the open air, and is readily dissolved by nitric acid. Hydrochloric acid attacks it feebly.

CERIUM.—LANTANIUM.

Cerium, named after the planet Ceres, was discovered in the year 1803 by Hisinger and Berzelius, in a rare Swedish mineral known by the name of Cerite, and its existence was recognized about the same time by Klaproth. Thomson has since found it to the extent of thirty-four per cent. in a mineral from Greenland, called *Allanite*, in honour of the late Mr. Allan, who first distinguished it as a distinct species.

Very lately, Mosander has shown that the oxide commonly considered as oxide of cerium contains a large proportion of the oxide of a new metal, to which he has given the name of Lantanium (from λανθανω, *I lurk*, it having lain concealed in the ores of cerium). The properties and compounds of this new metal have not yet been fully investigated, and of course those of pure cerium are equally unknown. There is, however, a great analogy between them, each forming two oxides, both of which unite with acids. The carbonates of both protoxides are white and insoluble; the sulphates soluble and crystallizable.

By the following process the two oxides may be conveniently separated. The mixed oxide is dissolved in nitric acid, the solution evaporated to dryness, and the residue calcined. The oxide is now powdered, and digested in weak nitric acid (1 of acid to 50 or 100 of water), which dissolves the oxide of lantanium, and leaves the oxide of cerium undissolved. The former may be precipitated as carbonate by a carbonated alkali; the latter may be dissolved by a strong acid, and also converted into carbonate. It would be absurd, in the present state of our knowledge, to give details as to the compounds of these two metals, which cannot possibly be correct.

The symbol of cerium is Ce; that of lantanium will be La. Both metals are more closely allied to yttrium and zirconium than to any others.*

SECTION XXII.

BISMUTH.—TITANIUM.—TELLURIUM.

BISMUTH.

Hist. and Prep.—This metal was known to the ancients, though often confounded by them with lead and tin; but it appears to have derived the name of *bismuth*, or properly *wismuth*, from the German miners. It occurs in the earth both native and in combination with other substances, such as sulphur, oxygen, and arsenic. That which is employed in the arts is derived chiefly from native bismuth, and commonly contains small quantities of sulphur, iron, and copper. It may be obtained pure for chemical purposes by heating the oxide or subnitrate to redness along with charcoal.

* Mosander has still more recently announced the existence of another new metal associated with cerium and lantanium, which he calls *Didym* or *Didymium*. (R.)

Prop.—Bismuth has a reddish-white colour and considerable lustre. Its structure is highly lamellated, and when slowly cooled it crystallizes in cubes or octohedrons. Its density is about 10. It is brittle when cold, but may be hammered into plates while warm. At 476° it fuses, and sublimes in close vessels at a red heat. It is a less perfect conductor of heat than most other metals.

Bismuth undergoes little change by exposure to air at common temperatures. When fused in open vessels, its surface becomes covered with a grey film, which is a mixture of metallic bismuth with the oxide of the metal. Heated to its subliming point, it burns with a bluish white flame, and emits copious fumes of oxide of bismuth. The metal is attacked with difficulty by hydrochloric or sulphuric acid, but it is readily oxidized and dissolved by nitric acid.

The eq. of bismuth, deduced by Lagerhjelm from the composition of its protoxide, is 71 (An. of Phil. iv. 357); *its symb.* is Bi. Its compounds described in this section are thus constituted:—

	Bismuth.		Equiv.	Formulæ.
Protoxide	71	1 eq.+Oxygen 8	1 eq.= 79	Bi+O or BiO.
Peroxide	142	2 eq.+do. 24	3 eq.=166	2Bi+3O or Bi_2O_3.
Chlorine	71	1 eq.+Chlorine 35·42	1 eq.=106·42	Bi+Cl or BiCl.
Bromide	71	1 eq.+Bromine 78·4	1 eq.=149·4	Bi+Br or BiBr.
Sulphuret	71	1 eq.+Sulphur 16·1	1 eq.= 87·1	Bi+S or BiS.

Protoxide of Bismuth.—This compound is readily prepared by heating to redness the nitrate or subnitrate of oxide of bismuth. Its colour is yellow; at a full red heat it is fused into a brown liquid, which on cooling becomes a yellow transparent glass of sp. gr. 8·211. At intense temperatures it is sublimed. It unites with acids, and most of its salts are white.

When nitrate of oxide of bismuth, either in solution or in crystals, is put into water, a copious precipitate, the subnitrate, of a beautifully white colour, subsides, which was formerly called the *magistery of bismuth.* From its whiteness it is sometimes employed as a paint for improving the complexion; but it is an inconvenient cosmetic, owing to the facility with which it is blackened by hydrosulphuric acid. If the nitrate with which it is made contains no excess of acid, and a large quantity of water is employed, nearly the whole of the bismuth is separated as a subnitrate.—By this character bismuth may be both distinguished and separated from other metals.

Its eq. is 79; *symb.* Bi + O, Bi, or BiO.

Peroxide.—This oxide was first noticed by Bucholz and Brandes, but its nature and composition have been recently examined by A. Stromeyer. It is generated when hydrate of potassa is fused at a moderate heat with protoxide of bismuth; but the best mode of preparation is first to prepare the protoxide by igniting the subnitrate, and then gently heating it for some time in a solution of chloride of potassa or soda. After washing with water, any unchanged protoxide is dissolved by a solution made with 1 part of nitric acid (quite free from nitrous acid) and 9 of water.

As thus prepared, peroxide of bismuth is a heavy powder of a brown colour, very like peroxide of lead, manifests little disposition to unite either with acids or alkalies, and is reconverted by heat with loss of oxygen into the protoxide. Heated with sulphuric or phosphoric acid, it gives off oxygen gas, and a sulphate or phosphate of the protoxide is formed; and with hydrochloric acid chlorine is

evolved, and the protochloride produced (An. de Ch. et Ph. li. 267). *Its eq. is* 166; *symb.* 2Bi + 3O, $\dot{\overline{Bi}}$, or Bi_2O_3.

Chloride of Bismuth.—When bismuth in fine powder is introduced into chlorine gas, it takes fire, burns with a pale blue light, and is converted into a chloride, formerly termed *butter* of bismuth. It may be prepared conveniently by heating two parts of corrosive sublimate with one of bismuth, and afterwards expelling the excess of the former, together with the metallic mercury, by heat.

Chloride of bismuth is of a greyish-white colour, opaque, and of a granular texture. It fuses at a temperature a little above that at which the metal itself is liquefied, and bears a red heat in close vessels without subliming.

Its eq. is 106·42; *symb.* Bi + Cl, or BiCl.

Bromide of Bismuth is prepared by heating the metal with a large excess of bromine in a long tube; when a grey-coloured bromide results, similar in its aspect to fused iodine. At 392° it enters into fusion, and at a low red heat sublimes. With water it is converted into oxide of bismuth and hydrobromic acid, the former of which combines with some undecomposed bromide of bismuth as an oxybromide. (Serullas.)

Its eq. is 149·4; *symb.* Bi + Br, or BiBr.

Sulphuret of Bismuth.—This sulphuret is found native, and may be formed artificially by fusing bismuth with sulphur, or by the action of hydrosulphuric acid on the salts of bismuth. It is of a lead-grey colour and metallic lustre.

Its eq. is 87·1; *symb.* Bi + S, or BiS.

TITANIUM.

Hist.—This metal was first recognized as a new substance by Mr. Gregor of Cornwall, and its existence was afterwards established by Klaproth, who fancifully gave it the name of *Titanium*, after the *Titans* of ancient fable. (Contributions, i.) But the properties of the metal were not ascertained in a satisfactory manner until the year 1822, when Wollaston was led to examine some minute crystals which were found in a slag at the bottom of a smelting furnace at the great iron works at Merthyr Tydvil in Wales, and presented to him by Buckland. (Philosophical Transactions, 1823.) These crystals, which have since been found at other iron works, are of a cubic form, and in colour and lustre resemble burnished copper. They are found in the blast furnaces, and are probably derived principally from the hearth-stone, which contains them abundantly. They conduct electricity, and are attracted slightly by the magnet, a property which seems owing to the presence of a minute quantity of iron. Their sp. gr. is 5·3; and their hardness is so great, that they scratch a polished surface of rock crystal. They are exceedingly infusible; but when exposed to the united action of heat and air, their surface becomes covered with a purple-coloured film, which is an oxide. They resist the action of nitric and nitro-hydrochloric acids, but are completely oxidized by being strongly heated with nitre. They are then converted into a white substance, which possesses all the properties of titanic acid.

Prep.—Liebig prepares metallic titanium by putting fragments of recently made chloride of titanium and ammonia in a glass tube half an inch wide and two or three feet long, transmitting through it a current of perfectly dry ammonia, and when atmospheric air is entirely displaced, applying heat until the glass softens. Complete decomposition ensues, nitrogen gas is disengaged, hydro-

chlorate of ammonia sublimes, and metallic titanium is left in the state of a deep blue-coloured powder. If exposed to the air while warm, it is apt to take fire.

The eq. of titanium, determined by Rose from his analysis of the bichloride, is 24·3; its symb. is Ti. The composition of its compounds described in this section is as follows:—

1 eq. Titanium.			Equiv.	Formulæ.
Oxide (probably)	24·3+Oxygen	8	1 eq.=32·3	Ti+O or TiO.
Titanic Acid .	24·3+do.	16	2 eq.=40·3	Ti+2O or TiO_2.
Bichloride .	24·3+Chlorine	70·84	2 eq.=95·14	Ti+2Cl or $TiCl_2$.
Bisulphuret .	24·3+Sulphur	32·2	2 eq.=56·5	Tl+2S or TiS_2.

Oxide of Titanium.—When titanic is exposed to a strong heat in a black-lead crucible, a mass is obtained, the exterior crust of which is metallic titanium, but the interior parts consist of the supposed protoxide. As thus prepared it is a black mass, which has an earthy fracture, is quite insoluble in all acids, and is very difficult to oxidize. Oxide of titanium is formed in the moist way, when a fragment of zinc or iron is introduced into a solution of titanic acid in hydrochloric acid. The solution soon acquires a purple tint, and after a time the whole of the titanic acid is thrown down in the form of a deep purple powder. This cannot be collected, owing to the facility with which it is reconverted into titanic acid; hence its composition and chemical properties are unknown.

Titanic Acid.—Hist. and Prep.—This compound, called also peroxide of titanium, has been carefully studied by H. Rose, who first pointed out its acid properties. It occurs in a nearly pure state in the minerals rutile and anatase, which are remarkable for presenting the same chemical compound crystallized in unconnected forms. It also exists in titanite or sphene as titanate and silicate of lime, and menaccanite as titanate of the oxides of iron and manganese, in the latter of which titanium was originally discovered by Gregor. It is best prepared from rutile. The mineral, after being reduced to an exceedingly fine powder, is fused in a platinum crucible with three times its weight of carbonate of potash, and the mass afterwards washed with water to remove the excess of alkali. A grey mass remains, which consists of potash and titanic acid. This compound is dissolved in concentrated hydrochloric acid; and on diluting with water, and boiling the solution, the greater part of the titanic acid is thrown down. It is then collected on a filter, and well washed with water acidulated with hydrochloric acid. In this state it is not quite pure; but contains a little oxide of manganese and iron, derived from the rutile. The best mode of separating these impurities is to digest the precipitate, while still moist, with hydrosulphate of ammonia, which converts the oxides of iron and manganese into sulphurets, but does not act on the titanic acid. The two sulphurets are readily dissolved by dilute hydrochloric acid; and the titanic acid, after being collected on a filter and well washed as before, may be dried and heated to redness. This method, proposed by Rose of Berlin, has been thus simplified by himself. Either rutile or titaniferous iron, after being pulverized and washed, is exposed in a porcelain tube at a very strong red heat to a current of hydrosulphuric acid gas, which acts upon the oxide of iron, giving rise to water and sulphuret of iron. As soon as water ceases to appear, the process is discontinued, the mass digested in hydrochloric acid to remove the iron, and the titanic acid separated from adhering sulphur by heat. A little iron is still usually retained; but the whole may be removed by a repetition of the same process. (An. de Ch. et Ph. xxiii. and xxxviii. 131.)

Prop.—Titanic acid, when pure, is quite white. It is exceedingly infusible; and after being once ignited it ceases to be soluble in acids, except in the hydrofluoric. In its chemical relations it is analogous to silicic acid, being a feeble acid, insoluble in water, without action on test paper, but combining with metallic oxides. In the state of hydrate, as when precipitated from hydrochloric acid by boiling, or when combined with an alkali after fusion, it has a singular tendency to pass through the pores of a filter when washed with pure water; but the presence of a little acid, alkali, or salt, prevents this inconvenience.

If previously ignited with carbonate of potassa, titanic acid is soluble in dilute hydrochloric acid; but it is retained in solution by so feeble an attraction, that it is precipitated merely by boiling. It is likewise thrown down by the pure and carbonated alkalies, both fixed and volatile. A solution of gall-nuts causes an orange red colour, which is very characteristic of titanic acid; an effect which appears owing to tannic, and not to gallic acid. When a rod of zinc is suspended in the solution, a purple-coloured powder, probably the protoxide, is precipitated which is gradually converted into titanic acid. *Its eq. is* 40·3; *symb.* $\dot{T}i + 2O$, $\ddot{T}i$, or TiO_2.

Bichloride of Titanium.—This substance was discovered in the year 1824 by Mr. George of Leeds, by transmitting dry chlorine gas over metallic titanium at a red heat. Rose prepared it for his analysis by heating a mixture of titanic acid and charcoal in a tube, through which dry chlorine gas was passing: the resulting bichloride was purified from adhering free chlorine by agitation either with mercury or potassium, and repeated distillation. At common temperatures it is a transparent colourless fluid, of considerable sp. gr., boils violently at a temperature a little above 212°, and condenses again without change. Dumas has shown that the density of its vapour may be estimated at 6·615. In open vessels it is attacked by the moisture of the atmosphere, and emits dense white fumes of a pungent odour similar to that of chlorine, but not so offensive. On adding a few drops of water to a few drops of the liquid, combination ensues with almost explosive violence, from the evolution of intense heat; and if the water is not in excess a solid hydrate is obtained. On exposure to the air it deliquesces, and on adding water the greater part is dissolved. The bichloride, when exposed to an atmosphere of dry ammonia, absorbs a large quantity of the gas, and becomes solid. It was from this compound Liebig prepared metallic titanium.

Its eq. is 95·14; *symb.* Ti + 3Cl, or $TiCl_2$.

Bisulphuret of Titanium.—This compound was discovered by Rose, who prepared it by transmitting the vapour of bisulphuret of carbon over titanic acid, heated to whiteness in a tube of porcelain. It occurs in thick green masses, which by the least friction acquire a dark yellow colour and metallic lustre. When heated in the open air it is converted into sulphurous and titanic acids. By acids it is slowly decomposed, and is dissolved by hydrochloric acid with disengagement of hydrosulphuric acid gas.

Its eq. is 56·5; *symb.* Ti + 2S, or TiS_2.

TELLURIUM.

Hist.—A rare metal, hitherto found only in the gold mines of Transylvania, and even there in very small quantity. Its existence was inferred by Müller in the year 1782, and fully established in 1798 by Klaproth, who gave it the name

of *tellurium*, from *tellus*, *the earth*, suggested by the source from which he drew the name of uranium. (Contributions, iii.) It occurs in the metallic state, chiefly in combination with gold and silver.

Prop.—It has a tin-white colour running into lead-grey, a strong metallic lustre, and lamellated texture. It is very brittle, and its density is 6·2578. It fuses at a temperature below redness, and at a red heat is volatile. When heated before the blowpipe it takes fire, burns rapidly with a blue flame bordered with green, and is dissipated in grey-coloured pungent inodorous fumes. The odour of decayed horse-radish is sometimes emitted during the combustion, and was thought by Klaproth to be peculiar to tellurium; but Berzelius ascribes it solely to the presence of selenium.

From some experiments of Berzelius the eq. of tellurium is 64·2; its symb. is Te. The compounds described in this section are thus constituted:—

	1 eq. Tellurium.		Equiv.	Formulæ.
Tellurous Acid	64·2 + Oxygen .	16	2 eq. = 80·2	Te + 2O or TeO_2.
Telluric Acid	64·2 + . . .	24	3 eq. = 88·2	Te + 3O or TeO_3.
Chloride	64·2 + Chlorine .	35·42	1 eq. = 99·62	Te + Cl or TeCl.
Bichloride	64·2 + . . .	70·84	2 eq. = 135·04	Te + 2Cl or $TeCl_2$.
Bisulphuret	64·2 + Sulphur .	32·2	2 eq. = 96·4	Te + 2S or TeS_2.
Persulphuret	Composition uncertain.			
Hydrotelluric Acid	64·2 + Hydrogen	1	1 eq. = 65·2	Te + H or TeH.

Tellurous Acid.—This compound, also called *oxide of tellurium*, is generated by the action of nitric acid on tellurium, by which acid it is dissolved; but the solution possesses such little permanence that mere effusion of water precipitates part of it, and the rest is obtained by evaporating to dryness. In this state it is a white granular anhydrous powder, which slowly reddens moist litmus paper, and is insoluble in water and acids. By pure potassa or soda in solution it is dissolved, and is rendered soluble by fusion with the alkaline carbonates, forming with those alkalies crystallizable salts. Acids added in slight excess to the alkaline solutions throw down tellurous acid as a white flaky hydrate, which if washed in ice-cold water, and dried at a temperature not exceeding 53°, may be preserved unchanged. In this state it is freely soluble in acids, in ammonia, in the alkaline carbonates, from which it expels carbonic acid, and even to considerable extent in pure water. Its aqueous solution reddens litmus paper: it becomes turbid at 68°, and the acid which falls is no longer soluble in acids. In these properties tellurous acid closely resembles the titanic and several other feeble acids, which have a soluble hydrated state easily convertible into an insoluble anhydrous one. Its salts are precipitated black by hydrosulphuric acid, bisulphuret of tellurium being formed. It is deoxidized and metallic tellurium falls as a black powder, when a piece of zinc, tin, iron or antimony is left in its solution. *Its eq. is* 80·2; *symb.* Te + 2O, $\ddot{T}e$, or TeO_2.

Telluric Acid.—The process which Berzelius recommends for preparing this compound is either to deflagrate tellurous acid with nitre, or to mix pure potassa freely with a solution of tellurite of potassa, and to saturate fully with chlorine. Nitric acid in slight excess and a little chloride of barium are added, in order to precipitate any traces of sulphuric and selenic acids; and after separating the precipitate by filtration, the liquid is exactly neutralized with ammonia, and chloride of barium added as long as it causes a precipitate. The tellurate of baryta

is washed, dried by a gentle heat, and then digested with a fourth of its weight of strong sulphuric acid previously diluted with water: the filtered solution is then concentrated by a water bath, and on cooling or subsequent spontaneous evaporation yields hydrated telluric acid in the form of flat six-sided prisms. Adhering sulphuric acid is removed by alcohol.

This hydrate consists of 1 eq. of acid and 3 eq. of water. When heated at 212° it loses 2 of its eq. of water; and on heating still further all its water is expelled, and the anhydrous acid of a lemon-yellow colour remains. In this state it is insoluble in all fluids, whereas the hydrated acid is soluble in water; and the salts of the former differ from those which the latter forms with the same bases. Hence heat modifies the character of telluric acid much in the same way as that of phosphoric acid. At a heat beyond that required to render it anhydrous, telluric acid loses oxygen and is reduced to tellurous acid. (Pog. Annalen. xxviii. 392.)

Its eq. is 88·2; *symb.* Te + 3O, $\dddot{\text{Te}}$, or TeO_3.

Chloride.—Rose obtained it by passing a feeble current of chlorine gas over tellurium at a strong heat, when the chloride passes over as a violet vapour, which at first condenses into a black liquid, and when quite cold becomes a solid of the same colour. By the action of water it deposits metallic tellurium, and the bichloride is dissolved.

Its eq. is 99·62; *symb.* Te + Cl, or TeCl.

Bichloride.—Rose obtained this in the same manner as the preceding chloride, except using a lower heat and a more liberal supply of chlorine. The bichloride is also volatile, and after being purified from free chlorine by agitation with mercury, and a second distillation, it condenses into a white crystalline solid. By a gentle heat it yields a brown liquid, but recovers its whiteness on cooling. (Pog. Annalen, xxi. 443.)

Its eq. is 135·04; *symb.* Te + 2Cl, or TeCl_2.

Bisulphuret.—This compound falls of a dark brown, nearly black colour, when hydrosulphuric acid gas is transmitted through a solution of bichloride of tellurium, tellurous acid, or any soluble tellurite. This sulphuret is what Berzelius calls a sulphur-acid, forming a soluble sulphur-salt by uniting with sulphuret of potassium. Hence a solution of caustic potassa dissolves bisulphuret of tellurium, producing the same kind of change as on sulphuret of antimony.

Its eq. 96·4; *symb.* Te + 2S, or TeS_2.

Persulphuret.—This compound falls of a deep yellow colour, when a salt of telluric acid is mixed in solution with persulphuret of potassium. Its existence is but transient, as it is quickly transformed into bisulphuret and becomes black.

Hydrotelluric Acid.—This gas, discovered by Davy in 1809, is formed by acting with hydrochloric acid on an alloy of tellurium with zinc or tin. It has the properties of a feeble acid, very analogous in odour, and apparently in composition, to hydrosulphuric acid; it is absorbed by water, forming a claret-coloured solution; and it precipitates many metallic salts, yielding an alloy of tellurium with the other metal. It is deprived of its hydrogen by chlorine, nitric acid, or oxygen of the atmosphere, tellurium being separated.

Its eq. is 65·2; *symb.* Te + H, or TeH.

CLASS II.

ORDER III.

METALS, THE OXIDES OF WHICH ARE REDUCED TO THE METALLIC STATE BY RED HEAT.

SECTION XXIII.

MERCURY OR QUICKSILVER.

Hist. and Prep.—This metal was well known to the ancients. The principal mines from which it is obtained are those of Idria in Carniola and Almaden in Spain, where it is found both in the native state and combined with sulphur as cinnabar, the latter being the most abundant. From this ore the metal is extracted by heating it with lime or iron filings, by which means the mercury is volatilized and the sulphur retained. As prepared on a large scale it is usually mixed in small quantity with other metals, from which it may be purified by cautious distillation.

Prop.—Distinguished from all other metals by being fluid at common temperatures. It has a tin-white colour and strong metallic lustre. It becomes solid at a temperature which is 39 or 40 degrees below zero; and in congealing, it evinces a strong tendency to crystallize in octohedrons. It contracts greatly at the moment of congelation; for while its density at 47° is 13·545, that of frozen mercury is 15·612. When solid it is malleable, and may be cut with a knife. At 662° or near that degree, it enters into ebullition, and condenses again on cool surfaces into metallic globules.

Mercury, if quite pure, is not tarnished in the cold by exposure to air and moisture; but if it contain other metals, the amalgam of those metals oxidizes readily, and collects as a film upon its surface. It is said to be oxidized by long agitation in a bottle half full of air, and the oxide so formed was called by Boerhaave *Ethiops per se*; but it is very probable that the oxidation of mercury observed under these circumstances was solely owing to the presence of other metals. When exposed to air or oxygen gas, while in the form of vapour, it slowly absorbs oxygen, and is converted into peroxide of mercury.

The only acids that act on mercury are the sulphuric and nitric acids. The former has no action whatever in the cold; but on the application of heat, the mercury is oxidized at the expense of the acid, pure sulphurous acid gas is disengaged, and a sulphate of mercury is generated. Nitric acid acts energetically upon mercury both with and without the aid of heat, oxidizing and dissolving it with evolution of binoxide of nitrogen.

From some late analyses on the peroxide and chlorides of mercury, I have inferred that its equivalent is 202* (Phil. Trans. 1833, part ii.); its symb. is Hg. The composition of its compounds described in this section is as follows:

	Mercury.			Equiv.	Formulæ.
Protoxide	202	1 eq. + Oxygen	8	1 eq. = 210	Hg + O or HgO.
Peroxide	202	1 eq. + do.	16	2 eq. = 218	Hg + 2O or HgO_2.
Protochloride	202	1 eq. + Chlorine	35·42	1 eq. = 237·42	Hg + Cl or HgCl.
Bichloride	202	1 eq. + do.	70·84	2 eq. = 272·84	Hg + 2Cl or $HgCl_2$.
Iodide	202	1 eq. + Iodine	126·3	1 eq. = 328·3	Hg + I or HgI.
Sesquiodide	404	2 eq. + do.	378·9	3 eq. = 782·9	2Hg + 3I or Hg^2I_3.
Biniodide	202	1 eq. + do.	252·6	2 eq. = 454·6	Hg + 2I or HgI_2.
Brotobromide	202	1 eq. + Bromine	78·4	1 eq. = 280·4	Hg + Br or HgBr.
Bibromide	202	1 eq. + do.	156·8	2 eq. = 358·8	Hg + 2Br or $HgBr_2$.
Protosulphuret	202	1 eq. + Sulphur	16·1	1 eq. = 218·1	Hg + S or HgS.
Bisulphuret	202	1 eq. + do.	32·2	2 eq. = 234·2	Hg + 2S or HgS_2.
Ioduretted bichloride of Mercury	$HgCl_2$		5456·8	20 eq.	= 5583·1	$20HgCl_2 + I$.
	I		126·3	1 eq.	
Iodo-bichloride of Mercury	$HgCl_2$		10913·6	40 eq.	= 11368·2	$40HgCl_2 + HgI_2$.
	HgI_2		454·6	1 eq.	

Protoxide.—Prep.—Best by the process recommended by Donovan (An. of Phil. xiv.): this consists in mixing calomel briskly in a mortar with pure potassa in excess, so as to effect its decomposition as rapidly as possible; the protoxide is then washed with cold water, and dried spontaneously in a dark place. These precautions are rendered necessary by the tendency of the protoxide to resolve itself into the peroxide and metallic mercury, a change which is easily effected by heat, by the direct solar rays, and even by daylight. It is on this account very difficult to procure protoxide of mercury in a state of absolute purity.

Prop.—A black powder, which is exceedingly prone to decomposition, is insoluble in water, unites with acids, but is a weak alkaline base. It is precipitated from a solution of its salts, of which the nitrate is the most interesting, as the black protoxide of pure alkalies; as a white carbonate, which soon becomes dark from the loss of carbonic acid, by alkaline carbonates; as calomel by hydrochloric acid or any soluble chloride; and as the black protosulphuret by hydrosulphuric acid. Of these tests, the action of hydrochloric acid is the most characteristic. The oxide is reduced to the metallic state by copper, phosphorous acid, or protochloride of tin.

Its eq. is 210; *symb.* Hg + O, Hg, or HgO.

Peroxide.—Prep.—Either by the combined agency of heat and air, as already mentioned, or by dissolving mercury in nitric acid, and exposing the nitrate so formed to a temperature just sufficient for expelling the whole of the nitric acid. It is commonly known by the name of *red precipitate*. The peroxide prepared from the nitrate almost always contains a trace of nitric acid, which may be detected by heating it in a clean glass tube by means of a spirit-lamp: a yellow-

* Some chemists regard the black oxide of mercury as a suboxide 2HgO, and the red oxide as the true protoxide, HgO; according to which view the equivalent of mercury is assumed to be 101, or one half the number adopted in the text. There are no positive data by which to decide this point, as we are ignorant of any isomorphous relations between mercury and copper or that class of metals to which the latter belongs. (R.)

ring, formed of subnitrate of oxide of mercury, collects within the tube just above the part which is heated. (Clark.)

As thus prepared, it is commonly in the form of shining crystalline scales of a nearly black colour while hot, but red when cold: when very finely levigated, the peroxide has an orange colour. It is soluble to a small extent in water, forming a solution which has an acrid metallic taste, and communicates a green colour to the blue infusion of violets. When heated to redness, it is converted into metallic mercury and oxygen. Long exposure to light has a similar effect. (Guibourt.)

Some of the neutral salts of this oxide, such as the nitrate and sulphate, are converted by water, especially at a boiling temperature, into insoluble yellow subsalts, leaving a strongly acid solution, in which a little of the original salt is dissolved. This oxide is separated from all acids as a yellow hydrate, by the pure fixed alkalies. Carbonate of potash or soda causes a dirty brownish red precipitate. Ammonia and its carbonate cause a white precipitate, which is a double salt, consisting of one equivalent of the acid, three equivalents of the peroxide, and one equivalent of ammonia. The oxide is readily reduced to the metallic state by metallic copper. Hydrosulphuric acid, phosphorous acid, and protochloride of tin, reduce the peroxide into the protoxide; and when added in larger quantity, the first throws down a black sulphuret, and the two latter metallic mercury. The action of hydrosulphuric acid on a solution of corrosive sublimate is, however, peculiar; for at first it occasions a white precipitate which, according to Rose, is a compound of two equivalents of bisulphuret to one of bichloride of mercury. This gas acts on bibromide and biniodide of mercury in a similar manner. (An. de Ch. et Ph. xl. 46.)

Its eq. is 218; *symb.* Hg + 2O, $\ddot{\text{H}}\text{g}$, or HgO_2.

Protochloride.—Prep.—Protochloride of mercury, or *calomel*, is a rare mineral production, called horn silver, which occurs crystallized in quadrangular prisms terminated by pyramids. It is always generated when chlorine comes in contact with mercury at common temperatures; and also by the contact of metallic mercury and the bichloride. It may be made by precipitation, by mixing nitrate of protoxide of mercury in solution with hydrochloric acid or any soluble chloride. It is more commonly prepared by sublimation. This is conveniently done by mixing 272·84 parts or 1 eq. of the bichloride with 202 parts or 1 eq. of mercury, until the metallic globules entirely disappear, and then subliming. When first prepared it is always mixed with some corrosive sublimate, and therefore should be reduced to powder and well washed before being employed for chemical or medical purposes.

Prop.—When obtained by sublimation it is in semi-transparent crystalline cakes; but as formed by precipitation, it is a white powder. Its sp. gr. is 7·2. At a heat short of redness, but higher than the subliming point of the bichloride, it rises in vapour without previous fusion; but during the sublimation a portion is always resolved into mercury and the bichloride. It is yellow while warm, but recovers its whiteness on cooling. It is distinguished from the bichloride by not being poisonous, by having no taste, and by being exceedingly insoluble in water. Acids have little effect upon it; but pure alkalies decompose it, separating the black protoxide of mercury. When calomel is boiled in a solution of hydrochlorate of ammonia, it is converted into corrosive sublimate and metallic mercury. Chloride of sodium has a similar effect, though in a less degree. *Its eq. is* 237·42; *symb.* Hg + Cl, or HgCl.

Bichloride.—Prep.—When mercury is heated in chlorine gas, it takes fire, and burns with a pale red flame, forming the well-known medicinal preparation and virulent poison *corrosive sublimate* or bichloride of mercury. It is prepared for medical purposes by subliming a mixture of bisulphate of the peroxide of mercury with chloride of sodium or sea-salt. The exact quantities required for mutual decomposition are 298·2 parts or 1 eq. of the bisulphate, to 117·44 parts or 2 eq. of the chloride. Thus,

Bisulphate of Mercury		1 eq.	Chloride of Sodium.		2 eq.
Sulphuric Acid .	80·2 or 2 eq.	$2SO_3$.	Chlorine .	70·84 or 2 eq.	2Cl.
Peroxide of Mer. .	218 or 1 eq.	HgO_2.	Sodium .	46·6 or 2 eq.	2Na.
	298·2	HgO_2+2SO_3.		177·44	2NaCl.

And by mutual interchange of elements they produce

Bichloride of Mercury		1 eq.	Sulphate of Soda		2 eq.
Mercury .	202 or 1 eq.	Hg.	Soda . .	62·6 or 2 eq. .	2 NaO.
Chlorine .	70·84 or 2 eq.	2Cl.	Sulphuric Ac.	80·2 or 2 eq. .	$2SO_3$.
	272.84	$HgCl_2$.		142·8	$2NaO,SO_3$.

The products have exactly the same weight (272·84 + 142·8 = 415·64) as the compounds (298·2 + 117·44 = 415·64) from which they were prepared.

Prop.—When obtained by sublimation, it is a semi-transparent colourless substance, of a crystalline texture. It has an acrid, burning taste, and leaves a nauseous metallic flavour on the tongue. Its sp. gr. is 5·2. When exposed to a heat short of incandescence, it is fused, enters into ebullition from the rapid formation of vapour, and is deposited without further change on cool surfaces as a white crystalline sublimate. It requires twenty times its weight of cold, and only twice its weight of boiling water for solution, and is deposited from the latter, as it cools, in the form of prismatic crystals. Strong alcohol and ether dissolve it in the same proportion as boiling water; and it is soluble in half its weight of concentrated hydrochloric acid at the temperature of 70°. With the chlorides of potassium and sodium, hydrochlorate of ammonia, and several other bases, it enters into combination, forming double salts, which are more soluble than the chloride itself. When its solution in water is agitated with ether, the latter abstracts the bichloride, and rises with it to the surface of the former, thus affording strong evidence of the bichloride having existed as such in the water. Its aqueous solution is gradually decomposed by light, calomel being deposited.

The pure and carbonated fixed alkalies throw down the peroxide of mercury, from a solution of corrosive sublimate. Ammonia, on the contrary, causes the deposition of a white matter, which is commonly known under the name of the white precipitate. This substance has been recently examined by Kane. (Trans. Irish Academy, xvii.) He finds that on adding a slight excess of ammonia just one half of the chlorine of the corrosive sublimate falls, the other half remaining in the solution with ammonia. The precipitate nevertheless does not contain calomel, as is proved by its complete solubility in hydrochloric and nitric acids. From his analysis it is composed of

Mercury . . .	78·6	Ammonia	6·77
Chlorine . . .	13·85	Hygrometric water, loss, & oxygen	0·78

Its atomic constitution would appear from this analysis to contain the compound radical which is the base of the amides. By the action of boiling water, it loses

half its chlorine and ammonia, peroxide of mercury being at the same time formed, and a canary-yellow powder is produced. Kane finds that on treating calomel with ammonia, it too loses only one half its chlorine, and a compound analogous to white precipitate is obtained.

The presence of mercury in a fluid supposed to contain corrosive sublimate, may be detected by concentrating and digesting it with an excess of pure potassa. Oxide of mercury, which subsides, is then sublimed in a small glass tube by means of a spirit-lamp, and obtained in the form of metallic globules. But in cases of poisoning, when the bichloride is mixed with organic substances, Christison recommends that the liquid, without previous filtration, be agitated with a fourth of its volume of ether, which separates the poison from the aqueous part, and rises to the surface. The ethereal solution is then evaporated on a watch-glass, the residue dissolved in hot water, and the mercury precipitated in the metallic state by protochloride of tin at a boiling temperature. If, as is probable, most of the poison is already converted into calomel, and thereby rendered insoluble, as many vegetable fibres should be picked out as possible, and the whole at once digested with protochloride of tin. The organic substances are then dissolved in a hot solution of caustic potassa, and the insoluble parts washed and sublimed to separate the mercury. (Christison on Poisons.)

A very elegant method of detecting the presence of mercury is to place a drop of the suspected liquid on polished gold, and to touch the moistened surface with a piece of iron wire or the point of a penknife, when the part touched instantly becomes white, owing to the formation of an amalgam of gold. This process was originally suggested by Sylvester, and has since been simplified by Paris. (Medical Jurisprudence, by Paris and Fonblanque.)

Many animal and vegetable solutions convert bichloride of mercury into calomel, a portion of hydrochloric acid being set free at the same time. Some substances effect this change slowly; while others, and especially albumen, produce it in an instant. Thus, when a solution of corrosive sublimate is mixed with albumen, a white flocculent precipitate subsides, which Orfila has shown to be a compound of calomel and albumen, and which he has proved experimentally to be inert. (Toxicologie, vol. i.) Consequently a solution of the white of eggs is an antidote to poisoning by corrosive sublimate. The muscular and membranous parts, even of a living animal, produce a similar effect; and the causticity of corrosive sublimate seems owing to the destruction of the animal fibre, by which the decomposition of the bichloride is accompanied, and which constitutes an essential part of the chemical change.*

Its eq. is 272·84; *symb.* Hg + Cl, or $HgCl_2$.

Protiodide of Mercury.—This compound is obtained by mixing nitrate of protoxide of mercury in solution with iodide of potassium. It is a green powder, insoluble in water, and disposed to resolve itself under the influence of heat or solar light into mercury and the biniodide. However, when the heat is quickly supplied, it is fused and sublimed without material change.

* M. Mialhi proposes the moist recently precipitated sulphuret of iron as an antidote for corrosive sublimate, and its value in this respect is said to have been tested by M. Orfila. When added to mixtures containing the minutest trace of corrosive sublimate, decomposition ensues immediately, from the reaction of two equivalents of the sulphuret of iron with one of the bichloride of mercury, giving rise to two eq. of the chloride of iron and 1 eq. of the bisulphuret of mercury, thus $HgCl_2$ and 2FeS yield HgS_2 and 2FeCl. The bisulphuret of mercury is inert. (R.)

Its eq. is 328·3; *symb.* Hg + I, or HgI.

Sesquiodide.—This compound falls as a yellow powder when iodide of potassium is added in solution to the mixed nitrates of the protoxide and peroxide of mercury, the latter being in excess. The precipitate is digested with a solution of sea-salt, which takes up any biniodide which may have fallen.

Its eq. is 782·9; *symb.* 2Hg + 3I, or Hg_2I_3.

Biniodide.—This compound is formed by mixing nitrate of the peroxide or bichloride of mercury with iodide of potassium in solution, and falls as a rich red-coloured powder of a tint which vies in beauty with that of vermilion, though, unfortunately, the colour is less permanent. Though insoluble in water, it dissolves freely in an excess of either of its precipitants. If taken up in a hot solution of nitrate of peroxide of mercury, the biniodide crystallizes out on cooling in scales of a beautiful red tint. The same crystals separate from a solution in iodide of potassium; but if the liquid be concentrated, a double iodide of mercury and potassium subsides.

The biniodide, when exposed to a moderate heat, gradually becomes yellow; and the particles, though previously in powder, acquire a crystalline appearance. At about 400° it forms a yellow liquid, which slowly sublimes in small transparent scales, or in large rhombic tables, when a considerable quantity is sublimed. The crystals retain their yellow colour at 60° if kept very tranquil; but if the temperature be below a certain point, or they are rubbed or touched, they quickly become red. This phenomenon is entirely due to a change in molecular arrangement: the different colours so often witnessed in the same substances at different temperatures, as in peroxide of mercury and the protoxides of lead and zinc, appear to be phenomena of the same nature.

Its eq. 454·6; *symb.* Hg + 2I, or HgI_2.

Ioduretted Bichloride of Mercury.—This compound has recently been described by Lassaigne. (An. de Ch. et Ph. lxiii. 106.) It is formed by adding to an alcoholic solution of iodine a solution of corrosive sublimate, when the deep colour of the iodine gradually disappears, and a colourless solution is obtained. It is remarkable, that in this combination the iodine cannot be detected by starch and chlorine or sulphurous acid, as in its other combinations. The compound is decomposed by heat, but may be obtained in crystals by evaporating a concentrated solution at a moderate temperature. *Its eq. is* 5583·1; *symb.* $20HgCl_2 + I$.

Iodo-bichloride of Mercury.—This compound was described by Boullay. (An. de Ch. et Ph. xxxvi. 366.) It is formed by dissolving biniodide of mercury in corrosive sublimate, when a colourless crystalline compound is obtained. It is composed of 40 eq. of the bichloride and one of the biniodide.

Its eq. is 11368·2; *symb.* $40HgCl_2 + HgI_2$.

Protobromide of Mercury.—It is precipitated as a white insoluble powder by mixing nitrate of protoxide of mercury with bromide of potassium. *Its eq. is* 280·4; *symb.* Hg + Br, or HgBr.

The bibromide is a white crystallizable compound, soluble in water and alcohol, fusible and volatile, and in many respects analogous to the bichloride. It is formed by acting on peroxide of mercury with hydrobromic acid, or digesting the preceding compound with bromine.

Its eq. is 358·8; *symb.* Hg + 2Br, or $HgBr_2$.

Sulphurets of Mercury.—The protosulphuret may be prepared by transmitting a current of hydrosulphuric acid gas through a dilute solution of nitrate of protoxide of mercury, or through water in which calomel is suspended. It is a black-

coloured substance, which is oxidized by digestion in strong nitric acid. When exposed to heat it is resolved into the bisulphuret and metallic mercury. *Its eq. is* 218·1; *symb.* Hg + S, or HgS.

The bisulphuret is formed by fusing sulphur with about six times its weight of mercury, and subliming in close vessels. When procured by this process it has a red colour, and is known by the name of *factitious cinnabar*. Its tint is greatly improved by being reduced to powder, in which state it forms the beautiful pigment *vermilion*. It may be obtained in the moist way by pouring a solution of corrosive sublimate into an excess of hydrosulphate of ammonia. A black precipitate subsides, which acquires the usual red colour of cinnabar when sublimed. The black precipitate formed by the action of hydrosulphuric acid on bicyanuret of mercury, is likewise a bisulphuret. Cinnabar, as already mentioned, occurs native.

When equal parts of sulphur and mercury are triturated together until metallic globules cease to be visible, the dark-coloured mass called *Ethiops mineral* results, which Mr. Brande has proved to be a mixture of sulphur and bisulphuret of mercury. (Journal of Science, vol. xviii. p. 294.)

Cinnabar is not attacked by alkalies, or any simple acid; but it is dissolved by the nitro-hydrochloric, with formation of sulphuric acid and peroxide of mercury.

Its eq. is 234·2; *symb.* Hg + 2S, or HgS_2.

SECTION XXIV.

SILVER.

Hist.—This metal was known to the ancients. It frequently occurs native in silver mines, both massive and in octohedral or cubic crystals. It is also found in combination with gold, tellurium, antimony, copper, arsenic, and sulphur. In the state of sulphuret it so frequently accompanies galena, that the lead of commerce is rarely quite free from traces of silver.

Prep.—Silver is extracted from its ores by two processes which are essentially distinct; one of them being contrived to separate it from lead, the other, the process by *amalgamation*, being especially adapted to those ores which are free from lead. The principle of its separation from lead is founded on the different oxidability of lead and silver, and on the ready fusibility of litharge. The lead obtained from those kinds of galena which are rich in sulphuret of silver is kept at a red heat in a flat furnace, with a draught of air constantly playing on its surface: the lead is thus rapidly oxidized; and as the oxide, at the moment of its formation, is fused, and runs off through an aperture in the side of the furnace, the production of litharge goes on uninterruptedly until all the lead is removed. The button of silver is again fused in a smaller furnace, resting on a porous earthen dish, made with lixiviated wood-ashes, called a *test*, the porosity of which is so great, that it absorbs any remaining portions of litharge which may be formed on the silver.

Mr. Pattinson of Newcastle has taken out a patent for a new and ingenious process, whereby the extraction of silver from lead is much facilitated. The lead is melted and allowed to cool slowly. The crystals which form first are much richer in silver than the original mass. They are removed by means of a perforated ladle, and the process is repeated both with them and with the residue, till there is obtained, on the one hand, lead almost free of silver, while on the other, the whole silver is collected in combination with a small part of the lead. This mixture is then subjected to cupellation, which from its smaller bulk is more easily and rapidly accomplished.

The ores commonly employed in the process of amalgamation, which has been long used at Freyberg in Saxony, and is extensively practised in the silver and gold mines of South America, are native silver and its sulphuret. At Freyberg the ore in fine powder is mixed with sea-salt, and carefully roasted in a reverberatory furnace. The production of sulphuric acid leads to the formation of sulphate of soda, while the chlorine of the sea-salt combines with silver. The roasted mass is ground to a fine powder, and, together with mercury, water, and fragments of iron, is put into barrels, which are made to revolve by machinery. In this operation, intended to insure perfect contact between the materials, chloride of silver is decomposed by the iron, the silver unites with the mercury, and the chloride of iron is dissolved by the water. The mercury is then squeezed through leathern bags, the pores of which permit the pure mercury to pass, but retain the amalgam of silver. The combined mercury is then distilled off in close vessels, and the metals obtained in a separate state.

Goldsmiths' silver commonly contains copper and traces of gold, the latter appearing in dark flocks when the metal is dissolved in nitric acid. It may be obtained pure for chemical use by placing a clean piece of copper in a solution of nitrate of oxide of silver, washing the precipitate with pure water, and then digesting it in ammonia, in order to remove any adhering copper. A better process is to decompose chloride of silver by means of carbonate of potassa. For this purpose precipitate a solution of nitrate of oxide of silver with chloride of sodium, wash the precipitate with water, and dry it. Then put twice its weight of carbonate of potassa into a clean hessian or black-lead crucible, heat it to redness, and throw the chloride by successive portions into the fused alkali. Effervescence takes place from the evolution of carbonic acid and oxygen gases, chloride of potassium is generated, and metallic silver subsides to the bottom. The pure metal may be granulated by pouring it while fused from a height of seven or eight feet into a vessel of water.

Prop.—It has the clearest white colour of all the metals, and is susceptible of receiving a lustre surpassed only by polished steel. In malleability and ductility it is inferior only to gold, and its tenacity is considerable. It is very soft when pure, so that it may be cut with a knife. Its density after being hammered is 10·51. At a full red heat, corresponding to 1873° F. according to Daniell, it enters into fusion. It does not rust by exposure to air and moisture. When fused in open vessels it absorbs oxygen in considerable quantity, amounting sometimes to 22 times its volume; but it parts with the whole of it in the act of becoming solid. This fact, first noticed by M. Lucas, has been studied by Gay-Lussac, who attributes to it the peculiarly beautiful aspect of granulated silver: he observed the absorption and subsequent evolution of oxygen to be most abundant in the purest silver, and is entirely prevented by a very small per centage of copper. If silver is heated to redness, without fusing, in contact with

glass or porcelain, it readily absorbs oxygen, and the oxide fuses with the earthy matters, forming a yellow enamel. When silver in the form of leaves or fine wire is intensely heated by means of electricity, galvanism, or the oxy-hydrogen blowpipe, it burns with vivid scintillations of a greenish-white colour.

The only pure acids that act on silver are the sulphuric and nitric acids, by both of which it is oxidized, forming with the first a sulphate, and with the second a nitrate of oxide of silver. It is not attacked by sulphuric acid unless by the aid of heat. Nitric acid is its proper solvent, and forms with its oxide a salt, which, after fusion, is known by the name of *lunar caustic*.

From recent experiments on the composition of the chloride and nitrate of the oxide of silver, I have deduced 108 as the eq. of silver, an estimate closely corresponding with the previous researches of Berzelius. (Phil. Trans. 1833, part ii.) Its *symb.* is Ag. The compounds of silver described in this section are thus constituted :—

	Silver.			Equiv.	Formulæ.
Dioxide .	216	2 eq.+Oxygen	8	1 eq.=224·2	Ag+O or Ag_2O.
Oxide .	108	1 eq.+Oxygen	8	1 eq.=116	Ag+O or AgO.
Chloride .	108	1 eq.+Chlorine	35·42	1 eq.=143·42	Ag+Cl or AgCl.
Iodide .	108	1 eq.+Iodine	126·3	1 eq.=234·3	Ag+I or AgI.
Sulphuret .	108	1 eq.+Sulphur	16·1	1 eq.=124·1	Ag+S or AgS.

[*Dioxide of Silver, suboxide.*—This oxide is obtained, according to Wöhler, by passing a current of hydrogen gas over the citrate of the protoxide, heated to 212°. The protoxide of this salt loses one half of its oxygen and is thereby reduced to the dioxide which remains in combination with one half of the citrate as a sub-salt, which along with the free citric acid, forms a dark brown solution in water. The dioxide is precipitated from this solution by potassa as a black powder, which is very easily decomposed and quite soluble in ammonia. A solution of the sub-salt is immediately resolved by heat into metallic silver which is precipitated, and a protosalt which remains in solution.]

Oxide of Silver.—This oxide is best procured by mixing a solution of pure baryta with nitrate of oxide of silver dissolved in water, [or, according to Gregory, by boiling recently precipitated chloride of silver with a strong solution of caustic potassa. By the first method it is brown in colour, by the second jet black.] It is insoluble in water, and completely reduced by a red heat. It is separated from its solution in nitric acid by pure alkalies and alkaline earths as the brown oxide, which is redissolved by ammonia in excess; by alkaline carbonates as a white carbonate, which is soluble in an excess of carbonate of ammonia; as a dark brown sulphuret by hydrosulphuric acid; and as a white curdy chloride of silver, which is turned violet by light, and is very soluble in ammonia, by hydrochloric acid or any soluble chloride. By the last character, silver may be both distinguished and separated from other metallic bodies.

Silver is precipitated in the metallic state by most other metals. When mercury is employed for this purpose, the silver assumes a beautiful arborescent appearance, called *arbor Dianæ*. A very good proportion for the experiment is 20 grains of lunar caustic to 6 drachms or an ounce of water. The silver thus deposited always contains mercury.

When oxide of silver, recently precipitated by baryta or lime-water, and separated from adhering moisture by bibulous paper, is left in contact for 10 or 12

hours with a strong solution of ammonia, the greater part of it is dissolved; but a black powder remains which detonates violently from heat or percussion. This substance, which was discovered by Berthollet, (An. de Chimie, i.) appears to be a compound of ammonia and oxide of silver; for the products of its detonation are metallic silver, water, and nitrogen gas. It should be made in very small quantity at a time, and dried spontaneously in the air.

On exposing a solution of oxide of silver in ammonia to the air, its surface becomes covered with a pellicle, which Faraday considers to be an oxide containing a smaller proportion of oxygen than that just described. This opinion he has made highly probable; but further experiments are requisite before the existence of this oxide can be regarded as certain.

Its eq. is 116; *symb.* Ag + O, Ag, or AgO.

Chloride of Silver.—*Prep.*—This compound, which sometimes occurs in silver mines, and constitutes the horn silver of mineralogists, is always generated when silver is heated in chlorine gas, and may be prepared conveniently by mixing hydrochloric acid, or any soluble chloride, with a solution of nitrate of oxide of silver. As formed by precipitation it is quite white; but by exposure to the direct solar rays it becomes violet, and almost black, in the course of a few minutes; and a similar effect is slowly produced by diffused day-light. On this principle is founded Mr. Talbot's method of photography. Hydrochloric acid is set free during this change, and, according to Berthollet, the dark colour is owing to separation of oxide of silver. (Statique Chimique, vol. i. p. 195.)

Prop.—It is insoluble in water, and is dissolved very sparingly by the strongest acids; but it is soluble in ammonia. Hyposulphurous acid likewise dissolves it. At a temperature of about 500° it fuses, and forms a semitransparent horny mass on cooling, which has a density of 5·524. It bears any degree of heat, or even the combined action of pure charcoal and heat, without decomposition; but hydrogen gas decomposes it readily with formation of hydrochloric acid. *Its eq. is* 143.42; *symb.* Ag + Cl, or AgCl.

Iodide of Silver.—This compound is formed when iodide of potassium is mixed with a solution of nitrate of oxide of silver. It is of a greenish-yellow colour, and is insoluble in water and ammonia. A film of this compound on the surface of a polished plate of silver, constitutes the substance which receives the impressions of light in Daguerré's beautiful invention of the Daguerréotype.

Its eq. is 234·3; *symb.* Ag + I, or AgI.

Sulphuret of Silver.—Silver has a strong affinity for sulphur. This metal tarnishes rapidly when exposed to an atmosphere containing hydrosulphuric acid gas, owing to the formation of a sulphuret. On transmitting a current of this gas through a solution of lunar caustic, a dark brown precipitate subsides, which is a sulphuret of silver. The *silver glance* of mineralogists is a similar compound, and the same sulphuret may be prepared by heating thin plates of silver with alternate layers of sulphur. This sulphuret is remarkable for being soft and even malleable.

Its eq. is 124·1; *symb.* Ag + S, or AgS.

Silver unites also by the aid of heat with phosphorus, forming a soft, brittle, crystalline compound.

SECTION XXV.

GOLD.

Hist. and Prep.—Gold appears to have been known to the earliest races of man, and to have been esteemed by them as much as by the moderns. It has hitherto been found only in the metallic state, either pure or in combination with other metals. It occurs massive, capillary, in grains, and crystallizes in octohedrons and cubes, or their allied forms. It is sometimes found in primary mountains; but more frequently in alluvial depositions, especially among sand in the beds of rivers, having been washed by water out of disintegrated rocks in which it originally existed. There are few countries in which gold washings have not formerly existed; but the principal supply of gold is from South America, from the gold mines of Hungary, and from the Uralian mountains of Siberia, especially on the Asiatic side of the chain, where separate masses in sand have been found weighing 18 or 20 pounds. Rich deposits of gold appear also to exist in some of the southern provinces of North America. Gold is generally separated from accompanying impurities by the process of amalgamation, similar to that described in the last section; by which means it is freed from iron and all associated metals, excepting silver. In Hungary the gold is purified by cupellation. The silver, which in variable quantity is present in native gold, may be brought into view by dissolving the gold in nitro-hydrochloric acid. The best mode of separation consists in fusing the gold with so much silver that the former may constitute one-fourth of the mass: nitric acid will then dissolve all the silver and leave the gold. The silver may also be removed by digestion in sulphuric acid.

Prop.—Gold is the only metal which has a yellow colour, a character by which it is distinguished from all other simple metallic bodies. It is capable of receiving a high lustre by polishing, but is inferior in brilliancy to steel, silver, and mercury. In ductility and malleability it exceeds all other metals; but it is surpassed by several in tenacity. Its density is 19·3; when pure it is exceedingly soft and flexible; and it fuses according to Daniell at 2016°.

Gold may be exposed for ages to air and moisture without change, nor is it oxidized by being kept in a state of fusion in open vessels. When intensely ignited by means of electricity or the oxy-hydrogen blowpipe, it burns with a greenish-blue flame, and is dissipated in the form of a purple powder, which is supposed to be an oxide.

Gold is not oxidized or dissolved by any of the pure acids; for it may be boiled even in nitric acid without undergoing any change. Its best solvents are chlorine and nitro-hydrochloric acid; and it appears from the observations of Davy that chlorine is the agent in both cases, since nitro-hydrochloric acid does not dissolve gold, except when it gives rise to the formation of chlorine. It is to be inferred, therefore, that the chlorine unites directly with the gold. It is also readily attacked by fluorine.

The most convenient method of dissolving it is to digest fragments of the

metal in a mixture composed of two measures of hydrochloric and one of nitric acid, until the acid is saturated. The excess of acid is then expelled by evaporating the orange-coloured solution until a ruby-red liquid remains, which is the neutral terchloride of gold. On adding water, the chloride is dissolved, forming a solution of a gold-yellow colour.

The eq. of gold, estimated from the analysis of the terchloride by Berzelius, is 199·2; its symb. is Au. The composition of its compounds described in this section is as follows:—

	1 eq. of Gold.		Equiv.	Formulæ.
Protoxide	199·2 + Oxygen	8	1 eq. = 207·2	Au + O or AuO.
Binoxide	199·2 + do.	16	2 eq. = 115·2	Au + 2O or AuO_2.
Peroxide	199·2 + do.	24	3 eq. = 123·2	Au + 3O or AuO_3.
Protochloride	199·2 + Chlorine	35·42	1 eq. = 234·62	Au + Cl or AuCl.
Terchloride	199·2 + do.	106·26	3 eq. = 305·46	Au + 3Cl or $AuCl_3$.
Protiodide	199·2 + Iodine	126·3	1 eq. = 325·5	Au + I or AuI.
Teriodide	199·2 + do.	378·9	3 eq. = 578·1	Au + 3I or AuI_3.
Tersulphuret	199·2 + Sulphur	48·3	3 eq. = 247·5	Au + 3S or AuS_3.

Protoxide of Gold.—It is obtained by the action of a cold solution of potassa on the protochloride of gold, and is separated as a green precipitate, which is partially soluble in the alkaline solution. It spontaneously changes soon after its preparation into metallic gold and the peroxide.

Its eq. is 207·2; *symb.* Au + O, Au, or AuO.

The *binoxide* is supposed to be the purple oxide which is formed by the combustion of gold; but its composition has not been demonstrated by analysis.

Peroxide.—Prep.—This, the only well known oxide of gold, is prepared by the action of alkalies on the terchloride, but is obtained quite pure with difficulty. Pelletier recommends that it should be formed by digesting a solution of the terchloride with pure magnesia, washing the precipitate with water, and removing the excess of magnesia by dilute nitric acid. It is apt, however, to retain magnesia, and I am informed by Wagner, of Pesth in Hungary, that the most certain mode of procuring the peroxide is the following. Dissolve one part of gold in the usual way, render it quite neutral by evaporation, and redissolve in 12 parts of water: to the solution add one part of carbonate of soda dissolved in twice its weight of water, and digest at about 170°. Carbonic acid gradually escapes, and the hydrated peroxide of a brownish-red colour subsides. After being well washed it is dissoved in colourless nitric acid of specific gravity 1·4, and the solution decomposed by admixture with water. The hydrated peroxide is thus obtained quite pure, and is rendered anhydrous by a temperature of 212°.

Prop.—Yellow in a state of hydrate, and nearly black when anhydrous, is insoluble in water, and completely decomposed by solar light or a red heat. Hydrochloric acid dissolves it readily, yielding the common solution of gold; but it forms no definite compound with any acid which contains oxygen. It may indeed be dissolved by nitric and sulphuric acids; but the affinity is so slight that the oxide is precipitated by the addition of water. It combines, on the contrary, with alkaline bases, such as potassa and baryta, apparently forming regular salts, in which it acts the part of a weak acid. This property, which constitutes the difficulty of procuring peroxide of gold quite pure, induced Pelletier to deny that the peroxide of gold is a salifiable base, and to propose for it the name of

auric acid, its compounds with alkalies being called *aurates*. (An. de Ch. et Ph. xv.)

When recently precipitated peroxide of gold is kept in strong ammonia for about a day, a detonating compound of a deep olive colour is generated, analogous to the fulminating silver described in the last section. According to the analysis of Dumas, its elements are in the ratio of 1 eq. of gold, 2 of nitrogen, 6 of hydrogen, and 3 of oxygen, as expressed by the symbols $Au + N_2 + H_6 + O_3$. With regard to the mode in which these elements are arranged, different opinions may be formed. Dumas thinks the real combination is indicated by the formula $AuN_2 + NH_3 + 3HO$, being a hydrated nituret of gold united with ammonia; but it appears more simple to consider it as a di-aurate of ammonia, expressed by the formula $AuO_3 + 2NH_3$. Its detonation should give rise to metallic gold, water, nitrogen, and ammonia. A similar compound is obtained, and this is the ordinary mode of procuring fulminating gold, by digesting terchloride of gold with an excess of ammonia: a yellow precipitate subsides, the fulminating ingredient of which appears identical with that above described; but a subchloride of gold and ammonia falls at the same time, and adheres so obstinately that it cannot be wholly removed by boiling water. Fulminating gold may be dried at 212°; but friction, or a heat suddenly raised to about 290° or upwards, produces a violent detonation. It is best to make it in small quantities at a time, and to dry it in the open air. (An. de Ch. et Ph. xliv. 167.)

Its eq. is 123·2; *symb.* Au + 3O, $\dot{A}u$, or AuO_3.

Chlorides of Gold.—On concentrating the solution of gold to a sufficient extent by evaporation, the terchloride may be obtained in ruby-red prismatic crystals, which are very fusible. It deliquesces on exposure to the air, and is dissolved readily by water without residue. It is also soluble in alcohol and ether; and the latter withdraws it from the aqueous solution. It begins to lose chlorine at a temperature of about 400°, being changed into a brown dry mass, which is a mixture of the protochloride and terchloride, soluble in water. At about 600° the terchloride is completely resolved into the yellow insoluble protochloride, which by boiling in water is changed into metallic gold and the soluble terchloride. At a red heat the protochloride loses its chlorine altogether, and metallic gold remains. *Its eq. is* 234·62; *symb.* Au + Cl, or AuCl.

The terchloride of gold is the usual and most convenient form of obtaining a solution of gold and examining its properties in that state. On adding to the solution sulphate of protoxide of iron, a brown precipitate ensues, which is gold in very fine division, and the solution contains sesquisulphate of peroxide and perchloride of iron. The action is such that

6 eq. Sulphate of Protoxide of Iron	6 (FeO, SO_3.)
and 1 eq. Terchloride of Gold . . .	$Au Cl_3$.

yield

2 eq. Sesquisulphate of Peroxide of Iron	2(Fe_2O_3, $3SO_3$.)
1 eq. Perchloride of Iron, Fe_2Cl_3, and 1 eq. of Gold .	Au.

The precipitate when duly washed with dilute hydrochloric acid, in order to separate adhering iron, is gold in a state of perfect purity. A similar reduction is effected by most of the metals, and by sulphurous and phosphorous acids, and by oxalic acid with escape of carbonic acid gas. When a piece of charcoal is immersed in a solution of gold, and exposed to the direct solar rays, its surface acquires a coat-

ing of metallic gold; and ribands may be gilded by moistening them with a dilute solution of gold, and exposing them to a current of hydrogen or phosphuretted hydrogen gas. When a strong aqueous solution of gold is shaken in a phial with an equal volume of pure ether, two fluids result, the lighter of which is an ethereal solution of gold. From this liquid flakes of metal are deposited on standing, especially by exposure to light, and substances moistened with it receive a coating of metallic gold.* The reduction in most of these instances is owing to the chlorine quitting the gold in obedience to some stronger attraction: metals deprive it directly of its chlorine; and deoxidizing agents do so indirectly by combining with the oxygen of water, while its hydrogen acts on the chlorine.

When protochloride of tin is added to a dilute aqueous solution of gold, a purple-coloured precipitate, called the *purple of Cassius*, is thrown down; and the same substance may be prepared by fusing together 150 parts of silver, 20 of gold, and 35·1 of tin, and acting on the alloy with nitric acid, which dissolves out the silver and leaves a purple residue, containing the tin and gold which were employed. To prevent the oxidation of the tin during fusion, the three metals should be projected into a red-hot black-lead crucible, which contains a little melted borax. When the powder of Cassius is fused with vitreous substances, such as flint-glass, or a mixture of sand and borax, it forms with them a purple enamel, which is employed in giving pink colours to porcelain. The essential cause of the colour is probably a compound of the purple or supposed binoxide of gold with earthy matters, similar to the enamel formed by glass and oxide of silver; the oxide of tin is not essential, since finely divided metallic gold alone will give the same tint of purple. Fuchs has shown that the purple of Cassius is best prepared by means of sesquioxide of tin dissolved in hydrochloric acid.

The chemical nature of the purple of Cassius is very obscure. From its formation by protochloride of tin it is inferred to contain peroxide of tin and gold either in the metallic state or oxidized to a degree inferior to the peroxide. According to Berzelius its sole loss when heated to redness is 7·65 per cent. of water, and the residue has a brick-red colour, arising from a mechanical mixture of metallic gold and peroxide of tin, a statement which is confirmed by Gay-Lussac. (An. de Ch. et Ph. xlix. 396.) The proportion of these products corresponds to 5 equivalents of peroxide of tin, 1 of gold, and 6 of water. Nevertheless, the purple of Cassius, as is indicated both by its colour and its solubility in ammonia, is not a mechanical mixture of these ingredients; nor can it well be regarded as a chemical compound of gold and peroxide of tin, since no definite compound of the kind is known to chemists. The more probable supposition is, that it is a hydrated double salt, composed of peroxide of tin as the acid, united with protoxide of tin and binoxide of gold as bases, in such proportion that the oxygen of the gold exactly suffices to convert the protoxide into peroxide of tin. A compound of this nature is expressed by the formula $2(SnO, SnO_2) + (AuO_2, SnO_2) + 6HO$.

Its eq. is 305·46; *symb.* Au + 3Cl, or $AuCl_3$.

Sulphuret of Gold.—On transmitting a current of hydrosulphuric acid gas through a solution of gold, a black precipitate is formed, which is a sulphuret. It is resolved by a red heat into gold and sulphur.

Its eq. is 247·5; *symb.* Au + 3S, or AuS_3.

* With respect to the revival of gold from its solutions, the reader may consult an Essay on combustion, by Mrs. Fulhame, and a paper by Count Rumford, in the Philosophical Transactions for 1798.

The compounds of gold with the other non-metallic bodies have been little examined.

Iodides of Gold.—These compounds have recently been studied by Johnston (Phil. Mag. and An. ix. 266.) The protiodide falls as a greenish-yellow powder, when iodide of potassium is added in excess to a solution of the terchloride of gold. Though insoluble in water, it dissolves in a dilute hot solution of iodide of potassium, from which it crystallizes on cooling in golden yellow scales with triangular and square faces. These crystals generally contain about 12 per cent. of metallic gold mechanically mixed with them. They gradually lose iodine at common temperatures, freely at 150°, and are almost wholly decomposed at 230°.

Its eq. is 325·5; *symb.* Au + I, or AuI.

The teriodide is formed when terchloride of gold is added to a solution of iodide of potassium. It falls as a dark green precipitate, which is insoluble in water, but is soluble in hydriodic acid and in solutions of the iodides of potassium and sodium. It is very prone to decomposition from the easy loss of iodine. It is a haloid acid, and forms crystallizable compounds with haloid bases. Thus, on setting aside the solution formed by digesting it in iodide of potassium, the auro-iodide of potassium is deposited in dark brownish-red, nearly black needles. These crystals are anhydrous, are more stable than the teriodide, and may be dried at 100° without decomposition. The corresponding salt of sodium is deliquescent. *Its eq. is* 578·1; *symb.* Au + 3I, or AuI_3.

SECTION XXVI.

PLATINUM.

Hist.—This valuable metal occurs only in the metallic state, associated or combined with various other metals, such as copper, iron, lead, titanium, chromium, gold, silver, palladium, rhodium, osmium, and iridium. It has hitherto been found chiefly in Brazil, Peru, and other parts of South America, in the form of rounded or flattened grains of a metallic lustre and white colour, mixed with sand and other alluvial depositions. The particles rarely occur so large as a pea; but they are sometimes larger, and a specimen brought from South America by Humboldt was rather larger than a pigeon's egg, and weighed 1088·6 grains. In the year 1826, however, Boussingault discovered it in a syenitic rock in the province of Antioquia in South America, where it occurs in veins associated with gold. Rich mines of gold and platinum have also been discovered in the Uralian Mountains. (Edinburgh Journal of Science, v. 323.)

Prop.—Pure platinum has a white colour very much like silver, but of inferior lustre. It is the heaviest of known metals, its density after forging being about 21·25, and 21·5 in the state of wire. Its malleability is considerable, though far less than that of gold and silver. It may be drawn into wires, the diameter of which does not exceed the 2000th part of an inch. It is a soft metal, and like iron ad-

mits of being welded at a high temperature. Wollaston* observed that it is a less perfect conductor of heat than several other metals.

Platinum undergoes no change from the combined agency of air and moisture; and it may be exposed to the strongest heat of a smith's forge without suffering either oxidation or fusion. On heating a small wire of it by means of galvanism or the oxy-hydrogen blowpipe, it is fused, and afterwards burns with the emission of sparks. Smithson Tennant showed that it is oxidized when ignited with nitre (Phil. Trans. 1797); and a similar effect is occasioned by pure potassa and lithia. It is not attacked by any of the pure acids. Its solvents are chlorine or solutions, such as nitro-hydrochloric acid, which supply chlorine; and it is dissolved with greater difficulty than gold.

The remarkable property observed by Döbereiner in spongy platinum of causing the union of oxygen and hydrogen gases, was formerly mentioned; a property which Dulong and Thenard showed to be also possessed, though in a lower degree, by platinum in its compact form of wire or foil, and by several other metals. (An. de Ch. et Ph. xxiii. and xxiv.) Faraday (Phil. Trans. 1834, part i.) has lately discussed, with his wonted ability and success, both the conditions required for the effective action of platinum, and the cause of the phenomenon. The sole conditions are purity of the gases and perfect cleanliness of the platinum. By cleanliness is meant perfect absence of foreign matter, pure water excepted; and this condition is easily secured by fusing pure potassa on its surface, washing off the alkali by pure water, then dipping the platinum in hot oil of vitriol, and again washing with water. In this state platinum foil acts so rapidly at common temperatures on oxygen and hydrogen gases mixed in the ratio of 1 to 2, that it often becomes red hot and kindles the mixture. Handling the platinum, wiping it with a towel, or exposing it to the atmosphere for a few days, suffices to soil the surface of the metal, and thereby diminish or prevent its action. These phenomena are supposed to result from the concurring influence of two forces, the self-repulsive energy of similar gaseous particles, and the adhesive attraction exerted between them and the platinum. Each gas, repulsive to itself and not repelled by the platinum, comes into the most intimate contact with that metal, and both gases are so condensed upon its surface that they are brought within the sphere of their mutual attraction and combine. Faraday has given several instances, similar to those which I had occasion to describe some years ago (Jameson's Journal, xi. 99 and 311), where the action of platinum is retarded or altogether prevented by small quantities of certain gases, such as hydrosulphuric acid, carbonic oxide, and olefiant gases. One would be tempted to suppose that these gases act by soiling the metallic surface, though in some respects this explanation is not satisfactory.

When solutions of platinum are heated with various deoxidizing agents, such as formic acid, formiates, alcohol with alkalies, &c., or when an alloy of zinc and platinum is acted on by nitric acid, platinum is obtained as a finely divided black powder, which absorbs oxygen without chemically combining with it, and transfers it to combustible substances, thus indirectly acting as a powerful oxi-

* The reader will find, in the Philosophical Transactions for 1829, some important directions by Dr. Wollaston, both as to the mode of extracting platinum from its ores, and of communicating to the pure metal its highest degree of malleability. The essay receives additional interest from being one of those which were composed during the last illness of this truly illustrious philosopher.

dizing agent. In this way alcohol and pyroxylic spirit may be converted into acetic and formic acids, sulphurous acid into sulphuric acid, &c. (Döbereiner.)

The eq. of platinum, deduced by Berzelius from the analysis of the bichloride, is 98·8; its symb. is Pt. The composition of its compounds described in this section is as follows:—

	Platinum.			Equiv.	Formulæ.
Protoxide	98·8	1 eq. + Oxygen	8	1 eq. = 106·8	Pt + O or PtO.
Binoxide	98·8	1 eq. + . .	16	2 eq. = 114·8	Pt + 2O or PtO_2.
Sesquioxide ?	197·6	2 eq. + . .	24	3 eq. = 221·6	2Pt + 3O or Pt_2O_3.
Protochloride	98·8	1 eq. + Chlorine	35·42	1 eq. = 134·22	Pt + Cl or PtCl.
Bichloride	98·8	1 eq. + . .	70·84	2 eq. = 169·64	Pt + 2Cl or $PtCl^2$.
Protiodide	98·8	1 eq. + Iodine	126·3	1 eq. = 225·1	Pt + I or PtI.
Biniodide	98·8	1 eq. + . .	252·6	2 eq. = 351·4	Pt + 2I or PtI_2.
Protosulphuret	98·8	1 eq. + Sulphur	16·1	1 eq. = 114·9	Pt + S or PtS.
Bisulphuret	98·8	1 eq. + . .	32·2	2 eq. = 131·0	Pt + 2S or PtS_2.

Protoxide of Platinum.—This oxide is prepared by digesting protochloride of platinum in a solution of pure potassa, avoiding a large excess of the alkali, since it dissolves a portion of the oxide and thereby acquires a green colour. In this state it is a hydrate which loses first its water and then oxygen when heated, and dissolves slowly in acids, yielding solutions of a brownish-green tint.

Its eq. is 106·8; *symb.* Pt + Cl, $\dot{P}t$, or PtO.

Binoxide.—This oxide is prepared with difficulty, owing to its disposition, like peroxide of gold, to act rather as an acid than an alkaline base, and either to fall in combination with any alkali by which it is precipitated, or to remain with it altogether in solution. Berzelius recommends that it should be prepared by exactly decomposing sulphate of binoxide of platinum with nitrate of baryta, and adding pure soda to the filtered solution, so as to precipitate about half of the oxide; since otherwise, a sub-salt would subside. The oxide falls in the form of a bulky hydrate, of a yellowish-brown colour: it resembles rust of iron when dry, and is nearly black when rendered anhydrous.

Its eq. is 114·8; *symb.* Pt + 2O, $\ddot{P}t$, or PtO_2.

Sesquioxide.—This oxide, of a grey colour, is prepared, according to its discoverer, Mr. E. Davy, by heating fulminating platinum with nitrous acid; but the nature of the compound so formed has not yet been decisively determined. (Phil. Trans. 1820.)

Protochloride.—When the bichloride is heated to 450°, half of its chlorine is expelled, and the protochloride of a greenish-grey colour remains. It is insoluble in water, sulphuric acid, and nitric acid; but hydrochloric acid partially dissolves it, yielding a red solution. At a red heat its chlorine is driven off, and metallic platinum is left. It is dissolved by a solution of the bichloride.

Its eq. is 134·22; *symb.* Pt + Cl, or PtCl.

Bichloride of Platinum.—This chloride is obtained by evaporating the solution of platinum in nitro-hydrochloric acid to dryness at a very gentle heat, when it remains as a red hydrate, which becomes brown when its water is expelled. It is deliquescent, and very soluble in water, alcohol, and ether; its solution, if free from the chlorides of palladium and iridium, being of a pure yellow colour. Its ethereal solution is decomposed by light, metallic platinum being deposited.

A solution of platinum is recognized by the following characters. When to an alcoholic or concentrated aqueous solution of the bichloride a solution of chloride of potassium is added, a crystalline double chloride of a pale yellow colour subsides, which is insoluble in alcohol, and sparingly soluble in water; at a red heat it yields chlorine gas, and the residue consists of metallic platinum and chloride of potassium. With a solution of hydrochlorate of ammonia a similar yellow salt falls, which when ignited leaves pure platinum in the form of a delicate spongy mass, the power of which in kindling an explosive mixture of oxygen and hydrogen gases has already been mentioned.

Its eq. is 169·64; *symb.* Pt + 2Cl, or $PtCl_2$.

Protiodide of Platinum.—Lassaigne prepared this compound by digesting the protochloride of platinum in a rather strong solution of iodide of potassium, when the protiodide gradually appeared in the form of a black powder, which is insoluble in water and alcohol. It is unchanged by the sulphuric, nitric, and hydrochloric acids, decomposed by the alkalies, and at a red heat gives off its iodine. *Its eq. is* 225·1; *symb.* Pt + I, or PtI.

Periodide of Platinum.—Lassaigne prepares this compound by the action of iodide of potassium on a rather dilute solution of bichloride of platinum. At first the liquid acquires an orange-red and then a claret colour, without any precipitation; but when the solution is boiled a black precipitate subsides, which should be washed with hot water and dried at a heat not exceeding 212°. This biniodide is a black powder, sometimes crystalline, is tasteless and inodorous, insoluble in water, and may be boiled in water without change. By alcohol it is sparingly dissolved, especially when heated. Acids act feebly upon it; but it is decomposed by alkalies, and begins to lose iodine at 270°. (An. de Ch. et Ph. li. 113.) *Its eq. is* 351·4; *symb.* Pt + 2I, or PtI_2.

Protosulphuret of Platinum.—It is formed by heating in a retort the yellow ammoniacal chloride of platinum with half its weight of sulphur until all the sal-ammoniac and excess of sulphur is expelled. The protosulphuret is then left as a grey powder of a metallic lustre. It may also be formed by the action of hydrosulphuric acid on protochloride of platinum.

Its eq. is 114·9; *symb.* Pt + S, or PtS.

Bisulphuret.—It is formed as a brown precipitate, which becomes black when dried, by letting fall a solution of bichloride of platinum drop by drop into a solution of sulphuret of potassium, or by transmitting hydrosulphuric acid gas into a solution of the double chloride of platinum and sodium. (Berzelius.) It should be dried in vacuo by aid of sulphuric acid, since by exposure to the air in a moist state sulphuric acid is generated.

Its eq. is 130; *symb.* Pt + 2S, or PtS_2.

Fulminating platinum may be prepared by the action of ammonia in slight excess on a solution of sulphate of oxide of platinum. (E. Davy.) It is analogous to the detonating compounds which ammonia forms with the oxides of gold and silver.

SECTION XXVII.

PALLADIUM.—RHODIUM.—OSMIUM.—IRIDIUM.

The four metals to be described in this section are all contained in the ore of platinum, and have hitherto been procured in very small quantity. When the ore is digested in nitro-hydrochloric acid, the platinum, together with palladium, rhodium, iron, copper, and lead, is dissolved; while a black powder is left consisting of osmium and iridium, mixed in general with a considerable quantity of titanate of iron, and siliceous minerals.

PALLADIUM.

Hist. and Prep.—Discovered in 1803, by Wollaston (Phil. Trans. 1804 and 1805). On adding bicyanuret of mercury dissolved in water to a neutral solution of the ore of platinum, either before or after the separation of that metal by hydrochlorate of ammonia, a yellowish-white flocculent precipitate is gradually deposited, which is cyanuret of palladium. When this compound is heated to redness, the cyanogen is expelled, and pure palladium remains. In order to obtain it in a malleable state, the metal should be heated with sulphur, and the resulting sulphuret purified by cupellation in an open crucible with borax and a little nitre. It is then roasted at a low red heat on a flat brick, and when reduced to a pasty consistence, it is pressed into a square or oblong perfectly flat cake. It is again to be roasted very patiently, at a low red heat, until it becomes spongy on the surface; and when quite cold, it is condensed by frequent tappings with a light hammer. By alternate roastings and tappings the sulphur is burned off, and the metal rendered sufficiently dense to be laminated. Thus prepared it is rather brittle while hot, which Wollaston supposed to arise from a small remnant of sulphur. (Phil. Trans. 1829, p. 7.)

Prop.—It resembles platinum in colour and lustre. It is ductile as well as malleable, and is considerably harder than platinum. Its sp. gr. varies from 11·3 to 11·8. In fusibility it is intermediate between gold and platinum, and is dissipated in sparks when intensely heated by the oxy-hydrogen blowpipe. At a red heat in oxygen gas its surface acquires a fine blue colour, owing to superficial oxidation; but the increase of weight is so slight as not to be appreciated. It is oxidized and dissolved by nitric acid, and even the sulphuric and hydrochloric acids act upon it by the aid of heat; but its proper solvent is nitro-hydrochloric acid. Its oxide forms beautiful red-coloured salts, from which metallic palladium is precipitated by sulphate of protoxide of iron, and by all the metals described in the foregoing sections, excepting silver, gold, and platinum.

From the analysis by Berzelius of the double chloride of palladium and potassium the *eq.* of palladium is inferred to be 53·3. *Its symb.* is Pd. The composition of its compounds described in this section is as follows:—

Palladium.			Equiv.		Formulæ
Protoxide	53·3	1 eq.+Oxygen	8	1 eq.= 61·3	Pd+O or PdO.
Binoxide	53·3	1 eq.+do.	16	2 eq.= 69·3	Pd+2O or PdO_2.
Protochloride	53·3	1 eq.+Chlorine	35·42	1 eq.= 88·72	Pd+Cl or PdCl.
Bichloride	53·3	1 eq.+do.	70·84	2 eq.=124·14	Pd+2Cl or $PdCl_2$.
Protosulphuret	53·3	1 eq.+Sulphur	16·1	1 eq.= 69·4	Pd+S or PdS.

Protoxide of Palladium.—This oxide is obtained as a hydrate of a deep brown colour by decomposing its salts with an excess of carbonate of potassa or soda; and, by washing and heating to low redness, the anhydrous protoxide of a black colour is left. It is also obtained by heating the nitrate at a low red heat. In the anhydrous state it is dissolved with difficulty by acids. When strongly heated it parts with its oxygen. Berzelius says it falls from its salts on the addition of the alkalies as a sub-salt, which is dissolved by the alkali in excess.

Its eq. is 61·3; *symb.* Pd + O, $\dot{P}d$, or PdO.

Binoxide.—To prepare this oxide Berzelius recommends that a solution of potassa or its carbonate in excess should be poured by little and little on the *solid* bichloride of palladium and potassium, and the materials be well intermixed: water is not first added, because it decomposes the double chloride; and the alkali is not added all at once, because the binoxide would then be dissolved at first, and afterwards separate out as a gelatinous hydrate, which could not be purified by washing. When prepared with the foregoing directions, the binoxide is obtained as a hydrate of a deep yellowish-brown colour, which retains a little potassa in combination; but on heating the solution to 212° the alkali is dissolved, and the anhydrous black oxide left.

Its eq. is 69·3; *symb.* Pd + 2O, $\ddot{P}d$, or PdO_2.

Protochloride of Palladium.—It is obtained by evaporating to dryness a solution of palladium in nitro-hydrochloric acid, being left as a brown crystalline hydrate, which becomes black when its water is expelled. It loses its chlorine when strongly heated, and is soluble in water. *Its eq. is* 88·72; *symb.* Pd + Cl, or PdCl.

The *bichloride* is formed by digesting the protochloride in nitro-hydrochloric acid, and exists only in solution, the colour of which is of so deep a brown as to appear nearly black. It is readily distinguished from the protochloride by yielding with chloride of potassium a double chloride of a red colour; whereas that formed with the protochloride is yellow.

Its eq. is 124·14; *symb.* Pd + 2Cl, or $PdCl_2$.

Protosulphuret of Palladium.—It is readily formed by heating the metal with sulphur, and is a fusible brittle compound of a grey colour. *Its eq. is* 69·4; *symb.* Pd + S, or PdS.

RHODIUM.

Hist. and Prep.—This metal was discovered by Wollaston at the time he was occupied with the discovery of palladium. On immersing a thin plate of clean iron into the solution from which palladium and the greater part of the platinum have been precipitated, the rhodium, together with small quantities of platinum, copper, and lead, is thrown down in the metallic state; and on digesting the precipitate in dilute nitric acid, the two last metals are removed. The rhodium and platinum are then dissolved by means of nitro-hydrochloric acid, and the

solution, after being mixed with some chloride of sodium, is evaporated to dryness. Two double chlorides result, that of platinum and sodium, and of rhodium and sodium, the former of which is soluble, and the latter insoluble in alcohol; and they may therefore be separated from each other by this menstruum. The double chloride of rhodium is then dissolved in water, and metallic rhodium precipitated by insertion of a rod of zinc.

Prop.—Thus procured, it is in the form of a black powder, which requires the strongest heat that can be produced in a wind furnace for fusion, and when fused has a white colour and metallic lustre. It is brittle, is extremely hard, and has a sp. gr. of about 11. It attracts oxygen at a red heat, a mixture of peroxide and protoxide being formed. It is not attacked by any of the acids when in its pure state; but if alloyed with other metals, such as copper or lead, it is dissolved by nitro-hydrochloric acid, a circumstance which accounts for its presence in the solution of crude platinum. It is oxidized by being ignited either with nitre, or bisulphate of potash. When heated with the latter, sulphurous acid gas is evolved, and a double sulphate of peroxide of rhodium and potash is generated, which dissolves readily in hot water, and yields a yellow solution. The presence of rhodium in platinum, iridium, and osmium may thus be detected, and by repeated fusion a perfect separation be accomplished. (Berzelius.)

Chemists are acquainted with two oxides of rhodium. The protoxide is black, and the peroxide, which is the base of the salts of rhodium, is of a yellow colour. Most of its salts are either red or yellow.

From the composition of the double chloride of rhodium and potassium Berzelius considers 52·2 as the *eq.* of rhodium; *its symb.* is R, and its compounds described in this section are thus constituted:—

	Rhodium.			Equiv.	Formulæ.
Protoxide	52·2	1 eq. + Oxygen	8	1 eq. = 60·2	R + O or RO.
Peroxide	104·4	2 eq. + do.	24	3 eq. = 128·4	2R + 3O or R_2O_3.
Protochloride	52·2	1 eq. + Chlorine	35·42	1 eq. = 87·62	R + Cl or RCl.
Perchloride	104·4	2 eq. + do.	106·26	3 eq. = 210·66	2R + 3Cl or R_2Cl_3.
Sulphuret	Probably a protosulphuret.				

Oxides of Rhodium.—The first grade of oxidation has not yet been insulated. The peroxide is generated when pulverulent rhodium is heated to redness in a silver crucible mixed with hydrate of potassa and a little nitre, when the rhodium is oxidized and acquires a coffee-brown colour. To remove the potassa united with the peroxide, the mass is first washed with water and then digested in hydrochloric acid, when it acquires a greenish-grey colour, and is left as a pure hydrate of the peroxide. In this state it is insoluble in acids. If an excess of carbonate of potassa or soda is added to the double chloride of rhodium and potassium, and the solution is evaporated, a gelatinous hydrate falls; but on attempting to dissolve in acid the potassa combined with the peroxide, the latter is also dissolved. ...

Its eq. is 128·4; *symb.* 2R + 3O, $\underline{R}$, or R_2O_3.

Chlorides of Rhodium.—The only chloride which has yet been insulated is the perchloride, which Berzelius obtained by adding to a solution of the double chloride of rhodium and potassium silico-hydrofluoric acid as long as the double fluoride of potassium and silicon was generated, after which the filtered liquid

was evaporated to dryness, and redissolved in water. This perchloride when dry has a dark brown colour, is uncrystalline, and decomposed by a full red heat into chlorine and metallic rhodium. It deliquesces in the air into a brown liquid, and its aqueous solution has a fine red colour, whence its name of rhodium (from ῥοδον, a rose) is derived. (An. de Ch. et Ph. xl. 51.)

Its eq. is 210·66; *symb.* 2R + 3Cl, or R_2Cl_3.

Sulphuret of Rhodium.—It may be formed by heating rhodium directly with sulphur, fuses at a white heat without decomposition, and has a bluish-grey colour, with a metallic lustre. Wollaston made use of it for procuring the metal in a coherent state, in the same manner as sulphuret of palladium.

IRIDIUM AND OSMIUM.

Hist.—These metals were discovered by the late Mr. Tennant in the year 1803 (Phil. Trans. 1804), and the discovery of iridium was made about the same time by Descotils in France. The black powder mentioned at the beginning of this section is a compound of iridium and osmium, an alloy which Wollaston detected in the form of flat white grains among fragments of crude platinum. This alloy, which is quite insoluble in nitro-hydrochloric acid, is the source from which iridium and osmium are extracted.

Osmium and Iridium.—Prep.—These metals are obtained from the pulverulent residue of the ores of platinum, after that metal together with palladium and rhodium have been removed by digestion in nitro-hydrochloric acid. Wollaston has recommended the following process (Phil. Trans. 1829, p. 8). The residue is ground into a fine powder with a third of its weight of nitre, and the mixture heated to redness in a silver crucible until it is reduced to a pasty state, when the characteristic odour of oxide of osmium will be perceptible. Dissolve the soluble parts, which contain oxide of osmium in combination with potassa, in the smallest possible quantity of water, and acidulate the solution, introduced into a retort, with sulphuric acid diluted with its own weight of water. By distilling rapidly into a clean receiver as long as osmic fumes pass over, the acid will be collected on its sides in the form of a white crust; and, there melting, it will run down in drops beneath the watery solution, forming a fluid flattened globule at the bottom. As the receiver cools, the acid becomes solid and crystallizes. Osmium is precipitated from the solution of its acid by all the metals, excepting gold and silver. A convenient mode of reduction is to agitate it with mercury, adding hydrochloric acid to decompose the protoxide of mercury which is formed, and then expelling the mercury and calomel by heat. The osmium is left as a black porous powder which acquires metallic lustre by friction.

The insoluble parts contain the iridium as oxide in combination with potassa. On digesting the mass in hydrochloric acid, a blue solution is obtained; but it afterwards becomes of an olive-green hue, and subsequently acquires a deep-red tint. This variety of colour, which suggested the name of iridium (Iris, the rainbow), is owing to the successive production of different compounds. The iridium may be precipitated from the solution by any metal except gold and platinum, or it may be obtained by exposing the chloride to a red heat. Wöhler has proposed a very elegant process by which both metals may be obtained on a large scale (Pog. An. xxi. 161). The great advantage of his method is, that it leaves the titanate of iron and other foreign minerals undecomposed. He mixes the residue with an equal weight of fused sea-salt in fine powder. The mixture

is introduced into a long and wide green glass tube, which is connected at one extremity with an apparatus for developing chlorine, at the other with a tubulated receiver. The latter is furnished with a small tube, the extremity of which is made to dip into a weak solution of ammonia. The tube containing the mixture of salt and ore being then brought to a low red heat, the chlorine is developed and the gas transmitted in a moderate stream through the glowing mass, by which in the first part of the process it is abundantly and completely absorbed. The operation is to be continued until the chlorine is observed to pass pretty freely into the solution of ammonia. The changes which occur are owing to the formation of two haloid acids, by the combination of the chlorine with both metals of the ore; and as these instantly combine with the chloride of sodium, two soluble salts, the iridio-chloride of sodium, and the osmio-chloride of sodium, are produced. But by the moisture of the chlorine gas the latter compound is decomposed, the chloride of osmium giving rise to the formation of osmic and hydrochloric acids, and the deposition of a part of the osmium in the metallic state. This by again combining with chlorine gives rise to a repetition of the same changes, and to the production of an additional quantity of osmic acid, which, being volatile, passes on and is deposited in crystals in the receiver. The solution of ammonia prevents the loss of any acid which might escape condensation. The solid matter in the tube is then digested in water, when a deep brown solution is obtained, and the clear liquid is separated by decantation from the insoluble parts, which consists principally of titanate of iron. As the solution still contains some osmic acid, it is submitted to a distillation until one-half has passed over into a weak solution of ammonia. The remainder is then evaporated in an open dish, while carbonate of soda is at the same time added in successive portions until a considerable excess is present. On evaporating to dryness a black mass is obtained, which is to be exposed to a low red heat in a hessian crucible. When cold, the saline matter is removed by boiling water, and the sesquioxide of iridium is left in the form of a black powder. It is readily reduced to the metallic state by a stream of hydrogen gas.

Osmium.—As obtained by precipitation it is a black porous powder, which acquires a metallic lustre by friction. After exposure to a very gentle heat, its sp. gr. is 7. It takes fire when heated in the open air, and is readily oxidized and dissolved by fuming nitric acid: but a red heat gives it greater compactness, and in that state it ceases to be attacked by acids, and may be freely heated without oxidation. In its densest state Berzelius found its sp. gr. to be 10. (An. de Ch. et Ph. xl. 257, and xlii. 185.) Its symb. is Os.

Berzelius, from his late researches on the compounds of osmium, considers 99·7 to be its eq., and gives the composition of its oxides, chlorides, and sulphurets, as follows;—

	Osmium.			Equiv.	Formulæ.
Protoxide	99·7	1 eq.+Oxygen	8	1 eq.=107·7	Os+O or OsO.
Sesquioxide	199·4	2 eq.+do.	24	3 eq.=223·4	2Os+3O or Os_2O_3.
Binoxide	99·7	1 eq.+do.	16	2 eq.=115·7	Os+2O or OsO_2.
Teroxide	99·7	1 eq.+do.	24	3 eq.=123·7	Os+3O or OsO_3.
Osmic Acid	99·7	1 eq.+do.	32	4 eq.=131·7	Os+4O or OsO^4.
Protochloride	99·7	1 eq.+Chlorine	35·42	1 eq.=135·12	Os+Cl or OsCl.
Sesquichlor.	199·4	2 eq.+do.	106·26	3 eq.=205·66	2Os+3Cl or Os_2Cl_3.
Bichloride	99·7	1 eq.+do.	70·84	2 eq.=170·54	Os+2Cl or $OsCl_2$.
Terchloride	99·7	1 eq.+do.	106·26	3 eq.=205·96	Os+3Cl or $OsCl_3$.

	Osmium.			Equiv.	Formulæ.
Protosulphuret	99·7	1 eq.+Sulphur	16·1	1 eq.=115·8	Os+S or Os or OsS.
Sesquisulph.	199·4	2 eq.+do.	48·3	3 eq.=247·7	$2Os+3S$ or Os_2S_3.
Bisulphuret	99·7	1 eq.+do.	32·2	2 eq.=131·9	$Os+2S$ or OsS_2.
Tersulphuret	99·7	1 eq.+do.	48·3	3 eq.=148·0	$Os+3S$ or OsS_3.

Oxides of Osmium.—For a minute description of these compounds I refer to the essays of Berzelius above cited. The protoxide is precipitated by pure alkalies from the protochloride, and falls as a deep green, nearly black, hydrate, which is soluble in acids, and detonates when heated with combustible matter. The binoxide is thrown down as a hydrate of a deep brown colour, when a saturated solution of the bichloride is heated with carbonate of soda. It retains a little alkali in combination; but the soda is easily removed by dilute hydrochloric acid, without the oxide being dissolved. The teroxide is prepared in like manner from the terchloride. [This, according to MM. Fremy and Claus, combines with potassa, forming a very beautiful salt, which crystallizes in regular octohedrons having a black, garnet, or rose-red colour, according to the quickness of their formation. They therefore rank this oxide with the metallic acids, under the name of osmious acid.] The sesquioxide has not been obtained in a separate state; but it is procured in combination with ammonia when the binoxide is treated with a large excess of pure ammonia, nitrogen gas being disengaged at the same time.

The highest stage of oxidation is the volatile acid, which is the product of the oxidation of osmium by acids, by combustion, or by fusion with nitre or alkalies; and it may be procured by the process above mentioned in colourless transparent elongated crystals, or as a colourless solution in water. Its vapour is very acrid, exciting cough, irritating the eyes, and producing a copious flow of saliva; and its odour is disagreeable and pungent, somewhat like that of chlorine; a property which suggested the name of *Osmium* (from οσμη, odour.) It does not combine with acids: on the contrary, though it has no acid reaction, it unites with alkalies, and the compound sustains a strong heat without decomposition. When touched, it communicates a stain which cannot be removed by washing. With the infusion of gall-nuts it yields a purple solution, which afterwards acquires a deep blue tint; a character which forms a sure and extremely delicate test for peroxide of osmium. By sulphurous acid it is deoxidized, and the colour of the solution passes through the shades of yellow, orange, brown, green, and lastly blue, when it resembles sulphate of indigo. These changes correspond to sulphates of the different oxides of osmium, the last or blue oxide being a compound of protoxide and sesquioxide of osmium.

Chlorides of Osmium.—Berzelius has described four chlorides of osmium, corresponding to the four first degrees of oxidation above mentioned. When osmium is heated in a tube in a current of dry chlorine gas, a deep green sublimate is formed, which is the protochloride. On continuing the process it yields a red sublimate, which is the bichloride. For the remaining details, which are rather minute, I may refer to the essay already cited. Several of these chlorides yield double compounds with sodium, potassium, and ammonia.

Osmium unites with sulphur in the dry way, or when precipitated from the chlorides by hydrosulphuric acid. The sulphurets obviously correspond to the number of the oxides. (Berzelius.)

Iridium.—Prop.—A brittle metal, and apt to fall into powder when burnished; but with care it may be polished, and then acquires the appearance of platinum.

Of all known metals it is the most infusible: Children, by means of his large galvanic battery, fused it into a globule of a brilliant metallic lustre and white colour, having a density of 18·68; but the attempts at fusion by Berzelius were unsuccessful. Breithaupt states that the sp. gr. of native iridium, lately found in the Russian mines of platinum, although not quite free from lighter metals, varies from 23 to 26.* This would make iridium the heavest of metals. It is also, according to Breithaupt, the hardest and the most indestructible by acids. Hence, if it could be easily wrought it would be invaluable for the edges of delicate balances. It is oxidized at a red heat in the open air, if in a state of fine division, but not otherwise; and it is attacked with difficulty even by nitro-hydrochloric acid.

The eq. of iridium is estimated by Berzelius at 98·8, being identical with that of platinum. It forms with oxygen four oxides exactly analogous in composition to the four first oxides of osmium in the foregoing table, and its four chlorides correspond to those of osmium. Its sulphurets have been little examined, but they doubtless correspond to the oxides. (An. de Ch. et Ph. xl. 257, and xliii. 185.) Its symb. is Ir.

Oxides of Iridium.—The protoxide, sesquioxide, and teroxide, are precipitated by alkalies from the chloride, to which each is respectively proportional. The protoxide is greenish-grey as a hydrate, and black when anhydrous. The sesquioxide is bluish-black in the dry state, and deep brown as a hydrate. The hydrated teroxide is of a yellowish-brown or greenish colour. The binoxide has not hitherto been insulated. Berzelius has not fully decided the nature of the compound which is considered as the blue oxide, that which forms a blue solution with acids; but he believes it to be a compound of the protoxide and sesquioxide. This variety of oxides, together with the facility with which they appear to pass from one to the other, amply accounts for the diversity of tints sometimes observed in solutions of iridium.

Chlorides of Iridium.—The protochloride is obtained as a light powder of a deep olive-green colour, by transmitting chlorine gas over pulverulent iridium heated to a commencing red heat. When heated to redness its chlorine is expelled. It is insoluble in water, and but sparingly dissolved by acids, even the nitro-hydrochloric; but when the hydrated protoxide is digested in hydrochloric acid, the protochloride is reproduced and dissolved, forming probably a soluble compound of the protochloride and hydrochloric acid. Its solution is a mixture of brown, green, and yellow. (Berzelius.)

The *sesquichloride* is best obtained by calcining iridium with nitre, digesting the product in nitric acid, and, after washing, dissolving the residual oxide in hydrochloric acid. Its solution has a dark yellowish-brown tint, which is so intense that a small quantity renders water opaque. By evaporation it yields a black mass, wholly uncrystalline, and deliquescent in the air.

The *bichloride* is formed by digesting at a moderate heat the sesquichloride in nitro-hydrochloric acid. It is deliquescent and very soluble, yielding a solution of a dark reddish-brown colour. When its solution is evaporated to dryness, except at a heat not exceeding 104°, it loses chlorine, and is reconverted into the sesquichloride.

The *terchloride* has not been obtained in a separate form, but only as a double chloride of potassium. It appears to be the principal compound formed in the

* Professor Hare has repeatedly fused it by means of his oxyhydrogen blowpipe, and found its sp. gr. to be 21·8.

process above given for extracting iridium from its ore, and is recognized by its rose-red tint.

Iridium has a considerable affinity for carbon, combining with it when a piece of metal is held in the flame of a spirit-lamp. The resulting carburet contains 19·8 per cent. of carbon.

[*Ruthenium* is the name given by M. Claus to a new metal which he discovered about two years ago in the platinum residues. It had escaped the notice of chemists from the close resemblance of its double chloride with potassium to the similar double salt of iridium. He has recently obtained the metal in perfect purity, and states that its highest chloride is of a fine orange colour, and its solution in water, unlike any of the other platina metals, is precipitated by ammonia at common temperatures. When a plate of zinc is immersed in this chloride, previously acidified by a little hydrochloric acid, the metal is after some time precipitated in the form of a black powder. (Jour. de Pharm. et de Ch. Juin. 1845.)]

SECTION XXVIII.

ON METALLIC COMBINATIONS.

Having completed the history of the individual metals, and of the compounds resulting from their union with the simple non-metallic bodies, I shall treat briefly in the present section of the combinations of the metals with each other. These compounds are called *alloys;* and to those alloys, of which mercury is a constituent, the term *amalgam* is applied. It is probable that each metal is capable of uniting in one or more proportions with every other metal, and on this supposition the number of alloys would be exceedingly numerous. This department of chemistry, however, owing to its having been cultivated with less zeal than most other branches of the science, is as yet limited, and our knowledge concerning it imperfect. On this account I shall mention those alloys only to which some particular interest is attached.

Metals do not combine with each other in their solid state, owing to the influence of chemical affinity being counteracted by the force of cohesion. It is necessary to liquefy at least one of them, in which case they always unite, provided their mutual attraction is energetic. Thus, brass is formed when pieces of copper are put into melted zinc; and gold unites with mercury at common temperatures by mere contact.

Metals appear to unite with one another in every proportion, precisely in the same manner as sulphuric acid and water. Thus there is no limit to the number of alloys of gold and copper. It is certain, however, that metals have a tendency to combine in definite proportion; for several atomic compounds of this kind occur native. The crystallized amalgam of silver, for example, is composed, according to the analysis of Klaproth, of 64 parts of mercury and 36 of silver; numbers which are so nearly in the ratio of 202 to 108, that the amalgam may be inferred to contain one eq. of each of its elements. It is indeed possible that the variety of proportion in alloys is rather apparent than real, arising from the mixture of a few definite compounds with each other, or with uncombined metal;

an opinion not only suggested by the mode in which alloys are prepared, but in some measure supported by observation. Thus, on adding successive small quantities of silver to mercury, a great variety of fluid amalgams are apparently produced; but, in reality, the chief, if not the sole compound, is a solid amalgam, which is merely diffused throughout the fluid mass, and may be separated by pressing the liquid mercury through a piece of thick leather.

This view is strengthened by some late experiments by Rudberg (An. de Ch. et Ph. xlviii. 363). He finds that variable mixtures of metals in cooling after fusion have generally two periods when the thermometer is stationary. In alloys of lead and tin one of these points is uniformly at 368½° for all mixtures, while the other point varies according as one or the other metal is predominant, and is near the fusing point of the predominating metal. From this it is inferred that the latter point is caused by the congelation of the predominating metal, and the constant point is the congealing temperature of an alloy of uniform composition present in all the mixtures. This alloy is composed of 3 eq. of tin and 1 eq. of lead, its congealing point being 368½°. In variable mixtures of bismuth and tin the constant point is 289½°, which is the congealing temperature of an alloy composed of single eq. of tin and bismuth.

Alloys are analogous to metals in their chief physical properties. They are opaque, possess the metallic lustre, and are good conductors of heat and electricity. They often differ materially in some respects from the elements of which they consist. The colour of an alloy is sometimes different from that of its constituents, of which brass is a remarkable example. The hardness of a metal is in general increased by being alloyed, and for this reason its elasticity and sonorousness are frequently improved. The malleability and ductility of metals, on the contrary, are usually impaired by combination. Alloys formed of two brittle metals are always brittle; and an alloy composed of a ductile and a brittle metal is generally brittle, especially if the latter predominate. An alloy of two ductile metals is sometimes brittle.

The density of an alloy is sometimes less, sometimes greater, than the mean density of the metals of which it is composed.

The fusibility of metals is greatly increased by being alloyed. Thus pure platinum, which cannot be completely fused in the most intense heat of a wind furnace, forms a very fusible alloy with arsenic.

The tendency of metals to unite with oxygen is considerably augmented by being alloyed. This effect is particularly conspicuous when dense metals are liquefied by combination with quicksilver. Lead and tin, for instance, when united with mercury, are soon oxidized by exposure to the atmosphere; and even gold and silver combine with oxygen, when the amalgams of those metals are agitated with air. The oxidability of one metal in an alloy appears in some instances to be increased in consequence of a galvanic action. Thus, Faraday observed that an alloy of steel with 100th of its weight of platinum was dissolved with effervescence in dilute sulphuric acid, which was so weak that it scarcely acted on common steel; an effect which he ascribes to the steel in the alloy being rendered positive by the presence of the platinum. De la Rive has noticed a similar instance in commercial zinc, the oxidability of which is increased by the presence of small quantities of iron. In these cases, however, the effect is due rather to one metal being mechanically enveloped in another than to actual combination.

AMALGAMS.

Quicksilver unites with potassium when agitated in a glass tube with that metal, forming a solid amalgam. When the amalgam is put into water, the potassium is gradually oxidized, hydrogen gas is disengaged, and the mercury resumes its liquid form. A similar compound may be obtained with sodium. These amalgams may also be procured by placing the negative wire in contact with a globule of mercury during the process of decomposing potassa and soda by galvanism.

A solid amalgam of tin is employed in making looking-glasses; and an amalgam made of one part of lead, one of tin, two of bismuth, and four parts of mercury, is used for silvering the inside of hollow glass globes. This amalgam is solid at common temperatures; but is fused by a slight degree of heat.

The amalgam of zinc and tin, used for promoting the action of the electrical machine, is made by fusing one part of zinc with one of tin, and then agitating the liquid mass with two parts of hot mercury placed in a wooden box. Mercury evinces little disposition to unite with iron, and, on this account, it is usually preserved in iron bottles.

The amalgam of silver, as already mentioned, is a mineral production. The process of separating silver from its ores by amalgamation, practised on a large scale at Freyberg in Germany, is founded on the affinity of mercury for silver. On exposing the amalgam to heat, the quicksilver is volatilized, and pure silver remains.

Gold unites with remarkable facility with mercury, forming a white-coloured compound. An amalgam composed of one part of gold and eight of mercury is employed in gilding brass. The brass, after being rubbed with nitrate of oxide of mercury, in order to give it a thin film of quicksilver, is covered with the amalgam of gold, and then exposed to heat for the purpose of expelling the mercury.

ALLOYS OF ARSENIC.

Arsenic has a tendency to render the metals, with which it is alloyed, both brittle and fusible. It has the property of destroying the colour of gold and copper. An alloy of copper, with a tenth part of arsenic, is so very similar in appearance to silver, that it has been substituted for it. The whiteness of this alloy affords a rough mode of testing it for arsenic; for if arsenious acid and charcoal be heated between two plates of copper, a white stain afterwards appears upon its surface, owing to the formation of an arseniuret of copper.

The presence of arsenic in iron has a very pernicious effect; for even though in small proportion it renders the iron brittle, especially when heated.

The alloy of tin and arsenic is employed for forming arseniuretted hydrogen gas by the action of hydrochloric acid. The tin of commerce sometimes contains a minute quantity of this alloy.

An alloy of platinum with ten parts of arsenic is fusible at a heat a little above redness, and may therefore be cast in moulds. On exposing the alloy to a gradually increasing temperature in open vessels, the arsenic is oxidized and expelled, and the platinum recovers its purity and infusibility.

ALLOYS OF TIN, LEAD, ANTIMONY, AND BISMUTH.

Tin and lead unite readily when fused together, constituting a solder, of which two kinds are distinguished. The alloy called *fine solder*, consists of two parts

of tin and one of lead, fuses at about 360°, and is much employed in tinning copper. The *coarse solder* contains 1-4th of tin, fuses at about 500°, and is the substance used for soldering by glaziers. Thus, by varying the relative quantity of the metals, a solder of different fusibility may be obtained. The process of hard soldering or *brazing*, by which two surfaces of copper are cemented together, is done with *hard solder*, which is made by fusing together brass and zinc: the copper requires to be heated, when this solder is used, to near its point of fusion.

It has been observed by Kupfer that most of the *alloys* of tin and lead, made in atomic proportion, have a sp. gr. less than their calculated density; from which it is manifest that they expand in uniting. The *amalgams* of lead and tin, on the contrary, occupy less space, when combined, than their elements did previously.

Tin alloyed with small quantities of antimony, copper, and bismuth, forms the best kind of pewter. Inferior sorts contain a large proportion of lead.

Tin, lead, and bismuth, form an alloy which is fused at a temperature below 212°. The best proportion, according to D'Arcet, is 8 parts of bismuth, 5 of lead, and 3 of tin.

An alloy of three parts of lead to one of antimony constitutes the substance of which types for printing are made.

A native alloy of antimony and nickel, found at Andreasberg in the Harz, was found by Stromeyer to consist of 29·5 parts or 1 eq. of nickel, and 64·4 parts or 1 eq. of antimony.

ALLOYS OF COPPER.

Copper forms with tin several valuable alloys, which are characterized by their sonorousness. Bronze is an alloy of copper with about eight or ten per cent. of tin, together with small quantities of other metals which are not essential to the compound. Cannons are cast with an alloy of a similar kind.

The best bell-metal is composed of 80 parts of copper and 20 of tin;—the Indian gong, celebrated for the richness of its tones, contains copper and tin in this proportion. A specimen of English bell-metal was found by Dr. Thomson to consist of 80 parts of copper, 10·1 of tin, 5·6 of zinc, and 4·3 of lead. Lead and antimony, though in small quantity, have a remarkable effect in diminishing the elasticity and sonorousness of the compound. *Speculum-metal*, with which mirrors for telescopes are made, consists of about two parts of copper and one of tin. The whiteness of the alloy is improved by the addition of a little arsenic.

Copper and zinc unite in several proportions, forming alloys of great importance in the arts. The best brass consists of four parts of copper to one of zinc; and when the latter is in a greater proportion, compounds are generated which are called *Tombac*, *Dutchgold*, and *Pinchbeck*. The *white copper* of the Chinese, which is the same as the German silver of the present day, is composed, according to the analysis of Fyfe, of 40·4 parts of copper, 25·4 of zinc, 31·6 of nickel, and 2·6 of iron.

The art of tinning copper consists in covering that metal with a thin layer of tin, in order to protect its surface from rusting. For this purpose, pieces of tin are placed upon a well-polished sheet of copper, which is heated sufficiently for fusing the tin. As soon as the tin liquefies, it is rubbed over the whole sheet of copper, and if the process is skilfully conducted, adheres uniformly to its surface. The oxidation of the tin, a circumstance which would entirely prevent the success of the operation, is avoided by employing fragments of resin or

muriate of ammonia, and regulating the temperature with great care. The two metals do not actually combine; but the adhesion is certainly owing to their actual affinity.—Iron, which has a weaker attraction than copper for tin, is tinned with more difficulty than that metal.

ALLOYS OF STEEL.

Messrs. Stodart and Faraday have succeeded in making some very important alloys of steel with other metals. (Phil. Trans. for 1822.) Their experiments induced them to believe that the celebrated Indian steel, called *wootz*, is an alloy of steel with small quantities of silicon and aluminium; and they succeeded in preparing a similar compound, possessed of all the properties of wootz. They ascertained that silver combines with steel, forming an alloy, which, although it contains only 1-500th of its weight of silver, is superior to wootz or the best cast steel in hardness. The alloy of steel with 100th part of platinum, though less hard than that with silver, possesses a greater degree of toughness, and is therefore highly valuable when tenacity as well as hardness is required. The alloy of steel with rhodium even exceeds the two former in hardness. The compound of steel with palladium, and of steel with iridium and osmium, is likewise exceedingly hard; but these alloys cannot be employed extensively, owing to the rarity of the metals of which they are composed.

ALLOYS OF SILVER.

Silver is capable of uniting with most other metals, and suffers greatly in malleability and ductility by their presence. It may contain a large quantity of copper without losing its white colour. The standard silver for coinage contains about 1-13th part of copper, which increases its hardness, and thus renders it more fit for coins and many other purposes.

ALLOYS OF GOLD.

The presence of other metals in gold has a remarkable effect in impairing its malleability and ductility. The metals which possess this property in the greatest degree are bismuth, lead, antimony, and arsenic. Thus, when gold is alloyed with 1-1920th part of its weight of lead, its malleability is surprisingly diminished. A very small proportion of copper has an influence over the colour of gold, communicating to it a red tint, which becomes deeper as the quantity of copper increases. Pure gold, being too soft for coinage and many purposes in the arts, is always alloyed either with copper or an alloy of copper and silver, which increases the hardness of the gold without materially affecting its colour or tenacity. Gold coins contain about 1-12th of copper.

Nearly all the gold found in nature is alloyed more or less with silver. In a late elaborate investigation into the constituents of the Uralian ores of gold, G. Rose found one specimen with 0·16 per cent. of silver, and another with 38·38 per cent.; but most of the specimens contained 8 or 9 per cent. of silver. It has been maintained that the native alloys of gold and silver are usually in atomic proportion. This statement, however, has been amply disproved by G. Rose: these metals appear to be isomorphous, and hence, like other isomorphous bodies, they crystallize with each other in proportions altogether indefinite. (Pog. An. xxiii. 161.)

SALTS.

GENERAL REMARKS ON SALTS.

The preceding pages contain the description either of elementary principles, or of compounds immediately resulting from the union of those elements. These compounds are chiefly bi-elementary, that is, arise from the union of two elements; their constituents are regarded, according to the electro-chemical theory, possessing opposite electric energies, and as combined by virtue of such energies; and the names applied to them are partly constructed in reference to this theory. Thus in compounds of oxygen and chlorine, chlorine and iodine, sulphur and potassium, the term expressive of the genus or class of bodies to which each compound belongs, is derived from the electro-negative element; so that we do not say, chloride of oxygen, iodide of chlorine, and potassiuret of sulphur, —but, oxide of chlorine, chloride of iodine, and sulphuret of potassium; because oxygen has a higher electro-negative energy than chlorine, chlorine than iodine, and sulphur than potassium. The metals as a class are electro-positive to the non-metallic elements; but in relation to each other some of the metals are electro-positive, and others electro-negative. To the former belong those metals, the oxides of which are strong alkaline bases, such as potassium, sodium, and calcium; and among the latter are enumerated those, such as arsenic, antimony, and molybdenum, which are prone to form acids when they unite with oxygen.

Some of the bi-elementary compounds above referred to, though composed of very energetic elements, are themselves chemically indifferent, manifesting little disposition to unite with any other body whatever; of which the peroxides of manganese and lead, and some of the chlorides are examples. Others, on the contrary, are surprisingly energetic in their chemical relations, and have an extensive range of affinity. The most remarkable instances of this are found among those oxidized bodies called *acids* and *alkalies*, the characters of which fixed the attention of chemists long before their composition was understood. The acids and alkalies, however, are indifferent to elementary substances: their affinities are exerted towards each other, and by uniting they give rise to compounds more complex than themselves, as containing at least three elements, and which are known by the name of *salts*. Acids and alkalies possess opposite electric energies in relation to each other, the former being — and the latter +. The electric energies evinced by them are related to the electric energies of their

elements. Thus acids generally abound in the electro-negative oxygen, and if they contain a metal, it is usually an electro-negative metal; whereas the powerful alkalies are the protoxides of electro-positive metals.

Acids and alkalies neutralize each other more or less completely, so that the resulting salt is generally neither acid nor alkaline, and is far less energetic as a chemical agent than acids and alkalies. Most of them, however, unite in definite proportion with certain substances, such as water, alcohol, ammonia, and with other salts, forming the extensive family of *double salts*. To these compounds the electro-chemical theory may be extended: the two simple salts which constitute a double salt, may be viewed as two molecules united by virtue of electric energies of an opposite character.

In the early period of modern chemistry an acid was considered to be an oxidized body which has a sour taste, reddens litmus paper, and neutralizes alkalies. But subsequent experience has shown the propriety of extending the definition of an acid. For, first, the discovery of the hydracids proved that oxygen is not essential to acidity. Secondly, some compounds, owing to their insolubility, neither taste sour nor redden litmus, and yet from their chemical relations are regarded as acids. Thirdly, some acknowledged acids, such as the carbonic and hydrosulphuric, are unable fully to destroy the alkaline reaction of potassa. Facts of this kind have induced chemists to consider as acids all those compounds which unite with potassa or ammonia, and give rise to bodies similar in their constitution and general character to the salts which the sulphuric or some admitted acid forms with those alkalies.

A similar extension is given to the notion of alkalinity, the characters of which, as exhibited in their most perfect form in potassa and soda, are causticity, a peculiar pungent alkaline taste, alkaline reaction with test paper, and power both of neutralizing acids and of forming with them neutral saline compounds. Of these, chemists agree to consider the last as the most characteristic, and place among the *alkaline or salifiable bases* all those bodies which unite definitely with admitted acids, such as the sulphuric and nitric, and form with them compounds analogous in constitution to the salts which admitted alkalies form with the acids. Thus, magnesia is a very strong alkaline base, seeing that 20·7 parts of it neutralize as much sulphuric acid as 47 of potassa; and yet magnesia, from being insoluble is all but tasteless, and has barely any alkaline reaction.

The progress of chemistry, which has gradually developed sounder views of the nature of acids and alkalies, is also causing an extension in the idea of a salt. The great mass of the salts are compounds of oxidized bodies, both the acid and the base containing oxygen. But ammonia, though not an oxide, has all the characters of alkalinity in an eminent degree, and its compounds with acids were at once admitted into the list of salts. Then came the discovery of the hydracids, such as the hydrochloric and hydriodic, which are so powerfully acid, that their compounds with alkaline bases were readily adopted as salts. Hence arose the division of the salts as a class into two orders, one containing the oxygen or oxy-salts, and the other the hydrogen or hydro-salts. Again, the gaseous terfluoride of boron, which contains neither oxygen nor hydrogen, combines definitely with ammonia, and forms with it a neutral compound, which was esteemed a salt as soon as it was known.

The notion of a salt has of late been still further extended. Chemists have long known that metallic sulphurets occasionally combine together, and constitute what is called a *double sulphuret*. In these compounds Berzelius, whose

labours have greatly added to their number, has traced an exact analogy with the salts, and applied to them the name of *sulphur-salts*. The simple sulphurets by the union of which a sulphur-salt is formed, are bi-elementary compounds, strictly analogous in their constitution to acids and alkaline bases, and which, like them, are capable of assuming opposite electric energies in relation to each other. Electro-positive sulphurets, termed *sulphur bases*, are usually the protosulphurets of electro-positive metals, and therefore correspond to the alkaline bases of those metals; and the electro-negative sulphurets, *sulphur-acids*, are the sulphurets of electro-negative metals, and are proportional in composition to the acids which the same metals form with oxygen. Hence, if the sulphur of a sulphur-salt were replaced by an equivalent quantity of oxygen, an oxy-salt would result. (An. de Ch. et Ph. xxxii. 60.)

The compounds which Berzelius has enumerated as sulphur-acids, are the sulphurets of arsenic, antimony, tungsten, molybdenum, tellurium, tin, and gold. To these he has added the sulphurets of several other substances not metallic, such as sulphuret of selenium, bisulphuret of carbon, and the hydrosulphuric and hydrosulphocyanic acids. He mentions, also, that just as two electro-positive oxides may combine, one becoming electro-negative in regard to the other, so may a sulphur-salt be generated by the union of electro-positive sulphurets. The native double sulphuret of copper and iron, and a considerable number of similar compounds, are instances of this nature. These analogies are rendered much closer by the facts that hydrosulphuric and hydrosulphocyanic acids act as hydro-acids with ammonia, and as sulphur-acids with sulphur-bases; and that all the sulphurets which are remarkable as *sulphur-acids*, have likewise the property of combining with ammonia.—I shall accordingly place the double sulphurets as a third order of the class of salts, and describe them under the name of sulphur-salts.

A fourth order of salts has been formed by Berzelius, comprising for the most part bi-elementary compounds, which consist of a metal on the one hand, and of chlorine, iodine, bromine, fluorine, and the radicals of the hydracids on the other. He has applied to them the name of *haloid-salts* (from ἁλς sea-salt, and ειδος form), because in constitution they are analogous to sea-salt. The whole series of the metallic chlorides, iodides, bromides, and fluorides, such as chloride of sodium, iodide of potassium, and fluor-spar, as well as the cyanides, sulphocyanides, and ferrocyanides, are included in the list of haloid-salts. (An. de Ch. et Ph. xxxii. 60.) The reader will at once perceive that these haloid-salts, as bi-elementary compounds, differ in composition from other salts, and are analogous to oxides and sulphurets.

The preceding pages contain an account of the different classes of compounds which have been termed salts. But since the last edition of this work was published, new views on this important class of bodies have begun to prevail. The researches of Graham on the phosphates, those of Liebig on the constitution of the organic acids and their salts, and the experiments of Dumas, Clark, Frémy, Thaulow, Péligot, and many others, have gradually converged to the point of recalling to the recollection of chemists certain profound views, first suggested by Davy in regard to chloric and iodic acids and their salts, and afterwards applied (apparently without previous knowledge of what Davy had done) by Dulong to the salts of oxalic acid. These views have the inestimable advantage of uniting all acids into one series, and all salts into another; nay, these two series may even be considered as one. I shall here briefly explain them; but in

describing the salts individually, I shall retain the usual views of the constitution of acids and salts, as the former have been thus described in the preceding part of this volume, and the chemical world is not yet ripe for a complete change in the theory of salts. The new views, however, are making such rapid progress, and are so closely entwined with the details of every part of chemistry, that a knowledge of them is indispensable to the student.

In regard to acids, then, the first point to be noticed is, that all so-called oxygen acids, in the free, or what may be called the *active* state, contain hydrogen. On referring to the description of the mineral acids it will be found, for example, that they are described as combining with water when separated from their combining actions. Oil of vitriol is SO_3,HO; nitric acid NO_5,HO, &c. The latter, indeed, cannot exist in the supposed anhydrous state, NO_5; and this is the case with a large majority of all known acids. Sulphuric acid and phosphoric acid, no doubt, may be obtained anhydrous, So_3 and P_2O_5; but it is worthy of especial notice, that in this state *they do not possess the properties of these acids*, and only acquire them on the addition of water. The compound of dry sulphuric acid and ammonia, SO_3,NH_3, *is not* sulphate of ammonia, but a distinct compound. Moreover, these anhydrous acids combine with water with the greatest vehemence, and then assume their active characters. The principal exceptions are carbonic acid and chromic acid; but, on the other hand, none of the organic acids can exist without water, that is, without hydrogen.

It is obvious that hydrogen is essential to the hydracids. Now the view which I wish here to explain considers both these classes of acids as hydracids, and thus unites in one class or series bodies having the most perfect analogy in properties. According to this view, therefore, the general formula of a hydracid is $X + H$: X being an acid-radical which may be either simple or compound. Thus in hydrochloric, hydriodic, and hydrosulphuric acids respectively, X is represented by Cl,I, or S. In hydrocyanic and hydrosulphocyanic acids, X is represented by $Cy = C_2N$, and by $CyS_2 = C_2NS_2$, respectively.

In the hydrated oxygen acids of the preceding pages, to which alone, and not to the anhydrous acids, this theory applies, X is always a compound, and always contains oxygen. Thus in hydrated sulphuric acid, commonly so called, and represented by SO_3,HO, X is represented by SO_4: in nitric acid, NO_5HO, $X = NO_6$; and in metaphosphoric acid, P_2O_5,HO, $X = P_2O_6$: and the true formulæ of these acids are SO_4,H,NO_6,H and P_2O_6,H, respectively.

Further, among the organic acids to be afterwards described, we find a corresponding constitution. In acetic acid (hydrated) $C_4H_3O_3$,HO, $X = C_4H_3O_4$; in hydrated formic acid, C_2HO_3,HO, $X = C_2HO_4$, &c.

The next point to be noticed is, that acids exist, the general formula of which is $X + H_n$; that is, in which X combines with two or more equivalents of H, and which are called polybasic acids. Those acids, above described, in which there is 1 eq. of H, are called monobasic acids. Where 2 eq. of H are present the acid is bibasic; with 3 eq. of H, tribasic, and so on. The reason of this nomenclature will appear when we come to salts.

Examples of this kind are, pyrophosphoric acid, P_2O_5,2HO, which is bibasic, its true formula being P_3O_7,H_2; phosphoric acid, P_2O_5,3HO, which is a tribasic acid, P_2O_8,H_3; and arsenic acid, As_2O_5,3HO; also a tribasic acid, As_2O_8,H_3.

But it is among the organic acids that we find the most numerous and striking

examples of polybasic acids. The following table contains the formulæ of some of these.

Meconic acid . . .	$C_{14}H\ O_{11} + 3HO$ (tribasic)	$= C_{14}H\ O_{14} + H_3$.
Cyanuric acid . . .	$Cy_3\ O_3 + 3HO$ (tribasic)	$= Cy_3\ O_6 + H_3$.
Citric acid	$C_{12}H_5O_{11} + 3HO$ (tribasic)	$= C_{12}H_5O_{14} + H_3$.
Tannic acid . . .	$C_{18}H_5O_9 + 3HO$ (tribasic)	$= C_{18}H_5O_{12} + H_3$.
Tartaric acid . . .	$C_8\ H_4O_{10} + 2HO$ (bibasic)	$= C_8\ H_4O_{12} + H_2$.
Komenic acid . . .	$C_{12}H_2O_8 + 2HO$ (bibasic)	$= C_{12}H_2O_{10} + H_2$.
Fulminic acid . . .	$Cy_2\ O_2 + 2HO$ (bibasic)	$= Cy_2\ O_4 + H_2$.
Mucic acid	$C_{12}H_8O_{14} + 2HO$ (bibasic)	$= C_{12}H_8O_{16} + H_2$.

Moreover there are also polybasic acids which contain no oxygen, analogous in this respect to hydrochloric and hydrocyanic acids. Thus ferrocyanic acid is represented by $Cy_3Fe + H_2$; and ferridcyanic acid is $Cy_3Fe_2 + H_3$.

It will be obvious at a glance, that this theory of acids possesses the advantages of simplicity and of uniting in classification a vast number of bodies, similar in properties, which have formerly been arbitrarily separated. But the chief advantage attending it is, that it enables us to effect the same union into one class of all the salts of the acids containing hydrogen. It is in examining the salts, moreover, that we find the strongest arguments in favour of the theory as applied to acids.

A salt is formed, whenever one of these acids is neutralized by a metallic oxide, by ammonia, or by an organic base, or combines with them, without being neutralized.

Now, when a salt is thus formed, one phenomena constantly occurs; this is the separation of *water*. In the simplest case, namely, where the hydracid of an elementary body acts on a metallic protoxide, the origin of the water is quite obvious. When hydrochloric acid, for example, acts on oxide of silver, chloride of silver is formed, and water is eliminated: $HCl + AgO = AgCl + HO$. There is here no doubt that the water is produced by the reaction.

But when hydrated sulphuric acid acts on the same oxide, although the phenomena are exactly the same, a different explanation is commonly given; and the water is assumed to have pre-existed in the acid, thus, $SO_3,HO + AgO = SO_3,AgO + HO$.

It is contrary to all sound principles of reasoning to adopt two explanations of facts precisely similar; where one will suffice, and only one explanation of the former case is possible, we must apply the same explanation to the latter. This is done by the new theory; and the following formulæ will show the identity of the reaction in the two cases:—

$$H,Cl + Ag,O = Ag,Cl + H,O.$$
$$H,SO_4 + AgO = Ag,SO_4 + HO.$$

In both cases the water is formed by the union of the hydrogen of the acid with the oxygen of the oxide; and consequently in both cases the hydrogen of the acid has been replaced by the metal.

Here, then, is the theory of salts. A salt is formed when the hydrogen of the acid is replaced by its equivalent of a metal. Consequently, acids may be viewed as the hydrogen salts of their radicals, and thus acids and salts, in regard to their constitution, will form but one class.

As the metals replace hydrogen equivalent for equivalent, it is obvious that polybasic acids will form polybasic salts. This has already been illustrated under phosphoric acid, but other examples may be given. Thus, when cyanuric acid acts on oxide of silver, 3 atoms of the latter are required for one of the former, $(Cy_3O_6 + H_3) + 3AgO = (Cy_3O_6 + Ag_3) + 3HO$. With fulminic acid 2 atoms are required, $(Cy_2O_4 + H_2) + 2AgO = (Cy_2O_4 + Ag_2) + 2HO$. It is unnecessary here to multiply these examples.

One remarkable consequence, deducible from the theory under consideration is, that those oxides which most easily lose oxygen should most readily replace by their metal the hydrogen of the acid. This is found to be the case. For example, potash can only replace by potassium 2 of the 3 eq. of hydrogen in cyanuric acid, and 1 of the 2 eq. of hydrogen in fulminic acid, forming the compounds, $Cy_3O_6 \left\{ \begin{matrix} K_2 \\ H \end{matrix} \right\}$ and $Cy_2O_4 \left\{ \begin{matrix} K \\ H \end{matrix} \right\}$ while with oxide of silver, an easily reducible oxide, the replacement as before mentioned, is complete. This fact furnishes an almost irresistible argument for the existence of hydrogen, as such, in acids; and further explains the formerly unaccountable fact, that the salts formed by the action of oxide of silver on organic acids are always anhydrous. In the case of phosphoric and arsenic acids also, oxide of silver forms anhydrous salts, or, in other words, replaces the hydrogen entirely, with much greater facility than potash or soda.

Another obvious consequence of this theory is, that the neutralizing power of an acid depends entirely on the number of equivalents of hydrogen replaceable by metals. Take, for example, hydrosulphuric acid, S + H; and add to the radical oxygen, &c., in almost any proportion, the neutralizing power remains unchanged, as the following table shows:—

	X=	
Hydrosulphuric acid . . .	S	+H.
Sulphurous acid	SO_2	+H.
Sulphuric acid	SO_3	+H.
Hyposulphurous acid . . .	S_2O_3	+H.
Hyposulphuric acid . . .	S_2O_6	+H.
Hydrosulphocyanic acid . . .	S_2Cy	+H.
Chlorosulphuric acid . . .	SO_3Cl	+H. (Regnault.)
Nitrosulphuric acid . . .	SNO_5	+H. (Pelouze.)

No substances can be more different in composition than the above; yet they all neutralize exactly the same quantity of base; a fact readily explained, when it is considered that neutral salts result from the complete replacement of the hydrogen by metals.

The salts of ammonia form no exception to our theory. They always contain 1 at. of water, essential to their existence. Thus, sulphate of ammonia, anhydrous, contains $SO_3,NH_3,HO = SO_3,NH_4O = SO_4 + NH_4$. In this last formula, NH_4 represents the supposed metal ammonium, which, if it be a metal, only differs from ordinary metals in being compound, just as cyanogen, a compound acid, radical, differs from chlorine.*

* This theory respecting the constitution of acids and salts, although captivating on account of its apparent simplicity, has not met the views of some distinguished chemists. It is ably opposed in a paper entitled, "An effort to refute the argument in favor of the

I shall resume this subject when treating of the organic acids; and meantime I return to the description of the salts, according to the views still prevailing, with which the student must also make himself well acquainted, as they pervade all chemical works.

Consistently with the views developed in the first part of this section, I have grouped together all saline compounds which have a certain similarity of composition into one great class of *salts*, which is divided into the four following orders:—

Order I. The oxy-salts. This order includes no salt the acid or base of which is not an oxidized body.

Order II. The hydro-salts. This order includes no salt the acid or base of which does not contain hydrogen.

Order III. The sulphur-salts. This order includes no salt the electro-positive or negative ingredient of which is not a sulphuret.

Order IV. The haloid-salts. This order includes no salt the electro-positive or negative ingredient of which is not haloidal.*

The nomenclature of the first order of salts was explained on a former occasion. The insufficiency of the division into *neutral*, *super*, and *sub*-salts will be made apparent by the following remarks. In the first place, some alkaline bases form more than one super-salt, in which case two or more different salts would be included under the same name. Secondly, some salts have an acid reaction, and might therefore be denominated super-salts, although they do not contain an excess of acid. Nitrate of oxide of lead, for instance, has the property of reddening litmus paper; whereas it consists of 1 eq. of oxide of lead and 1 eq. of nitric acid, and therefore in composition is precisely analogous to nitrate of potassa, which is a neutral salt. This fact was noticed some years ago by Berzelius, who accounted for the circumstance in the following manner:—The colour of litmus is naturally red, and it is only rendered blue by the colouring matter combining with an alkali. If an acid be added to the blue compound, the colouring matter is deprived of its alkali, and thus, being set free, resumes its red tint. Now on bringing litmus paper in contact with a salt, the acid and base of which have a weak attraction for each other, it is possible that the alkali contained in the litmus paper may have a stronger affinity for the acid of the salt than the base has with which it was combined; and in that case the alkali of the litmus being neutralized, its red colour will necessarily be restored. It is hence apparent that a salt may have an acid reaction without having an excess of acid.

The nomenclature of the hydro-salts is framed on the same principles as that applied to the salts which contain oxygen. With respect to the third and fourth orders of salts no general principle of nomenclature has yet been agreed on. Berzelius has extended to them the same nomenclature which he employs for the oxy-salts, and some chemists seem disposed to follow his example; but as

existence in amphide salts of radicals," by Robert Hare, M. D., Professor of Chemistry, University of Pennsylvania," &c. (R.)

* This order of salts is founded upon the assumption that the binary compounds which form them have opposite electro-chemical relations, and act relatively to each other as acids and bases. This doctrine was proposed by Bornsdorff (An. de Ch. et de Ph. xliv. 189), and entertained by Professor Hare, before he became aware that Bornsdorff held similar opinions. More recently he has ably advocated it in a letter to Professor Silliman on the Berzelian nomenclature. June, 1834. (R.)

new views are apt to be obscured, and their intrinsic value overlooked, by being expressed in new language, I shall confine myself as much as possible to terms with which every chemist is familiar. It is worthy of consideration whether the nomenclature of the sulphur and haloid salts, instead of being purposely assimilated to that of the other salts, should not designedly be kept distinct, in order the more readily to distinguish between analogous compounds.

Nearly all salts are solid at common temperatures, and most of them are capable of crystallizing. The colour of salts is very variable, having no necessary connection with the colour of their elements. Salts composed of a colourless acid and base are colourless; but a salt, though formed of a coloured oxide or acid, may be colourless; or, if coloured, the tint may differ from that of both its constituents.

All soluble salts are more or less sapid, while those that are insoluble in water are insipid. Few salts are possessed of odour: the most remarkable one for this property is carbonate of ammonia.

Salts differ remarkably in their affinity for water. Thus some salts, such as the nitrates of lime and magnesia, are *deliquescent*, that is, attract moisture from the air, and become liquid. Others, which have a less powerful attraction for water, undergo no change when the air is dry, but become moist in a humid atmosphere; and others may be exposed without change to an atmosphere loaded with watery vapour.

Salts differ likewise in the degree of solubility in water. Some dissolve in less than their weight of water; while others require several hundred times their weight of this liquid for solution, and others are quite insoluble. This difference depends on two circumstances, namely, on their affinity for water, and on their cohesion; their solubility being in direct ratio with the first, and in inverse ratio with the second. One salt may have a greater affinity for water than another, and yet be less soluble; an effect with may be produced by the cohesive power of the salt which has the stronger attraction for water being greater than that of the salt which has a less powerful affinity for that liquid. The method proposed by Gay-Lussac for estimating the relative degrees of affinity of salts for water (An. de Ch. lxxxii.) is by dissolving equal quantities of salts in equal quantities of water, and applying heat to the solutions. That salt which has the greatest affinity for the menstruum will retain it with most force, and will therefore require the highest temperature for boiling.

Salts which are soluble in water crystallize more or less regularly when their solutions are evaporated. If the evaporation is rendered rapid by heat, the salt is usually deposited in a confused crystalline mass; but if it take place slowly, regular crystals are formed. The best mode of conducting the process is to dissolve a salt in hot water, and when it has become quite cold to pour the saturated solution into an evaporating basin, which is to be set aside for several days or weeks without being moved. As the water evaporates, the salt assumes the solid form; and the slower the evaporation, the more regular are the crystals. Some salts which are much more soluble in hot than in cold water, crystallize with considerable regularity when a boiling saturated solution is slowly cooled. The form which salts assume in crystallizing is constant under the same circumstances, and constitutes an excellent character by which they may be distinguished from one another.

Many salts during the act of crystallizing unite chemically with a definite portion of water, which forms an essential part of the crystal, but not of the salt,

and is termed *water* of *crystallization*. The quantity of combined water is very variable in different saline bodies, but is uniform in the same salt. A salt may contain more than half its weight of water, and yet be quite dry. On exposing a salt of this kind to heat, it is dissolved, if soluble, in its own water of crystallization, undergoing what is termed the *watery fusion*. By a strong heat, the whole of the water is expelled; for no salt can retain its water of crystallization when heated to redness. Some salts, such as sulphate and phosphate of soda, lose a portion of their water, and crumble down into a white powder, by mere exposure to the air; a change which is called *efflorescence*. The tendency of salts to undergo this change depends on the dryness and coldness of the air; for a salt which effloresces rapidly in a moderately dry and warm atmosphere, may often be kept without change in one which is damp and cold.

The water of crystallization is retained by a very feeble affinity, as is proved by the phenomena of efflorescence, and by the facility with which such water is separated from the saline matter by a moderate heat, or by exposure to the vacuum of an air-pump at common temperatures. It is frequently observed, however, that a portion of the water is retained with such obstinacy that it cannot be expelled by a temperature short of that at which the salt is totally decomposed. This water, as in the case of the hydrated acids, is considered to act the part of a base, and is hence commonly called basic water, as has already been explained in the section on phosphorus. But from the observations of Graham it would appear that the water thus retained does not always act the part of a base, but is in a peculiar state of combination, characteristically different both from basic water and water of crystallization (Ph. Tr. Ed. xii. 297). In his original paper he distinguished it as saline water; but in a recent report read to the meeting of the British Association in Liverpool, he has called it constitutional water. It is readily distinguished from water of crystallization, by being retained by a stronger affinity, and by being essential to the existence of the salt of which it constitutes a part. From basic water it differs by not being removed from its combinations even by the most powerful alkalines, whereas it is readily removed, and its place in the compound assumed by certain anhydrous salts: it is also expelled from an acid more readily than the basic water. From an example the character of water in these different states of combination will be readily understood. The crystals of the common phosphate of soda are composed of 1 eq. of phosphoric acid, 2 eq. of soda, and 25 eq. of water. On exposing them to a temperature of 212°, 24 eq. of the water are readily expelled; but the 25th eq. is retained with such power, that a red heat is necessary to effect its complete separation. By the loss of the 24 eq. of water, the crystalline form and texture of the salt is entirely destroyed, but the residual amorphous mass has all the properties of the common phosphate; whereas by the loss of the 25th, an entirely different salt, the pyrophosphate of soda, is produced. It will hence appear, that the 24 eq. of water which were lost at 212° were only essential to the existence of the crystal, while the loss of the 25th eq. affected that of the salt.

The same thing is observed in the case of sulphate of oxide of zinc. Its common crystals are composed of 1 eq. of sulphuric acid, 1 eq. of oxide of zinc, and 7 eq. of water, six of which are readily lost at 212°, the crystal being at the same time destroyed, while the 7th eq. is not expelled until the temperature rises above 410°. Thus far the 7th eq. of water in sulphate of zinc appears analogous to the 25th in the common phosphate of soda; but Graham has pointed

out the remarkable difference that in the latter salt the eq. of water is readily removed from its combination by an eq. of any base which supplies its place in the compound; while in sulphate of zinc, the eq. of water is not affected by bases, but may be removed by anhydrous sulphates, which occupy its place and give rise to the formation of double salts. The former, as acting the part of a base, is called basic water; the latter, as influencing the constitution of a salt, is called constitutional water. The difference is denoted in symbols, by writing the basic water, as is the case with all bases, on the left side of the acid with which it is combined, and the constitutional water on the right. Hence the symb. of the crystals of phosphate of soda is $2NaO, HO. P_2O_5 + 24$ aq.; and of the sulphate of zinc, $ZnO\ SO_3\ HO + 6$ aq. In the phosphate the water may be removed by soda, forming $3NaO. P_2O_5 + 24$ aq.; in the sulphate, by anhydrous sulphate of potassa, forming the double salt $ZnO\ SO_3\ (KO\ SO_3) + 6$ aq.

In pursuing the study of this subject, Graham has been led to the conclusion that all salts are neutral in their constitution with the exception of certain classes. Thus he finds that the bisulphate of potassa is a double salt, formed by the constitutional water of sulphate of water being replaced by sulphate of potassa: thus

$$\begin{matrix} HO\ SO_3HO \\ \&\ Ko\ SO_3 \end{matrix} \quad \text{yield} \quad \begin{matrix} HO\ SO\ (KO_3\ SO_3. \\ \&\ HO. \end{matrix}$$

To illustrate the constitution of a subsalt, the nitrates were selected. Nitric acid of sp. gr. 1·42 he considers to be nitrate of water with 3 eq. of constitutional water. Its symb. is therefore $HO\ NO_5. 3HO$. But water corresponds with the class of isomorphous oxides of which magnesia, the oxides of zinc or of copper, may be taken as the type. Hence these oxides are capable of supplying the place of water in either state of combination, as is seen in the neutral and subnitrate of copper, in the former of which the basic water is replaced by an eq. of oxide of copper, while in the sub-salt the 3 eq. of constitutional water are replaced by 3 eq. of oxide of copper. Their constitution is therefore represented by the formulæ

$$KuO\ NO_5. 3HO.$$
$$\text{And } HO\ NO_5. 3KuO.$$

In applying these views in other cases, however, difficulties arise, owing to the existence of anhydrous bisalts, as the anhydrous bisulphate and bichromate of potassa. These are accounted for by Graham, by supposing the existence of a class of bodies, called by him basic adjuncts, which admit of being attached to the oxide of hydrogen, or to the oxides of metals — the only true bases. The arguments in support of this view are principally drawn from the composition of the ammoniacal salts: it must be remembered, however, that the whole subject is in many respects hypothetical, and has not yet been sufficiently tested by experiment.

Salts, in crystallizing, frequently enclose mechanically within their texture particles of water, by the expansion of which, when heated, the salt is burst with a crackling noise into smaller fragments. This phenomenon is known by the name of *decrepitation*. Berzelius has correctly remarked that those crystals decrepitate most powerfully, such as the nitrates of baryta and oxide of lead, which contain no water of crystallization.

The atmospheric pressure is said to have considerable influence on the crys-

tallization of salts. If, for example, a concentrated solution, composed of about three parts of sulphate of soda in crystals, and two of water, is made to boil briskly, and the flask which contains it is then tightly corked, while its upper part is full of vapour, the solution will cool down to the temperature of the air without crystallizing, and may in that state be preserved for months without change. Before removal of the cork, the liquid may often be briskly agitated without losing its fluidity; but on readmitting the air, crystallization commonly commences, and the whole becomes solid in the course of a few seconds. The admission of the air sometimes, indeed, fails in causing the effect; but it may be produced with certainty by agitation or the introduction of a solid body. The theory of this phenomenon is not very apparent. Gay-Lussac has shown that it does not depend on atmospheric pressure (An. de Ch. vol. lxxxvii.); for he finds that the solution may be cooled in open vessels without becoming solid, provided its surface be covered with a film of oil; and I have frequently succeeded in the same experiment without the use of oil, by causing the air of the flask to communicate with the atmosphere by means of a moderately narrow tube. It appears from some experiments of Graham (Phil. Trans. Edin. 1828), that the influence of the air may be ascribed to its uniting chemically with water: for he has proved that gases which are more freely absorbed than atmospheric air, act more rapidly in producing crystallization. Indeed, the rapidity of crystallization, occasioned by the contact of gaseous matter, seems proportional to the degree of its affinity for water.

The same quantity of water may hold several different salts in solution, provided they do not mutually decompose each other. The solvent power of water with respect to one salt is, indeed, sometimes increased by the presence of another, owing to combination taking place between the two salts.

Most salts produce cold during the act of solution, especially when they are dissolved rapidly and in large quantity. The greatest reduction of temperature is occasioned by those which contain water of crystallization.

All the oxy-salts are decomposed by voltaic electricity, provided they are either moistened or in solution. The acid appears at the positive pole of the battery, and the oxide at its opposite extremity; or if the oxide is of easy reduction, the metal itself goes over to the negative side, and its oxygen accompanies the acid to the positive wire.

The hydro-salts, and doubtless also the sulphur and haloid-salts, are subject to a similar change; but the phenomena as respects the two last orders of salts have been little examined.

ON CRYSTALLIZATION.

The particles of liquid and gaseous bodies, during the formation of solids, sometimes cohere together in an indiscriminate manner, and give rise to irregular shapeless masses; but more frequently they attach themselves to each other in a certain order, so as to constitute solids possessed of a symmetrical form. The process by which such a body is produced is called *crystallization*; the solid itself is termed a *crystal*; and the science, the object of which is to study the form of crystals, is *crystallography*.

Most bodies crystallize under favourable circumstances. The condition by which the process is peculiarly favoured is the slow and gradual change of a fluid into a solid, the arrangement of the particles being at the same time undis-

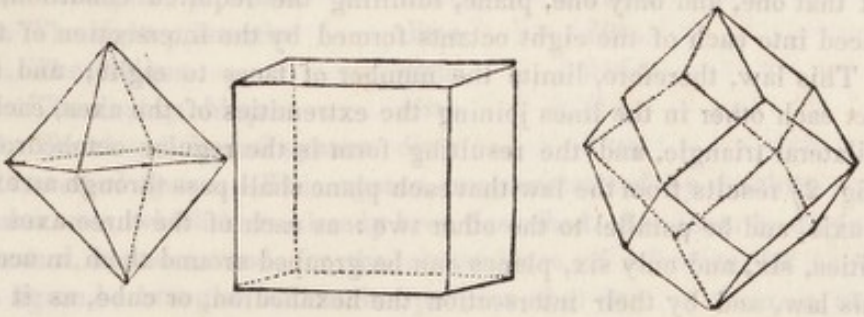
turbed by motion. This is exemplified during the slow cooling of a fused mass of sulphur or bismuth, or the spontaneous evaporation of a saline solution; and the origin of the numerous crystals, which are found in the mineral kingdom, may be ascribed to the influence of the same cause.

All substances are limited in the number of their crystalline forms. Thus, calcareous spar crystallizes in rhombohedrons, fluor-spar in cubes, and quartz in six-sided pyramids; and these forms are so far peculiar to those substances, that fluor-spar never crystallizes in rhombohedrons or six-sided pyramids, nor calcareous spar or quartz in cubes. Crystalline form may therefore serve as a ground of distinction between different substances. It is accordingly employed by mineralogists for distinguishing one mineral species from another; and it is very serviceable to the chemist as affording a physical character for salts. On this account I have thought it would be useful, before describing the individual salts, to introduce a few pages on crystallization; but from the great extent of the subject, which now constitutes a separate science, my remarks must necessarily be limited, and comprehend little else than a brief outline of its more important principles. To those who are desirous of more ample information, I may recommend the "Elements of Crystallography," by Gustav. Rose, or Mr. Whewell's Essay in the Phil. Trans. of London for 1825.

Every perfect crystal is bound by plane surfaces, which are called its faces. The straight line formed by the intersection of two faces is called an edge; the meeting of three or more edges in a point forms a solid angle. Thus in the octohedron, fig. 1, the bounding planes are the faces, the lines formed by their intersection the edges, the meeting of four of which in the same point produces a solid angle of the crystal.

The forms of crystals are exceedingly diversified. They are divided by crystallographers into simple and compound: a simple form has all its faces equal and similar to each other, while a compound form is bounded by at least two different classes of faces. Thus, figs. 1, 2, and 3, are simple forms; for the

Fig. 1. Fig. 2. Fig. 3.



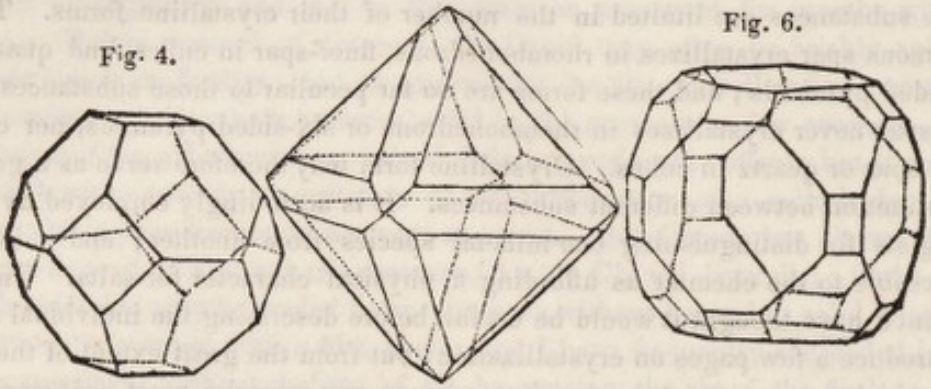
first is bounded by eight faces, each of which is an equilateral triangle, the second by six squares, and the third by twelve equal and similar rhombi. The forms represented by 4, 5, and 6, are, on the contrary, compound crystals: for fig. 4 is composed of two classes of faces, eight which are hexagonal, and six square; while fig. 6 contains three classes, eight faces being hexagonal, six octagonal, and twelve quadratic. This division into compound and simple is not artificial, but is founded on the fact that the compound forms are really produced by the combination of two or more of the simple crystals, as will be seen by a careful inspection of the forms and relative situations of the faces in the accom-

panying figures. The character of the faces in figures 1, 2, and 3, which represent respectively the regular octohedron, the cube, and the rhombic dodecahedron,

Fig. 5.

Fig. 4.

Fig. 6.



is too obvious to demand comment; but to obtain a correct idea of the relative positions of the faces in these three forms requires a more careful investigation.

It will be observed that in each of these figures three right lines, which are equal in length, perpendicular to each other, and pass through the centre of the crystal, may be obtained;—in the octohedron by joining the opposite angles, in the cube by joining the centres of the opposite faces, and in the rhombic dodecahedron by connecting the opposite angles formed by the meeting of four edges, these angles being six in number and corresponding in situation to the six angles of the octohedron. The lines around which the different parts of the crystals are thus symmetrically grouped are called crystalline axes. Hence the above forms are connected by being possessed of the same axes of crystallization, and proceeding from these three equal and rectangular axes, either the octohedron, the cube, or the rhombic dodecahedron may be constructed, the resulting form being solely dependent on the law in accordance with which planes are symmetrically arranged or grouped around the axes. The octohedron (fig. 1) results from the law that every plane shall pass through an extremity of each axis: it will be evident that one, and only one, plane, fulfilling the required condition, may be introduced into each of the eight octants formed by the intersection of the three axes. This law, therefore, limits the number of faces to eight; and as these intersect each other in the lines joining the extremities of the axes, each face is an equilateral triangle, and the resulting form is the regular octohedron. The cube (fig. 2) results from the law that each plane shall pass through an extremity of one axis, and be parallel to the other two: as each of the three axes has two extremities, six, and only six, planes can be grouped around them in accordance with this law, and by their intersection the hexahedron, or cube, as it is more commonly called, is produced. In a similar manner may the rhombic dodecahedron (fig. 3) be shown to be formed according to the law that each plane shall pass through the extremities of two axes, and be parallel to the third.

The groups of simple forms, which are thus associated by being reducible from the same axes, constitute what is called by crystallographers a system of crystallization. Thus the octohedron, the cube, and the rhombic dodecahedron, are three forms of what is called the octohedral or regular system. Such forms are associated not merely by the similarity of their axis, but are connected still more intimately by the remarkable fact, that any substance which in crystallizing assumes one form of a system, may, and frequently does, assume other forms

belonging to that system. Examples of this may be seen in the well-known salt alum, and in the black oxide of iron, the magnetic ore of mineralogists; the former generally crystallizing in the octohedron (fig. 1), but it may also be obtained in the form of the cube (fig. 2); and the magnetic iron ore is found not only in the form of octohedrons and cubes, but likewise in that of the rhombic dodecahedron (fig. 3). But, what is still more remarkable, the same substance is not only capable of assuming different forms of the same system, but during the act of crystallization the faces of two, three, four, and in some cases even more, of these forms are simultaneously developed, whereby compound crystals of the greatest diversity of form and appearance are produced. Thus, in the crystallization of alum either the cube or octohedron may be formed, but it is by far more common that the faces of both be produced, giving rise to the compound crystal represented in fig. 4, where the faces of the cube appear truncating the angles of the octohedron. Another form frequently observed in alum is represented by fig. 5, where in addition to the octohedron the faces of the rhombic dodecahedron are also developed; and as these are twelve in number, and correspond in situation to the twelve edges of the octohedron, their developement removes, or as it is technically expressed, truncates the twelve edges of the latter form. Fig. 6 represents a combination of all three forms. Similar and still more complicated combinations are observed on magnetic iron ore.

The importance of a knowledge of all the simple forms of a system, as being those in which the same substance may occur, and which alone can give rise to compound crystals, for simple forms of different systems are never combined, will be felt from what has already been stated. The first person who proved the existence of a mathematical connection between them was the celebrated crystallographer Haüy; but it is to Weiss, Professor of Mineralogy in Berlin, that we are indebted for the distinction of the system of crystallization,—a discovery which justly entitles him to the honour of being the founder of modern crystallography. He has shown that all crystalline forms may be brought under one of the six following systems, which may be conveniently distinguished as,

1. The octohedral, or regular system of crystallization.
2. The square prismatic ditto ditto.
3. The right prismatic ditto ditto.
4. The oblique ditto ditto.
5. The doubly oblique ditto ditto.
6. The rhombohedral system ditto ditto.

The Octohedral System.—This system is characterized by the three equal and rectangular axes, which have already been described. Let them be distinguished as the axes *a*, *b*, and *c*; and, for the convenience of reference, let us consider that the figure be brought into such a position that two of them, *a* and *b*, be horizontal, and *c* vertical. The figs. 1, 2, and 3 are drawn under this supposition. The law of crystalline symmetry is such, that if a face of a crystal be observed to bear a certain relation to one of the axes *a*, other faces must fulfil the same condition to the equal axes *b* and *c*. Thus, if a plane be seen to pass through the extremity of *a*, or be parallel to it, other planes must pass through the extremity of *b* and *c*, or be parallel to them. Owing to the perfect symmetry in the different parts of the crystal, this group is frequently called the regular system of crystallization.

It consists of but few simple forms, the number being necessarily limited to

the number of different ways in which a plane can intersect the three axes. These, it will be seen, are only seven :—

1. The plane may cut each at an equal distance from the centre. The crystal the faces of which obey this law is the octohedron, fig. 1.

2. The plane may cut two axes at an equal, and the third at a greater distance from the centre. The resulting form is called the triakisoctohedron.

3. The plane may cut two axes at an equal, and the third at a less distance from the centre. The resulting form is the ikositetrahedron.

4. The plane may cut all three axes unequally. The form is the herakisoctohedron.

5. The plane may cut two axes at unequal distances from the centre, and be parallel to the third. The resulting crystal is the tetrakishexahedron.

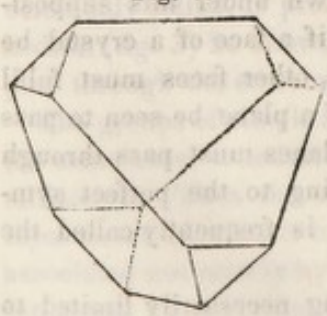
6. The plane may cut two axes in points equally distant from the centre, and be parallel to the third. The form is the rhombic dodecahedron, fig. 3.

7. The plane may cut one axis, and be parallel to the other two. This law gives rise to the cube or hexahedron, fig. 2.

Of these forms, 1, 6, and 7 are of frequent occurrence; but the others are usually found only in combination, when their faces are generally small, and appear symmetrically arranged around the angles and on the edges of the former. Hence, in most compound crystals of this system, the faces either of the octohedron cube or rhombic dodecahedron may be readily recognized; and as these suffice to fix the position of the crystalline axes, they serve as a guide to determine the forms of the combination. Their prevalence presents also a remarkable instance of the tendency to simplicity which may be observed in all the processes of nature. This is not only seen in the greater simplicity of exterior form, but in the more definite nature of the laws by which the faces of these three crystals are determined; for while a plane has but one position in which it can satisfy the laws 1, 6, and 7, an unlimited number of planes may be found to satisfy the conditions expressed by 2, 3, 4, and 5. Thus, for example, there is but one way in which a plane can satisfy the law 1; while there are as many ways of satisfying the law 4, as there are of taking three lines which shall be unequal. Hence it follows that there can be but one octohedron, while the number of herakisoctohedrons is unlimited, and the faces of two different ones have been observed on the same crystals. The latter observation also applies to the forms produced according to the laws 2, 3, and 5: but the number of varieties which have been observed is very limited, and the relative lengths of the unequal axes may be expressed, almost without an exception, by the numbers 1, $\frac{1}{2}$, $\frac{1}{3}$, $\frac{1}{4}$, and $\frac{1}{5}$.

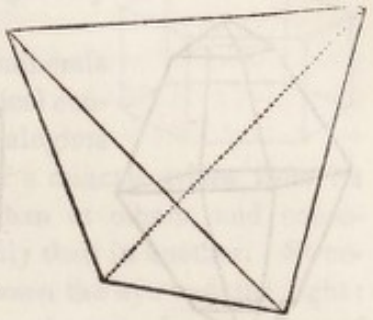
It is frequently observed in crystals of this system, that one-half of the faces of the crystals are much more developed than the other. This may be seen in figure 7, a crystal of the red oxide of copper, where four out of the eight faces of the octohedron have increased, and the other four proportionally diminished. The faces which increase, as well as those which diminish, always form two similar and symmetrically arranged groups, the increasing faces or groups of faces touching each other at the angular points of the crystal. Thus, in the octohedron, the four alternating faces which do not intersect in edges, but merely touch each

Fig. 7.



other in the angular points, increase, as represented in figure 7, and by increasing till they form a perfect figure, give rise to the well known crystal the tetrahedron, fig. 8. These forms are called hemiedral, as denoting their origin: hence the tetrahedron is commonly known as the hemi-octohedron. Each of the simple forms of this system, with the exception of the cube and rhombic dodecahedron, gives rise to hemihedral crystals: the exception evidently results from the impossibility of dividing the faces of the cube and rhombic dodecahedron into two groups, which fulfil the necessary conditions.

Fig. 8.



The Square Prismatic System.—The forms of this system are, like those of the preceding, characterized by three axes, which intersect each other at right angles; but they differ from them by two only out of the three being equal. Let the third, which may be either greater or less than the two equal axes be called *c*, and let it be placed in a vertical position. The octohedron formed by joining the extremities of these axes, is either longer or shorter in the direction of the axis *c* than in that of its horizontal axes, as is seen in figure 9. From this it follows that these octohedrons may be compared to a double four-sided pyramid constructed on either side of a square base. The parts of the crystal about this base are therefore similar to each other, but differ from those about its upper or lower extremity; and as this observation applies equally to all forms of this system, it is the character by which the system is best distinguished. This difference is owing to the inequality of the vertical axis, which causes the relations of the faces to it to be unconnected with those they bear to the two horizontal axes. Hence it is common to find the lateral edges truncated without those connected with the extremities of the crystal being affected, whereby a square prism terminated by four-sided pyramids, as represented in figure 10, is produced. The same may occur on the lateral angles as well as edges, as in figure 11. In other cases, the terminal edges and angles are modified, but always in a different manner from the lateral.

Fig. 9.

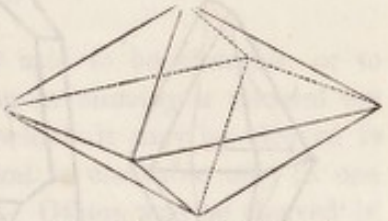


Fig. 10.

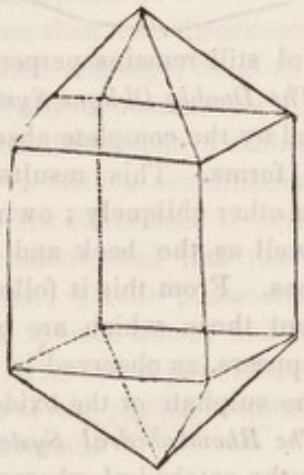
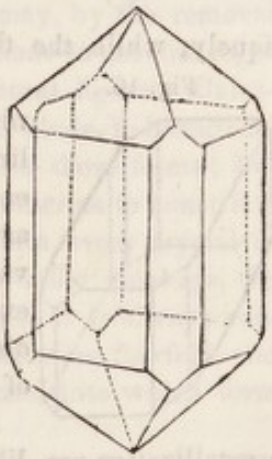


Fig. 11.



The Right Prismatic System.—The crystals of this system are like the preceding, characterized by three rectangular axes, and are distinguished from both by no two of these axes being equal. Its forms are therefore not only distinguished by a difference in the lateral and terminal parts, but are still further marked by the difference between the front and back of the crystal, as

Fig. 12.

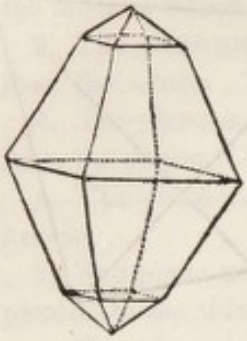
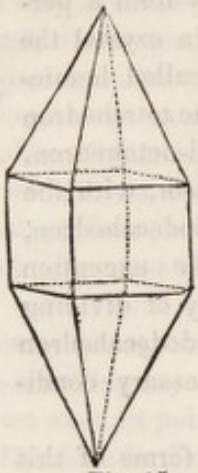


Fig. 13.



compared with its sides. Thus in figures 12, 13, and 14, which represent three of the common forms of sulphur, the different magnitude in the parts of the crystals about each axis is perceptible, and sufficiently marks the different crystalline values of the three axes. But this is still better pointed out by the three different and independent modifications of the rhombic octohedron, which forms the basis of all three crystals.

Fig. 14.

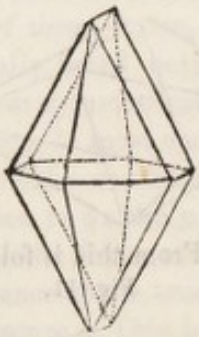
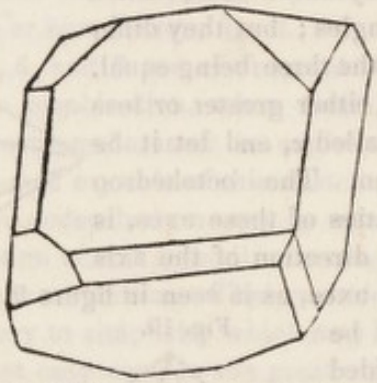
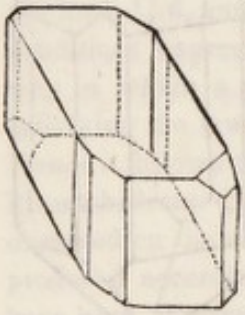


Fig. 15.



The Oblique Prismatic System.—The crystals of this system, of which an example may be seen in sulphate of the protoxide of iron, figure 15, differ from those of the right prismatic system by the front and back parts being dissimilar. This difference is owing to two of the axes intersecting each other obliquely, while the third still remains perpendicular to both.

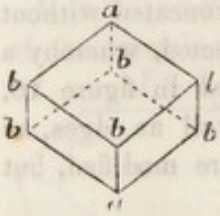
Fig. 16.



The Doubly Oblique System.—This system is readily recognized by the complete absence of all symmetry in its crystalline forms. This results from all three axes intersecting each other obliquely ; owing to which the left and right sides, as well as the back and front, are of different crystalline values. From this it follows that no two faces are connected except those which are parallel, and all symmetry of form disappears, as observed in fig. 16, which represents a crystal of the sulphate or the oxide of copper.

The Rhombohedral System.—The forms of this system of crystallization are, like the octohedral, characterized by three equal and similar axes ; but these axes intersect each other at equal, but not at right angles. Its most simple form is the rhombohedron, fig. 17, which is bound by six equal and similar rhombic faces. The axes are obtained by joining the centre of the opposite faces. Although the faces of the rhombohedron are equal, two only of its angles, marked *a*, are regular, being formed by the meeting of three equal edges, while the other six are irregular. The line joining *a a* is called the principal axis of the rhombohedron, the angles *a* the terminal, and *b* the lateral angles of the rhombohedron.

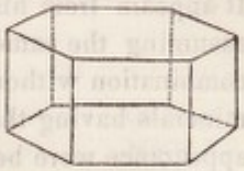
Fig. 17.



The form which most commonly occurs associated with the rhombohedron is a hexagonal prism, fig. 18, two of which are observed, the one truncating the six angles, the other the lines joining these angles, the faces of the prism

being in both cases parallel to the rhombohedral axes *aa*. The terminal angles *a* are frequently truncated by terminal planes.

Fig. 18.



The different forms of the system may be advantageously studied on crystals of quartz and calcareous spar.

Besides the distinction arising from external form, minerals are further distinguished by differences in the mechanical connection of their particles, peculiarities which mineralogists designate by the name of *structure*. The structure of a mineral arises from its particles adhering at some parts less tenaciously than at others, and consequently yielding to force in one direction more readily than in another. Structure is sometimes visible by holding a mineral between the eye and the light; but in general it is brought into view by effecting the actual separation of parts by mechanical means.

The structure of minerals may be *regular* or *irregular*. It is regular when the separation takes place in such a manner, that the detached surfaces are smooth and even like the planes of a crystal; and it is irregular, when the new surface does not possess this character.

A mineral which possesses a regular structure is said to be *cleavable*, or to admit of *cleavage*; the surfaces exposed by splitting or *cleaving* a mineral are termed the *faces of cleavage*; and the direction in which it may be cleaved is called the *direction of cleavage*. Sometimes a mineral is cleavable only in one direction, and is then said to have a *single* cleavage. Others may be cleaved in two, three, four, or more directions, and are said to have a *double*, *treble*, *fourfold* cleavage, and so on, according to their number.

Minerals that are cleavable in more than two directions may, by the removal of layers parallel to the planes of their cleavage, be often made to assume regular forms, though they may originally have possessed a different figure. Calcareous spar, for example, occurs in rhombohedrons of different kinds, in hexagonal prisms, in six-sided pyramids, and in various combinations of these forms; but it has three sets of cleavage, which are so inclined to each other as to constitute a rhombohedron of invariable dimensions, and into that form every crystal of calcareous spar may be reduced. Lead glance possesses a treble cleavage, the planes of which are at right angles to each other; and hence it is always convertible by cleavage into the cube. The cleavages of fluor-spar are fourfold, and in a direction parallel to the planes of the regular octohedron, into which form every cube of fluor-spar may be converted.

Since the forms enumerated as belonging to the octohedral system of crystallization are possessed of fixed invariable dimensions, it is obvious that minerals, or other crystallized bodies included in that system, must often in their primary forms be identical with each other. In the other systems of crystallization this identity is not necessary, because the dimensions of their forms are variable. Thus octohedrons with a square base may be distinguished by the relative length of their axis, some being flat and others acute. Rhombic octohedrons may be distinguished from each other by the relative length of their axis, and the angles of their base. By Haüy it was regarded as an axiom in crystallography, that minerals not belonging to the octohedral system are characterized by their form; that though two minerals may in form be analogous, each for instance being a rhombic prism, the dimensions of those prisms are different. Identity of form in crystals not included in the octohedral system was thought to indicate identity of composition. But in the year 1819 a discovery, extremely

important both to mineralogy and chemistry, was made by Mitscherlich of Berlin, relative to the connection between the crystalline form and composition of bodies. It appears from his researches,* that certain substances have the property of assuming the same crystalline form, and may be substituted for each other in combination without affecting the external character of the compound. Thus minerals having the crystallization and structure of garnet, and which from their appearance were believed to be such, have been found on analysis to contain different ingredients. Crystals possessed of the form and aspect of alum may be made with sulphates of potassa and peroxide of iron, without a particle of aluminous earth; and a crystal composed of selenic acid and soda will have a perfect resemblance to Glauber's salts. The axiom of Haüy, therefore, requires an essential modification.

To the new branch of science laid open by the discovery of Mitscherlich, the term *isomorphism* (from ισος equal, and μορφη form) is applied; and those substances which assume the same figure are said to be *isomorphous*. Of these isomorphous bodies several distinct groups have been described by Mitscherlich. One of the most instructive of these includes the salts of arsenic and phosphoric acid. Thus, the neutral phosphate and biphosphate of soda have exactly the same form as the arseniate and binarseniate of soda; phosphate and biphosphate of ammonia correspond to arseniate and binarseniate of ammonia; and the biphosphate and binarseniate of potassa have the same form. Each arseniate has a corresponding phosphate, possessed of the same form, possessing the same number of eq. of acid, alkali, and water of crystallization, and differing in fact in nothing, except that one series contains arsenic and the other an equivalent quantity of phosphorus. A second remarkable group contains the salts of sulphuric, selenic, chromic, and manganic acids. The salts of baryta, strontia, and oxide of lead, constitute a third group; and a fourth consists of lime, magnesia, and the protoxides of manganese, iron, cobalt, nickel, zinc. and copper. A fifth includes alumina, peroxide of iron, and the green oxide of chromium; and a sixth group includes the salts of permanganic and perchloric acids. In comparing together isomorphous bodies of the same group, identity of form is not to be expected unless there is similarity of composition. A neutral phosphate does not correspond to a binarseniate, nor a biphosphate to a neutral arseniate; an anhydrous sulphate is not comparable to a hydrated seleniate of the same base; nor is sulphate of protoxide of iron, with 6 eq. of water, isomorphous with sulphate of protoxide of manganese with 5 eq. In all such instances, if chemical composition differ, crystalline form is also different.

The following table contains the principal groups of isomorphous substances at present observed by chemists: a more extended one, partly theoretical, has been drawn up by Professor Johnston, of Durham, in his Report on Chemistry to the British Association:—

1.		3.	
Silver	Ag.	Alumina	Al_2O_3.
Gold	Au.	Peroxide of Iron	Fe_2O_3.
2.		**4.**	
Arsenious Acid in its unusual form.	As_2O_3.	Salts of Phosphoric Acid	P_2O_5.
Sesquioxide of Antimony	Sb_2O_3.	Arsenic Acid	As_2O_5.

* Annales de Ch. et de Physique, vol. xiv. 172, xix. 350, and xxiv. 264 and 355.

5.	
Salts of	
Sulphuric Acid	SO_3.
Selenic Acid	SeO_3.
Chromic Acid	CrO_3.
Manganic Acid	MnO_3.

6.	
Salts of	
Perchloric Acid	Cl_2O_7.
Permanganic Acid	Mn_2O_7.

7.	
Salts of	
Potassa	KO.
Ammonia with 1 eq. of water	H_4NO.

8.	
Salts of	
Soda	NaO.
Oxide of Silver	AgO.

9.	
Salts of	
Baryta	BaO.
Strontia	SrO.
Lime (in Arragonite)	CaO.
Protoxide of Lead	PbO.

10.	
Salts of	
Lime	CaO.
Magnesia	MgO.
Protoxide of Iron	FeO.
Manganese	MnO.
Zinc	ZnO.
Nickel	NiO.
Cobalt	CoO.
Copper	CuO.
Lead in Plumbo-calcite	PbO.

11.	
Salts of	
Alumina	Al_2O_3.
Peroxide of Iron	Fe_2O_3.
Oxide of Chromium	Cr_2O_3.
Sesquioxide of Manganese	Mn_2O_3.

The facts above mentioned afford indubitable proof that the form of crystals is materially dependent on their atomic constitution; and they at first induced Mitscherlich to suspect that crystalline form is determined solely by the number and arrangement of atoms, quite independently of their nature. Subsequent observation, however, induced him to abandon this view; and his opinion now appears to be, that certain elements, which are themselves isomorphous, when combined in the same manner with the same substance, communicate the same form. Similarly constituted salts of arsenic and phosphoric acid yield crystals of the same figure, because the acids, it is thought, are themselves isomorphous; and as the atomic constitution of these acids is similar, each containing the same number of atoms of oxygen united with the same number of atoms of the other ingredient, it is inferred that phosphorus is isomorphous with arsenic. In like manner it is believed that selenic acid must be isomorphous with sulphuric acid, and selenium with sulphur; and the same identity of form is ascribed to all those oxides above enumerated, the salts of which are isomorphous. The accuracy of this ingenious view has not yet been put to the test of extensive observation, because the crystalline forms of the substances in question are for the most part unknown. But our knowledge, so far as it goes, is favourable; for peroxide of iron and alumina, the salts of which possess the same form, are themselves isomorphous. It may hence be inferred as probable, that isomorphous compounds in general arise from isomorphous elements uniting in the same manner with the same substance.

Isomorphous substances have often very close points of resemblance, quite independently of form. Thus, arsenic and phosphorus have the same odour, they both form gaseous compounds with hydrogen, they differ from nearly all other bodies in their mode of combining with oxygen, and yet agree with one another, and their salts are disposed to combine with the same quantity of water of crystallization. A similar analogy subsists between selenium and sulphur,

both being fusible, volatile, and combustible in nearly the same degree, forming with hydrogen colourless gases which are similar in odour and in their chemical relations, and giving rise to analogous compounds with oxygen. The characters of sulphuric and selenic acids in particular are very similar; and the salts of these acids are equally allied. Sulphate of soda, for example, has the unusual property of being less soluble in water at 212° than at 100°, and the very same peculiarity is observable in seleniate of soda. The same intimacy of relation exists between baryta and strontia, between lime and magnesia, and between cobalt and nickel.

Isomorphous substances, owing doubtless to the various points of resemblance which have just been traced, crystallize together with great readiness, and are separated from each other with difficulty. Daubeny has remarked that a weak solution of lime, which in pure water would be instantly indicated by oxalate of ammonia, is very sluggishly affected by that test when much sulphate of magnesia is present; and I find that chloride of manganese cannot be purified from lime by oxalate of ammonia. A mixture of the sulphates of the protoxides of copper and iron yields crystals which have the same quantity of water of crystallization (6 equivalents), and the same form, as green vitriol, though they may contain a large quantity of copper. The sulphates of the protoxides of zinc and copper, of copper and magnesium, of copper and nickel, of zinc and manganese, and of magnesium and manganese, crystallize together, contain 6 equivalents of water, and have the same form as green vitriol, without containing a particle of iron. These mixed salts may be crystallized over and over again without the ingredients being separated from each other, just as it is extremely difficult to purify alum from peroxide of iron, with which alumina is isomorphous. In these instances the isomorphous salts do not occur in definite proportions: they are not chemically united as double salts, but merely crystallize together.

The same intermixture of isomorphous substances which takes place in artificial salts is found to occur in minerals, and affords a luminous explanation of the great variety both in the kind and proportion of substances which may coexist in a mineral species, without its external character being thereby essentially affected. Thus, garnet is a double silicate of alumina and lime, expressed by the formula $Al_2O_3 + SiO_3) + 3(CaO + SiO_3)$, but in garnet, as in alum, the alumina may be replaced by peroxide of iron, yielding the compound $(Fe_2O_3 + SiO_3) + (3CaO + SiO_3)$, or they may be both present in any proportion, provided that their sum is equivalent to either singly. So, while peroxide of iron displaces the alumina, the lime may be exchanged for protoxide of iron; and a mineral would result, $(Fe_2O_3 + SiO_3) + (3FeO + SiO_3)$, which contains neither alumina nor lime, though it has still the form of garnet. Instead of protoxide of iron, the lime may be replaced by magnesia, protoxide of manganese, or any other isomorphous base; or any equivalent quantity of some or all of these may take the place of the lime, without the crystallographic character being destroyed. In like manner epidote is a double silicate of alumina and lime, expressed by $(Al_2O_3 + SiO_3) + (CaO + SiO_3)$; and here again varieties of epidote are to be expected, in which alumina and lime are replaced partially or wholly by an equivalent quantity of isomorphous bases.

The discovery of Mitscherlich, while it accounts for difference of composition in the same mineral, and serves as a caution to mineralogists against too exclusive reliance on crystallographic character, is in several other respects of deep interest to the chemist. It tends to lay open new paths of research by unfolding

analogies which would not otherwise have been perceived.—The tendency of isomorphous bodies to crystallize together accounts for the difficulty of purifying mixtures of isomorphous salts by crystallization.—The same property sets the chemist on his guard against the occurrence of isomorphous substances in crystallized minerals. The native phosphates, for example, frequently contain arsenic acid, and conversely the native arseniates phosphoric acid, without the form of the crystals being thereby affected in the slightest degree.—It is a useful guide in discovering the atomic constitution of compounds. All chemists are agreed, from the composition of the oxides of iron, and from the compounds which this metal forms with other bodies, that the peroxide consists of two atoms of iron and three atoms of oxygen; and therefore it is inferred that alumina, which is isomorphous with peroxide of iron, has a similar constitution. The green oxide and acid of chromium, the oxygen of which is as 1 to 2, afford a still better illustration. As the chromates and sulphates are isomorphous, it was inferred that chromic, like sulphuric, acid was composed of one atom of the combustible to three atoms of oxygen. On this presumption it follows that the green oxide, containing half as much oxygen as the acid, must contain two atoms of chromium to three atoms of oxygen; and agreeably to this inference it is found that the green oxide is isomorphous with alumina and peroxide of iron.—The phenomena presented by isomorphous bodies afford a powerful argument in favour of the atomic theory. The only mode of satisfactorily accounting for the striking identity of crystalline form observable, first, between two substances, and, secondly, between all their compounds which have an exactly similar composition, is by supposing them to consist of ultimate particles possessed of the same figure, and arranged in precisely the same order. Hence it appears, that, in accounting for the connection between form and composition, it is necessary to employ the very same theory, by which alone the laws of chemical union can be adequately explained.

It has been objected to some of the facts adduced in favour of isomorphism, that the forms of substances considered isomorphous are sometimes *approximate* rather than *identical*. The primary form of sulphate of strontia is a rhombic prism very similar to that of sulphate of baryta; but on measuring the inclination of corresponding sides in each prism, the difference is found to exceed two degrees; and similar differences are observable in the rhombohedron of the carbonates of lime and protoxide of iron. This has induced Professor Miller of Cambridge to indicate this *approximation* by the term *plesiomorphism* (πλησιος, near); and it has been brought forward in a clever essay by Brooke, as an argument against the whole doctrine of isomorphism, an essay which has received an able reply from the pen of Whewell. (Phil. Mag. and An. N. S. x. 161 and 401.)

In one of the essays above referred to, Mitscherlich observed that biphosphate of soda is capable of yielding two distinct kinds of crystals, which, though different in form, in composition appear to be identical. The more uncommon of the two forms resembled binarseniate of soda; but the more usual form is quite dissimilar. He has since discovered, that sulphur is capable of yielding two distinct kinds of crystals. The crystals of carbonate of lime in calcareous spar and in arragonite belong to different systems of crystallization, the former being rhombohedral, and the latter derived from a rhombic prism. Arsenious acid, and probably metallic arsenic also, affords an instance of the same kind. It would thus seem that elementary and compound bodies are capable of assuming two

distinct crystalline forms. In the case of biphosphate of soda an explanation may be derived from the experiments of Graham on metaphosphoric acid; but the fact that an elementary substance is susceptible of assuming different forms is wholly unexplained.

Mitscherlich has also noticed that the form of salts is sometimes changed by heat, without losing their solid state. This change was first noticed in sulphate of magnesia, and also in the sulphates of the protoxides of zinc and iron. It appears, in these instances at least, to be owing to decomposition of the hydrous salt effected by increased temperature; a change of composition which is accompanied with a new arrangement in the molecules of the compound.

SECTION I.

CLASS OF SALTS, ORDER I.

OXY-SALTS.

This order of salts includes no compound the acid or base of which does not contain oxygen. With the apparent exception of the ammoniacal salts, both the acid and base of the salts described in this section are oxidized bodies. As each acid, with few exceptions, is capable of uniting with every alkaline base, and frequently in two or more proportions, it is manifest that the salts must constitute a very numerous class of bodies. It is necessary, on this account to facilitate the study of them as much as possible by classification. They may be conveniently arranged by placing together those salts which contain either the same salifiable base or the same acid. It is not very material which principle of arrangement is adopted; but I give the preference to the latter, because, in describing the individual oxides, I have already mentioned the characteristic features of their salts, and have thus anticipated the chief advantage that arises from the former mode of classification. I shall therefore divide the salts into families, placing together those saline combinations which consist of the same acid united with different salifiable bases. The salts of each family, in consequence of containing the same acid, possess certain characters in common by which they may all be distinguished; and, indeed, the description of many salts, to which no particular interest is attached, is sufficiently comprehended in that of its family, and may therefore be omitted.

All the powerful alkaline bases, excepting ammonia, are the protoxides of an electro-positive metal, such as potassium, barium, or iron; so that if M represent an eq. of any one of those metals, M + O or MO is the strongest alkaline base, and often the only one, which that metal can form. A single eq. of a monobasic acid neutralizes MO, forming with it a neutral salt. Thus, indicating an equivalent of sulphuric and nitric acid by the signs SO_3 and NO_5, all the neutral sulphates and nitrates of protoxides are indicated by $MO + SO_3$ and $MO + NO_5$. There is, therefore, in the neutral protosalts of each family, a constant ratio in the oxygen of the base and acid, resulting from the composition of each acid, that ratio for the sul-

phates being as 1 to 3, and for nitrates as 1 to 5. If the metal M of a neutral sulphate pass into a higher grade of oxidation, becoming a binoxide MO_2, then will that binoxide be disposed to unite with 2 eq. of acid, and form a bisalt, $MO_2 + 2SO_3$, in which the oxygen of base and acid is still as 1 to 3; and if the metal yield a sesquioxide, M_2O_3, then if sufficient acid be supplied, the resulting salt will consist of $M_2O_3 + 3SO_3$, the ratio of 1 to 3 being preserved. This curious law relative to oxy-salts, which is very general, was first noticed by Gay-Lussac (Mémoires d'Arcueil, ii.); and Berzelius has found it to hold in earthy minerals, and employed it as a guide in studying their composition.

The combination of salts with one another gives rise to compounds which were formerly called *triple* salts; but as the term *double* salt, proposed by Berzelius, gives a more correct idea of their nature and constitution, it will always be employed by preference. These salts may be composed of one acid and two bases, of two acids and one base, and of two different acids and two different bases. Most of the double salts hitherto examined consist of the same acid and two different bases.

The difference in the constitution of ammonia and that of all other bases capable of uniting with ox-acids, gives great interest to its salts. In another place, the probable existence of a compound radical formed of 1 eq. of nitrogen and 4 of hydrogen, and called by Berzelius ammonium, was pointed out. The oxide of this radical, which has not yet been obtained in an uncombined state, he considers as the basis of the oxy-salts of ammonia. This view is not supported by analogy alone, but is based on the remarkable fact, that in all the neutral salts of ammonia the quantity of water necessary to convert the ammonia into oxide of ammonium is always present, nor can it be removed without the total decomposition of the salt. H. Rose has indeed succeeded in obtaining anhydrous compounds of ammonia with the ox-acids; but he has at the same time shown that they cannot be considered as salts, for although containing the elements for forming an anhydrous and neutral salt of ammonia, and produced by direct combination, neither the acid nor the alkali is present in the compound. This he has proved particularly in the substance formed by the union of anhydrous sulphuric acid with ammonia (An. de Ch. et Ph. lxii. 389). Strong evidence in its favour is likewise obtained from the views of isomorphism. It has been proved by Mitscherlich that in all the crystallized salts of potassa, whether simple or double, the potassa may be replaced either partially or completely by an equivalent quantity of protohydrate of ammonia without any change in the form of the crystal. Ammonia with an eq. of water is therefore isomorphous with potassa. But all isomorphous substances, with this exception, have the same chemical constitution, and it is incompatible with the theory of isomorphism to suppose one alkali to be isomorphous with the hydrate of another. But that the oxide of a compound radical should be isomorphous with the oxide of a simple metal is consistent with—nay, might be expected from their known analogies.

Another view of the constitution of the oxy-salts of ammonia has recently been proposed by Graham. He supposes ammonia not to be a base, but to be one of a class of bodies which he calls basic adjuncts; a term used to denote a substance which, without being a base, is capable of entering into the constitution of a salt by attaching itself to other bases. Thus, the oxy-salts of ammonia he conceives to be salts of water, to the base of which ammonia is added as an adjunct. It is scarcely necessary to remark, that this view is not only inconsistent with the

theory of isomorphism, but that the existence of adjunct bases is hypothetical, and arises from an endeavour to support another hypothesis, that all salts are neutral in composition.

SULPHATES.

The salts of sulphuric acid in solution may be detected by chloride of barium. A white precipitate, sulphate of baryta, invariably subsides, which is insoluble in acids and alkalies; a character by which the presence of sulphuric acid, whether free or combined, may always be recognized. An insoluble sulphate, such as sulphate of baryta or strontia, may be detected by mixing it, in fine powder, with three times its weight of carbonate of potassa or soda, and exposing the mixture in a platinum crucible for half an hour to a red heat. Double decomposition ensues; and on digesting the residue in water, filtering the solution, neutralizing the free alkali by pure hydrochloric, nitric, or acetic acid, and adding chloride of barium, the insoluble sulphate of that base is precipitated.

Several sulphates exist in nature, but the only ones which are abundant are the sulphates of lime and baryta. All of them may be formed by the action of sulphuric acid on the metals themselves, on the metallic oxides or their carbonates, or by way of double decomposition.

The solubility of the sulphates is very variable. There are six only which may be regarded as really insoluble; namely, the sulphate of baryta, and of the oxides of tin, antimony, bismuth, lead, and mercury. The sparingly soluble sulphates are those of strontia, lime, zirconia, yttria, and oxide of silver. All the others are soluble in water.

All the sulphates, those of potassa, soda, lithia, baryta, strontia, and lime excepted, are decomposed by a white heat. One part of the sulphuric acid of the decomposed sulphate escapes unchanged, and another portion is resolved into sulphurous acid and oxygen. Those which are easily decomposed by heat, such as sulphate of oxide of iron, yield the largest quantity of undecomposed sulphuric acid.

When a sulphate, mixed with carbonaceous matter, is ignited, the oxygen both of the acid and of the oxide unites with carbon, carbonic acid is disengaged, and a metallic sulphuret remains. A similar change is produced by hydrogen gas at a red heat, with formation of water, and frequently of some hydrosulphuric acid. In some instances the hydrogen entirely deprives the metal of its sulphur.

The composition of neutral protosulphates is expressed, as above stated, by the formula $MO + SO_3$. Consequently the acid contains three times as much oxygen as the base; and if both were deprived of their oxygen, a metallic protosulphuret would result, as indicated by the formula $M + S$.

In accordance with the views of Graham already given, the sulphates may be divided into three classes;—the first consisting of the anhydrous sulphates, being such as can exist without the eq. of constitutional water; the second, those in which the constitutional water forms an essential part; and the third composed of the double salts, which he considers as produced from the second by the eq. of constitutional water being replaced by an eq. of a sulphate of the first class. If dilute sulphuric acid be exposed in an open dish to a temperature not exceeding 380°, the evaporation proceeds without the slightest loss of acid until the sp. gr. is raised to 1·78, when it ceases entirely, and there remains a definite compound of 1 eq. of sulphuric acid and 2 eq. of water. One of these he considers as basic,

the other as constitutional water, the acid of the mentioned strength being a salt the constitution of which is represented by the formula HO, SO_3, HO. From it any one of the three classes of sulphates may be formed, the eq. of basic water being readily replaced by any stronger base, while the eq. of constitutional water can only be removed by a neutral salt producing the double salts, among which the bisulphates must also be included. There are, however, exceptions to the last observation, as Graham has remarked that magnesia and its class of isomorphous oxides are capable of acting the part of constitutional water. Although it would be highly advantageous to treat of the sulphates under the three classes above mentioned, it cannot yet be attempted; for although the constitutional water of several of them has been determined by Graham in his valuable essay already quoted, many of them have not yet been examined in reference to this point. The following table represents the constitution of the more important, both in their amorphous and crystallized state:—

Names.	Base.	Acid.	Equiv.	Formulæ.
Sulphate of Potassa . .	47·15	1 eq.+ 40·1	1 eq.= 87·25	$KO+SO_3$.
Sesquisulph. do. . .	94·3	2 eq.+120·3	3 eq.=214·6	$2KO+3SO_3$.
Do. in crystals with	9 or	1 eq. of water	=223·6	
Bisulph. Potassa . .	47·15	1 eq.+ 80·2	2 eq.=127·35	$KO+2SO_3$.
Do. with 9 or 1 eq. of water			=106·35	
Sulphate of Soda . .	31·3	1 eq.+ 40·1	1 eq.= 71·4	$NaO+SO_3$.
Do. in crystals with	90 or	10 eq. of water	=161·4	
Bisulph. Soda . . .	31·3	1 eq.+ 80 2	2 eq.=115·5	$NaO+2SO_3$.
Do. in crystals with	36 or	4 eq. of water	=147·5	
Sulphate of Lithia . .	18	1 eq.+ 40·1	1 eq.= 58·1	$LO+SO_3$.
Do. in crystals with	9 or	1 eq. of water	= 67·1	
Sulph. of ox. of Ammonium	26·15	1 eq.+ 40·1	1 eq.= 66·25	H_4No+3O_3.
Do. in crystals with	9 or	1 eq. of water	= 75·25	
Sulphate of Baryta . .	76·7	1 eq.+ 40·1	1 eq.=116·8	$BaO+SO_3$.
Do. Strontia .	51·8	1 eq.+ 40·1	1 eq.= 91·9	$SrO+SO_3$.
Do. Lime . .	28·5	1 eq.+ 40·1	1 eq.= 68·6	$CaO+SO_3$.
Do. as Gypsum with	18 or	2 eq. of water	= 86·6	
Sulphate of Magnesia .	20·7	1 eq.+ 40·1	1 eq.	
		+9 aq. 1 eq.	= 69·8	$MgO+SO_3HO$.
Do. in crystals with	54 or	6 eq. of water	=123·8	
Sulphate of Alumina ·	51·4	1 eq.+ 40·1	1 eq.= 91·5	$Al_2O_3+SO_3$.
Do. in crystals with	81 or	9 eq. of water	=172·5	
Tersulph. Alumina . .	51·4	1 eq.+120·3	3 eq.=171·7	$Al_2O_3+3SO_3$.
Do. in crystals with	162 or	18 eq. of water	=333·7	
Sulph. protox. Manganese	35·7	1 eq.+ 40·1	1 eq.	
		+9 aq. 1 eq.	= 84·8	$MnO+SO_3HO$.
Do. in crystals with	36 or	4 eq. of water	=120·8	
Sulph. protox. Iron . .	36	1 eq.+ 40·1	1 eq.	
		+9 aq. 1 eq.	= 85·1	$FeO+SO_3HO$.
Do. in crystals with	45 or	5 eq. of water	=130·1	
Tersulph. perox. Iron .	80	1 eq.+120·3	3 eq.=210·3	$Fe_2O_3+3SO_3$.
Disulph. do. . .	160	2 eq.+ 40·1	1 eq.=200·1	$2FeO_3+SO_3$.
Do. as a hydrate with	54 or	6 eq. of water	=254·1	
Sulph. protox. Zinc .	40·3	1 eq.+ 40·1	1 eq.	
		+9 aq. 1 eq.	= 89·4	$ZnO+SO_3HO$.
Do. in crystals with	54 or	6 eq. of water	=143·4	
Sulph. protox. Nickel .	37·5	1 eq.+ 40·1	1 eq.	
		+9 aq. 1 eq.	= 86·6	$NiO+SO_3HO$.
Do. in crystals with	54 or	6 eq. of water	=140·6	

Names.	Base.	Acid.	Equiv.	Formulæ.
Sulph. protox. Cobalt .	37·5	1 eq.+ 40·1	1 eq.	
		+9 aq.	1 eq. = 86·6	$CoO+SO_3HO$.
Do. In crystals with	49 or	5 eq. of water	=131·6	
Tersulph. Ox. Chromium	80	1 eq.+120·3	3 eq.=200·3	$Cr_2O_3+3SO_3$.
Sulp. protox. Copper .	39·6	1 eq.+ 40·1	1 eq.	
		+9 aq.	1 eq. = 88·7	$CuO+SO_3HO$.
Do. in crystals with	37 or	4 eq. of water	=124·7	
Disulphate do. . .	79·2	2 eq.+ 40·1	1 eq.=119·3	$2CuO+SO_3$
Sulp. protox. Mercury .	210	1 eq.+ 40·1	1 eq.=250·1	$HgO+SO_3$.
Subsulp. perox. do. .	872	4 eq.+120·3	3 eq.=992·3	$4HgO_2+3SO_3$.
Bisulp. do. . .	218	1 eq.+ 80·2	2 eq.=298·2	HgO_2+2SO_3.
Sulp. ox. Silver . .	116	1 eq.+ 40·1	1 eq.=156·1	$AgO+SO^3$.

DOUBLE SULPHATES.

Sulphate of Soda and Lime	Sulphate of Soda	71·4	1 eq.	=140·0	$NaO,SO_3 + CaO,SO_3$.
	do. Lime	68·6	1 eq.		
Sulp. of Potassa & Magnesia	Sulph. Potassa	87·25	1 eq.	=148.05	$KO,SO_3 + MgO,SO_3$.
	do. Magnesia	60·8	1 eq.		
Do. with 54 or 6 eq. of water . . .				=202·05	
Sulp. ox. of Ammonium & Mag.	Sulp. ox. Ammonium	57·25	1 eq.	=127·05	$H_4NO,SO_3 + MgO,SO_3$.
	do Magnesia	60·8	1 eq.		
Do. with 54 or 6 eq. of water . . .				=181·05	
Sulp. of Soda and Magnesia	Sulph. Soda	71·4	1 eq.	=132·2	$NaO,SO_3 + MgO,SO_3$.
	do. Magnesia	60·8	1 eq.		
Do. with 54 or 6 eq. of water . . .				=186·2	
Sulp. of Potassa & Alumina	Sulph. Potassa	67·25	1 eq.	=258·95	$KO,SO_3, + Al_2O_3 3SO_2$.
	Tersulph. Alumina	171·7	1 eq.		
Do. with 216 or 24 eq. of water . . .				=474·95	
Sulph. of Soda & Alumina	Sulph. Soda	71·4	1 eq.	=243·1	$NaO,SO_3 + Al_2O_3,3SO_3$.
	Tersulph. Alumina	171·7	1 eq.		
Do. with 234 or 26 eq. of water . . .				=477·1	
Sulph. ox. Am. & Alumina	Sulp. ox. Ammonium	57·25	1 eq.	=228·95	$H_4NO,SO_3+Al_2O_3,3SO_3$.
	Tersulph. Alumina	171·7	1 eq.		
Do. with 216 or 24 eq. of water . . .				=444·95	
Sulph. Potassa & protox. Mang.	Sulph. Potassa	87·25	1 eq.	=163·05	$KO,SO_3 + MnO,SO_3$.
	do. ox. Mangan.	75·8	1 eq.		
Do. with 54 or 6 eq. of water . . .				=217·05	
Sulph. ox. Am. & protox. Mang.	Sulph. Ammonium	57·25	1 eq.	=133·05	$H_4NO,SO_3 + MnO,SO_3$.
	do. ox. Mang.	75·8	1 eq.		
Do. with 54 or 6 eq. of water . . .				=196·05	

The protoxides of iron, zinc, nickel, and cobalt yield with potassa and ammonia double salts exactly agreeing in form and composition with the preceding double salts of magnesia and oxide of manganese.

Sulphate of Potassa.—This salt is easily prepared artificially by neutralizing carbonate of potassa with sulphuric acid; and it is procured abundantly by neutralizing with carbonate of potassa the residue of the operation for preparing nitric acid. Its taste is saline and bitter. It crystallizes in forms belonging to the right prismatic system, and its general form closely resembles the regular hexagonal prism, terminated by pyramids with six sides; the size of which is said to be much increased by the presence of a little carbonate of potassa. According to Mitscherlich it is isomorphous with chromate and seleniate of potassa. (Pog. Annalen, xviii. 168.) The crystals contain no water of crystal-

lization, and suffer no change by exposure to the air. They decrepitate when heated, and enter into fusion at a red heat. They require 16 times their weight of water at 60°, and five of boiling water for solution.

Bisulphate of potassa is easily formed by exposing the neutral sulphate with half its weight of strong sulphuric acid to a heat just below redness, in a platinum crucible, until acid fumes cease to escape. It is obtained in crystals from a concentrated solution at high temperatures, as in the cold the neutral sulphates are formed. The form is a right rhombic prism, which is in general so flattened as to be tabular. According to Graham they contain 1 eq. of water, which he considers to be basic; the bisulphate being a double sulphate of water and potassa. The anhydrous bisulphate has been prepared by Rose. It has a strong sour taste, and reddens litmus paper. It is much more soluble than the neutral sulphate, requiring for solution only twice its weight of water at 60°, and less than an equal weight at 212° F. It is resolved by heat into sulphuric acid and the neutral sulphate.

Phillips has described a sesquisulphate, obtained in the form of acicular crystals like asbestos, from the residue of the process for making nitric acid. The conditions for insuring its production have not been determined. (Phil. Mag. and Annals, ii. 421.)

Sulphate of Soda.—This compound, commonly called *Glauber's salt*, is occasionally met with on the surface of the earth, and is frequently contained in mineral springs. It may be made by the direct action of sulphuric acid on carbonate of soda; and it is procured in large quantity as a residue in the processes for forming hydrochloric acid and chlorine.

Sulphate of soda has a cooling, saline, and bitter taste. It commonly yields forms belonging to the right prismatic system, and containing 10 eq. of water of crystallization, the whole of which is rapidly lost by efflorescence on exposure to the air. When heated they readily undergo the watery fusion. At 32°, 100 parts of water dissolve 12 parts of the crystals, 48 parts at 64·5°, 100 parts at 77°, 270 at 89·5°, and 322 at 91·5°. On increasing the heat beyond this point, a portion of the salt is deposited, being less soluble than at 91·5°. (Gay-Lussac.) If a solution saturated at 91·5° is evaporated at a higher temperature, the salt is deposited in opaque anhydrous prisms, unconnected, but of the same system as the hydrous crystals. Its sp. gr. in this state is 2·462. (Haidinger.)

Bisulphate of Soda may be formed in the same manner as the analogous salt of potassa.

Sulphate of Lithia.—This salt is very soluble in water, fuses by heat more readily than the sulphates of the other alkalies, and crystallizes in flat prisms, which resemble sulphate of soda in appearance, but do not effloresce on exposure to the air. Its taste is saline without being bitter.

Sulphate of Oxide of Ammonium.—This salt is easily prepared by neutralizing carbonate of ox. of ammonium with dilute sulphuric acid; and it is contained in considerable quantity in the soot from coal. It crystallizes in long flattened six-sided prisms. It dissolves in two parts of water at 60°, and in an equal weight of boiling water. In a warm dry air it effloresces and loses 1 eq. of water. When sharply heated, it fuses, and is decomposed, yielding nitrogen gas, water, and sulphite of ox. of ammonium.

The anhydrous compound was formed by Rose by conducting dry ammoniacal gas into a glass vessel coated by a thin film of perfectly anhydrous sulphuric acid. When no excess of acid is present, it undergoes no change in the air, and

is soluble without change in water, from which it crystallizes irregularly, but in forms different from those of the common sulphate. It is remarkable that the sulphuric acid is only partially precipitated by chloride of barium in the cold, and no precipitate whatever is produced by chlorides of strontium or lime until heat is applied, and even then the action is imperfect. Nor, on the other hand, can the ammonia be separated by the chloride of platinum. From this it follows that neither the sulphuric acid nor the ammonia can be present in the solution, although their elements are present in equivalent proportions. It is not improbable it may be an amide, and formed of $H_2NSO_2 + HO$.

Sulphate of Baryta.—Native sulphate of baryta, commonly called *heavy spar*, occurs abundantly, chiefly massive, but sometimes in anhydrous crystals, the form of which is variable, being sometimes prismatic and sometimes tabular, deducible from a right rhombic prism. Its density is about 4·4. It is easily formed artificially by double decomposition. This salt bears an intense heat without fusing or undergoing any other change, and is one of the most insoluble substances with which chemists are acquainted. It is sparingly dissolved by hot and concentrated sulphuric acid, but is precipitated by the addition of water.

Sulphate of Strontia.—This salt, the *celestine* of mineralogists, is less abundant than heavy spar. It occurs in anhydrous prismatic crystals of peculiar beauty in Sicily, and is isomorphous with the sulphate of baryta. Its density is 3·858. As obtained by the way of double decomposition, it is a white heavy powder, very similar to sulphate of baryta, and requires about 3840 times its weight of boiling water for solution.

Sulphate of Lime.—This salt is easily formed by mixing in solution a salt of lime with any soluble sulphate. It occurs abundantly as a natural production. The mineral called *anhydrite* is anhydrous sulphate of lime; and all the varieties of *gypsum* are composed of the same salts, united with water. The pure crystallized specimens of gypsum are sometimes called *selenite*; and the white compact variety is employed in statuary under the name of *alabaster*. The crystals of anhydrite belong to the right prismatic system, and are isomorphous with the sulphates of baryta and strontia, while the forms of gypsum are oblique prismatic. The latter, which are by far the more general, are readily recognized by the perfect cleavage plane which truncates the acute angle of the prism. They contain 2 eq. of water, one only of which is considered by Graham to be water of crystallization, the other being constitutional. The former is readily lost by exposing pounded gypsum to a temperature of 212° *in vacuo*, and the whole water is expelled by a temperature below 300°. Thus dried, it constitutes the well-known plaster of Paris, which, when mixed with a proper proportion of water, rapidly becomes dry and solid, owing to the reproduction of gypsum. It is remarkable, however, that gypsum which has lost only 1 eq. of water, as well as that which is dried by a heat exceeding 270°, will not act in a similar manner. In the latter case, the powder is a perfect anhydrite. (Phil. Mag. vi. 417.)

Sulphate of lime has hardly any taste. It is considerably more soluble than the sulphate of baryta or strontia, requiring for solution about 500 parts of cold, and 450 of boiling water. Owing to this circumstance, and to its existing so abundantly in the earth, it is frequently contained in spring water, to which it communicates the property called hardness. When freely precipitated, it may be dissolved completely by dilute nitric acid. It is commonly believed to sustain a white heat without decomposition; but Thomson states that it parts with some of its acid when heated to redness.

Sulphate of Magnesia.—This sulphate, generally known by the name of *Epsom* salt, is frequently contained in mineral springs. It may be made directly, by neutralizing dilute sulphuric acid with carbonate of magnesia; but it is procured for the purposes of commerce by the action of dilute sulphuric acid on magnesian limestone, native carbonate of lime and magnesia.

Sulphate of magnesia has a saline, bitter, and nauseous taste. It crystallizes readily in small quadrangular prisms, which effloresce slightly in a dry air. It is obtained also in larger crystals, the principal form in which is a right rhombic prism, the angles of which are 90° 30′ and 89° 30′.—(Brooke.) Its crystals are soluble in an equal weight of water at 60°, and in three-fourths of their weight of boiling water. They undergo the watery fusion when heated; and the anhydrous salt is deprived of a portion of its acid at a white heat. Dried at 212° it retains 2 eq. of water; but one of these is expelled at 270°, while the other is retained till the temperature rises to 460°.

Sulphates of Alumina.—The tersulphate is prepared by saturating dilute sulphuric acid with hydrated alumina, and evaporating. It crystallizes with difficulty in thin flexible plates of a pearly lustre, which contain 18 eq. of water, and require twice their weight of water for solution. Berzelius says it occurs native at Milo in the Grecian Archipelago. It has an acid reaction.

The hydrated disulphate is known to mineralogists under the name of *aluminite*, which occurs at Halle, on the river Saal, and at Newhaven in Sussex; and Berzelius says the same compound falls when ammonia is added to a solution of the tersulphate. It is insoluble in water, and by heat is first rendered anhydrous, and then its acid is expelled, leaving pure alumina. The composition given in the table is from an analysis of aluminite from both its localities by Stromeyer.

Sulphate of Protoxide of Manganese.—This salt is best obtained by dissolving pure carbonate of manganese in moderately dilute sulphuric acid, and setting the solution aside to crystallize by spontaneous evaporation. The crystals are transparent and of a slight rose tint, in taste resemble Glauber's salt, and belong to the doubly oblique prismatic system. It is insoluble in alcohol, but dissolves in twice and a half its weight of cold water. If the heat is gradually applied, it may be increased to redness without expelling any of the acid.

Sulphates of the Oxides of Iron.—Sulphate of the protoxide, commonly called *green vitriol*, is formed by the action of dilute sulphuric acid on metallic iron, or by exposing protosulphuret of iron in fragments to the combined agency of air and moisture. The salt has a strong styptic, inky taste. When perfectly pure it does not change vegetable blue colours, though generally stated to do so, the reddening effect being only produced when some of the iron passes into a higher state of oxidation, as has been shown by Bonsdorff (Pogg. An. xxxi. 81). He finds that the oxidation, which occurs with extreme facility in a perfectly neutral solution, is completely prevented by a few drops of sulphuric acid in excess, and the resulting crystals have a distinctly blue colour. The common green tint is consequently a delicate test of the presence of peroxide of iron. The crystals belong to the oblique prismatic system, and contain 6 eq. of water, one of which is retained, according to Graham, till the temperature rises to 535°. By operating carefully it may be rendered anhydrous without the loss of acid. It is soluble in two parts of cold and in three-fourths of its weight of boiling water. This salt is employed in the manufacture of fuming sulphuric acid.

The tersulphate of the peroxide is formed by mixing with a solution of the

protosulphate exactly half as much sulphuric acid as that salt contains, and adding to the mixture in a boiling state successive portions of nitric acid until nitrous acid fumes cease to appear. The solution is then evaporated to dryness to expel the excess of nitric acid, and the tersulphate remains as a white salt. After being strongly heated, it dissolves slowly in water; but if evaporated at a gentle heat, it is deliquescent, and very soluble in water and alcohol, but insoluble in strong sulphuric acid. At a red heat it gives out all its acid, and peroxide of iron is all left. Its solution in water has an orange colour, which is yellow when much diluted.

The disulphate of the peroxide falls as a hydrate of an ochreous colour, when a solution of the protosulphate is kept in an open vessel.

Sulphate of Oxide of Zinc.—This salt, frequently called *white vitriol*, is the residue of the process for forming hydrogen gas by the action of dilute sulphuric acid on metallic zinc; but it is also made, for the purposes of commerce, by roasting native sulphuret of zinc. It crystallizes by spontaneous evaporation in transparent flattened four-sided prisms of the right prismatic system, and isomorphous with Epsom salts. The crystals dissolve in two parts and a half of cold, and are still more soluble in boiling water. The taste of this salt is strongly styptic. It reddens vegetable blue colours, though in composition it is strictly a neutral salt.

Sulphate of Protoxide of Nickel.—This salt, like the salts of nickel in general, is of a green colour, and crystallizes from its solution in pure water in right rhombic prisms exactly similar to the sulphates of zinc and magnesia. If an excess of sulphuric acid is present, the crystals are square prisms, which, according to R. Phillips and Cooper, contain rather less water and more acid than the preceding: though the difference is not so great as to indicate a different atomic constitution. (Annals of Philosophy, xxii. 439.) Thomson says he analyzed both kinds, and found their composition identical. It is soluble in about three times its weight of water at 60° F.

Sulphate of Protoxide of Cobalt.—When protoxide of cobalt is digested in dilute sulphuric acid, a red solution is formed, which by evaporation deposits crystals of the same colour. Mitscherlich has shown that the crystals are identical in composition with sulphate of protoxide of iron; and Brooke's measurements prove these salts to be isomorphous. (An. of Phil. N. S. vi. 120.) They are insoluble in alcohol, and dissolve in about 24 parts of cold water.

Tersulphate of Oxide of Chromium.—This salt may be formed by saturating dilute sulphuric acid with hydrated sesquioxide of chromium; but it has not been obtained in crystals.

Sulphates of the Oxides of Copper.—Sulphate of the red oxide of copper has not been obtained in a separate state. The sulphate of the black, or protoxide, *blue vitriol*, employed by surgeons as an escharotic and astringent, may be prepared by roasting the native sulphuret; but it is more generally made by directly dissolving the protoxide in dilute sulphuric acid, and crystallizing by evaporation. This salt forms crystals of a blue colour, reddens litmus paper, and is soluble in about four of cold, and in two parts of boiling water. The crystals contain 5 eq. of water, four of which are lost at 212° in a dry air, but the fifth is retained till the temperature exceeds 430°. It is then a white powder, which combines readily with water, with the development of considerable heat. It is isomorphous with sulphate of protoxide of manganese.

When pure potassa is added to a solution of the sulphate of protoxide of cop-

per in a quantity insufficient for separating the whole of the acid, a pale bluish-green precipitate, the disulphate, is thrown down.

Sulphate of protoxide of copper and ammonia is generated by dropping pure ammonia into a solution of the sulphate, until the sub-salt at first thrown down is nearly all dissolved. It forms a dark blue solution, from which, when concentrated, crystals are deposited by the addition of alcohol. It may be formed also by rubbing briskly in a mortar two parts of crystallized sulphate of protoxide of copper with three parts of carbonate of ammonia, until the mixture acquires an uniform deep blue colour. Carbonic acid gas is disengaged with effervescence during the operation, and the mass becomes moist, owing to the water of the blue vitriol being set free.

This compound, which is the *ammoniuret of copper* of the pharmacopœia, contains sulphuric acid, protoxide of copper, and ammonia; but its precise nature has not been determined in a satisfactory manner. It parts gradually with ammonia by exposure to the air.

Sulphates of the Oxides of Mercury.—When two parts of mercury are gently heated in three parts of strong sulphuric acid, so as to cause slow effervescence, a sulphate of the protoxide of mercury is generated. But if a strong heat is employed in such a manner as to excite brisk effervescence, and the mixture is brought to dryness, a bisulphate of the peroxide results, both being anhydrous. (Donovan in An. of Phil. xiv.) When this bisulphate, which is the salt employed in making corrosive sublimate, is thrown into hot water, decomposition ensues, and a yellow sub-salt, formerly called *turpeth mineral*, subsides. This salt is said by Phillips to consist of 3 eq. of acid and 4 of the peroxide. The hot water retains some of the bisulphate in solution, together with free sulphuric acid.

Sulphate of Oxide of Silver.—As this salt is rather sparingly soluble in water, it may be formed by double decomposition from concentrated solutions of nitrate of oxide of silver and sulphate of soda. It may also be procured by dissolving silver in sulphuric acid which contains about a tenth part of nitric acid, or by boiling silver in an equal weight of concentrated sulphuric acid. It requires about 80 times its weight of hot water for solution, and the greater part is deposited in small needles on cooling. By slow evaporation from a solution containing a little nitric acid, Mitscherlich obtained it in the form of a rhombic octohedron, the angles of which are almost identical with that of anhydrous sulphate of soda. Seleniate of oxide of silver is isomorphous with the sulphate.

Sulphate of oxide of silver forms with ammonia a double salt, which crystallizes in rectangular prisms, the solid angles and lateral edges of which are commonly replaced by tangent planes. It consists of 1 eq. of oxide of silver, 1 of acid, and 2 of ammonia; and it is formed by dissolving sulphate of oxide of silver in a hot concentrated solution of ammonia, from which on cooling the crystals are deposited. This salt is isomorphous with a double chromate and seleniate of oxide of silver and ammonia, which have a similar constitution, and are formed in the same manner. (Mitscherlich in An. de Ch. et Ph. xxxviii. 62.)

DOUBLE SULPHATES.

Sulphates of Lime and Soda.—This compound, the glauberite of mineralogists, occurs in very flat oblique rhombic prisms. Berthier prepared it by fusing together sulphate of lime with sulphate of soda in the ratio of their equivalents.

Sulphate of soda fused in similar proportions with the sulphates of magnesia, baryta, and oxide of lead, gives analogous compounds. In these instances however, the affinity is so feeble, that it is overcome by the mere action of water. (An. de Ch. et Ph. xxxviii. 255.)

Sulphate of Potassa and Magnesia.—On mixing solutions of these salts in atomic proportion, the double salt is formed either by spontaneous evaporation or on cooling from a hot rather concentrated solution. The crystals are prismatic, and of a complicated form, belonging to the oblique prismatic system. (Brooke.) A similar double salt, isomorphous with the preceding, is formed by substituting ammonia for potassa. Their composition is given in the table.

Similar pairs of double salts may be formed with the protoxides of iron, zinc, cobalt, and nickel. These salts have the same form and composition as the corresponding salt of magnesia.

Alum.—This well-known substance is a double sulphate of potassa and alumina, which crystallizes with great facility from a solution containing its elements. It is prepared in this country from alum-slate, an argillaceous slaty rock highly charged with pyrites: on roasting this rock, the sulphuret of iron is oxidized, the resulting sulphuric acid unites with alumina and potassa present in the slate, and the alum is dissolved out by water. By frequent crystallization it is purified from the oxide of iron, which obstinately adheres to it. In Italy it is prepared from *alum-stone*, which occurs at Tolfa near Rome, and in most volcanic districts, being formed apparently by the action of sulphurous acid vapours on felspatic rocks. The materials of the alum exist in the stone ready formed; and they are extracted by gently heating the rock, exposing it for a time to the air, and lixiviation. The alum from this source has been long prized, in consequence of being quite free from iron. In both of these processes the alkali contained in the alum-rock is inadequate for uniting with the sulphate of alumina which is obtained, and hence a salt of potassa must be added.

Alum has a sweetish astringent taste, and reddens litmus paper. It is soluble in five parts of water at 60°, and in little more than its own weight of boiling water. It crystallizes readily in octohedrons, or in segments of the octohedron, and the crystals contain 24 eq. or almost 50 per cent. of water of crystallization. On being exposed to heat, they froth up remarkably, and part with all the water, forming anhydrous alum, the *alumen ustum* of the pharmacopœia. At a full red heat the alumina is deprived of its acid.

Alum is employed in the formation of a spontaneously inflammable mixture long known under the name of *Homberg's pyrophorus*. It is made by mixing equal weights of alum and brown sugar, and stirring the mass over the fire in an iron or other convenient vessel till quite dry: it is then put into a glass tube or bottle, and heated to moderate redness without exposure to the air, until inflammable gas ceases to be evolved. A more convenient mixture is made with three parts of lamp-black, four of burned alum, and eight of carbonate of potassa. When the pyrophorus is well made, it speedily becomes hot on exposure to the air, takes fire, and burns like tinder; but the experiment frequently fails from the difficulty of regulating the temperature.

From some recent experiments by Gay-Lussac, it appears that the essential ingredient of Homberg's pyrophorus is sulphuret of potassium in a state of minute division. The charcoal and alumina act only by being mechanically interposed between its particles; but when the mass once kindles, the charcoal takes fire and continues the combustion. He finds that an excellent pyrophorus is

made by mixing 27 parts of sulphate of potassa with 15 parts of calcined lamp-black, and heating the mixture to redness in a common hessian crucible, of course excluding the air at the same time. (An. de Ch. et. Ph. xxxvii. 415.)

Alum, having exactly the same form, composition, appearance, and taste, as the salt just described, may be made with ammonia, the sulphate of which replaces sulphate of potassa. It is met with occasionally as a natural product, and may be prepared by evaporating a solution of sulphate of ammonia with tersulphate of alumina.

A soda alum may also be prepared, similar in form and composition to the preceding alums, except that it contains 26 equivalents of water. (Berzelius.) This salt is disposed to effloresce in the air.

Iron Alum.—By mixing sulphate of potassa with tersulphate of peroxide of iron, and crystallizing by spontaneous evaporation, crystals are obtained similar to common alum in form, *colour*, *taste*, and composition. This salt has often a pink tint, but is sometimes quite colourless. A similar double salt, quite colourless, may be made with ammonia instead of potassa. In both these alums the alumina is simply replaced by an equivalent quantity of peroxide of iron.

Chrome Alums.—The tersulphate of oxide of chromium forms with the sulphates of potassa and ammonia double salts, which are exactly similar in form and composition to the preceding varieties of alum. They appear black by reflected, but ruby-red by transmitted light.

Manganese Alum.—Mitscherlich obtained this salt by mixing a solution of tersulphate of sesquioxide of manganese with sulphate of potassa, and evaporating to the consistence of syrup by a very gentle heat. On cooling, octohedral crystals of a brownish-violet colour were deposited, which were similar in composition to common alum. The tersulphate used for the purpose is prepared by macerating sesquioxide of manganese in very fine powder with strong sulphuric acid: it is made with difficulty, owing to the indisposition of that oxide to unite with acids, and to its ready conversion by heat into sulphate of the protoxide.

From the descriptions of the salts to which the term alum has been applied, it will be observed that they are characterized by two common properties: they all crystallize in the octohedral system, and they are all constituted as represented by the formula $RO,SO_3 + R_2O_3,3SO_3 + 24$ aq., where RO represents an eq. of potassa, or oxide of ammonium, and R_2O_3 any of the isomorphous oxides of aluminium, iron, manganese, and chromium. As Berzelius has ably remarked, the formula and crystalline form serve to determine the genus alum, and the oxidized bases its species.

Sulphate of Protoxide of Iron and Alumina.—This salt, which has recently been formed by Klauer, is obtained by the spontaneous evaporation of a mixture of sulphate of protoxide of iron and tersulphate of alumina in eq. proportions, a large excess of sulphuric acid being present (Lieb. An. xiv. 261). The salt is deposited in long acicular crystals, the constitution of which, being $FeO,SO_3 + Al_2O_3,3SO_3 + 24HO$, is similar to that of an alum; but as the crystals do not belong to the octohedral system, it has been improperly described as one of that class.

A compound, exactly analogous, in which protoxide of manganese is substituted for protoxide of iron, occurs native on the gold coast of Africa, in beautiful silvery fibres, many inches long. It has been described and analyzed by Apjohn, who found its formula to be $MnO,SO_3 + Al_2O_3,3SO_3 + 24HO$.

A similar salt of magnesia was obtained in the same manner; and it is exceed-

ingly probable that a similar compound might be formed with the isomorphous oxides of zinc, copper, nickel, cobalt, and with lime. These, in their turn, might again be varied by substituting for the alumina the sesquioxides of iron, manganese, and chromium.

Anhydrous Sulphates with Ammonia.—Rose has observed that some sulphates possess the property of absorbing ammonia, and of forming with it definite compounds, which differ from sulphates of ammonia prepared in the moist way, both by containing no water of crystallization, and by the facility with which the alkali is again given out. They are formed by placing the anhydrous sulphate in a glass tube, and transmitting over it at common temperatures ammoniacal gas, well dried by fused potassa, as long as any increase of weight is observed: some sulphates absorb the gas very rapidly at first, and with disengagement of heat; but the absorption afterwards becomes slow, and requires a day or two in order to be complete. The salts most remarkable for this property are those which, in solution, are disposed to unite with ammonia. Sulphate of protoxide of copper greedily absorbs ammonia, and acquires a deep blue colour similar to the ammoniaret of copper, prepared with moisture; but the former compound consists of 2 eq. of sulphate of protoxide of copper and 5 eq. of ammonia, while the latter contains 1 eq. of sulphate of copper, 2 of ammonia, and 1 eq. of water. Sulphate of protoxide of cobalt, as well as that of nickel, unites with 3 eq. of ammonia; that of zinc with 2·5, and that of manganese with 2 eq. The latter when heated loses all its ammonia, and returns to its original condition; whereas most of the other ammoniaco-sulphates suffer partial decomposition at the same time. Sulphate of oxide of silver unites with 1 eq. of ammonia; and a similar compound was prepared by C. G. Mitscherlich, but with 2 eq. of ammonia. With most of the other anhydrous sulphates ammonia refuses to unite.

On considering the nature of these compounds, one is at first disposed to associate them with double salts, supposing the acid to be divided between the two bases. But this opinion is rendered unlikely by the large quantity of combined ammonia, by the facility with which the alkali is given off, and by the absence of water, so constantly present in other ammoniacal sulphates. Rose, with much plausibility, compares these compounds to hydrates: water acts as a feeble base to saline compounds, combining with some in one or more proportions, and not at all with others, differing greatly in the ratio in which it combines with different salts, and being abandoned with great facility, often by mere exposure to the air. The same features characterize the combinations of ammonia with the anhydrous sulphates. (Pog. Annalen, xx. 149.)

The sulphates are not the only salts which absorb ammonia. Rose found that the nitrate of oxide of silver unites with 3 eq. of ammonia, and the gas, if freely supplied, is at first absorbed with such rapidity, and the corresponding increase of temperature is so great, that the salt enters into fusion. Heat expels the ammonia before the nitrate of oxide of silver is decomposed. A similar compound, but with less ammonia, was formed by C. Mitscherlich.

SULPHITES.

The salts of sulphurous acid have not hitherto been minutely examined. The sulphites of potassa, soda, and ammonia, which are made by neutralizing those alkalies with sulphurous acid, are soluble in water; but most of the other sulphites, so far as is known, are of sparing solubility. The sulphites of baryta,

strontia, and lime, are very insoluble; and consequently the soluble salts of these earths decompose the alkaline sulphites.

The stronger acids, such as the sulphuric, hydrochloric, phosphoric, and arsenic acids, decompose all the sulphites with effervescence, owing to the escape of sulphurous acid, which may easily be recognized by its odour. Nitric acid, by yielding oxygen, converts the sulphites into sulphates.

When the sulphites of the fixed alkalies and alkaline earths are strongly heated in close vessels, a sulphate is generated, and a portion of sulphur sublimed. In open vessels at a high temperature they absorb oxygen, and are converted into sulphates; and a similar change takes place even in the cold, especially when they are in solution. Gay-Lussac has remarked, that a neutral sulphite always forms a neutral sulphate when its acid is oxidized; a fact from which it may be inferred, that neutral sulphites consist of 1 eq. of the acid and 1 eq. of the base.

The hyposulphates and hyposulphites are of such little practical importance, that it is unnecessary to describe individual salts: their general character has been already given. For a particular description of the hyposulphates, the reader is referred to an essay by Heeren. (An. de Ch. et Ph. xl. 30.)

NITRATES.

The nitrates may be prepared by the action of nitric acid on metals, on the salifiable bases themselves, or on carbonates. As nitric acid forms soluble salts with all alkaline bases, the acid of the nitrates cannot be precipitated by any reagent. They are readily distinguished from other salts, however, by the characters already described.

All the nitrates are decomposed without exception by a high temperature; but the changes which ensue are modified by the nature of the oxide. Nitrate of oxide of palladium is decomposed at such a moderate temperature, that a great part of the acid passes off unchanged. Nitrate of oxide of lead requires a red heat, by which it is resolved, as already mentioned, into oxygen and nitrous acid. In some instances the changes are more complicated. With nitre, for example, nitrite of potassa is at first generated, with escape of oxygen gas: as the heat increases, the nitrous acid is resolved into binoxide of nitrogen and oxygen, the former of which remains in combination with potassa; the binoxide is then resolved into protoxide of nitrogen and oxygen, the former being retained by the alkali; and, lastly, nitrogen gas is disengaged, and peroxide of potassium remains. If the operation is performed in an earthen vessel, the peroxide will be more or less decomposed, in consequence of the affinity of the earthy substances for potassa. The preceding facts have been chiefly collected from the observations of Phillips and Berzelius. The tendency of potassa and soda to unite with protoxide of nitrogen was first discovered by Davy; and Hess has lately remarked that similar compounds are obtained with soda, baryta, and lime, as well as potassa, when their nitrates are heated until the disengaged gas is found to extinguish a light.

As the nitrates are easily decomposed by heat alone, they must necessarily suffer decomposition by the united agency of heat and combustible matter. The nitrates on this account are much employed as oxidizing agents, and frequently act with greater efficacy even than nitro-hydrochloric acid. Thus metallic titanium, which resists the action of these acids, combines with oxygen when heated

with nitre. The efficiency of this salt, which is the nitrate usually employed for the purpose, depends not only on the affinity of the combustible for oxygen, but likewise on that of the oxidized body for potassa. The process for oxidizing substances by means of nitre is called *deflagration*, and is generally performed by mixing the inflammable body with an equal weight of the nitrate, and projecting the mixture in small portions at a time into a red-hot crucible.

All the neutral nitrates of the fixed alkalies and alkaline earths, together with most of the neutral nitrates of the common metals, are composed of 1 eq. of nitric acid, and 1 eq. of a protoxide. Consequently, the oxygen of the oxide and acid in all such salts must be in the ratio of 1 to 5, the general formula being $MO + NO_5$.

The only nitrates found native are those of potassa, soda, lime, and magnesia.

The composition of the principal nitrates is exhibited in the following table:

Names.	Base.	Acid.	Equiv.	Formulæ.
Nitrate of Potassa	47·15	1 eq. + 54.15	1 eq. = 101·3	$KO + NO_5$.
——— Soda	31·3	1 eq. + 54·15	1 eq. = 85·45	$NaO + NO_5$.
Oxide of Ammonium	26·15	1 eq. + 54·15	1 eq. = 80·3	$H_4NO + NO_5$.
Nitrate of Baryta	76·7	1 eq. + 54·15	1 eq. = 130·85	$BaO + NO_5$.
——— Strontia	51·8	1 eq. + 54·15	1 eq. = 105·95	$SrO + NO_5$.
Do. in prisms with 45 or 5 eq. of water			= 150·95	
Nitrate of Lime	28·5	1 eq. + 54·15	1 eq. = 82·65	$CaO + NO_5$.
——— Magnesia	20·7	1 eq. + 54·15	1 eq. = 74·85	$MgO + NO_5$.
——— Protox. Copper	39·6	1 eq. + 54·15	1 eq. = 93·75	$CuO + NO_5$.
Do. in prisms with 63 or 7 eq. of water ?			= 156·75	
Nitrate of protox. Lead	111·6	1 eq. + 54·15	1 eq. = 165·75	$PbO + NO_5$.
Dinitrate of ditto	223·2	2 eq. + 54·15	1 eq. = 277·35	$2PbO + NO_5$.
Nitrate of protox. Mercury	210	1 eq. + 54·15	1 eq. = 264·15	$HgO + NO_5$.
Do. in crystals with 18 or 2 eq. of water			= 282·15	
Nitrate of perox. Mercury	218	1 eq. + 54·15	1 eq. = 272·15	$HgO_2 + NO_5$.
Dinitrate do.	436	2 eq. + 54·15	1 eq. = 490·15	$2HgO_2 + NO_5$.
Nitrate of ox. Silver	116	1 eq. + 54·15	1 eq. = 170·15	$AgO + NO_5$.

Nitrate of Potassa.—This salt is generated spontaneously in the soil, and crystallizes upon its surface, in several parts of the world, and especially in the East Indies, whence the greater part of the nitre used in Britain is derived. In some parts of the Continent, it is prepared artificially from a mixture of common mould or porous calcareous earth with animal and vegetable remains containing nitrogen. When a heap of these materials, preserved moist and in a shady situation, is moderately exposed to the air, nitric acid is gradually generated, and unites with the potassa, lime, and magnesia, which are commonly present in the mixture. On dissolving these salts in water, and precipitating the two earths by carbonate of potassa, a solution is formed, which yields crystals of nitre by evaporation. The nitric acid is possibly generated under these circumstances by the nitrogen of the organic matters combining during putrefaction with oxygen of the atmosphere, a change which must be attributed to the affinity of oxygen for nitrogen, aided by that of nitric acid for alkaline bases. The nitre made in France is often said to be formed by this process; but the greater part is certainly obtained by lixiviation from certain kinds of plaster of old houses, when nitrate of lime is gradually generated. Liebig, in his profound work on the application of organic chemistry to Agriculture and Physiology, has rendered it highly probable, if not certain, that the nitric acid is formed by the oxidation of

ammonia, which exists in the atmosphere, and is brought by absorption in contact with organic matters in a state of slow combustion or *eremacausis*. Ammonia is more easily oxidized than any other compound of nitrogen; probably because it contains hydrogen, the oxidation of which yields water, which is essential to the existence of nitric acid. Animal matters only act as a source of ammonia, and nitric acid may be formed where the decaying organic matter contains no nitrogen, from the ammonia present in the atmosphere. For the details of his argument I must refer to Dr. Playfair's translation of the above work recently (Sept. 1840) published.

Nitrate of potassa is a colourless salt, which crystallizes readily in six-sided prisms. Its taste is saline, accompanied with an impression of coolness. It requires for solution seven parts of water at 60°, and its own weight of boiling water. It contains no water of crystallization, but its crystals are never quite free from water lodged mechanically within them. At 616° it undergoes the igneous fusion, and like all the nitrates, is decomposed by a red heat.

Nitre is chiefly employed in chemistry as an oxidizing agent, and in the formation of nitric acid. Its chief use in the arts is in making gunpowder, which is a mixture of nitre, charcoal, and sulphur. In the East Indies it is employed for the preparation of cooling mixtures; an ounce of powdered nitre dissolved in five ounces of water reduces its temperature by fifteen degrees. It possesses powerful antiseptic properties, and is therefore much employed in the preservation of meat and animal matters in general.

Nitrate of Soda.—This salt is analogous in its chemical properties to the preceding compound. It sometimes crystallizes in oblique rhombic prisms; but it more commonly occurs as an obtuse rhombohedron. (Brooke.) It is plentifully found in the soil in some parts of India; and at Atacama in Peru it covers large districts, and occurs in immense quantity. With charcoal and sulphur it forms a mixture which burns much slower than common gunpowder, and therefore cannot be substituted for nitre; but it may be advantageously used in the manufacture both of sulphuric and nitric acid. It is disposed to deliquesce in the air, and is soluble in twice its weight of cold water, and still more freely by the aid of heat.

Nitrate of Oxide of Ammonium.—It may be formed by neutralizing dilute nitric acid by carbonate of ammonia, and evaporating the solution. This salt may be procured in three different states, which have been described by Davy. (Researches concerning the nitrous oxide.) If the evaporation is conducted at a temperature not exceeding 100°, the salt is obtained in prismatic crystals isomorphous with nitre. If the solution is evaporated at 212°, fibrous crystals are procured; and if the heat be gradually increased to 300°, it forms a brittle compact mass on cooling. The fibrous and compact varieties still contain water, the former 8·2 per cent. and the latter 5·7. All these varieties deliquesce in a moist air, and are very soluble in water.

The change which nitrate of ammonia undergoes at a temperature varying between 400° and 500° has already been explained. When heated to 600°, it explodes with violence, being resolved into water, nitrous acid, binoxide of nitrogen, and nitrogen. The fibrous variety was found by Davy to yield the largest quantity of protoxide of nitrogen. From one pound of this salt he procured nearly three cubic feet of the gas.

Nitrate of Baryta.—This salt is sometimes used as a reagent and for preparing pure bartya. It is easily prepared by digesting the native carbonate,

reduced to powder, in nitric acid diluted with 8 or 10 times its weight of water The salt crystallizes readily by evaporation in transparent anhydrous octohedrons, and is very apt to decrepitate by heat unless previously reduced to powder. It requires 12 parts of water at 60° and 3 or 4 of boiling water for solution, but is insoluble in alcohol. It undergoes the igneous fusion in the fire before being decomposed.

Nitrate of Strontia.—This salt may be made from strontianite in the same manner as the foregoing compound, to which it is exceedingly analogous. It commonly crystallizes in anhydrous octohedrons which undergo no change in a moderately dry atmosphere, and are insoluble in alcohol; but sometimes it contains 30 per cent. of water of crystallization, and then assumes the form of the oblique prismatic system.

Nitrates of Lime and Magnesia.—These salts crystallize in hydrated prisms when their solutions are concentrated to the consistence of syrup, but the quantity of water which they contain is not ascertained. They deliquesce rapidly in the air, are very soluble in water, and are dissolved by alcohol, the nitrate of lime more freely than nitrate of magnesia.

Nitrate of Protoxide of Copper.—This salt is prepared by the action of nitric acid on copper. It crystallizes, though with some difficulty, in prisms of a deep blue colour, which are very soluble in water and alcohol, and deliquesce on exposure to the air. The green insoluble subsalt, procured by exposing the neutral nitrate to a heat of 400°, or by dropping an alkali into a solution of that salt, the latter being in excess, is a trinitrate, consisting of 3 eq. of oxide of copper, 1 eq. of acid, and 1 eq. of water. From the observations of Graham, the neutral salt contains 3 eq. of constitutional water, and therefore may be represented by the formula $CuO, NO_5, 3HO$: from this it would appear that the subsalt is similarly constituted, being a nitrate of water with 3 eq. of constitutional oxide of copper. It is on this supposition represented by the formula $HO, NO_5, 3CuO$. It is probable that the nitrates of lime and magnesia are similarly constituted, as has been shown to be the case with nitric acid of sp. gr. 1·42. When heated to redness it yields pure oxide of copper.

Nitrate of Protoxide of Lead.—This salt is formed by digesting litharge in dilute nitric acid, and crystallizes readily in octohedrons, which are anhydrous and almost always opaque. It has an acid reaction, but is neutral in composition.

A dinitrate was formed by Berzelius by adding to a solution of the neutral nitrate a quantity of pure ammonia insufficient for separating the whole of the acid.

Nitrates of the Oxides of Mercury.—The protonitrate is conveniently formed by digesting mercury in nitric acid diluted with three or four parts of water, until the acid is saturated, and then allowing the solution to evaporate spontaneously in an open vessel. The solution always contains, at first, some nitrate of the peroxide; but if metallic mercury is left in the liquid, a pure protonitrate is gradually deposited. The salt thus formed has hitherto been regarded as the neutral protonitrate; but according to the analysis of M. C. Mitscherlich (Pog. Annalen, ix. 387), it is a subsalt, in which the protoxide and acid are in the ratio of 208 to 36. This result, however, requires confirmation. The neutral protonitrate is said by C. Mitscherlich to be obtained in crystals, by dissolving the former salt in pure water acidulated with nitric acid, and evaporating spontaneously without the contact of metallic mercury or uncombined oxide. These

salts dissolve completly in water slightly acidulated with nitric acid, but in pure water a small quantity of a yellow subsalt is generated.

When mercury is heated in an excess of strong nitric acid, it is dissolved with brisk effervescence, owing to the escape of binoxide of nitrogen, and transparent prismatic crystals of the pernitrate are deposited as the solution cools. When put into hot water it is resolved into a soluble salt, the composition of which is unknown, and into a yellow dinatrate of the peroxide. (An. de Ch. et Phys. xix.)

Nitrate of Oxide of Silver.—Silver is readily oxidized and dissolved by nitric acid diluted with two or three times its weight of water, forming a solution which yields transparent tabular crystals by evaporation. These crystals, which are anhydrous, undergo the igneous fusion at 426°, and yield a crystalline mass in cooling; but when the temperature reaches 600° or 700°, complete decomposition ensues, the acid being resolved into oxygen and nitrous acid, while metallic silver is left. When liquefied by heat, and received in small cylindrical moulds, it forms the *lapis infernalis* or *lunar caustic*, employed by surgeons as a cautery. The nitric acid appears to be the agent which destroys the animal texture, and the black stain is owing to the separation of oxide of silver. It is sometimes employed for giving a black colour to the hair, and is the basis of the indelible ink for marking linen.

The pure nitrate, whether fused or in crystals, is colourless and transparent, and does not deliquesce by exposure to the air; but common lunar caustic is dark and opaque, and dissolves imperfectly in water, owing to some of the nitrate being decomposed during its preparation. It is impure also, always containing nitrate of protoxide of copper, and frequently traces of gold. The pure salt is soluble in its own weight of cold, and in half its weight of hot water. It dissolves also in four times its weight of alcohol. Its aqueous solution, if preserved in clean glass vessels, especially with the addition of a minute quantity of free nitric acid, undergoes little or no change even in the direct solar rays; but when exposed to light, especially to sunshine, in contact with paper, the skin, or any organic substance, a black stain is quickly produced, owing to decomposition of the salt and reduction of its oxide to the metallic state. This change is so constant, that nitrate of oxide of silver constitutes an extremely delicate test of the presence of organic matter, and has been properly recommended as such by Dr. Davy. Its solution is always kept in the laboratory as a test for chlorine and hydrochloric acid.

Nitrate of oxide of silver, even after fusion, reddens vegetable colouring matters; but it is quite neutral in composition.

NITRITES.

Little is known with certainty concerning the compounds of nitrous acid with alkaline bases. Nitrite of potassa is formed by heating nitre to redness, and removing it from the fire before the decomposition is complete. On adding a strong acid to the product, red fumes of nitrous acid are disengaged, a character which is common to all the nitrites. The nitrite of soda, baryta, and strontia, may be obtained in the same manner, and doubtless several others. Two nitrites of oxide of lead have been described in the Annales de Chimie, lxxxiii. by Chevreul and Berzelius. It is possible, however, that these compounds are hyponitrites.

CHLORATES.

The salts of chloric acid are very analogous to the nitrates. As the chlorates of the alkalies, alkaline earths, and most of the common metals, are composed of 1 eq. of chloric acid and 1 eq. of a protoxide, $MO + ClO_5$, it follows that the oxygen of the latter to that of the former is in the ratio of 1 to 5. The chlorates are decomposed by a red heat, nearly all of them being converted into metallic chlorides, with evolution of pure oxygen gas. They deflagrate with inflammable substances with greater violence than nitrates, yielding oxygen with such facility that an explosion is produced by slight causes. Thus, a mixture of sulphur with three times its weight of chlorate of potassa explodes when struck between two hard surfaces. With charcoal and the sulphurets of arsenic and antimony, this salt forms similar explosive mixtures: and with phosphorus it detonates violently by percussion. One of the mixtures, employed in the percussion locks for guns, consists of sulphur and chlorate of potassa, with which a little charcoal or gunpowder is mixed; but as the use of these materials is found corrosive to the lock, fulminating mercury is now generally preferred.

All the chlorates hitherto examined are soluble in water, excepting the chlorate of protoxide of mercury, which is of sparing solubility. These salts are distinguished by the action of strong hydrochloric and sulphuric acids, the former of which occasions the disengagement of chlorine and protoxide of chlorine, and the latter of peroxide of chlorine.

None of the chlorates are found native, and the only ones that require particular description are those of potassa and baryta.

Chlorate of Potassa.—This salt, formerly called *oxymuriate* or *hyper-oxymuriate of potash*, is colourless and crystallizes in four and six-sided scales of a pearly lustre. Its forms are stated by Brooke to belong to the oblique prismatic system. It is soluble in sixteen times its weight of water at 60°, and in two and a half of boiling water. It is quite anhydrous, and when exposed to a temperature of 400° or 500° undergoes the igneous fusion. On increasing the heat almost to redness, effervescence ensues, and pure oxygen gas is disengaged, phenomena which have been explained in the section on oxygen. It can bear a heat of 600° without decomposition.

Chlorate of potassa is made by transmitting chlorine gas through a concentrated solution of pure potassa, until the alkali is completely neutralized. The solution which, after being boiled for a few minutes, contains nothing but chloride of potassium and chlorate of potassa, is gently evaporated till a pellicle forms upon its surface, and is then allowed to cool. The greater part of the chlorate crystallizes, while the chloride remains in solution. The crystals, after being washed with cold water, may be purified by a second crystallization.

Chlorate of Baryta is of interest, as being the compound employed in the formation of chloric acid; and the readiest mode of preparing it is by the process of Wheeler. On digesting for a few minutes a concentrated solution of chlorate of potassa with a slight excess of silicated hydrofluoric acid, the alkali is precipitated in the form of an insoluble double fluoride of silicium and potassium, while chloric acid remains in solution. The liquid after filtration is neutralized by carbonate of baryta, which throws down the excess of silicated hydrofluoric acid, and chlorate of baryta is left in solution. By evaporation it yields prismatic

crystals, which require for solution 4 times their weight of cold, and a still smaller quantity of hot water. They are composed of 76·7 parts or 1 eq. of baryta, 75·42 or 1 eq. of chloric acid, and 9 or 1 eq. of water.

[Waechter states that light is evolved during the crystallization of this salt, and that it communicates to the flame of alcohol an intense green colour. (Jour. fur prakische Chem. i. xxx. p. 321.)]

Perchlorates.—The neutral proto-salts of perchloric acid consist of 1 eq. of acid and base, as is expressed by the formula $MO + Cl_2O_7$. Most of these salts are deliquescent, very soluble in water, and soluble in alcohol: four only were found by Serullas to be not deliquescent,—the perchlorates of potassa, ammonia, protoxide of lead and protoxide of mercury. When heated to redness they yield oxygen gas and metallic chlorides; and they are distinguished from the chlorates by not acquiring a yellow tint on the addition of hydrochloric acid. The perchlorate of potash is prepared from the chlorate by the action of heat or sulphuric or nitric acid, as already mentioned. It is the most insoluble of the perchlorates, and on this account perchloric acid precipitates potassa from its salts, being a test of about the same delicacy as tartaric acid. The other perchlorates are made by neutralizing the base with perchloric acid. The solubility in alcohol of the perchlorates of baryta, soda, and oxide of silver, is a property which the analytical chemist may avail himself of in analysis for the separation of potassa and soda from each other.

CHLORITES.

The alkaline salts of chlorous acid are readily made, as mentioned at page 226, by transmitting a current of chlorous acid gas into a solution of the pure alkalies. All that have as yet been examined are soluble in water, and are remarkable for their highly bleaching and oxidizing properties. By the latter properties and the evolution of chlorous acid on the addition of any of the stronger acids their presence is readily recognized.

Hypochlorites.—The hypochlorites may be produced by the action of chlorine gas on the salifiable bases. The most important of them is the hypochlorite of lime, the well-known bleaching powder, which has commonly been described as the oxymuriate or chloride of lime. It is prepared for commercial purposes by exposing thin strata of recently slaked lime in fine powder to an atmosphere of chlorine. The gas is absorbed in large quantity, and the chloride of calcium and hypochlorite of lime are produced in equivalent proportions.

It is a dry white powder, which smells faintly of chlorine, and has a strong taste. It dissolves partially in water, and the solution possesses powerful bleaching properties, and contains both chlorine and lime; while the undissolved portion is hydrate of lime, retaining a small quantity of chlorine. The aqueous solution, when exposed to the atmosphere, is gradually decomposed; chlorine is set free, and carbonate of lime generated. On boiling the liquid, chloride of calcium, and, I presume, chlorate of lime are formed; and by long keeping, the dry chloride appears to undergo a similar change,—at least chloride of calcium is produced in large quantity. It is also decomposed by a strong heat: at first, chlorine is evolved; but pure oxygen is afterwards disengaged, and chloride of calcium remains in the retort.

The composition of chloride of lime was first carefully investigated by Dalton,*

* Annals of Philosophy, i. 15, and ii. 6.

and it has since been analyzed by Thomson,* Welter,† and Ure.‡ The three first-mentioned chemists infer from their researches that bleaching powder is a hydrated *subchloride* or *dichloride* of lime in which one equivalent of chlorine is united with two equivalents of lime. They are also of opinion, that on mixing this dichloride with water, the chloride is dissolved, and one equivalent of lime separated as an insoluble powder. Dr. Ure, on the contrary, denies that bleaching powder is a dichloride, and maintains that the elements of this powder do not constitute a regular atomic combination. He found that the quantity of chlorine absorbed by hydrate of lime is variable, depending not only on the pressure and degree of exposure, but on the quantity of water present. From these experiments it appears that the commercial bleaching powder is essentially a hypochlorite with single equivalents of its elements, but mixed with variable quantities of hydrate of lime.

According to Millon, bleaching-powder is an oxychloride of calcium, $Ca\left\{\begin{matrix}Cl\\O\end{matrix}\right\}$ $=$ CaO, ClO + CaCl. It is now certain that even if hypochlorites exist, the bleaching compounds of lime, potash, and soda contain the chlorides of these metals as an essential constituent, according to the second of the above formulæ. But according to the view of Millon, these compounds must be viewed as oxychlorides, corresponding to the peroxides of the metals, in which part of the oxygen is replaced by chlorine. The peroxides of sodium and calcium are NaO_2 and CaO_2, and the bleaching compounds are $Na\left\{\begin{matrix}Cl\\O\end{matrix}\right\}$ and $Ca\left\{\begin{matrix}Cl\\O\end{matrix}\right\}$. But the peroxide of potassium is KO_3, and consequently its bleaching compound ought to be $K\left\{\begin{matrix}Cl_2\\O\end{matrix}\right\}$. In point of fact, it contains twice as much chlorine as the corresponding compound of sodium, which renders this view extremely probable. Similar oxychlorides are formed by adding these compounds to solutions of lead, iron, and copper; and by the action of these compounds on hydrochloric acid, Millon has obtained a new bleaching compound, perchloride of hydrogen, HCl_2 perfectly analogous to peroxide of hydrogen, which is the type of the class of bodies just described, as well as of the super-oxides of the metals, its formula being $H\left\{\begin{matrix}O\\O\end{matrix}\right\}$. For details the reader is referred to Millon's paper in the Journal de Pharmacie for September, 1839, p. 595.

Several methods have been proposed for estimating the value of different specimens of bleaching powder. Perhaps the most convenient for the artist is that of Welter, which consists in ascertaining the power of the bleaching liquid to deprive a solution of indigo of known strength of its colour; and directions have been drawn up by Gay-Lussac for enabling manufacturers to employ this method with accuracy. (Annals of Philosophy, xxiv. 218.) For analytical purposes, the best method is to decompose chloride of lime, confined in a glass tube over mercury, by means of hydrochloric acid. Chloride of calcium is generated, and the chlorine being set free, its quantity may easily be measured.

* An. of Phil. xv. 401. † Ann. de Ch. et. Ph. vol. viii. ‡ Quarterly Journal, xiii. 1.

IODATES.

From the close analogy in the composition of chloric and iodic acids, it follows that the general character of the iodates must be similar to that of the chlorates. Thus in all neutral protiodates the oxygen contained in the oxide and acid is in the ratio of 1 to 5. They form deflagrating mixtures with combustible matters; and on being heated to low redness, oxygen gas is disengaged and a metallic iodide remains. As the affinity of iodine for metals is less energetic than that of chlorine, many of the iodates part with iodine as well as oxygen when heated, especially if a high temperature is employed.

The iodates are easily recognized by the facility with which their acid is decomposed by deoxidizing agents. Thus, the sulphurous, phosphorous, hydrochloric, and hydriodic acids, deprive iodic acid of its oxygen, and set iodine at liberty. Hydrosulphuric acid not only decomposes the acid of these salts, but occasions the formation of hydriodic acid by yielding hydrogen to the iodine. Hence an iodate of potassa may be converted into the iodide by transmitting a current of hydrosulphuric acid gas through its solution. None of the iodates have been found native. They are all of very sparing solubility, or actually insoluble in water, excepting the iodates of the alkalies.

Iodate of Potassa.—This salt may be procured by adding iodine to a concentrated hot solution of pure potassa, until the alkali is completely neutralized. The liquid, which contains an iodate and iodide, is evaporated to dryness by a gentle heat, and the residue, when cold, is treated by repeated portions of boiling alcohol. The iodate, which is insoluble in that menstruum, is left, while the iodide of potassium is dissolved. A better process has been recommended by M. Henry, Jr., founded on the property which iodide of potassium possesses, of absorbing oxygen while in the act of escape from decomposing chlorate of potassa. For this purpose iodide of potassium is fused in a capacious hessian crucible, and when, after removal from the fire, it is yet semi-fluid, successive portions of pulverized chlorate of potassa are projected into it, stirring well after each addition. The materials froth up considerably, and when the action is over, a white, opaque, cellular mass remains, easily separable from the crucible: tepid water dissolves out the chloride of potassium, and leaves the iodate. Convenient proportions are one part of iodide of potassium and rather more than one and a half of chlorate of potassa. (Journ. de Pharmacie, July, 1832.)

All the insoluble iodates may be procured from this salt by double decomposition. Thus iodate of baryta may be formed by mixing chloride of barium with a solution of iodate of potassa.

A biniodate of potassa has been described by Serullas. It is formed by incompletely neutralizing a hot solution of chloride of iodine with potassa or its carbonate, and setting it aside to cool. A peculiar compound of chloride of potassium and biniodate of potassa falls; but on dissolving this substance, filtering and exposing the solution to a temperature of 77°, the biniodate is gradually deposited in right rhombic prisms terminated by dihedral summits. It is soluble in 75 times its weight of water at 59°.

A teriodate may be formed by mixing a large excess of sulphuric acid with a moderately dilute solution of iodate of potassa. On evaporating at 77°, the teriodate is deposited in regular rhomboidal crystals, which require 25 times their weight of water at 60° for solution.

Serullas states that the compound of chloride of potassium and biniodate of

potassa, above mentioned, may be formed by the action of hydrochloric acid on iodate of potassa. By spontaneous evaporation it is obtained, sometimes in brilliant, transparent, elongated prisms, and at other times in hexagonal laminæ; but generally it crystallizes in right quadrangular prisms with their lateral edges truncated, and terminated by four-sided summits. (An. de Ch. et Ph. xliii. 113.)

Bromates.—These compounds have many characters in common with the chlorates and iodates; but hitherto they have been but partially examined.

PHOSPHATES.

In studying these salts, the reader must bear in mind that there are three isomeric modifications of the same acid, which have been described under the names of *phosphoric*, *pyrophosphoric*, and *metaphosphoric acid*; and therefore it will be necessary to have three corresponding families of salts, the *phosphates*, *pyrophosphates*, and *metaphosphates*. This distinction, and the other facts lately recorded by Graham, render it necessary either to change the names of the phosphates, or to retain their old names in opposition to the principles of nomenclature. The most consistent conduct will be to describe each salt under its scientific name, and add at the same time its ordinary one. An eq. of each of the three acids, is a compound of 31·4 parts or 2 eq. of phosphorus + 40 parts or 5 eq. of oxygen = 71·4, expressed by the formula P_2O_5. To form a salt *neutral in composition*, 1 eq. of an alkaline base is requisite; and in the case of any protoxide, indicated by MO, the general formula will be $MO + P_2O_5$. If 2 eq. of a protoxide are united with one of the acid, we have a *disalt*, $2MO + P_2O_5$; and if 3 eq. of a base combine with 1 eq. of the acid, it is a *trisalt*, $3MO + P_2O_5$. It seems also that water plays the part of an alkaline base towards each of the three acids, either alone or conjointly with another base: the salts with such compound bases can scarcely be viewed in the light of double salts, since the two bases act together as one electro-positive element.

All the protophosphates which are neutral in composition are soluble in water, and redden litmus paper; whence they are commonly called superphosphates. The triphosphates, except those of the pure alkalies, are either sparingly soluble or insoluble in water; but they are all dissolved by dilute nitric or phosphoric acid, being converted into the soluble phosphates. All the triphosphates with fixed and strong bases bear a red heat without change; but the phosphates and diphosphates, to judge from experiments on the soda salts, are converted into metaphosphates and pyrophosphates. Most of the phosphates of the second class of metals are resolved into phosphurets by the conjoint agency of heat and combustible matter. The phosphates of the alkalies are only partially decomposed under these circumstances, and the phosphates of baryta, strontia, and lime, undergo no change.

The presence of a soluble phosphate may be distinguished by the tests already mentioned for phosphoric acid. The insoluble phosphates are decomposed when boiled with a strong solution of carbonate of potassa or soda, the acid uniting with the alkali so as to form a soluble phosphate: the earthy phosphates, indeed, are decomposed with difficulty, requiring continued ebullition, and should preferably be fused with an alkaline carbonate, like an insoluble sulphate.

Several phosphates are met with in nature, such as those of lime, alumina, and the oxides of manganese, iron, uranium, copper, and lead.

The composition of the principal phosphates is given in the following table:

Names.	Base.		Acid.	Equiv.	Formulæ.
Triphosphate of Soda	93·9	3 eq.	+ 71·4 1 eq.	= 165·3	$3NO + P_2O_5$.
Do. in crystals with 216 or 24 eq. of water				= 381·3	
Triphosph. Soda and Basic Water { Soda	62·6	2 eq.	+ 71·4 1 eq.	= 143	$2NaO,HO + P_2O_5$.
Water	9	1 eq.			
Do. in crystals with 216 or 24 eq. of water				= 359	
Do. . . . 135 or 15 eq. of water				= 278	
Acid Triphos. Soda and Basic Water { Soda	31·3	1 eq.	+ 71·4 1 eq.	= 120·7	$NaO,2HO + P_2O_5$.
Water	18	2 eq.			
Do. in crystals with 18 or 2 eq. of water				= 138·7	
Triphosphate of Potassa	141·45	3 eq.	+ 71·4 1 eq.	= 212·85	$3KO + P_2O_5$.
Triphosp. of Potassa and Basic Water { KO	94·3	2 eq.	+ 71·4 1 eq.	= 174·7	$2KO,2HO + P_2O_5$.
HO	9	1 eq.			
Acid Triphosphate { Potassa	47·15	1 eq.	+ 71·4 1 eq.	= 136·55	$KO,2HO + P_2O_5$.
ditto Water	18	2 eq.			
Triphosph. of Soda, Oxide Ammonium, and Basic Water { Soda	31·3	1 eq.	+ 71·4 1 eq.	= 137·85	$NaO,H_4NO,HO + P_2O_5$.
Ox. Am.	26·15	1 eq.			
Water	9	1 eq.			
Do. in crystals with 72 or 8 eq. of water				= 209·85	
Triphos. of oxide of Am. & Basic Water { Ox. Am.	52·30	2 eq.	+ 71·4 1 eq.	= 132·70	$2H_4NO,HO + P_2O_5$.
Water	9	1 eq.			
Acid Triphosphate { Ox. Am.	26·15	1 eq.	+ 71·4 1 eq.	= 115·55	$H_4NO,2HO + P_2O_5$.
ditto Water	18	2 eq.			
Bone Phosphate of Lime	228	8 eq.	+ 214·2 3 eq.	= 442·2	$8CaO + 3P_2O_5$.
Triphosphate do.	85·5	3 eq.	+ 71·4 1 eq.	= 156·9	$3CaO + P_2O_5$.
Triphos. of Lime & Basic Water { Lime	57	2 eq.	+ 71·4 1 eq.	= 127·4	$2CaO,2HO + P_2O_5$.
Water	9	1 eq.			
Acid Triphos. do. { Lime	28·5	1 eq.	+ 71·4 1 eq.	= 117·9	$CaO,2HO + P_2O_5$.
Water	18	2 eq.			

For the new and more simple views of the constitution of the phosphates, pyrophosphates, and metaphosphates, which are becoming prevalent, the reader is referred to the account of them given in the general section on salts.

The triphosphate of baryta, strontia, protoxides of manganese, iron, copper, lead, silver, &c. precisely correspond to the triphosphate of lime, simply substituting 3 eq. of those oxides. These oxides in like manner form soluble phosphates analogous in composition to that of lime.

Triphosphate of Soda.—This salt, described by Graham as the *subsesquiphosphate*, is made by adding pure soda to a solution of the succeeding compound until the liquid feels soapy to the fingers, an excess of soda not being injurious. The liquid is then evaporated until a pellicle appears, and the crystals which form on cooling are quickly redissolved in water and recrystallized. Though the crystals do not change in the air, the solution absorbs carbonic acid, and the resulting carbonate of soda adheres to the triphosphate.

This salt crystallizes in colourless six-sided slender prisms, which have a strong alkaline taste and reaction, require 5 times their weight of water at 60°, and still less of hot water, for solution, and at 170° fuse in their water of crystallization. They may be exposed to a red heat without losing the characters of a phosphate. The feeblest acids deprive the salt of one-third of its soda.

When this salt is mixed in solution with nitrate of oxide of silver in excess, there is an exact interchange of elements, such that

1 eq. Triphosphate of Soda	$3NO + P_2O_5$	yield	1 eq. Triphosph. of Silver $3AgO + P_2O_5$.
& 3 eq. Nitrate of Silver	$3(AgO + NO_5)$		& 3 eq. Nitrate of Soda $3(NaO + NO_5)$.

The resulting solution is therefore quite neutral. The triphosphate of oxide of lead, and other insoluble triphosphates may be prepared in like manner.

Triphosphate of Soda and Basic Water.—This salt is the most common of the phosphates, being manufactured on a large scale by neutralizing with carbonate of soda the acid phosphate of lime procured by the action of sulphuric acid on burned bones. It is generally described as the neutral phosphate of soda, and for distinction's sake is sometimes termed *rhombic phosphate*, from its crystals having the form of oblique rhombic prisms.

This salt crystallizes best out of an alkaline solution; but however prepared it is always alkaline to test paper, and requires a considerable quantity of acid before losing its alkalinity. The crystals effloresce on exposure to the air, and require 4 times their weight of cold, and twice their weight of hot water for solution. It often contains traces of sulphuric acid, from which it may be purified by repeated solution and crystallization. When mixed with nitrate of oxide of silver, the interchange of elements is such that

1 eq. Rhombic Phos. $2\,NaO,HO+P_2O_5$	yield	1 eq. Triphosph. of Silver $3AgO+P_2O_5$.
& 3 eq. Nitrate of Silver $3(AgO+NO_5)$		& 2 eq. Nitrate of Soda $2(NaO+NO_5$.

The yellow triphosphate of oxide of silver falls exactly as with the former salt, but 1 eq. of nitric acid is left free in the solution.

When a solution of the rhombic phosphate is evaporated at a temperature of 90°, it crystallizes with 14 instead of 24 equivalents of water, and the crystals differ, as might be expected, from the other salt in figure, and are permanent in the air. Both salts lose their basic water at a red heat, and are converted into a pyrophosphate.

Acid Triphosphate of Soda and Water.—This salt, commonly called *biphosphate of soda* from its acid reaction, may be formed by adding phosphoric acid to a solution of carbonate of soda, or to either of the preceding phosphates, until it ceases to give a precipitate with chloride of barium. Being very soluble in water, the solution must be concentrated in order that it may crystallize. This salt is capable of yielding two different kinds of crystals without varying its composition. The more unusual form, isomorphous with binarseniate of soda, is a right rhombic prism, the smaller lateral edge of which is 78° 30′, terminated by pyramidal planes. The form of its ordinary crystals is a right rhombic prism, the larger angle of which is 93° 54′.

The crystals of this salt consist, as stated at page 481, of $NaO,2HO,P_2O_5+2HO$. When heated to 212°, the water of crystallization is expelled, and the anhydrous salt remains, still yielding a yellow precipitate with silver when neutralized by ammonia; but if exposed to a heat of 400°, it loses half its basic water, being reduced to NaO,HO,P_2O_5, and has the character of pyrophosphate of soda. At a red heat it is converted into metaphosphate of soda.

Triphosphate of Potassa.—Graham formed this salt by adding caustic potassa in excess to a solution of phosphoric acid, as well as by fusing phosphoric acid with a slight excess of carbonate of potassa. He obtained it in acicular crystals, which were very soluble in water, but not deliquescent.

Triphosphate of Potassa and Basic Water.—This salt may be prepared by neutralizing the superphosphate of lime from bones with carbonate of potassa. It is deliquescent, and has not been obtained in regular crystals.

Acid Triphosphate of Potassa and Basic Water may be formed by adding phosphoric acid to carbonate of potassa until the liquid ceases to give a precipitate

with chloride of barium, and setting it aside to crystallize. The crystals belong to the square prismatic system, and they usually occur in square prisms terminated by the planes of an octohedron. They are acid to test paper.

When this compound is neutralized by carbonate of soda, and the solution set to crystallize, a phosphate of soda and potassa is deposited in crystals, the form of which is an oblique rhombic prism, which frequently occurs without modification.

Triphosphate of Soda and Oxide of Ammonia and Basic Water.—This salt is easily prepared by mixing together 1 eq. of hydrochlorate of ammonia and 2 eq. of the rhombic phosphate of soda, each being previously dissolved in a small quantity of boiling water. As the liquid cools, prismatic crystals of the double phosphate are deposited, while chloride of sodium remains in solution. Their form is an oblique rhombic prism. This salt has been long known by the name of *microcosmic salt*, and is much employed as a flux in experiments with the blowpipe. When heated it parts with its water and ammonia, and a very fusible metaphosphate of soda remains.

Triphosphate of Ox. Ammonium and Basic Water.—This salt is formed by adding ammonia to concentrated phosphoric acid until a precipitate appears. On applying heat, the precipitate is dissolved, and on abandoning the solution to itself, the neutral salt crystallizes. The form of the crystals is an oblique rhombic prism, the smaller angle of which is 84° 30′. They often occur in rhombic prisms with diedral summits. (Mitscherlich.)

The acid triphosphate is made in the same manner as the preceding triphosphate of potassa. The crystals are less soluble than the preceding salt, and undergo no change on exposure to the air. Their form is an octohedron with a square base; but the right square prism, terminated by the faces of the octohedron, is the most frequent.

Phosphates of Lime.—The peculiar compound called the *bone phosphate*, exists in bones after calcination, and falls as a gelatinous precipitate on pouring chloride of calcium into a solution of the rhombic phosphate of soda, or on adding ammonia to a solution of any phosphate of lime in acids.

Triphosphate of Lime and Basic Water, commonly called *neutral phosphate*, falls as a granular precipitate, consisting of fine crystalline particles, when the rhombic phosphate of soda is added in solution drop by drop to chloride of calcium in excess. The residual liquid reddens litmus, owing to a small quantity of triphosphate of lime being generated.

Triphosphate of Lime cannot be formed by precipitation, but occurs in hexagonal prisms in the mineral called *apatite*.

Acid Triphosphate of Lime and Basic Water, called the *biphosphate* from its acid reaction, is formed by dissolving either of the preceding salts in a slight excess of phosphoric acid. The compound is deliquescent, very soluble, and crystallizes with great difficulty. It exists in the urine. The solution formed by the action of sulphuric acid on bones is probably a compound of lime with 2 or more eq. of phosphoric acid, being really a *superphosphate*.

Triphosphate of Magnesia and Basic Water.—It is formed by mixing together hot saturated solutions of the rhombic phosphate of soda and sulphate of magnesia, and separates on cooling in small crystals which contain 13 eq. of water to one of the salt. The triphosphate of magnesia is principally formed when the solutions are intermixed in the cold. These salts have been but little examined.

The phosphate of ammonia and magnesia subsides as a pulverulent granular

precipitate from neutral or alkaline solutions, containing phosphoric acid, ammonia, and magnesia. It is readily dissolved by acids, and is sparingly soluble in pure water, especially when carbonic acid is present: but it is insoluble in a solution of most neutral salts, such as hydrochlorate of ammonia. It constitutes one variety of urinary concretions. According to Berzelius it consists of

Phosphoric Acid . .	71·4	1 eq.	P_2O_5.
Magnesia . . .	41·4	2 eq.	2MgO.
Ammonia . . .	34·3	2 eq.	$2H_3N$.
Water . . .	90	10 eq.	10HO.

The mode in which these elements are arranged is unknown. When heated to redness it loses its water and ammonia, and the residue is diphosphate of magnesia, which contains 36·67 per cent. of pure magnesia. At a strong red heat it fuses, and appears when cold as a white enamel.

When the materials for forming the preceding salt are mixed while hot, small acicular crystals subside on cooling, which are said by Berzelius to contain less of the two bases than the other salt.

Phosphates of Protoxide of Lead.—The triphosphate is precipitated when acetate of oxide of lead is mixed with a solution of the rhombic phosphate of soda, acetic acid being set free. The triphosphate with basic water is best formed by adding the rhombic phosphate of soda gradually to a hot solution of chloride of lead. The nitrate should not be used for the purpose, as it combines with the precipitate. Both these phosphates are white, and are frequently formed at the same time. The latter fuses readily into a yellow bead, which in cooling acquires crystalline facettes.

Triphosphate of Oxide of Silver.—This compound subsides, of a characteristic yellow colour, when the rhombic phosphate of soda is mixed in solution with nitrate of oxide of silver, nitric acid being set free at the same time. It is apt to retain some of the nitrate in combination. This salt is very soluble in nitric and phosphoric acid, forming the soluble phosphate, and in ammonia. By exposure to light it is speedily blackened; but when protected from this agent, it yields on drying an anhydrous yellow powder, which has a sp. gr. of 7·321 (Stromeyer). Its colour changes on the application of heat to a reddish-brown, but its original tint returns on cooling. It bears a red heat without fusion: at a white heat it fuses, and if kept for some time in a fused state a portion of pyrophosphate is generated.

PYROPHOSPHATES.

The discovery of these salts by Clark has also been mentioned. That modification of phosphoric acid termed *pyrophosphoric acid*, is procured by forcing with the aid of heat phosphoric acid to combine with 2 eq. either of water or some fixed base. The only pyrophosphates which have as yet been studied are those of soda and oxide of silver. These salts are thus constituted:—

Names.	Base.	Acid.	Equiv.	Formulæ.
Dipyrophosphate of Soda . . .	62·6	2 eq.+71·4	1 eq.=134·0	$2NaO+P^2O^5$.
Do in crystals with 90 or 10 eq. of water .			=224	
Acid Dipyrophos. Soda and Basic Water (Soda / Water)	31·3 / 9	1 eq.+71·4	1 eq.=111·7	$NaO,HO+P_2O_5$
Pyrophosphate of Soda . . .	31·3	1 eq.+71·4	1 eq.=102·7	$NaO+P^2O^5$.
Dipyrophos. Oxide of Silver . .	232	2 eq.+71·4	1 eq.=303·4	$2AgO+P^2O^5$.

Dipyrophosphate of Soda.—This is the compound first prepared by Clark from the rhombic phosphate, by expelling its basic water. When the residual mass is dissolved in water and set to evaporate, crystals are obtained, having the outline of an irregular six-sided prism, derived from a rhombic prism. These crystals are permanent in the air, much less soluble in water than the original rhombic phosphate, and quite neutral to test paper. Ignited with carbonate of soda, a phosphate is reproduced, because the acid is forced to unite with 3 eq. of a base.

Dipyrophosphate of soda is permanent both in crystals and in solution in the cold; but by long boiling, or quickly when boiled with an acid, a phosphate is reproduced. With a salt of lead it yields a white dipyrophosphate of oxide of lead; and on washing the precipitate and decomposing by hydrosulphuric acid gas, a solution of pyrophosphoric acid is obtained, which again forms dipyrophosphate of soda when neutralized with soda.

The oxides of most metals of the second class yield with pyrophosphoric acid insoluble or sparingly soluble salts, which may be prepared by double decomposition with dipyrophosphate of soda. It should be held in view, however, as Stromeyer has remarked, that most of these salts are more or less soluble in an excess of dipyrophosphate of soda; and that some of them, such as the dipyrophosphate of the oxides of lead, copper, nickel, cobalt, uranium, bismuth, manganese, and mercury, are dissolved by it with great facility.

Acid Dipyrophosphate of Soda and Water.—This salt is formed by exposing, as stated at page 482, the acid triphosphate to a heat of 400°, when it loses one half of its basic water, and acquires the character of a pyrophosphate. This salt dissolves readily in water, has an acid reaction, and has not been obtained in crystals.

Pyrophosphate of Soda.—When the preceding salt, $NaOHO + P_2O_5$, is heated to 600° or a little higher, it loses its basic water, and yet the acid does not lose the character of pyrophosphoric acid. It is left, therefore, as a simple pyrophosphate of soda, $NaO + P_2O_5$. On adding water part of it dissolves, and part is left as an insoluble white powder. The solution is *quite neutral to test paper;* but on adding nitrate of oxide of silver, the dipyrophosphate of that oxide falls, and free nitric acid remains in solution. The soluble and insoluble pyrophosphate of soda appear identical in composition, and the former at a heat just short of redness may be wholly converted into the latter.

Dipyrophosphate of Oxide of Silver.—This salt is readily formed by double decomposition with dipyrophosphate of soda and nitrate of oxide of silver, the residual liquid being quite neutral to test paper. It falls as a snow-white granular precipitate, which fuses readily at a heat short of incandescence into a dark brown liquid, which becomes a crystalline enamel on cooling.

METAPHOSPHATES.

The only metaphosphates which have yet been examined are those of soda, baryta, and oxide of silver, which are thus constituted :—

Names.	Base.	Acid.	Equiv.	Formulæ.
Metaphosphate of Soda . .	31·3	1 eq.+71·4	1 eq.=102·7	$NaO+P_2O_5$.
Do. Baryta . .	76·7	1 eq.+71·4	1 eq.=148·1	$BaO+P_2O_5$.
Do. Ox. Silver .	116	1 eq.+71·4	1 eq.=187·4	$AgO+P_2O_5$.
Submetaphos. do. . .	348	3 eq.+142·8	2 eq.=490·8	$3AgO+2P_2O_5$.

Metaphosphate of Soda.—When the pyrophosphate or acid dipyrophosphate of soda is heated to low redness, it fuses, and on cooling becomes a transparent glass, which deliquesces in a damp air, and is very soluble. The solution has a feeble acid reaction. When mixed with nitrate of oxide of silver, the metaphosphate of that oxide falls in gelatinous flakes, wholly unlike the pyrophosphate, and aggregates together as a soft solid when heated to near 212°. The metaphosphate of soda does not change by keeping, and has not hitherto been made to crystallize. When its solution is evaporated, and kept for some time at 400°, it is reconverted into the acid dipyrophosphate of soda and basic water. All the preceding facts are drawn from Graham's essay. (Phil. Trans. 1833, Part ii.)

Metaphosphate of Baryta falls in gelatinous flakes on adding metaphosphate of soda to a solution of chloride of barium, the latter being in excess as the soda salt dissolves the precipitate. By long-continued boiling metaphosphate of baryta is at length dissolved, and at the same time converted into a phosphate.

The metaphosphate of silver is obtained by precipitation, as above stated. When put, while moist, into boiling water, part of its acid is removed, and the submetaphosphate is generated.

ARSENIATES.

Arsenic acid resembles the phosphoric in composition and in many of its properties, but as far as is yet known is only capable of forming tribasic salts. Those which contain 2 eq. of basic water are, like the phosphates, soluble in water and redden litmus, whence they are commonly considered as bisalts. If only 1 eq. of basic water be present, in which the oxygen of the alkaline base and acid is as 2 to 5, the salt is usually termed a neutral arseniate. When no basic water is present, the salt is usually described as a subarseniate. The two last series of salts, except those with the alkalies, are of sparing solubility in water: but they are dissolved by phosphoric or nitric acid, as well as most acids which do not precipitate the base of the salt.

Many of the arseniates bear a red heat without decomposition, or being otherwise modified in their characters; but they are all decomposed when heated to redness along with charcoal, metallic arsenic being set at liberty. The arseniates of the fixed alkalies and alkaline earths require a rather high temperature for reduction; while the arseniates of the second class of metals, as of lead and copper, are easily reduced in a glass tube by means of a spirit-lamp without danger of melting the glass. Of all the arseniates that of oxide of lead is the most insoluble.

The soluble arseniates are easily recognized by the tests described in the section on arsenic; and the insoluble arseniates, when boiled in a strong solution of the fixed alkaline carbonates, are deprived of their acid, which may then be detected in the usual manner. The free alkali, however, should first be exactly neutralized by pure nitric acid.

The arseniates of lime, and of the oxides of nickel, cobalt, iron, copper, and lead, are natural productions.

The composition of the principal arseniates is contained in the following table:—

Names.	Base.		Acid	Equiv.	Formulæ.
Triarseniate of Soda .	93·9	3 eq.	+115·4	1 eq.=209·3	$3Na+As_2O_5$.
Do. in crystals with 216 or 24 eq. of water .				=425·3	
Triarsen. Soda and Basic Water { Soda	62·6	2 eq.	+115·4	1 eq.=187	$2NaO,HO+As_2O_5$.
Water	9	1 eq.			
Do. in crystals with 216 or 24 eq. of water				=403	
Do. in crystals with 126 or 14 eq. of water				=313	
Acid Triarsen. Soda and Basic Water { Soda	31·3	1 eq.	+115·4	1 eq.=164·7	$NaO,2HO+As_2O_5$.
Water	18	2 eq.			
Do. in crystals with 18 or 2 eq. of water				=182·7	
Triarseniate of Potassa	141·45	3 eq.	+115·4	1 eq.=256·85	$3KO+As_2O_5$.
Triarsen. of Potassa and Basic Water { Potassa	94·3	2 eq.	+115·4	1 eq.=218·7	$2KO,HO+As_2O_5$.
Water	9	1 eq.			
Acid Arsen. of Potas. and Basic Water { Potassa	47·15	1 eq.	+115·4	1 eq.=162·55	$KO,2HO+As_2O_5$.
Water	18	2 eq.			
Triarseniate of Oxide Am. and Basic Water { Ox. Am.	52·30	2 eq.	+115·4	1 eq.=176·7	$2H_4NO,HO+As_2O_5$.
Water	9	1 eq.			
Acid Triarsen. of Ox. Am. and Basic Water { Ox. Am.	26·15	1 eq.	+115·4	1 eq.=159·55	$H_4NO,2HO+As_2O_5$.
Water	18	2 eq.			
Triarseniate of Baryta .	230·1	3 eq.	+115·4	1 eq.=345·5	$3BaO+As_2O_5$.
Triarseniate do. with Basic Water { Baryta	153·4	2 eq.	+115·4	1 eq.=277·8	$2BaO,HO+As_2O_5$.
Water	9	1 eq.			
Acid Triarsen. do with Basic Water { Baryta	76·7	1 eq.	+115·4	1 eq.=210·1	$BaO,2HO+As_2O_5$.
Water	18	2 eq.			
Triarseniate of Lime .	85·5	3 eq.	+115·4	1 eq.=200·9	$3CaO+As_2O_5$.
Triarseniate do. and Basic Water { Lime	57	2 eq.	+115·4	1 eq.=181·4	$2CaO,Ho+As_2O_5$.
Water	9	1 eq.			
Acid Triarsen. do. and Basic Water { Lime	28·5	1 eq.	+115·4	1 eq.=161·9	$CaO,2HO+As_2O_5$.
Water	18	2 eq.			
Triarseniate of Ox. Lead .	334·8	3 eq.	+115·4	1 eq.=450·2	$3PbO+As_2O_5$.
Triarseniate do. and Basic Water { Lead	223·2	2 eq.	+115·4	1 eq.=347·6	$2PbO,HO+As_2O_5$.
Water	9	1 eq.			
Triarseniate of Ox. Silver .	348	3 eq.	+115·4	1 eq.=463·4	$3AgO+As_2O_5$.

Arseniates of Soda.—The triarseniate is made in the same manner as triphosphate of soda, with which it is isomorphous. At 60°, 100 parts of water dissolve 28 of the crystals, and still more by the aid of heat. At 186° they fuse in their water of crystallization.

The triarseniate of soda and basic water corresponds precisely in form and constitution with the corresponding phosphate, and like it parts with its last eq. of water at a red heat; but does not, on losing it, receive any change in its characters. It is efflorescent and alkaline to test paper, and crystallizes best out of an alkaline solution. It is prepared by adding soda or its carbonate in slight excess to a solution of arsenic acid. The salt with 14 eq. of water coincides with the corresponding phosphate.

The acid triarseniate of soda and basic water is prepared like the corresponding phosphate.

The same observation applies to the arseniates of potassa and ammonia, each having its isomorphous arseniate. The triarseniate of potassa crystallizes in needles and with difficulty, like the corresponding phosphate. The arseniate of potassa may be formed by heating nitre to redness mixed with an equal weight of arsenious acid.

The compound arseniate of potassa and soda agrees in form and composition with the phosphate of those bases.

Arseniates of Baryta.—The triarseniate is best prepared by gradually adding in

solution triarseniate of soda to chloride of barium in excess, and falls as a pulverulent heavy precipitate, which is apt to contain a little triarseniate of baryta and basic water as well as the soda salt, and should therefore be well washed with boiling water. On adding chloride of barium to an excess of triarseniate of soda, the latter salt always falls with the precipitate.

To prepare the triarseniate of baryta and basic water a solution of the rhombic triarseniate of soda is added drop by drop to chloride of barium in solution, when the triarseniate soon appears in white crystalline scales, which contain 3 eq. of water. On reversing the process by adding chloride of barium to the arseniate, the precipitate is a mixture of the triarseniate of baryta, and triarseniate of baryta and water. By the continued action of hot water on the latter, it is partly changed into the acid triarseniate and insoluble triarseniate. The acid triarseniate is obtained by dissolving either of the two former salts, in a moist state, by dilute arsenic acid.

Triarseniates of Lime.—The three salts analogous to those of baryta are obtained by precisely similar processes. The triarseniate of lime and basic water occurs in silky acicular crystals as a rare mineral named *pharmacolite*, which contains 5 eq. of water of crystallization.

Triarseniates of Protoxide of Lead.—The triarseniate is formed by adding in solution acetate of oxide of lead gradually to an excess of triarseniate of soda. The same salt falls when acetate of oxide of lead and the rhombic triarseniate of soda are intermixed, acetic acid being set free. It is a white very insoluble powder, which at a low red heat acquires a yellow tint, which it loses again on cooling.

The triarseniate with basic water may be made by a similar process as for forming the corresponding triphosphate, and is a white insoluble, easily fusible powder.

Triarseniate of Oxide of Silver.—This salt falls as a brick-red powder when nitrate of oxide of silver is mixed in solution with triarseniate of soda or the rhombic triarseniate, in the latter case nitric acid being set free. It is apt to retain some of the nitrate, which cannot be removed by washing; a property which the yellow phosphate of oxide of silver also possesses.

ARSENITES.

These salts have as yet been but little examined. The arsenites of potassa, soda, and ammonia may be prepared by acting with those alkalies on arsenious acid: they are very soluble in water, have an alkaline reaction, and have not been obtained in regular crystals. Most of the other arsenites are insoluble, or sparingly soluble, in pure water; but they are dissolved by an excess of their own acid, with great facility by nitric acid, and by most other acids with which their bases do not form insoluble compounds. The insoluble arsenites are easily formed by double decomposition.

All the arsenites are decomposed when heated in close vessels, the arsenious acid being either dissipated in vapour, or converted, with disengagement of some metallic arsenic, into arseniates. Heated with charcoal or black-flux, the acid is reduced with facility. Formiate of soda answers still better.

The soluble arsenites, if quite neutral, are characterized by forming a yellow arsenite of oxide of silver when mixed with the nitrate of that base, and a green arsenite of protoxide of copper, *Scheele's green*, with sulphate of that oxide.

When acidulated with acetic or hydrochloric acid, hydrosulphuric acid causes the formation of orpiment. The insoluble arsenites are all decomposed when boiled in a solution of carbonate of potassa or soda.

The arsenite of potassa is the active principle of Fowler's arsenical solution.

CHROMATES.

The salts of chromic acid are mostly either of a yellow or red colour, the latter tint predominating whenever the acid is in excess. The chromates of oxides of the second class of metals are decomposed by a strong red heat, by which the acid is resolved into the green oxide of chromium and oxygen gas; but the chromates of the fixed alkalies sustain a very high temperature without decomposition. They are all decomposed, without exception, by the united agency of heat and combustible matter. The neutral chromates of protoxides are similar in constitution to the sulphates, being formed of 1 eq. of the base and 1 of chromic acid, the formula being $MO + CrO_3$.

The chromates are in general sufficiently distinguished by their colour. They may be known chemically by the following character:—On boiling a chromate in hydrochloric acid mixed with alcohol, the chromic acid is at first set free, and is then decomposed, a green solution of the chloride of chromium being generated.

The only native chromate hitherto discovered is the red dichromate of protoxide of lead from Siberia, in the examination of which Vauquelin made the discovery of chromium.

Chromates of Potassa.—The neutral chromate from which all the compounds of chromium are directly or indirectly prepared, is made by heating to redness the native oxide of chromium and iron, commonly called *chromate of iron*, with nitrate of potassa, when chromic acid is generated, and unites with the alkali of the nitre. The object to be held in view is to employ so small a proportion of nitre, that the whole of the alkali may combine with chromic acid, and constitute a neutral chromate, which is easily obtained pure by solution in water and crystallization. For this purpose the chromate of iron is mixed with about a fifth of its weight of nitre, and exposed to a strong heat for a considerable time; and the process is repeated with those portions of the ore which are not attacked in the first operation. It is deposited from its solution in small prismatic anhydrous crystals of a lemon-yellow colour, which, according to Brooke, belong to the right prismatic system.

Chromate of potassa has a cool, bitter, and disagreeable taste. It is soluble to great extent in boiling water, and in twice its weight of that liquid at 60°; but it is insoluble in alcohol. It has an alkaline reaction, and on this account Tassaert* regards it as a subsalt; but Thomson has proved that it is neutral in composition, consisting of 52 parts or 1 eq. of chromic acid, and 47·15 parts or 1 eq. of potassa.†

Bichromate of potassa, which is made in large quantity at Glasgow for dyeing, is prepared by acidulating the neutral chromate with sulphuric, or still better with acetic acid, and allowing the solution to crystallize by spontaneous evaporation. When slowly formed it is deposited in four-sided tabular crystals, the form of which is an oblique rhombic prism. They have an exceedingly rich red

* An. de Ch. et Ph. vol. xxii. † Annals of Philosophy, vol. xvi.

colour, are anhydrous, and consist of 1 eq. of the alkali, and 2 eq. of chromic acid. (Thomson.) They are soluble in about ten times their weight of water at 60°, and the solution reddens litmus paper.

The insoluble salts of chromic acid, such as the chromates of baryta and oxides of zinc, lead, mercury, and silver, are prepared by mixing the soluble salts of those bases with a solution of chromate of potassa. The three former are yellow, the fourth orange-red, and the fifth deep red or purple. The yellow chromate of lead, which consists of 1 eq. of acid and 1 eq. of oxide, is now extensively used as a pigment, and the chromate of oxide of zinc may be used for the same purpose.

A dichromate, composed of 1 eq. of chromic acid and 2 eq. of protoxide of lead, may be formed by boiling the carbonate of that oxide with excess of chromate of potassa. It is of a beautiful red colour, and has been recommended by Badams as a pigment. (An. of Phil. xxv. 303.) It may be also made by boiling the neutral chromate with ammonia or lime-water. Liebig and Wöhler prepare it by fusing nitre at a low red heat, and adding chromate of oxide of lead by degrees until the nitre is nearly exhausted. The chromate of potassa and nitre are then removed by water, and the dicromate is left crystalline in texture, and of so beautiful a tint that it vies with cinnabar. (Pog. An. xxi. 580.)

Chromates of Silver.—When a soluble salt of chromic acid is added to a solution of nitrate of silver, a deep red-coloured precipitate is obtained, which has usually been considered as the neutral chromate of silver. But it has recently been proved by Warington (Phil. Mag. xi. 489) that if the precipitation be made with acid solutions a bichromate is formed. He also obtained the latter salt by the direct oxidation of metallic silver by a solution of bichromate of potassa acidulated with sulphuric acid. The silver is oxidized at the expense of a part of the chromic acid; while another part, by uniting with the resulting oxide, forms the bichromate, which is deposited in tabular crystals of a rich crimson colour. A chrome alum is at the same time formed, and the oxidation of this silver would appear to be induced by the affinity of the sulphuric acid for the oxide of chromium.

On boiling the bichromate in distilled water, a part is dissolved and separated as the solution cools in beautiful micaceous crystals; but, at the same time, a portion of the salt is decomposed into chromic acid and neutral chromate of silver. As thus formed, the latter is of a dark green colour: it is crimson, however, by transmitted light, and yields by trituration a powder similar in colour to the precipitated chromate.

Bichromate of Chloride of Potassium.—Peligot has described a crystalline compound in which chloride of potassium acts the part of an alkaline base in relation to chromic acid. It is prepared from bichromate of potassa and concentrated hydrochloric acid in the ratio by weight of about 3 to 4, which are to be boiled together for some time in a rather small quantity of water; and it is deposited in flat quadrangular prisms of the same colour as bichromate of potassa.

In this process there is a mutual interchange between the elements of potassa and hydrochloric acid; such that

2 eq. Chromic acid	$2CrO_3$		2 eq. Chromic acid	$2CrO_3$.
1 eq. Potassa	KO	yield	1 eq. Chlo. of Potassium	KCl.
1 eq. Hydrochloric acid	HCl		1 eq. Water	HO.

For this change to ensue there ought to be a certain excess of hydrochloric acid, and yet not so much as to decompose the chromic acid.

This salt should be dried on bibulous paper. It is permanent in the air. In pure water it is decomposed, the materials from which it was formed, bichromate of potassa and hydrochloric acid, being reproduced; but it may be dissolved without such change in water acidulated by hydrochloric acid. Peligot has made similar bichromates with the chlorides of sodium, calcium, and magnesium, and with hydrochlorate of ammonia, this last salt being exactly similar in appearance to the bichromate of chloride of potassium. (An. de Ch. et Ph. lii. 267.)

BORATES.

As the boracic is a feeble acid, it neutralizes alkalies imperfectly, and hence the borates of soda, potassa, and oxide of ammonium have always an alkaline reaction. For the same reason, when the borates are digested in any of the more powerful acids, such as the sulphuric, nitric, or hydrochloric, the boracic acid is separated from its base. This does not happen, however, at high temperatures; for boracic acid, owing to its fixed nature, decomposes at a red heat all salts, not excepting sulphates, the acid of which is volatile.

The borates of the alkalies are soluble in water, but most of the other salts of this acid are of sparing solubility. They are not decomposed by heat, and the alkaline and earthy borates resist the action of heat and combustible matter. They are remarkably fusible in the fire, a property obviously owing to the great fusibility of boracic acid itself.

The borates are distinguished by the following character:—By digesting any borate in a slight excess of strong sulphuric acid, evaporating to dryness, and boiling the residue in strong alcohol, a solution is formed which has the property of burning with a green flame.

Biborate of Soda.—This salt, the only borate of importance, occurs native in some of the lakes of Thibet and Persia, and is extracted from this source by evaporation. It is imported from India in a crude state, under the name of *Tincal*, which, after being purified, constitutes the *refined borax* of commerce. It is frequently called *sub-borate of soda*, a name suggested by the inconsistent and unphilosophical practice, now quite inadmissible, of regulating the nomenclature of salts merely by their action on vegetable colouring matter. It crystallizes in prisms of the oblique system, which effloresce on exposure to the air, and require twenty parts of cold, and six of boiling water, for solution. When exposed to heat, the crystals are first deprived of their water of crystallization, and then fused, forming a vitreous transparent substance called *glass of borax*. The crystals are composed of 69·8 parts or 2 eq. of boracic acid, 31·3 or 1 eq. of soda, and 90 or 10 eq. of water.

The chief use of borax is as a flux, and for the preparation of boracic acid. Biborate of magnesia is a rare natural production, which is known to mineralogists by the name of *Boracite*.

A new biborate of soda, which contains half as much water of crystallization as the preceding, has been lately described by Buran. It is harder and denser than borax, is not efflorescent, and crystallizes in regular octohedrons. It is made by dissolving borax in boiling water until the sp. gr. of the solution is at 30° or 32° of Beaumé's hydrometer: the solution is then very slowly cooled;

and when the temperature descends to about 133°, the new salt is deposited. It is found to be more convenient for the use of jewellers than common borax. (An. de Ch. et Ph. xxxvii. 419.)

The neutral borate of soda has been obtained by Berzelius by the action of boracic acid on carbonate of soda at a boiling heat, when carbonic acid is evolved. The solution on cooling yields crystals of the oblique prismatic system, and containing 8 eq. of water. Their constitution is there NaO,BaO_3+8 HO. They are powerfully alkaline, and on exposure to the air readily attract carbonic acid, forming the carbonate and biborate of soda. He also obtained the neutral borate of potassa, but was prevented by its great solubility from procuring it in crystals.

CARBONATES.

The carbonates are distinguished from other salts by being decomposed with effervescence, owing to the escape of carbonic acid gas, by nearly all the acids; and all of them, except the carbonates of potassa, soda, and lithia, may be deprived of their acid by heat. The carbonates of baryta and strontia, especially the former, require an intense white heat for decomposition; those of lime and magnesia are reduced to the caustic state by a full red heat; and the other carbonates part with their carbonic acid when heated to dull redness.

All the carbonates, except those of potassa, soda, and ammonia, are of sparing solubility in pure water; but all of them are more or less soluble in an excess of carbonic acid, owing doubtless to the formation of supersalts.

Several of the carbonates occur native, among which may be enumerated the carbonates of soda, baryta, strontia, lime, magnesia, and the protoxides of manganese, iron, copper, and lead; together with some double carbonates, such as dolomite or the double carbonate of lime and magnesia, and baryto-calcite or the double carbonate of baryta and lime.

The composition of the principal carbonates is stated in the following table:—

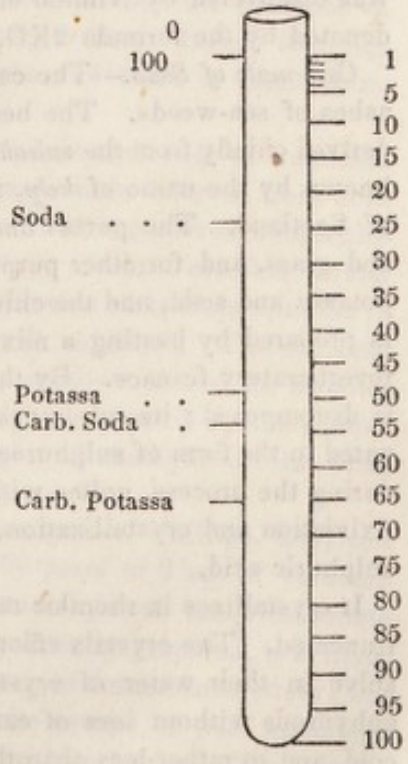
Names.	Base.	Acid.	Equiv.	Formulæ.
Carbonate of Potassa . .	47·15	1 eq.+22·12	1 eq.= 69 27	$KO+CO_2$.
Bicarbonate do. . .	47·15	1 eq.+44·24	2 eq.= 91·39	$KO+2CO_2$.
Do. in crystals with 9 or 1 eq. of water .			=100·39	
Carbonate of Soda . .	31·3	1 eq.+22·12	1 eq.= 53·42	$NaO+CO_2$.
Do. in crystals with 90 or 10 eq. of water			=143·42	
Do. . . .	63 or 7 eq. of water		. =116·42	
Bicarbonate of Soda . .	31·3	1 eq.+44·24	2 eq.= 75·54	$NaO+2CO_2$.
Do. in crystals with 9 or 1 eq. of water .			= 84·54	
Carbonate of Ammonia . .	17·15	1 eq.+22·12	1 eq.= 39·27	H_3N+CO_2.
Bicarbonate ditto . .	17 15	1 eq.+44·24	2 eq.= 61·39	$H_4NO+2CO_2$.
Carbonate of Baryta . .	76·7	1 eq.+22·12	1 eq.= 98·82	$BaO+CO_2$.
——— Strontia . .	51·8	1 eq.+22·12	1 eq.= 73·92	$SrO+CO_2$.
——— Lime . .	28·5	1 eq.+22·12	1 eq.= 50·62	$CaO+CO_2$.
——— Magnesia . .	20·7	1 eq.+22·12	1 eq.= 42·82	$MgO+CO_2$.
——— Do. in crystals with 27 or 3 eq. of water			. = 69·82	
Carbonate Protox. of Iron .	36	1 eq.+22·12	1 eq.= 58·12	$FeO+CO_2$.
Dicarbonate Protox. Copper .	79·2	2 eq.+22·12	1 eq.=101·32	$2CuO+CO_2$.
Do. in malachite with 9 or 1 eq. of water .			. =110·32	
Carbonate Protox. Lead .	111·6	1 eq.+22·12	1 eq.=133·72	

Names.	Base.	Acid.	Equiv.	Formulæ.
Dicarbon. Perox. Mercury	436	2 eq. + 22·12	1 eq. = 458·12	$2HgO + CO_2$.
Double Carbonates.				
Carbonate of Lime and Magnesia	Carb. Lime 50·62 1 eq. Carb. Magnesia 42·82 1 eq.		= 93·44	$MgO,CO_2 + CaO,CO_2$.
Carbon. of Baryta and Lime	Carb. Baryta 98 82 1 eq. Carb. Lime 50·62 1 eq.		= 149·44	$CaO,CO_2 + BaO,CO_2$.

Carbonate of Potassa.—This salt is procured in an impure form by burning land plants, lixiviating their ashes, and evaporating the solution to dryness; a process which is performed on a large scale in Russia and America. The carbonate thus obtained, is known in commerce by the names of *potash* and *pearlash*, and is much employed in the arts, especially in the formation of soap and the manufacture of glass. When derived from this source it always contains other compounds, such as sulphate of potassa and chloride of potassium; and therefore, for chemical purposes, it should be prepared from cream of tartar. On heating this salt to redness, the tartaric acid is decomposed, and a pure carbonate of potassa mixed with charcoal remains. The carbonate is then dissolved in water, and, after filtration, is evaporated to dryness in a capsule of platinum or silver.

Pure carbonate of potassa has a taste strongly alkaline, is slightly caustic, and communicates a green tint to the blue colour of the violet. It dissolves in less than an equal weight of water at 60°, deliquesces rapidly on exposure to the air, and crystallizes with much difficulty from its solution. In pure alcohol it is insoluble. It fuses at a full red heat, but undergoes no other change.

It is often necessary, for commercial purposes, to ascertain the value of different samples of pearlash; that is, to determine the quantity of real carbonate of potassa contained in a given weight of impure carbonate. A convenient mode of effecting this object is described by Faraday in his excellent work on *Chemical Manipulation*. Into a tube sealed at one end, 9½ inches long, ¾ of an inch in diameter, and as cylindrical as possible in its whole length, pour 1000 grains of water, and with a file or diamond mark the place where its surface reaches, and divide the space occupied by the water into 100 equal parts, as is shown in the annexed woodcut. Opposite to the numbers 23·44, 48·96, 54·63, and 65, draw a line, and at the first write soda, at the second potassa, at the third carbonate of soda, and at the fourth carbonate of potassa. Then prepare a dilute acid having the specific gravity of 1·127 at 60°, which may be made by mixing one measure of concentrated sulphuric acid with four measures of distilled water. This is the standard acid to be used in all the experiments, being of such strength that when poured into the tube till it reaches either of the four marks just mentioned, we shall obtain the exact quantity necessary for neutralizing 100 grains of the alkali written opposite to it. If, when the acid reaches the word *carb. potassa*, and when, consequently, we have the exact



quantity which will neutralize 100 grains of that carbonate, pure water be added until it reaches 1, or the beginning of the scale, each division of this mixture will neutralize one grain of carbonate of potassa. All that is now required, in order to ascertain the quantity of real carbonate in any specimen of pearlash, is to dissolve 100 grains of the sample in warm water, filter to remove all the insoluble parts, and add the dilute acid in successive small quantities, until by the test of litmus paper, the solution is exactly neutralized. Each division of the mixture indicates a grain of pure carbonate. It is convenient, in conducting this process, to set aside a portion of the alkaline liquid, in order to neutralize the acid, in case it should at first be added too freely. To this instrument the term *alkalimeter* is given, a name obviously derived from the use to which it is applied.

Bicarbonate of Potassa is made by transmitting a current of carbonic acid gas through a solution of the carbonate; or by evaporating a mixture of the carbonates of ammonia and potassa, the ammonia being dissipated in a pure state. By slow evaporation, the bicarbonate is deposited from the liquid in hydrated prisms with eight sides, terminated with dihedral summits.

Bicarbonate of potassa, though far milder than the carbonate, is alkaline both to the taste and to test paper. It does not deliquesce on exposure to the air. It requires four times its weight of water at 60° for solution, and is much more soluble at 212°; at this temperature it has been stated to be converted into sesquicarbonate, but H. Rose has shown that, though gradually, it at length parts with half its carbonic acid. The escape of the gas he finds to be much retarded by pressure, that of one inch of mercury making a difference; hence the loss of carbonic acid is much more rapid when a cold solution is evaporated in vacuo, both the gas and aqueous vapour being absorbed by quicklime (Pog. An. xxxiv. 149). At a low red heat it is converted into the carbonate.

Thomson, in his "First Principles," has described a sesquicarbonate, which was discovered by Nimmo of Glasgow. Its crystals contain 12 eq. of water, as denoted by the formula $2KO,3CO_2+12HO$.

Carbonate of Soda.—The carbonate of commerce is obtained by lixiviating the ashes of sea-weeds. The best variety is known by the name of *barilla*, and is derived chiefly from the *salsola soda* and *salicornia herbacea*. A very inferior kind, known by the name of *kelp*, is prepared from sea-weeds on the northern shores of Scotland. The purest barilla, however, though well fitted for making soap and glass, and for other purposes in the arts, always contains the sulphates of potassa and soda, and the chlorides of potassium and sodium. A purer carbonate is prepared by heating a mixture of sulphate of soda, saw-dust, and lime, in a reverberatory furnace. By the action of carbonaceous matter, the sulphuric acid is decomposed; its sulphur partly uniting with calcium, and partly being dissipated in the form of sulphurous acid, while the carbonic acid, which is generated during the process, unites with soda. The carbonate of soda is then obtained by lixiviation and crystallization. It is difficult to obtain this salt quite free from sulphuric acid.

It crystallizes in rhombic octohedrons, the acute angles of which are generally truncated. The crystals effloresce on exposure to the air, and, when heated, dissolve in their water of crystallization. By continued heat they are rendered anhydrous without loss of carbonic acid. They dissolve in about two parts of cold, and in rather less than their weight of boiling water, and the solution has a strong alkaline taste and reaction. The crystals commonly found in commerce

contain 10 eq. of water; but when formed at a temperature of about 80°, they retain only 7 eq.

The purity of different specimens of barilla, or other carbonates of soda, may be obtained by means of the alkalimeter above described.

Bicarbonate of Soda.—This salt is made by the same process as bicarbonate of potassa, and is deposited in hydrated crystalline grains by evaporation. Though still alkaline it is much milder than the carbonate, and far less soluble, requiring about ten times its weight of water at 60° for solution. It is found by Rose to undergo the same changes on boiling as the bicarbonate of potassa; it is converted into the carbonate by a red heat.

Sesquicarbonate.—This compound occurs native on the banks of the lakes of soda in the province of Sukena in Africa, whence it is exported under the name of *Trona*. It was first distinguished from the two other carbonates by Phillips (Journal of Science, vii.), whose analysis corresponds with that of Klaproth. Its formula is $2NaO,3CO_2+4HO$.

Carbonate of Ammonia.—The only method of obtaining the substance so called is by mixing perfectly dry carbonic acid and ammoniacal gases. In whatever proportion the two gases be mixed, they unite only in the ratio of one volume of the former to two of the latter, and condense into a white light powder. This substance therefore contains carbonic acid and ammonia in equivalent proportions, but it is probable that the elements are not arranged as expressed by the name. By the action of water it is instantly decomposed into ammonia and the sesquicarbonate.

Bicarbonate of Oxide of Ammonium.—This salt was formed by Berthollet by transmitting a current of carbonic acid gas through a solution of the common carbonate of ammonia of the shops. On evaporating the liquid by a gentle heat, the bicarbonate is deposited in small prisms of the right rhombic system, which have no smell, and very little taste. Berthollet ascertained that it contains twice as much acid as the carbonate. It cannot exist without the presence of water, of which it contains 22·7 per cent. (Berzelius), or 2 eq. It may therefore be considered as carbonate of basic water and carbonate of oxide of ammonium, or HO,CO_2+H_4NO,CO_2.

Sesquicarbonate of Oxide of Ammonium.—The common carbonate of ammonia of the shops, *sub-carbonas ammoniæ* of the pharmacopœia, is different from both these compounds. It is prepared by heating a mixture of one part of hydrochlorate of ammonia with one part and a half of carbonate of lime, carefully dried. Double decomposition ensues during the process: chloride of calcium remains in the retort, and hydrated sesquicarbonate of ammonia is sublimed. The carbonic acid and ammonia are, indeed, in proper proportion in the mixture for forming the real carbonate; but, owing to the presence of water generated by the combination of the oxygen of the lime with the hydrogen of the hydrochloric acid, part of the ammonia is disengaged in a free state.

The salt thus formed consists, according to the analysis of Phillips, Ure, and Thomson, of 34·3 parts or 2 eq. of ammonia, 66·36 parts or 3 eq. of carbonic acid, and 18 parts or 2 eq. of water. It is therefore anhydrous sesquicarbonate of oxide of ammonium, or $2H_4NO+3CO_2$. When recently prepared, it is hard, compact, translucent, of a crystalline texture, and pungent ammoniacal odour; but if exposed to the air, it loses weight rapidly from the escape of pure ammonia, and becomes an opaque brittle mass, which is the bicarbonate. The results

obtained by Rose, who has lately studied the carbonates of ammonia with care, will be given in the organic chemistry, where ammonia, as containing a compound radical, is more properly placed.

Carbonate of Baryta occurs abundantly in the lead mines of the north of England, where it was discovered by Dr. Withering, and has hence received the name of *Witherite*. It may be prepared by way of double decomposition, by mixing a soluble salt of baryta with any of the alkaline carbonates or bicarbonates. It is anhydrous, exceedingly insoluble in distilled water, requiring 4300 times its weight of water at 60°, and 2300 of boiling water for solution; but when recently precipitated, it is dissolved much more freely by a solution of carbonic acid. It is highly poisonous.

Carbonate of Strontia, which occurs native at Strontian in Argyleshire, and is known by the name of *Strontianite*, may be prepared in the same manner as carbonate of baryta. It is anhydrous, and very insoluble in pure water, but is dissolved by an excess of carbonic acid.

Carbonate of Lime.—This salt is a very abundant natural production, and occurs under a great variety of forms, such as common limestone, chalk, marble, and Iceland spar, and in regular anhydrous crystals, the density of which is 2·7. It may also be formed by precipitation. Though sparingly soluble in pure water, it is dissolved by carbonic acid in excess; and hence the spring-water of limestone districts always contains carbonate of lime, which is deposited when the water is boiled.

Daniell noticed that an aqueous solution of sugar and lime deposited crystallized carbonate of lime by exposure to the air. Gay-Lussac has proved that the sugar merely acts as a solvent, presenting lime in a favourable state for combining with the carbonic acid of the atmosphere; and that all the lime is deposited in acute rhombohedrons, which contain 5 eq. of water to 1 eq. of carbonate of lime. These crystals are insoluble and remain unchanged in cold water; but in water at 86°, or in air, they lose their combined water, and fall to powder. When boiled in alcohol they retain their form, but lose 2 eq. of water and retain 3 eq. in combination. (An. de Ch. et Ph. xlviii. 301.)

Carbonate of Magnesia.—It is met with occasionally in rhombohedral crystals, and in a pulverulent earthy state, but more commonly as a compact mineral of an earthy fracture called *Magnesite*. A specimen of magnesite from the East Indies, where, I am informed, it is abundant, has been analyzed by Henry, who found it to be nearly pure anhydrous carbonate of magnesia: it is of a snow-white colour, of density 2·56, and so hard that it strikes fire with steel. (An. of Phil. xvii. 252.) It is obtained in minute transparent hexagonal prisms with 3 eq. of water, when a solution of bicarbonate of magnesia evaporates spontaneously in an open vessel. The crystals lose their water and become opaque by a very gentle heat, and even in a dry air at 60°. By cold water they are decomposed, yielding a soluble bicarbonate and an insoluble white compound of hydrate and carbonate of magnesia; and hot water produces the same change with disengagement of carbonic acid, without dissolving any magnesia. The formula of the crystals is $MgO,CO_2 + 3HO$. (Berzelius.) Fritsche obtained in the same way, besides the salt of Berzelius, another in tabular crystals, containing 5 at. water, $MgO, CO_2 + 5HO$. When heated, it loses carbonic acid, and leaves a new compound, $4(MgO,CO_2) + MgO,5HO$.

When carbonate of potassa is added in excess to a hot solution of sulphate of

magnesia, a white precipitate falls, which after being well washed has been long considered as pure carbonate of magnesia; but Berzelius has shown that it consists of the following ingredients:—

Magnesia	44·75	82·8 or 4 eq.	Probable formula is
Carbonic Acid	35·77	66·36 or 3 eq.	
Water	19·48	36 or 4 eq.	$MgO,4HO + 3MgO,CO_2$.
	100·00	185·16 or 1 eq.	

This compound is said to require 2493 parts of cold, and 9000 of hot water for solution. It is freely dissolved by a solution of carbonic acid, bicarbonate of magnesia being generated; but on allowing the solution to evaporate spontaneously, carbonic acid is given off, and crystals of the hydrated carbonate above mentioned are obtained.

Carbonate of Protoxide of Iron.—Carbonic acid does not form a definite compound with peroxide of iron, but with the protoxide it constitutes a salt which is an abundant natural production, occurring sometimes massive, and at other times crystallized in rhombohedrons. This protocarbonate is obtained also in most of the chalybeate mineral waters, being held in solution by free carbonic acid; and it may be formed by mixing an alkaline carbonate with the sulphate of protoxide of iron. When prepared by precipitation it attracts oxygen rapidly from the atmosphere, and the protoxide of iron, passing into the state of peroxide, parts with carbonic acid. For this reason, the carbonate of iron of the pharmacopœia is of a red colour, and consists chiefly of the peroxide.

Dicarbonate of Protoxide of Copper.—It occurs as a hydrate in the beautiful green mineral called *malachite;* and the same compound, as a green powder, the *mineral green* of painters, may be obtained by precipitation from a hot solution of sulphate of protoxide of copper by carbonate of soda or potassa. When obtained from a cold solution, it falls as a bulky hydrate of a greenish-blue colour, which contains more water than the green precipitate. By careful drying its water may be expelled. When the hydrate is boiled for a long time in water, it loses both carbonic acid and combined water, and the colour changes to brown. The rust of copper, prepared by exposing metallic copper to air and moisture, is a hydrated dicarbonate.

The blue-coloured mineral, called *blue copper ore*, appears to be a hydrate and carbonate of the protoxide of copper, and consists, according to the analysis of Phillips, of (Quarterly Journal of Science, iv.)

Protoxide of Copper	69·08	118 or 3 eq.	Probable formula is
Carbonic Acid	25·46	44·24 2 eq.	
Water	5 46	9 1 eq.	$CuO,HO + 2CuO,CuO_2$.
	100·00	171·24 1 eq.	

The blue pigment called *verditer*, prepared by decomposing nitrate of oxide of copper with chalk, has a similar composition. (Phillips.)

Carbonate of Protoxide of Lead.—This salt, which is the *white lead*, or *ceruse* of painters, occurs native in white prismatic crystals derived from a right rhombic prism, the sp. gravity of which is 6·72. It is obtained as a white pulverulent precipitate by mixing solutions of an alkaline carbonate with acetate of protoxide of lead; and it is prepared as an article of commerce from the subacetate by a current of carbonic acid, by exposing metallic lead in minute division to air and moisture, and by the action on thin sheets of lead of the vapour of vinegar, by which the metal is both oxidized and converted into a carbonate.

Dicarbonate of Peroxide of Mercury.—When a solution of the nitrate of peroxide of mercury is decomposed by carbonate of soda, an ochre-yellow precipitate falls, which Phillips finds to be a dicarbonate. The protoxide appears to form no compound with carbonic acid; for when a nitrate of that oxide is decomposed by any alkaline carbonate, the precipitate is either black at first or speedily becomes so, and after being washed is quite free from carbonic acid.

Double Carbonates.—One of the most remarkable of these is the double carbonate of lime and magnesia, which constitutes the minerals called bitter-spar, pearl-spar, and dolomite. The two former occur in rhombohedrons of nearly the same dimensions as carbonate of lime. The latter is met with in great perfection in the Alps, and there usually occurs in white masses of a granular texture; the grains often cohere loosely, but other specimens are hard and compact, and when broken present the crystalline aspect of marble. Its density is 2·884. Some specimens consist of the two constituent carbonates in the ratio of their eq., as stated in the table; but the ratio of the ingredients, as may be expected, is very variable, since isomorphous substances crystallize together in all proportions. Carbonate of protoxide of manganese is often associated with them. The rock called *magnesian limestone* may be viewed as an impure earthy variety of dolomite.

The double carbonate of baryta and lime constitutes the mineral called *barytocalcite*, which Mr. Children found to contain the two carbonates in atomic proportion.

Berthier has made some interesting experiments on the production of double carbonates by fusion. Carbonate of soda, when fused with carbonate of baryta, strontia, or lime, in the ratio of their eq., yields uniform crystalline compounds, which have all the appearance of being definite. An eq. of dolomite fuses in like manner with 4 eq. of carbonate of soda. Five parts of carbonate of potassa and four of carbonate of soda, corresponding to an eq. of each, fuse with remarkable facility; and this mixture, by reason of its fusibility, may be advantageously employed in the analysis of earthy minerals.

Compounds similar to the foregoing may be generated by heating sulphate of soda with carbonate of baryta, strontia, or lime, in the ratio of their eq.; or by employing the sulphate of these bases and carbonate of soda. In like manner carbonate of soda fuses with chloride of barium or calcium; and chloride of sodium with carbonate of baryta or lime. (An. de Ch. et Ph. xxxviii.)

SECTION II.

CLASS OF SALTS. ORDER II.

HYDRO-SALTS.

In this section are included those salts only, the acid or base of which is a compound containing hydrogen as one of its elements. For reasons already assigned (page 286–7) I have already described all those salts which were for-

merly called *muriates* or *hydrochlorates* of metallic oxides as chlorides of metals, considering that in general the neutralizing power of hydrochloric acid is not due to its direct combination with an oxide, but to chlorine uniting with the metal itself. The same remark applies to the hydriodic and other hydracids, the salts of which are consequently reduced to a small number. The only salts, indeed, which are included in this section, are compounds of the hydracids with ammonia and phosphuretted hydrogen. Some of the compounds which might, as containing an hydracid, be comprehended in this section, may with greater propriety be placed in the fourth, seeing that in them the hydracid acts rather as a base or electro-positive ingredient than as an acid or electro-negative substance. This double function, which chemists have long recognized in certain metallic oxides, such as alumina and oxide of zinc, appears to be performed even by so powerful an acid as the hydrochloric. Some judicious observations on this subject have been made by Professor Kane of Dublin. (Dublin Journal of Science, i. 265.)

The compounds of ammonia with the hydracids may be described as chlorides of the hypothetical radical ammonium. The argument for doing so is derived from the similarity of the hydrochlorate of ammonia to the chloride of potassium in its crystalline form, and all its relations to other chlorides. But the argument does not apply with equal force in both cases; for to suppose a direct compound of ammonia and an hydracid is perfectly consistent with observation, whereas the existence of a compound of ammonia and an ox-acid is directly opposed to it. In the former case, therefore, we have two ways of accounting for the phenomena observed; in the latter we have but one, and that one, therefore, though hypothetical, must be adopted. As this necessity does not exist in the compounds of ammonia with the hydracids, they are treated as direct binary combinations of their constituents.

Ammonia unites with fluoride of boron, bisulphuret of carbon, and some other bi-elementary compounds, which contain neither oxygen nor hydrogen, constituting saline combinations, which are included in this section, and to which, considering the distinct alkaline character of ammonia, the ordinary nomenclature of salts is applicable.

AMMONIACAL SALTS.

These compounds are readily recognized by the addition of pure potassa or lime, when the odour of ammonia may be perceived. Those which contain a volatile acid may in general be sublimed without decomposition; but the ammonia is expelled by heat from those acids which are much more fixed than itself. The most important of these salts are thus constituted:—

Names.	Base.	Acid.	Equiv.	Formulæ.
Hydrochlorate of Ammonia	17·15	1 eq.+ 36·42	1 eq.= 53·57	H_3N+HCl.
Hydriodate do.	17·15	1 eq.+127·3	1 eq.=144·45	H_3N+HI.
Hydrobromate do.	17·15	1 eq.+ 79·4	1 eq.= 96·55	H_3N+HBr.
Hodrofluate do.	17·15	1 eq.+ 19·68	1 eq.= 36·83	H_3N+HF.
Hydrosulphate do.	17·15	1 eq.+ 17·1	1 eq.= 34·25	H_3N+HS.
Trifluoborate do.	51·45	3 eq.+ 66·94	1 eq.=118·39	$3H_3N+BF_3$.
Difluoborate do.	34·30	2 eq.+ 66·94	1 eq.=101·24	$2H_3N+BF_3$.
Fluoborate do.	17·15	1 eq.+ 66·94	1 eq.= 84·09	H_3N+BF_3.
Fluosilicate do.	17·15	1 eq.+ 78·54	1 eq.= 95·69	H_3N+SiF_3.
Carbosulphate do.	17·15	1 eq.+ 38·32	1 eq.= 55·47	H_3N+CS_2.

Hydrochlorate of Ammonia.—This salt, *sal-ammoniac* of commerce, was formerly imported from Egypt, where it is procured by sublimation from the soot of camel's dung; but it is now manufactured in Europe by several processes. The most usual is to decompose sulphate of ammonia by the chloride either of sodium or magnesium, when double decomposition ensues, giving rise in both cases to hydrochlorate of ammonia, and to sulphate of soda when chloride of sodium is used, and to sulphate of magnesia when chloride of magnesium is employed. The sal-ammoniac is afterwards obtained in a pure state by sublimation. The method now generally used in this country for obtaining sulphate of oxide of ammonium is, to decompose with sulphuric acid the hydrosulphate and hydrocyanate of ammonia which is collected in the manufacture of coal-gas; but it may also be procured either by lixiviating the soot of coal, which contains sulphate of oxide of ammonium in considerable quantity, or by digesting with gypsum impure sesquicarbonate of oxide of ammonium, procured from the destructive distillation of bones and other mineral substances, so as to form an insoluble carbonate of lime and a soluble sulphate of oxide of ammonium.

Hydrochlorate of ammonia has a pungent saline taste, a density of 1·45, and is tough and difficult to be pulverized. It is soluble in alcohol and water, requiring for solution three times its weight of water at 60°, and an equal weight at 212°. It usually crystallizes from its solution in feathery crystals, but sometimes in cubes or octohedrons. At a temperature below that of ignition it sublimes without fusion or decomposition, and condenses on cool surfaces as an anhydrous salt, which absorbs humidity in a damp atmosphere, but is not deliquescent. It is generated by the direct union of hydrochloric and ammoniacal gases, which unite in equal volumes.

Hydriodate of Ammonia.—It is formed as a white powder by the direct union in equal measures of hydriodic and ammoniacal gases, or by neutralizing a solution of hydriodic acid with ammonia, and evaporating. It crystallizes with difficulty in anhydrous cubes, is very soluble in water, and deliquesces in a moist atmosphere. In close vessels it may be sublimed without change; but it suffers partial decomposition when heated in the open air.

When a concentrated solution of this salt is digested with iodine, a brown solution is obtained, the nature of which is not understood.

Hydrobromate of Ammonia is a white anhydrous salt, which may be formed by similar processes as the hydriodate. It is soluble in water and crystallizes by evaporation in quadrilateral prisms.

Hydrofluate of Ammonia.—It is prepared by mixing one part of sal-ammoniac with 2¼ of fluoride of sodium, both dry and in fine powder, gently heating the mixture in a platinum vessel, and receiving the sublimed salt in a second platinum vessel, the temperature of which is not allowed to exceed 212°. Chloride of sodium is generated, and hydrofluate of ammonia is obtained in small anhydrous prismatic crystals, which may be preserved unchanged in the air, is partly soluble in alcohol, and dissolves readily in water. At an elevated temperature it fuses before subliming. It acts powerfully on glass even in its dry state.

When this salt is introduced in a dry state into ammoniacal gas, absorption ensues, and the resulting salt appears to be a dihydrofluate of ammonia. By sublimation it loses ammonia and becomes neutral. An acid salt, apparently a bi-hydrofluate, is obtained by evaporating the aqueous solution of the neutral hydrofluate, ammonia being disengaged. If the evaporation take place at 100°,

it separates in crystalline grains, which redden litmus, and deliquesce rapidly at common temperatures.

Hydrosulphate of Ammonia.—This salt, also called hydrosulphuret of ammonia, and formerly the *Fuming Liquor of Boyle*, is prepared by heating a mixture of one part of sulphur, two of sal-ammoniac, and two of unslaked lime. The changes which ensue have been explained by Gay-Lussac. The volatile products are ammonia and hydrosulphate of ammonia; and the fixed residue consists of sulphate of lime with chloride and sulphuret of calcium. The hydrosulphuric acid is formed from the hydrogen of hydrochloric acid uniting with sulphur, and the oxygen of the sulphuric acid is derived from decomposed lime, the calcium of which is divided between the chlorine of the hydrochloric acid and sulphur. Hydrosulphate of ammonia may also be formed by the direct union of its constituent gases, and if they are mixed in a glass globe kept cool by ice, the salt is deposited in crystals. It is much used as a reagent, and for this purpose is usually prepared by saturating a solution of ammonia with hydrosulphuric acid gas, or by precipitating sulphuret of barium with carbonate of ammonia. A mixture of sulphuret of barium, water, and sal-ammoniac, when distilled, also yields this compound. It is frequently called, by the continental chemists, sulphuret of ammonium, and has all the characters of a sulphuret.

Fluoborates of Ammonia.—Fluoboric acid combines with three times and with twice its volume of ammoniacal gas, forming a trifluoborate and difluoborate, which are liquid at common temperatures. The neutral fluoborate is formed of equal volumes of its constituent gases, and is a white volatile salt, soluble in water, but which cannot be recovered from the solution; for on evaporation, a subfluoborate of ammonia is expelled, and boracic acid is left in solution. The neutral fluoborate is formed by heating gently either of the subfluoborates.

Fluosilicate of Ammonia.—Fluosilic acid and ammoniacal gases unite by volume in the ratio of 1 to 2, forming a white volatile salt which is decomposed by water.

Carbosulphate of Ammonia.—When dry ammoniacal gas is brought into contact with bisulphuret of carbon, direct combination ensues, and there results an uncrystalline solid mass of a straw-yellow colour, which may be sublimed without decomposition. By contact with water or exposure to a moist air, an interchange ensues between the elements of water and bisulphuret of carbon, giving rise to hydrosulphuric and carbonic acids; and a sulphur-salt of an orange-yellow colour, the hydro-carbosulphuret of ammonia, is generated.

Arsenio-persulphate of Ammonia.—Berzelius states that when dry persulphuret of arsenic is exposed to ammoniacal gas, absorption ensues, and a yellowish-white compound results; but the elements are united by a feeble attraction, and on mere exposure to the air, the ammonia escapes.

SALTS OF PHOSPHURETTED HYDROGEN.

Rose has lately called the attention of chemists to the close analogy which exists in the composition of ammonia and phosphuretted hydrogen, and in some of their properties. The latter is a feeble alkaline base, which combines with some of the hydracids. The salt best known is the hydriodate of phosphuretted hydrogen, first noticed by Gay-Lussac, which is formed of 137·3 parts or 1 eq. of acid and 31·4 parts or 1 eq. of base, and crystallizes in cubes. The crystals are permanent while quite dry; but with water, or the moisture of the air, they

yield a solution of hydriodic acid, and phosphuretted hydrogen gas escapes. These salts are all decomposed by water, and exist only in the anhydrous state.

SECTION III.

CLASS OF SALTS. ORDER III.

SULPHUR-SALTS.

The compounds described in this section are double sulphurets, just as the oxy-salts in general are double oxides. Their resemblance in composition to salts is perfect. The principal *sulphur-bases* are the protosulphurets of potassium, sodium, lithium, barium, strontium, calcium, and magnesium, and hydrosulphate of ammonia; and the principal *sulphur-acids* are the sulphurets of arsenic, antimony, tungsten, molybdenum, tellurium, tin, and gold, together with hydrosulphuric acid, bisulphuret of carbon, and sulphuret of selenium. The sulphur-salts with two metals are so constituted, that if the sulphur in each were replaced by an eq. quantity of oxygen, an oxy-salt would result. The analogy between oxy-salts and sulphur-salts is rendered still closer by the circumstance that hydrosulphuric and hydrosulphocyanic acids have the characteristic properties of acidity, and unite both with ammonia and with sulphur-bases.

The sulphur-salts may be divided into families, characterized by containing the same sulphur-acid. For the purpose of indicating that such salts are double sulphurets, as well as to distinguish them readily from other kinds of salts, I shall construct the generic name of each family from the sulphur acid terminated with sulphuret. Thus the salts which contain persulphuret of arsenic or hydrosulphuric acid as the sulphur-acid are termed *arsenio-sulphurets* and *hydro-sulphurets*; and a salt composed of each of these sulphur-acids with sulphuret of potassium is termed *arsenio-sulphuret* and *hydro-sulphuret* of sulphuret of potassium. For the sake of brevity the metal of the base may alone be expressed, it being understood that the positive metal in a sulphur-salt enters as a protosulphuret into the compound.

HYDRO-SULPHURETS.

The sulphur-salts contained in this group have hydrosulphuric acid for their electro-negative ingredient. Most of them which have been studied are soluble in water, and may be obtained in crystals by evaporation. They are decomposed by exposure to the air, yielding at first bisulphurets of the metal, and then a hyposulphite. By acids the hydrosulphuric acid is expelled with effervescence. They are thus constituted:—

Name.	Sulphur-base.	Sulphur-acid.	Equiv.	Formulæ.
Hydro-sulphuret of Potassium	55·25	1 eq.+17·1	1 eq.= 72·35	KS+HS.
Ditto Sodium	40·4	1 eq.+17·1	1 eq.= 57·5	NaS+HS.

Name.	Sulphur-base.	Sulphur-acid.	Equiv.	Formulæ.
Ditto	Lithium . 26·1	1 eq.+17·1	1 eq.= 43·2	LS+HS.
Ditto	Barium . 84·8	1 eq.+17·1	1 eq.=10·19	BaS+HS.
Ditto	Strontium . 59·9	1 eq.+17·1	1 eq.= 77·0	SrS+HS.
Ditto	Calcium . 36·6	1 eq.+17·1	1 eq.= 53·7	CaS+HS.
Ditto	Magnesium . 28.8	1 eq.+17·1	1 eq.= 45·9	MgS+HS.

Hydro-sulphuret of Potassium.—This salt is obtained in the anhydrous state by introducing anhydrous carbonate of potassa into a tubulated retort, transmitting through it a current of hydrosulphuric acid gas, and heating the salt to low redness. The mass becomes black, fuses, and boils from the escape of carbonic acid gas and aqueous vapour; and after the ebullition has ceased, the gas is continued to be transmitted, until the retort is quite cold. The resulting anhydrous hydro-sulphuret of potassium, though black while in fusion, is white when cold, and of a crystalline texture; but if air had not been perfectly excluded, it has a yellow tint, owing to the presence of some bisulphuret of potassium.

The same salt is prepared in the moist way by introducing a solution of pure potassa, free from carbonic acid, into a tubulated retort, expelling atmospheric air by a current of hydrogen gas, and then saturating the solution with hydrosulphuric acid. At first the potassa, as in the former process, interchanges elements with the gas, yielding water and protosulphuret of potassium: after which the protosulphuret unites with hydrosulphuric acid. The solution should be evaporated in the retort to the consistence of syrup, a current of hydrogen gas being transmitted through the apparatus the whole time; and on cooling the salt crystallizes in large four or six-sided prisms, which are colourless if air was perfectly excluded. The crystals contain water of crystallization, have an acrid, alkaline, and bitter taste, deliquesce in open vessels, and dissolve freely in water and alcohol. On exposure to the air it acquires a yellow colour, from the formation of bisulphuret of potassium.

Hydro-sulphuret of Sodium.—It is prepared on the same principles as the former salt, and yields by evaporation colourless crystals. When a hot concentrated solution is mixed with a solution of hydrate of soda also concentrated, the mixture on cooling deposits four-sided prisms, which are protosulphuret of sodium with water of crystallization. The interchange of elements is such that

1 eq. Hydro-sulphuret and 1 eq. Soda			2 eq. Sulphuret and 1 eq. water.
NaS+HS	NaO	yield	2NaS HO.

Hydro-sulphuret of Lithium may be prepared in the same way as the two former salts, and is left by evaporation as a crystalline solid. When heated in close vessels it parts with its water of crystallization, and like the two former salts retains its acid even at a red heat.

Hydro-sulphuret of Barium.—It is prepared by the action of hydrosulphuric acid on a solution of baryta with the precautions already mentioned for excluding atmospheric air, and crystallizes by evaporation in four-sided prisms, which are very soluble in water, but dissolve sparingly in alcohol. The crystals part with their water of crystallization when heated, and at a commencing red heat give out hydrosulphuric acid, leaving pure sulphuret of barium.

Hydro-sulphuret of Strontium is prepared like the former salt, and crystallizes in large radiated prisms, which when quite dry may be kept several days ex-

posed to the air without change. When heated it loses its water and acid, and protosulphuret of strontium as a white powder is left.

Hydro-sulphuret of Calcium is formed in the same manner as the preceding salts; but it exists only in solution; for on attempting to crystallize by evaporation, hydrosulphuric acid is driven off, and the sulphuret of calcium in prisms of a silky lustre, is deposited. The hydro-sulphuret of magnesium likewise exists only in solution.

CARBO-SULPHURETS.

The acid of these sulphur-salts is bisulphuret of carbon; and the salts themselves are thus constituted :—

Names.	Sulphur.	Sulphur-acid.	Equiv.	Formulæ.
Carbo-sulphuret of Potassium	55·25	1 eq.+38·32	1 eq.= 93·57	$KS+CS_2$.
Ditto Sodium	40·4	1 eq.+38·32	1 eq.= 78·72	$NaS+CS_2$.
Ditto Lithium	26·1	1 eq.+38·32	1 eq.= 64·42	$LS+CS_2$.
Ditto Hydrosulphate of Ammonia	34·25	1 eq.+38·32	1 eq.= 72.57	$(H_3N+HS)+CS_2$.
Ditto Barium	84·8	1 eq.+38·32	1 eq.=123·12	$BaS+CS_2$.
Ditto Strontium	59·9	1 eq.+38·32	1 eq.= 98·22	$SrS+CS_2$.
Ditto Calcium	36·6	1 eq.+38·32	1 eq.= 74·92	$CaS+CS_2$.
Ditto Magnesium . . .	28.8	1 eq.+38·32	1 eq.= 67·12	$MgS+CS_2$.

Carbo-sulphuret of Potassium.—On agitating bisulphuret of carbon with a strong alcoholic solution of protosulphuret of potassium, the liquid when set at rest separates into three layers, the lowest of which is carbo-sulphuret of potassium, and is of the consistence of syrup. Another process is to digest bisulphuret of carbon at 86° in a corked bottle full of a strong aqueous solution of protosulphuret of potassium, until the latter is saturated. A concentrated solution of this salt is of a deep orange, almost red, colour; and when evaporated at 86° to the consistence of syrup, a deliquescent yellow crystalline salt is deposited, which is sparingly soluble in alcohol. On heating it to 150° it gives off water of crystallization; and when more strongly heated it is resolved into trisulphuret of potassium and charcoal.

Carbo-sulphuret of Sodium.—It is prepared like the former salt, and separates in yellow crystals from a very concentrated solution. It is deliquescent, and dissolves readily in alcohol as well as water.

The *Carbo-sulphuret of Lithium* resembles the preceding salt, and is very soluble in water and alcohol. Similar carbo-sulphurets are obtained by the action of solutions of sulphuret of barium, strontium, and calcium, on bisulphuret of carbon: the solutions are of an orange colour, and yield crystalline salts by evaporation.

Carbo-sulphuret of Hydrosulphate of Ammonia.—Zeise prepares this salt by filling a bottle with ten measures of nearly absolute alcohol saturated with ammoniacal gas and one measure of bisulphuret of carbon, and inserting a tight cork. As soon as the liquid has acquired a yellowish-brown colour, the bottle is plunged into ice-cold water, when the carbo-sulphuret is deposited either in yellow penniform crystals or as a crystalline powder. The whole is thrown upon a linen filter, and the salt after being washed, first with absolute alcohol and then with ether, is dried by pressure within folds of bibulous paper. This salt is very volatile, passing off entirely at common temperatures, and can only be preserved

in well-corked bottles. Exposed to the air it absorbs humidity and acquires a red colour. Its solution may be kept unchanged in bottles filled with it and tightly corked.

The carbo-sulphurets of barium, strontium, and calcium may be obtained by acting on bisulphuret of carbon with a solution of the protosulphurets of those metals. The resulting solutions are of an orange or brown colour, and the salts deposited by evaporation are of a citron-yellow when quite dry. The carbo-sulphuret of barium is of sparing solubility. The carbo-sulphuret of magnesium is best prepared by adding sulphate of magnesia to a solution of carbo-sulphuret of barium. Berzelius has also prepared several carbo-sulphurets of the metals of the second class.

ARSENIO-SULPHURETS.

Berzelius finds that each of the three sulphurets of arsenic is capable of acting as a sulphur-acid, giving rise to three distinct families of sulphur-salts, distinguishable by the terms *arsenio-persulphurets*, *arsenio-sesquisulphurets*, and *arsenio-protosulphurets*.

Persulphuret of arsenic is a very-powerful sulphur-acid, violently displacing hydrosulphuric acid from its combinations with sulphur-bases, even at common temperatures; and when digested with earthy or alkaline carbonates, it expels carbonic acid. The salts of this sulphur-acid may be prepared by several different methods:—

1. By digesting the persulphuret of arsenic in a solution of a sulphur-base, such as sulphuret of potassium or sodium, until it is saturated. The resulting soluble arsenio-persulphuret may be employed to prepare insoluble salts of the same sulphur-acid by means of double decomposition. If a persulphuret of potassium is used, sulphur is deposited.

2. By decomposing a hydrosulphuret of a sulphur-base with persulphuret of arsenic, in which case hydrosulphuric gas is disengaged with effervescence.

3. By decomposing a solution of an arseniate by means of hydrosulphuric acid or hydrosulphate of ammonia.

4. By dissolving persulphuret of arsenic in a solution of caustic alkali, such as potassa; when an interchange of elements between portions of the alkali and persulphuret ensues, whereby arsenic acid and protosulphuret of potassium are generated. In this case

1 eq. Persulphuret	& 5 eq. Potassa	yield	1 eq. Arsenic Acid	& 5 eq. Protosulphuret.
As_2S_5	5KO		As_2O_5	5KS.

Two salts are thus generated and co-exist in the solution, namely, arseniate of potassa and arsenio-sulphuret of potassium. Similar changes invariably occur when sesquisulphuret of arsenic, sesquisulphuret of antimony, and other sulphur-acids are boiled with alkaline solutions: an oxy-salt, the acid of which is formed of oxygen and the electro-negative metal, is always generated; and this salt, if soluble in water, remains together with the sulphur-salt in solution. An alkaline carbonate may be substituted for a pure alkali, but then carbonic acid is expelled. These principles are concerned in the production of kermes, as already explained.

5. The last method which requires mention, is by exposing a mixture of persulphuret of arsenic and an alkaline carbonate to a red heat in a covered vessel.

Carbonic acid gas is disengaged; and an interchange of elements, similar to that just explained, takes place between a portion of the alkali and the sulphuret. The fused mass, accordingly, contains an arseniate of the alkali, as well as a sulphur-salt. This tendency to the formation of a double sulphuret is the reason why, in decomposing orpiment by black flux, the whole of the arsenic is never sublimed; a part is uniformly retained in the form of a sulphur-salt, the arsenio-sesquisulphuret of sulphuret of potassium.

Most of the arsenio-persulphurets of the second class of metals are insoluble; but those of the metals of the alkalies and alkaline earths are very soluble in water, have a lemon-yellow colour in the anhydrous state, and are colourless when combined with water of crystallization or in solution. When exposed to heat in close vessels they give off sulphur, and an arsenio-sesquisulphuret is generated. In the solid state they are very permanent in the air, and even in solution oxidation takes place with great slowness. When decomposed by an acid, persulphuret of arsenic subsides, hydrosulphuric acid gas escapes, and a salt of the alkali is generated. Some chemists may doubt the possibility of the arsenio-persulphurets dissolving as such in water: they may consider the arsenic and the metal of the sulphur-base to be united with oxygen, and all the sulphur with hydrogen; but this supposition, if followed out, leads into such complex and improbable modes of combination, that I see no alternative but implicitly to admit the views here adopted.

The following table exhibits the composition of the principal arsenio-persulpurets:—

Names.	Sulph.-base.	Sulph.-acid.	Equiv.	Formulæ.
Triarse.-persulph. of Potassium	165·75	3 eq. + 155·9	1 eq. = 321.65	$3KS + As_2S_5$.
Diarse.-persulph. do.	110·5	2 eq. + 155·9	1 eq. = 266·4	$2KS + As_2S_5$.
Arsenio-persulph. do.	55·25	1 eq. + 155·9	1 eq. = 211·15	$KS + As_2S_5$.
Triarse.-persulph. of Sodium	121·2	3 eq. + 155·9	1 eq. = 277·1	$3NaS + As_2S_5$.
Do. in crystals with 270 or 30 eq. of water			= 547·1	
Diarse.-persulph. of Sodium	80·8	2 eq. + 155·9	1 eq. = 236·7	$2NaS + As_2S_5$.
Arsenio-persulph. do.	40·4	1 eq. + 155·9	1 eq. = 196·3	$NaS + As_2S_5$.
Triarse.-persulph. of Hydrosulphate of Ammonia	102·75	3 eq. + 155·9	1 eq. = 258·65	$3(H_3N + HS) + As_2S_5$.
Diarse.-persulph. do.	68·5	2 eq. + 155·9	1 eq. = 224·4	$2(H_3N + HS) + As_2S_5$.
Arsenio-persulph. do.	34·25	1 eq. + 155·9	1 eq. = 190·15	$(H_3N + HS) + As_2S_5$.

Arsenio-persulphurets of Potassium.—The diarsenio-persulphuret is best obtained by the action of hydrosulphuric acid gas on the diarseniate of potassa, and yields a colourless solution. By evaporation in vacuo it is reduced to a yellowish viscid mass which dries imperfectly, but when exposed for some time to the open air at length becomes a crystalline mass of a lemon-yellow colour, in which rhomboidal tables are perceptible. When this salt is mixed with alcohol, it is resolved into the triarsenio-persulphuret, which is insoluble in the alcohol, and the arsenio-persulphuret, which remains in solution. The latter has not been obtained in the solid state. The former is deliquescent and very soluble in water; but when its solution is gently evaporated, the residue has a radiated crystalline texture.

Arsenio-persulphurets of Sodium.—The diarsenio-persulphuret is formed like

the corresponding salt of potassium, is very soluble in water, and by evaporation yields a lemon-yellow mass, which attracts humidity from the air. On mixing its solution with alcohol it is resolved into the arsenio-persulphuret and triarsenio-persulphuret of sodium, and the latter falls in scaly crystals of snowy whiteness, which may be collected on a filter, washed with alcohol, and dried without change. This salt by solution in water and evaporation may be obtained in rhomboidal tables or prisms derived from a rhombic prism. The crystals undergo no change in the air, and contain 30 eq. of water. The arsenio-persulphuret has been obtained only in solution. The *Arsenio-persulphurets of lithium* are very analogous to those of sodium.

Arsenio-persulphurets of hydrosulphate of Ammonia.—The diarsenio-persulphuret is obtained as a colourless solution by decomposing with hydrosulphuric acid gas a solution of triarseniate of oxide of ammonium and basic water. By spontaneous evaporation it becomes a viscid mass of a reddish-yellow colour, and which cannot be fully dried without decomposition. When its solution is mixed with hydrosulphate of ammonia and agitated with hot alcohol, the triarsenio-sulphuret is deposited in colourless prisms, which, after being well washed with alcohol and dried on bibulous paper, undergo no change by exposure to the air. The arsenio-persulphuret remains in the alcoholic solution.

Analogous salts may be similarly prepared with barium, strontium, calcium, and magnesium; and insoluble compounds of the same nature may be formed by way of double decomposition by mixing soluble arsenio-persulphurets with oxy-salts of the second class of metals.

The salts in which sesquisulphuret of arsenic acts as an acid, resemble those of the persulphuret both in their general characters and mode of formation. Those formed with the protosulphuret of arsenic cannot be made in the moist way by direct union of their ingredients; but when solutions of the arsenio-sesquisulphurets are evaporated, spontaneous decomposition takes place, the salts of protosulphuret of arsenic of a reddish-brown colour subsides, while arsenio-persulphurets remain in solution.

MOLYBDO-SULPHURETS.

The electro-negative ingredient of these salts is the tersulphuret of molybdenum, and the most remarkable of them is the molybdo-sulphuret of potassium, which is readily formed by decomposing with hydrosulphuric acid gas a rather strong solution of molybdate of potassa. If no iron is present, the liquid acquires a beautiful red colour like the solution of bichromate of potassa, and on evaporation prismatic crystals with four and eight sides are deposited. Berzelius describes this compound as one of the most beautiful which chemistry can produce: the crystals, by transmitted light, are ruby-red, and their surfaces, while moist with the solution which yielded them, shine like the wings of certain insects with a metallic lustre of a rich green tint. The crystals are anhydrous, dissolve readily in water, but are insoluble in alcohol. On the addition of sulphuric or any of the stronger acids, a salt of potassa is generated with escape of hydrosulphuric acid, and precipitation of tersulphuret of molybdenum.

Soluble molybdo-sulphurets of sodium, lithium, and ammonia of a red colour, may be obtained by a process similar to that for preparing the preceding compound. The composition of these salts is as follows:—

Names.	Sulphur-base.	Sulphur-acid.	Equiv.	Formulæ.
Molybdo-sulphuret of Potassium	55·25	1 eq.+96·26	1 eq.=151·51	$KS+MoS_3$.
Molybdo-sulphuret of Sodium	40·4	1 eq.+96·26	1 eq.=136·66	$NaS+MoS_3$.
Molybdo-sulphuret of Lithium	26·1	1 eq.+96·26	1 eq.=122·36	$LS+MoS_3$.
Molybdo-sulphuret of Hydrosulphate of Ammonia	34·25	1 eq.+96·26	1 eq.=130·51	$(H_3N+HS)+MoS_3$.

Similarly constituted soluble salts of a red or orange colour may be obtained by boiling solutions of sulphuret of barium, strontium, and calcium, with an excess of tersulphuret of molybdenum. The insoluble molybdo-sulphurets may be prepared from the former by way of double decomposition.

ANTIMONIO-SULPHURETS.

When two parts of carbonate of potassa are intimately mixed with four of sesquisulphuret of antimony and one part of sulphur, and the mixture is fused, an antimonio-persulphuret of potassium is generated. On digesting in water, a subantimonio-persulphuret is dissolved, and is deposited by gentle evaporation in large colourless tetrahedrons, which become yellow on exposure to the air. The salts which this sulphur-acid forms with other bases have not been examined.

A sulphur-salt of potassium, in which sesquisulphuret of antimony is the acid, remains in solution after the kermes is deposited (page 377), and may be obtained by evaporation in vacuo in colourless irregular crystals which deliquesce rapidly in the air.

TUNGSTO-SULPHURETS.

The best known of these salts is that of potassium, in which tersulphuret of tungsten is combined with protosulphuret of potassium. It is formed when a solution of tungstate of potassa is decomposed by hydrosulphuric acid, and crystallizes by evaporation in flat quadrilateral prisms, which are anhydrous, and are of a pale red colour. It dissolves sparingly in alcohol, but is freely soluble in water, yielding an orange-coloured solution. When mixed with a quantity of acid insufficient for entire decomposition, it forms a bitungsto-sulphuret of a brown colour.

The tungsto-sulphuret of potassium unites with tungstate of potassa as a double salt, which yields a yellow solution, and crystallizes in rectangular tables of a lemon-yellow colour. It combines also with nitrate of potassa, and the resulting double salt crystallizes in large transparent crystals of a ruby-red tint, and when heated detonates like gunpowder.

The tungsto-sulphuret of sodium is prepared from tungstate of soda by hydrosulphuric acid, and crystallizes with difficulty in irregular crystals of a red colour. It deliquesces in the air, and is soluble in water and alcohol.

SECTION IV.

CLASS OF SALTS. ORDER IV.

HALOID-SALTS.

In this section are included substances composed like the preceding salts of two bi-elementary compounds, one or both of which are analogous in composition to sea-salt. The principal groups consist of double chlorides, double iodides, and double fluorides. In these the haloid-bases belong usually to the electro-positive metals, and the haloid-acids to the metals which are electro-negative. I shall apply to them the same principle of nomenclature as to the sulphur-salts.

HYDRARGO-CHLORIDES.

The haloid-acid of this family is bichloride of mercury, which reddens litmus paper, and loses the property when a haloid-base is present, thus bearing a close analogy to ordinary acids. Its principal salts which have been examined are thus constituted:—

Names.	Basic Chloride.	Bichlor. Merc.	Equiv.	Formulæ.
Dihydrargo-chloride of Potassium	149·14	2 eq.+273·84	1 eq.=422·98	$2KCl+HgCl_2$.
Do. in rhombic prisms with 18 or 2 eq. of water			=440·98	
Hydrargo-chloride of Potassium	74·57	1 eq.+273·84	1 eq.=348·41	$KCl+HgCl_2$.
Do. in acicular crystals with 18 or 2 eq. of water			=366·41	
Bihydrargo-chloride of Potassium	74·57	1 eq.+547·68	2 eq.=622·25	$KCl+2HgCl_2$.
Do. in acicular crystals with 36 or 4 eq. of water			=658·25	
Hydrargo-chloride of Sodium	59·72	1 eq.+273·84	1 eq.=333·56	$NaCl+HgCl_2$.
Do. in crystals with 36 or 4 eq. of water			=369·56	
Dihydrargo-chloride of hydrochlo. of Ammonia	105·14	1 eq.+273·84	1 eq.=378·98	$2(H_3N+HCl)+HgCl_2$.
Do. in flat rhombic prisms with 18 or 2 eq. of water			=396·98	

The preceding salts, except the last, were first prepared and examined by Bonsdorff (An. de Ch. et Ph. xliv. 189); and they are obtained by mixing the ingredients in the ratio for combining, and setting aside the solution to crystallize. The ammoniacal salt has long been known under the name of *salt of alembroth*. Bonsdorff obtained similar compounds with the chlorides of lithium, barium, strontium, calcium, magnesium, manganese, iron, cobalt, nickel, and copper. Those of lithium, calcium, magnesium and zinc are deliquescent. The hydrargo-chlorides of iron and manganese are isomorphous, and crystallize in rhombic prisms. Hydrochloric acid combines with bichloride of mercury, and yields a very soluble salt, which may be obtained in crystals: the electro-posi-

tive ingredient is here probably hydrochloric acid, and as such will be considered as chloride of hydrogen, with properties analogous to the chlorides of electro-positive metals.

AURO-CHLORIDES.

These salts, the electro-negative ingredient of which is the terchloride of gold, have been studied by Berzelius, Johnston, and Bonsdorff. They are prepared by mixing the chlorides in atomic proportions, and setting aside the solution to crystallize.

Most of them have an orange or yellow colour, and consist of single equivalents of their constituent chlorides, as is exemplified by the composition of the three following salts :—

Names.	Basic Chlorides.	Terch. Gold.	Equiv.	Formulæ.
Auro-chloride of Potassium	74·57 1 eq.	+ 305·46 1 eq.	= 380·03	$KCl + AuCl_3$.
Do. in prisms with 45 or 5 eq. of water			= 425·03	
Auro-chloride of Sodium	59·72 1 eq.	+ 305·46 1 eq.	= 365·18	$NaCl + AuCl_3$.[1]
Do. in 4-sided prisms with 36 or 4 eq. of water			= 401·18	
Auro-chloride or hydrochlorate of Ammonia	105·14 1 eq.	+ 305·46 1 eq.	= 410·60	$\left\{\begin{matrix}(H_3N + HCl)\\ AuCl_3\end{matrix}\right.$
Do. in acicular crystals with 36 or 4 eq. of water			= 446·6	

Auro-chloride of Potassium.—This salt crystallizes either in striated prisms or thin hexagonal tables, which effloresce in a dry air, and lose all their water at 212°. At a red heat the terchloride of gold is decomposed, leaving chloride of potassium and metallic gold. This salt is soluble both in water and alcohol.

Auro-chloride of Sodium crystallizes in long quadrilateral prisms, which may be exposed to the air without change, and fuse readily in their water of crystallization. The *auro-chloride of lithium* is deliquescent.

Auro-chloride of Hydrochlorate of Ammonia.—It crystallizes in transparent needles or small prisms, which become opaque by exposure to the air, and are soluble in water and alcohol.

Auro-chloride of Hydrogen.—In this compound hydrochloric acid is probably the positive chloride. It crystallizes readily in long acicular crystals of a light yellow colour when an acid solution of gold is cautiously evaporated. The crystals undergo no change in dry air, but in a moist atmosphere deliquesce into a yellow liquid.

Bonsdorff has prepared the auro-chlorides of barium, strontium, calcium, magnesium, manganese, zinc, cadmium, cobalt, and nickel. Most of them crystallize in prisms and contain water of crystallization.

PLATINO-CHLORIDES.

Both the protochloride and bichloride of platinum act as haloid-acids. Magnus prepared the platino-protochloride of potassium by mixing chloride of potassium with a solution of protochloride of platinum in hydrochloric acid. It crystallizes by evaporation in red, anhydrous, four-sided prisms, which are insoluble in alcohol, but dissolve readily in water. It consists of single equivalents of its constituent chlorides.

The *platino-protochloride of sodium* may also be prepared, is soluble in water

and alcohol, and crystallizes with difficulty. A similar salt may be formed with hydrochlorate of ammonia, and is isomorphous with that of potassium, which it also resembles in its properties, composition, and mode of preparation.

The solution of protochloride of platinum in hydrochloric acid, which has a deep red tint, is doubtless a double chloride, but it has not been obtained in crystals.

The principal salts of bichloride of platinum are those of potassium, sodium, and ammonia, which are thus constituted :—

Names.	Basic Chlorides.	Bichl. of Plat.	Equiv.	Formulæ.
Platino-bichloride of Potassium	74·57	1 eq. + 169·64	1 eq. = 244·21	$KCl + PlCl_2$.
——— Sodium	59·72	1 eq. + 169·64	1 eq. = 229·36	$NaCl + PlCl_2$.
Do. in prisms with 54 or 6 eq. of water			= 283·36	
Platino-bichloride of hydrochlorate of Ammonia	105·14	1 eq. + 169·64	1 eq. = 274·78	$(H_3N + HCl) + PlCl_2$.

Platino-bichloride of Potassium.—The production of this salt by mixing its constituents in solution, constitutes one of the best tests for potassa. It is commonly obtained as a powder, of a pale lemon-yellow colour; but by slow evaporation it yields small octohedrons of a brilliant lustre. It is anhydrous, insoluble in alcohol, and is sparingly dissolved by cold, but more freely by hot water. Heated to redness it yields chlorine, and the residue consists of platinum and chloride of potassium.

Platino-bichloride of Sodium.—This salt crystallizes in fine transparent prisms of a deep yellow-colour, which are soluble in water and alcohol. When gently heated it loses its water of crystallization, and becomes a pale yellow powder.

Platino-bichloride of Hydrochlorate of Ammonia falls as a lemon-yellow powder when sal-ammoniac is mixed with a strong solution of bichloride of platinum. It resembles the double salt of potassium in its properties and form, crystallizing in small anhydrous octohedrons when its aqueous solution is slowly evaporated. This salt is employed in the preparation of platinum, and when heated to redness leaves that metal in a spongy state.

Bonsdorff has prepared the platino-bichlorides of barium, strontium, calcium, and several other metals. Most of them crystallize with water of crystallization, and have a yellow or orange colour.

PALLADIO-CHLORIDES.

Both of the chlorides of palladium act as haloid-acids, combining with many of the metallic chlorides, when their respective solutions are mixed and evaporated. The principal ones which have been examined are those with potassium, sodium, and ammonia, which consist of single equivalents of their ingredients.

The palladio-protochloride of potassium crystallizes in four-sided prisms of a dirty yellow colour, which are anhydrous, insoluble in alcohol, and freely soluble in water. The corresponding salt of sodium is deliquescent and soluble both in water and alcohol. That of hydrochlorate of ammonia is isomorphous with the salt of potassium, which it resembles in its other properties.

The palladio-bichloride of potassium is obtained by evaporating the palladio-protochloride with nitro-hydrochloric acid, when microscopic crystals of a cinnabar-red colour are deposited which by a glass are found to be regular octohedrons.

It is anhydrous, insoluble in alcohol, and nearly so in water. When heated, or by continued ebullition, it is reconverted into the palladio-protochloride of potassium. The corresponding salt of hydrochlorate of ammonia is obtained in a similar manner, and resembles the former in form and other properties.

RHODIO-CHLORIDES.

The sesquichloride of rhodium combines with the chlorides of potassium and sodium, and the resulting salts are thus constituted:—

Names.	Basic Chlor.	Sesquichl. Rhod.	Equiv.	Formulæ.
Dirhodio-chloride of Potassium	419·14	2 eq. + 210·66	1 eq. = 359·80	$2KCl + R_2Cl_3$.
Do. in four sided prisms with 18 or 2 eq. of water			= 377·8	
Trirhodio-chloride of Sodium	179·16	3 eq. + 210·66	1 eq. = 389·82	$3NaCl + R_2Cl_3$.
Do. in prisms with 162 or 18 eq. of water			= 551·82.	

Dirhodio-chloride of Potassium.—It is obtained by mixing the respective chlorides in the ratio above assigned, and crystallizes in four-sided rectangular prisms, which are of a deep red colour, insoluble in alcohol, and contain 18 parts or 2 eq. of water combined with 359·8 parts or 1 eq. of the salt.

Hydrochlorate of ammonia yields a similar double salt, analogous in its properties to the preceding.

Trirhodio-chloride of Sodium.—This salt crystallizes in large prismatic crystals of a deep red colour, which lose part of their water in a dry air, and become covered with a red powder. They are insoluble in alcohol.

IRIDIO-CHLORIDES.

The chlorides of iridium act as haloid-acids. The most remarkable of its salts is the iridio-bichloride of potassium, which in form and properties resembles the platino-bichloride of potassium, crystallizing in brilliant octohedrons, but of a black colour, which are sparingly soluble in water. Hydrochlorate of ammonia forms with it a similar salt, which is of a deep cherry-red colour.

OSMIO-CHLORIDES.

Berzelius has described the osmio-bichloride of potassium, which resembles in form, composition, and most of its properties, the corresponding salts of platinum and iridium. It is insoluble in alcohol, and but sparingly dissolved in water; but its aqueous solution, when gently evaporated, yields octohedral crystals of a deep brown colour.

OXY-CHLORIDES.

Chemists are acquainted with a considerable number of compounds in which a metallic oxide is united with a chloride either of the same metal, which is the most frequent, or of some other chloride. These compounds are commonly termed *sub-muriates*, on the supposition that they consist of hydrochloric acid combined with two or more eq. of an oxide.

Oxy-chlorides of Iron.—When the crystallized protochloride of iron is heated without exposure to the air, the last portions of its water exchange elements

with part of the chloride of iron, yielding hydrochloric acid, which is evolved, and protoxide of iron. On raising the heat so as to expel the pure chloride of iron, a deep green oxy-chloride in scaly crystals remains. (Berzelius.)

The ochreous matter which falls when a solution of the protochloride of iron is exposed to the air, is hydrated peroxide of iron combined with some perchloride. A similar hydrate is obtained by mixing with a solution of the perchloride of iron a quantity of alkali insufficient for complete decomposition. When a solution of the perchloride is evaporated to dryness without exposure to the air, the last portions of water exchange elements with the perchloride, hydrochloric acid is disengaged, and after subliming the pure anhydrous perchloride, a compound in large, brown, shining laminæ is left, which consists of peroxide and perchloride of iron. (Berzelius.)

Mr. Phillips has described a soluble oxy-chloride which appears to consist of 1 eq. of perchloride of iron with 9 eq. of the peroxide. It is prepared by digesting hydrochloric acid with the required proportion of the moist hydrated peroxide. The solution is of a brownish-red colour, and a precipitate is occasioned either by a little more of the peroxide or a little acid, indicating the formation of other oxy-chlorides which are insoluble. (Phil. Mag. and An. viii. 406.)

By adding bleaching-liquor to protonitrate of iron, Millon obtained an oxy-chloride, corresponding to the sesquioxide, which it resembles in appearance. Its formula is $Fe_2 \left\{ \begin{matrix} O_2 \\ Cl \end{matrix} \right\}$.

Oxy-chlorides of Tin.—When a large quantity of water is poured on crystallized protochloride of tin, a portion of water and protochloride exchange elements, an acid solution is formed, containing the double chloride of tin and hydrogen, and a white powder subsides, which is a compound of the protoxide and protochloride of tin.

Oxy-chloride of Chromium.—This compound, which was long considered as the terchloride, was first shown to be an oxy-chloride by Rose. It has already been mentioned at page 383.

Oxy-chloride of Tungsten.—This compound, the nature of which was first pointed out by Rose, has already been described at page 395.

Oxy-chloride of Molybdenum.—Formerly described as the terchloride, but shown by Rose to be really similar in constitution to the two preceding compounds (page 393).

Oxy-chloride of Antimony.—It falls as a white curdy precipitate when sesquichloride of antimony is thrown into water (page 376), and, according to an analysis by Phillips, contains 7·8 per cent. of chlorine.

Oxy-chloride of Cerium.—This compound is generated by heating the hydrated protochloride, just as when the protochloride of iron is distilled.

Oxy-chloride of Bismuth.—It is prepared by pouring a neutral solution of nitrate of oxide of bismuth into a concentrated solution of sea-salt; and a similar compound, but with more oxide, is formed when a dilute solution of sea-salt is used. They are both heavy insoluble powders of a very white colour.

Oxy-chloride of Copper.—This compound falls as a green hydrate when potassa is added to a solution of chloride of copper in quantity insufficient for its complete decomposition. When its water is expelled, it becomes of a liver-brown colour. Berzelius states it to consist of 1 eq. of the chloride and 3 eq. of oxide of copper. It is used as a pigment under the name of *Brunswick green*, being

prepared for that purpose by exposing metallic copper to hydrochloric acid or a solution of sal-ammoniac. The same compound is generated during the corrosion of copper in sea-water. Millon, by the process above mentioned, obtained an oxy-chloride of copper, $Cu_2 \left\{ \begin{matrix} O \\ Cl \end{matrix} \right\}$, which seems to be a basic compound.

Oxy-chlorides of Lead.—A compound of 1 eq. protochloride to 2 eq. of protoxide of lead has been found as a colourless mineral. Another oxy-chloride with 3 eq. of the protoxide is prepared by adding pure ammonia to a hot solution of chloride of lead. It falls as a heavy white hydrate; but on expelling its water by heat, it acquires a pale yellow colour. A third oxy-chloride with a still larger proportion of oxide is used as a pigment under the name of *mineral* or *patent yellow*; and it is prepared by the action of moist sea-salt on litharge, by which means portions of the protoxide and sea-salt exchange elements, yielding soda and chloride of lead. After washing away the alkali, the mixed oxide and chloride are dried and fused. Millon states that bleaching liquor, added to nitrate of lead, throws down a white precipitate, which soon becomes brown. These colours indicate different mechanical states of the same compound, $Pb \left\{ \begin{matrix} O \\ Cl \end{matrix} \right\}$; that is an oxychloride, corresponding to the peroxide, $Pb \left\{ \begin{matrix} O \\ O \end{matrix} \right\}$.

Oxy-chloride of Mercury.—This compound is obtained as a shining crystalline powder, of a brownish-black colour, when peroxide of mercury is boiled with a solution of the bichloride. It is anhydrous, and consists of single equivalents of the oxide and chloride. Formula, $HgO_2 + HgCl_2$ or $Hg \left\{ \begin{matrix} O \\ Cl \end{matrix} \right\}$.

Millon's experiments alluded to above, and in the section on the hypochlorites, if confirmed, will add the bleaching compounds to the order of oxy-chlorides; and render it probable that oxy-chlorides in general are not compounds of oxides and chlorides, but compounds of the metal with oxygen and chlorine corresponding to the peroxides of the respective metals.

CHLORIDES WITH AMMONIA.

Several interesting compounds of chlorides with ammonia have been studied by Persoz and Rose. (An. de Ch. et Ph. xliv. 315, and li. 5, and Pog. Annalen, xx. 149.) The perchlorides of tin, titanium, antimony and iron, and the oxychloride of chromium, absorb ammonia at common temperatures; and most of the other chlorides absorb it when gently warmed. The chlorides of potassium, sodium, and barium, do not absorb ammonia; while those of strontium and calcium combine with 4 eq. of the alkali. Chloride of copper absorbs 3 eq. and acquires the same deep blue tint as the ammoniaco-sulphate of copper. Chloride of nickel unites with 3, and chloride of cobalt with 2 eq. of ammonia. Chloride of silver takes up slowly 1½ eq. Calomel absorbs half an eq. and forms a black compound; but on exposure to the air the ammonia flies off, and pure white calomel remains. Corrosive sublimate, by the aid of heat, rapidly absorbs half an eq. of ammonia, and forms a white compound, which is insoluble in water, and bears a considerable temperature without decomposition: the white precipitate of pharmacy is probably analogous in nature, though the ratio of its ingredients is different. Perchloride of titanium combines with 2 eq. and that of tin with 1. The bromides and iodides, as well as the bicyanuret of mercury, absorb ammonia in the same manner as the chlorides. Nearly all of these com-

pounds depend on very feeble affinities. Most of them lose their ammonia by mere exposure to the air, and it is expelled from nearly all by a very moderate heat. in some, as with perchloride of titanium, heat occasions reactions between the chlorine and ammonia, and the metal is insulated; but in general the alkali is simply expelled, and the chloride returns to its former condition. Though these ammoniacal chlorides may be viewed as salts in which a metallic chloride acts as an acid, they appear to be more closely allied to those singular compounds of ammonia with the oxy-salts which have already been noticed. To this remark some of them, of which the ammoniacal chloride of mercury is an instance, are probably exceptions, and are rather, as Kane has shown, to be viewed as compounds of amide. They will be referred to in this form in the organic chemistry.

CHLORIDES WITH PHOSPHURETTED HYDROGEN.

The analogy which Rose has traced between ammonia and phosphuretted hydrogen is especially remarkable in the compounds which they both form with metallic chlorides. He has examined the compounds of phosphuretted hydrogen with the perchlorides of titanium, tin, antimony, iron and alumina, all of which correspond to ammoniacal chlorides of similar composition. The phosphuretted hydrogen is in all readily displaced by water, or a solution of ammonia. Rose observed that the resulting compound is the same in character and composition whichever of the two kinds of phosphuretted hydrogen were used in its preparation. He also found that the gas, when displaced from perchloride of titanium by water, does not inflame spontaneously; whereas, if displaced by a solution of potassa or its carbonate, by carbonate of ammonia or hydrochloric acid, the gas is spontaneously inflammable. He was thus able to disengage at will either variety of phosphuretted hydrogen from the same compound, without reference to the kind which had been used in its preparation. These facts first led Rose to the opinion that the two gases of phosphorus and hydrogen must be identical in composition.

DOUBLE IODIDES.

These compounds have not as yet been closely studied; but there is no doubt that the iodides are capable of forming with each other an extensive series of compounds. Bonsdorff obtained the hydrargo-biniodide of potassium by saturating a strong solution of iodide of potassium with biniodide of mercury: it may also be formed by dissolving corrosive sublimate in a solution of iodide of potassium, evaporating to dryness, and digesting in alcohol, when the double iodide is dissolved, and chloride of potassium is left. A variety of double iodides have been described by Boullay, and among them a compound of biniodide of mercury and hydriodic acid. (An. de Ch. et Ph. xxxiv.) In general the double hydrargo-biniodides contain single equivalents of the respective iodides. Liebig obtained a compound of the bichloride and biniodide of mercury, consisting of 2 eq. of the former to 1 eq. of the latter, as indicated by the formula $HgI_2+2HgCl_2$.

Several compounds of biniodide of platinum with other iodides have been studied by Kane and Lassaigne. (Dublin Journal of Science, i. 304, and An. de Ch. et Ph. li. 125.) The compounds at present known are thus constituted:—

Names.	Basic Iod.	Biniod. Plat.	Equiv.	Formulæ.
Platino-biniodide of Potassium	165·45	1 eq.+351·4	1 eq.=516·85	KI+Pt I_2.
Do. of Sodium . . .	150·6	1 eq.+351·4	1 eq.=502·0	NaI+Pt I^2.
Do. of Hydriodate of Ammonia	144·45	1 eq.+351·4	1 eq.=495·85	NH_4I+Pt I_2.
Do. of Barium . . .	195	1 eq.+351·4	1 eq.=546·4	BaI+Pt I_2.
Do. of Zinc . . .	158·6	1 eq.+351 4	1 eq.=510·0	ZnI+Pt I_2.
Do. of Hydrogen . .	127·3	1 eq.+351·4	1 eq.=478·7	HI+Pt I_2.

The platino-biniodide of potassium is prepared by digesting an excess of biniodide of platinum in a rather concentrated solution of iodide of potassium. By spontaneous evaporation it crystallizes in small rectangular plates surmounted sometimes with a four-sided pyramid, which are anhydrous, unchanged in the air, and insoluble in alcohol. The colour of the crystals is black with a metallic lustre, and they yield a deep claret-coloured solution with water. The biniodide of platinum appears to combine also with the iodide of platinum; but the compound has only been obtained in solution.

The platino-biniodides of sodium, barium, and zinc are obtained in the same manner as that of potassium, crystallize with difficulty, are deliquescent in the air, and dissolve in water and alcohol. The ammoniacal salt is analogous in its properties to that of potassium, with which it appears also to be isomorphous.

Platino-biniodide of Hydrogen.—This compound consists of hydriodic acid and biniodide of platinum, in which the former is regarded as the electro-positive element. It is prepared by acting on biniodide of platinum with a cold dilute solution of hydriodic acid, which gradually acquires a deep claret colour, and by evaporation under a bell-jar with quicklime, deposits black acicular crystals. The crystals become moist by exposure to the air.

Oxy-iodides.—The principal oxy-iodides at present known to chemists are those formed by the oxide and iodide of lead. When iodide of potassium is mixed with acetate of oxide of lead in excess, the yellow chloride at first formed combines with oxide of lead and acquires a white colour; and the same compound is obtained directly by employing a subacetate. Denot finds that there are three oxy-iodides, in which 1 eq. of iodide of lead is united with 1, 2, and 5 eq. of oxide of lead.

DOUBLE BROMIDES.

These compounds have not yet been studied; but Bonsdorff has proved the possibility of forming compounds similar in composition and properties to the double chlorides. He obtained the hydrargo-bibromide of potassium in crystals, consisting of 1 eq. of each bromide united with 2 eq. of water.

DOUBLE FLUORIDES.

The researches of Berzelius have led to the formation of several extensive families of double fluorides, in which the fluorides of boron, silicon, titanium, and of other electro-negative metals are the acids, and the flourides of electro-positive metals are bases. In some instances hydrofluoric acid is a haloid-acid; but more commonly it acts the part of a base.

Hydro-fluorides.—In this family hydrofluoric acid is combined with the fluorides of electro-positive metals. If an equivalent of any electro-positive metal be indicated by M, then the general formula for this family is MF + HF.

The hydro-fluoride of potassium is made by mixing hydro-fluoric acid with a solution of fluoride of potassium, and evaporating by a gentle heat in a platinum capsule. It commonly crystallizes in confused laminæ; but by slow evaporation in square tables or cubes, which are anhydrous and dissolve freely in pure water. It fuses readily when heated, and loses all its hydrofluoric acid at a low red heat.

The hydro-fluoride of sodium is prepared as the preceding salt, and by spontaneous evaporation yields anhydrous rhombohedral crystals. It is sparingly soluble in cold, but much more freely in hot water. The hydrofluoride of lithium is also of sparing solubility. The fluorides of barium, strontium, calcium, and magnesium do not combine with hydrofluoric acid.

BORO-FLUORIDES.

When the terfluoride of boron (fluoboric acid gas) is acted upon by water, one out of every four eq. of the gas interchanges elements with water, giving rise to hydrofluoric and boracic acids, the former of which combines as a haloid-base with undecomposed terfluoride of boron, constituting the boro-hydrofluoric acid, but which may be viewed as the *boro-fluoride of hydrogen*. This change is such that

4 eq. Terfluoride of Boron	$4BF_3$	yield	3 eq. Terfluoride of Boron	$3BF_3$.
			3 eq. Hydrofluoric Acid	3HF.
and 3 eq. of water	3HO		and 1 eq. Boracic Acid	BO_3.

By careful concentration and cooling, the boracic acid separates as a crystalline powder, and the boro-fluoride of hydrogen remains in solution. It is strongly acid to test paper, and its composition is indicated by the formula $HF + BF_3$, being an eq. of each fluoride. On adding potassa to this compound, it interchanges elements with hydrofluoric acid, and there results the boro-fluoride of potassium, $KF + BF_3$, the hydrogen being simply displaced by potassium. The protoxides of most other metals act precisely like potassa, and therefore the general formula of these compounds is $MF + BF_3$. When exposed to a strong heat, they all give off terfluoride of boron, and a metallic fluoride is left.

Boro-fluoride of Potassium.—It is prepared by dropping boro-fluoride of hydrogen drop by drop into a solution of a salt of potassa, and falls as a gelatinous transparent hydrate, which is a white very fine powder when dried It has a slightly bitter taste, and is quite neutral to test paper, is very sparingly soluble in alcohol and cold water, but is dissolved freely by hot water, and subsides on cooling in small brilliant anhydrous crystals. At a strong red heat it gives off the terfluoride of boron, and fluoride of potassium remains.

The *boro-fluoride of sodium* is very soluble in water, and is therefore best obtained by the direct action of boro-fluoride of hydrogen on fluoride of sodium. It crystallizes by slow evaporation in large rectangular prisms, which redden litmus paper strongly. The boro-fluoride of lithium also crystallizes in large prisms, is very soluble in water, and deliquesces in the air.

The *boro-fluoride of barium* is prepared by adding carbonate of baryta to boro-fluoride of hydrogen till it ceases to be dissolved, avoiding any further addition On evaporating to the consistence of a syrup long acicular crystals form, and by keeping the solution in a warm place it yields flat, four-sided, rectangular prisms

It is acid to test paper, and deliquescent. The boro-fluoride of calcium and magnesium may be prepared in a similar manner, and are soluble in water. Lead forms a soluble boro-fluoride, which crystallizes in the same manner as the boro-fluoride of barium.

SILICO-FLUORIDES.

The acid solution, called *silico-hydrofluoric acid* may be viewed as the *subsesqui-silico-fluoride of hydrogen*, a compound of 157·16 parts or 2 eq. of fluoride of silicon and 59·04 or 3 eq. of fluoride of hydrogen (hydrofluoric acid), as indicated by the formula $3HF + 2SiF_3$. When the solution is neutralized with potassa, the alkali interchanges elements with the fluoride of hydrogen, water and fluoride of potassium are generated, and the latter combines with the fluoride of silicon. This double fluoride consists, therefore, of 157·16 parts or 2 eq. of fluoride of silicon, and 173·49 or 3 eq. of fluoride of potassium, the formula of which is $3KF + 2SiF_3$. A similar change ensues with the protoxides of most other metals, and hence the general formula of the silico-fluorides is $3MF + 2SiF_3$. On exposing these compounds to a red heat fluoride of silicon is disengaged.

Silico-fluoride of Potassium.—This salt falls as a semi-transparent jelly, which has the property of reflecting the colours of the rainbow; but when collected on a filter and dried, it becomes a dense white powder. By evaporating a saturated aqueous solution, it separates in minute anhydrous crystals. It is sparingly soluble in hot water, and still less so in cold water.

The *silico-fluoride of sodium* resembles the former salt, but is much more soluble in hot water. By evaporation it is obtained in minute anhydrous hexagonal prisms. The silico-fluoride of lithium forms similar crystals, but is more soluble in water.

The *silico-fluoride of barium* gradually falls in microscopic crystals, which through a glass appear as elongated prisms, when chloride of barium is mixed with the silico-fluoride of hydrogen, hydrochloric acid remaining in solution. This salt is very sparingly soluble in water whether hot or cold.

The silico-fluorides of strontium, calcium, magnesium, and lead are best prepared by dissolving their respective carbonates in silico-fluoride of hydrogen. The salt of strontium crystallizes in short quadrilateral prisms, which lose their water of crystallization at a gentle heat and become opaque. For complete solubility in water, they require a slight excess of hydrofluoric acid to be present, and then they dissolve freely. The salt of calcium crystallizes in regular quadrilateral prisms. It dissolves readily in water acidulated with hydrofluoric or hydrochloric acids, but is decomposed by pure water, yielding an acid soluble salt, and an insoluble sub-salt. The salts of magnesium and lead are very soluble, and leave a gummy mass by evaporation.

The silico-fluorides of manganese, iron, zinc, cobalt, nickel, and copper are soluble in water, and crystallize in similar hexagonal prisms, probably isomorphous, which contain respectively 1 eq. of the silico-fluoride and 7 eq. of water of crystallization.

TITANO-FLUORIDES.

Hydrofluoric acid dissolves titanic acid, and forms with it an acid solution which may be viewed as the titano-fluoride of hydrogen, consisting of 61·66

parts or 1 eq. of bifluoride of titanium, and 19·68 or 1 eq. of fluoride of hydrogen, expressed by the formula $HF + TiF_2$. When mixed with potassa, water and fluoride of potassium are generated, and the titano-fluoride of potassium results, the formula of which is $KF + TiF_2$. By substituting most other protoxides for potassa similar salts may be prepared, the general formula being $MF + TiF_2$.

Few of the titano-fluorides have as yet been studied. That of potassium crystallizes by evaporation in scales like boracic acid, which are anhydrous, and but sparingly soluble in cold water. The titano-fluoride of sodium is very soluble, and crystallizes with difficulty.

Similar double fluorides may be formed, in which the fluorides of molybdenum, tellurium, and platinum act as the electro-negative ingredients. Few of them, however, have as yet been studied. Berzelius has prepared the alumino-fluorides of potassium and sodium, and the zircono-fluoride of potassium. He employed the latter in the preparation of metallic zirconium. The alumino-fluoride of sodium is found in nature as a rare mineral called *cryolite*.

OXY-FLUORIDES.

Several fluorides combine with oxides in the same manner as chlorides and iodides. An oxy-fluoride of aluminium is prepared as an insoluble gelatinous hydrate by digesting hydrate of alumina in a solution of the sesquifluoride of aluminium. This oxy-fluoride, combined with silicate of alumina, constitutes the topaz. The neutral fluorides of cobalt, nickel, and copper are decomposed by hot water, being resolved into soluble hydro-fluorides, and insoluble oxy-fluorides. Several other fluorides doubtless undergo a similar change. The oxy-fluoride of lead is generated either by digesting fluoride of lead in solution of ammonia, or by fusing together the fluoride and oxide of lead. It is more soluble than the fluoride, and the solution by exposure to the air gives a precipitate of carbonate of oxide of lead. The fluoride of lead also combines by fusion with chloride of lead. Fluoride of calcium forms a very fusible compound with sulphate of lime.

PART III.

ORGANIC CHEMISTRY.

INTRODUCTORY.

Organic Chemistry is so called because it treats of the substances which form the structure of organized beings, and of their products, whether animal or vegetable. It has long been known, that all organized structures, as well as all the substances formed in or by these, are, in great part, composed of a very limited number of elements; insomuch that a large proportion of them may be described as consisting, almost exclusively, of only four simple substances, namely, Carbon, Hydrogen, Oxygen, and Nitrogen.

But while these four elements undoubtedly constitute the chief part of all organized tissues, and while such products as woody fibre, sugar, starch, gum, fat, oils, and many organic acids, contain only the first three, that is, Carbon, Hydrogen and Oxygen, we must not forget that other elements occur in the organized kingdoms of nature; some of them, such as those of Phosphate of Lime, in large quantity; and all, whether they occur in smaller or greater proportion, as truly essential to animal and vegetable life, as the four elements above mentioned, the predominance of which characterizes the organic world.

Thus, no plant can grow, or form cells, or even fibre, without the presence of certain mineral, or saline compounds, which are derived from the soil, and which, when the plant is burned, constitute its ashes. These are, Potash, Soda, Lime, Magnesia, with, occasionally, oxides of Iron and Manganese, as bases; and Silicic Acid, Phosphoric Acid, Sulphuric Acid, Chlorine and Fluorine, as acids and acid-radicals.

Again, the juices of all plants, and more especially their roots and seeds, contain some one or more of the compounds known by the names of albumen, fibrine, and caseine. Now these compounds contain small, but absolutely essential proportions of sulphur and phosphorus, besides earthy and alkaline phosphates.

Lastly, the bones of animals contain not only phosphate of lime, but also phosphate of magnesia and fluoride of calcium, both in considerable quantity; and Iron is an unfailing constituent of blood.

To the four elements first mentioned, as constituting the chief mass of organic substances, we must therefore add, as no less essential, although for the most part in smaller proportion, the following metalloids, Chlorine, Fluorine, Sulphur, Phosphorus, and Silicon; and the following metals, Potassium, Sodium, Calcium, Magnesium, Iron, and occasionally Manganese.

It thus appears that the fourteen or fifteen elements which constitute the chief mass of the mineral or inorganic world, are almost the same which occur in organized matter: the difference being chiefly this, that in inorganic nature the *predominant* elements, nearly in the order of their abundance, are, Oxygen, Hydrogen, Nitrogen, Silicon, Chlorine, Sodium, Aluminum, Carbon, and Iron, after which follow Potassium, Calcium, Magnesium, Sulphur, Phosphorus, and Fluorine; while in the organic department the order is nearly as follows, Carbon, Oxygen, Hydrogen, Nitrogen, Potassium, Calcium, Phosphorus, Silicon, Sulphur, Sodium, Magnesium, Chlorine, Iron, and Fluorine. Aluminum, so very abundant in the mineral kingdom, hardly ever occurs in organic compounds, and when it does occur, is perhaps accidental.

The above considerations are sufficient to show, that there is no essential distinction to be made between organic and inorganic Chemistry, founded on the nature of the elements concerned.

Neither is there any such distinction to be pointed out in regard to the laws of combination and decomposition which prevail in these different departments of chemistry; for we find the same affinities operating; and although organized tissues, and their products, have, in general, a more complicated constitution than inorganic compounds, containing a larger number of equivalents of their elements, and consequently having much higher atomic weights, we cannot consider such characters as forming a valid ground of distinction.

But while we should find it very difficult, if not impossible, to draw the line between inorganic and organic Chemistry on scientific principles, we may still recognize, for convenience sake, a certain distinction, founded, first, on the origin of substances, whether animal and vegetable, or mineral; and secondly, on the uniform predominance of carbon in animal and vegetable matter.

In reference to the first point, it is to be observed, that, although the elements concerned are those common to the inorganic and organic kingdoms, the compounds which constitute the latter are formed under peculiar circumstances, such as, for the most part, cannot be imitated in our experiments.

It is true that chemistry has succeeded, in some cases, in forming artificially certain compounds which occur as products of organic life, such as Urea, Formic Acid, and Oil of Spiræa. But, in the first place, most, if not all of these, require for their production the aid of an organic product; thus, Formic Acid is produced from Starch, Oil of Spiræa from Salicine; and although Urea may be obtained from Cyanic Acid and Ammonia, it is doubtful if either Cyanogen or Ammonia can be obtained except from organic compounds, directly or indirectly. Secondly, it is particularly to be noticed, that we have not yet succeeded in forming, artificially, either an organized tissue, or even any one of the compounds (albumen, &c.) of which such tissues are made. Those organic compounds which have been artificially formed, are invariably *products of decomposition*, or, in other words, the excretions or secretions of organized bodies; and are far less complex in their constitution than organized structures.

From these facts we draw the conclusion, that certain circumstances, of which the most important is the *vital force*, so modify the play of affinities in organized

beings, as to produce the compounds usually termed organic, which, so far as they are capable of entering into the composition of tissues, cannot be imitated by art.

In regard to the second peculiarity of organic compounds, namely, the predominance of carbon in their composition, we observe that, as this carbon is united to the three gases, Oxygen, Hydrogen, and Nitrogen, with each of which it forms gaseous compounds, and as, further, the latter elements, among themselves, form compounds, such as water and ammonia, which are also volatile, so the action of heat on organic compounds is characteristic; producing *combustion* of all, save the ashes, when there is free access of air; and *charring* them, or, in other words, causing the separation of part of their carbon, in close vessels, while the greater part is dissipated in the form of volatile products.

Here, then, we have a ready test of organic matter, which is so characteristic, that we might almost define Organic Chemistry as the Chemistry of such compounds as are charred when heated to redness in close vessels. There are very few substances, indeed, of organic origin, which do not exhibit this character.

Organic Chemistry has been defined as the Chemistry of Compound Radicals; but, although we must admit the existence of many such radicals in Organic Chemistry, we cannot adopt this definition in contradistinction to that of Inorganic Chemistry, as the Chemistry of Simple Radicals, because the recent progress of science has led, or almost compelled us to admit the existence of compound radicals in Inorganic Chemistry, as has been explained in the first Part of this work.

It is, perhaps, worth while to point out, that all the organic compound radicals hitherto established, or supposed to exist, are compounds of carbon, if we except amidogen, which contains only hydrogen and nitrogen.

It is also proper here to state, that, under the name of organic compounds, many substances are treated of which do not occur in nature, but which have been obtained by subjecting true organic products to various influences: to that, for example, of heat, as in what is called the destructive distillation, which yields such substances as naphtha, naphthaline, &c.; or to the action of chlorine or bromine, of sulphuric or nitric acids, of alkalies, &c., by all which means whole series of new compounds are obtained. Lastly, some very interesting and important compounds are included under the term organic, which arise from the addition of elements not naturally occurring in the organic kingdom; as for example, kakodyle and its compounds, which contain arsenic as an essential constituent; and the very singular bases in which platinum is added to the usual elements of organic alkalies.

But while, as has just been stated, compound radicals are not exclusively characteristic of organic chemistry, we may still derive great assistance from attending to the compound radicals of organic chemistry. For while we admit the existence of such radicals in inorganic chemistry, along with simple radicals, we must bear in mind that all the organic radicals as yet discovered are compound, and many of them exceedingly complex, containing three or four elements.

It is true that we are not yet acquainted with the radicals of a very large proportion of organic compounds; such as the principal organic acids, the organic alkalies, &c. But the known organic radicals furnish us with the means of classifying many most important substances, just as we classify the compounds of any metalloid or of any metal together. As to those groups or series of

organic compounds, the radicals of which are not yet known, we can only class them according to analogies of properties, of composition, or of both.

With these introductory remarks, we shall proceed to consider the known organic compound radicals, and their derivatives.

COMPOUND ORGANIC RADICALS.

A compound radical is a substance which, although containing two or more elements, enters into combination with elementary bodies as if it were itself elementary, and in ordinary circumstances performs exactly the part of an element.

In the first Part of this work, we have already admitted as probable the existence of inorganic compound radicals, such as SO_4, the radical of sulphuric acid, and NO_6, that of nitric acid. These bodies are, in their relations to others, entirely analogous to chlorine. Thus we may represent the acids of these three radicals, with their potassium and silver salts as follows :—

		Acid.	Potassium Salt.	Silver Salt.
Radicals	Chlorine	H+Cl	K+Cl	Ag+Cl
	SO_4	H+SO_4	K+SO_4	Ag+SO_4
	NO_6	H+NO_6	K+NO_6	Ag+NO_6

The compound inorganic radicals, SO_4, and NO_6, therefore, perform exactly the part of a metalloid of the group of chlorine.

But there have also been briefly mentioned, in the first Part, certain compound organic radicals, which not only exhibit, in their relations, characters analogous to those of chlorine, but actually exist, like chlorine, in the separate state, which is not the case with SO_4 and NO_6, these latter being only known in combination.

The organic radicals here alluded to are Cyanogen, C_2 N=Cy, and Mellone C_6N_4=Me (see Part II., p. 271). They may be compared to chlorine exactly like the two above mentioned inorganic compound radicals. Thus,

		Acid.	Potassium Salt.	Silver Salt.
Radicals	Chlorine Cl	H+Cl	K+Cl	Ag+Cl
	Cyanogen Cy	H+Cy	K+Cy	Ag+Cy
	Mellone Me	H+Me	K+Me	Ag+Me

Cyanogen and Mellone are, therefore, radicals of the nature of the chlorine group of metalloids. The bisulphuret or cyanogen, or sulphocyanogen, C_2N S_2=CyS_2, although it contains three elements, plays the same part as chlorine or cyanogen, and forms with hydrogen the acid H + CyS_2, and with potassium the salt K + CyS_2.

Some compound organic radicals appear more analogous to the combustible group of metalloids, that is, to carbon, sulphur, or phosphorus; inasmuch as they form acids with oxygen, or rather with the elements of water like those metalloids, and are besides capable of entering into combination with chlorine, iodine, &c. Such radicals are carbonic oxide, CO, or rather an isomeric modification of it, C_2O_2; acetyle, C_4H_3; and formyle, C_2H. Each of these may be

viewed as the radical of a powerful acid; for $C_2O_3 + O = C_2O_3$ is dry oxalic acid; $C_4H_3 + O_3$ is dry acetic acid; and $C_2H + O_3$ is dry formic acid. Again, the first forms with chlorine the compound $C_2O_2 + Cl_2$, called phosgene gas or chlorocarbonic acid, while the two others yield $C_4H_3 + Cl$, the chloride of acetyle, and $C_2H + Cl_3$ the perchloride of formyle.

Further, there are organic compound radicals which play the part of metals, forming salts with chlorine, iodine, sulphur, cyanogen, &c., and yielding, with oxygen, compounds possessing basic properties analogous to those of metallic oxides. Such radicals are ethyle, C_4H_5, methyle, C_2H_3, and kakodyle, $C_4H_6As_2$.

Radicals.	Oxygen Compound.	Chlorine Compound.	Cyanogen Compound.	Sulphur Compound.
Ethyle C_4H_5=Ae	AeO	AeCl	AeCy	AeS
Methyle C_2H_3=Mt	MtO	MtCl	MtCy	MtS
Kakodyle $C_4H_6As_2$=Kd	KdO	KdCl	KdCy	KdS

Lastly, there are some compound organic radicals, which partake of the characters of the two last groups, forming, like the acetyle group, acids and not bases with oxygen; but yielding, with chlorine, sulphur, cyanogen, &c., compounds analogous to those formed by the ethyle group. To this division belong Benzoyle, $C_{14}H_5O_2$=Bz; Cinnamyle, $C_{18}H_8O_2$=Ci: and several others. Benzoyle and cinnamyle, with the addition of oxygen and the elements of water, produce benzoic acid, BzO,HO, and cinnamic acid, CiO,HO. This group is characterized by forming with hydrogen certain essential oils. Thus, benzyle yields, with hydrogen, the essential oil of bitter almonds, BzH; cinnamyle yields the oil of cinnamon, CiH; and salicyle, $C_{14}H_5O_4$=Sa, another radical of this group, forms, with hydrogen, the oil of spiræa, SaH.

These brief statements will serve to show that there are different kinds or groups of compound radicals, just as there are of simple ones; and further, that these compound radicals exhibit a very remarkable tendency to combine with simple radicals, and, in fact, to act the part of elementary bodies. And let us here bear in mind that the only real difference, in this point of view, between cyanogen and chlorine is this, that in the case of the former we can prove the radical to be compound, while we cannot as yet do this in the case of the latter. But, as formerly pointed out, we call chlorine, and indeed all other elements simple, only because we have not been able to show them to be compound; without having any certainty that they are really and absolutely simple. If we could not resolve cyanogen into carbon and nitrogen, we should be compelled to add it to the list of elements.

But although compound radicals usually act towards other bodies as if simple, and consequently combine generally with simple substances, they are also capable of uniting with each other. In fact, this is but another proof of their close resemblance to elementary bodies in their relations; for as simple metals, such as potassium and silver, unite with cyanogen just as with chlorine, so also such compound radicals as are analogous to metals can combine with cyanogen, itself a compound radical. Thus ethyle, methyle, benzoyle, and kakodyle all combine with cyanogen, yielding compounds formed of two organic radicals, one playing the part of a metalloid, the other that of a metal.

Compounds of this nature furnish the very best proof and illustration of the advantages which we derive from the doctrine of compound radicals, acting like

elements, whenever we are justified by facts in adopting and applying it. Thus a compound has been formed by the mutual action of a compound of kakodyle and a compound of cyanogen, the analysis of which proves that it contains carbon, hydrogen, nitrogen, and arsenic, in the relative proportions indicated by the formula $C_6H_6NAs_2$. What view are we to take of such a formula? and if we look on the compound as one formed of these four elements indiscriminately united, how are we to retain such an isolated fact in the memory? But if, on the other hand, we view it as the cyanide of kakodyle, $= C_4H_6As_2 + C_2N$, or using the abbreviated notation appropriate to compound radicals, KdCy, we are at once enabled to retain the composition and chemical relations of the compound. Moreover, when we find that the radical, Kd ($=C_4H_6As_2$) exists in a separate form, and that it forms, with oxygen, two compounds, KdO and KdO_3; with chlorine, KdCl; with sulphur, KdS; and that, in short, it plays the part of a metal in all its compounds, and may in fact be separated from some of these by metals having stronger affinities than itself, we are supplied with an idea which serves to connect and to fix all these any many more analogous facts in the memory.

When we further observe, to pursue the same example, that the cyanide of kakodyle, KdCy, when acted on by hydrochloric acid, gives rise to hydrocyanic acid and chloride of kakodyle; and that, when acted on by potassa, it yields cyanide of potassium and oxide of kakodyle, we acquire so many additional proofs of the entire analogy between simple and compound radicals in their relations to other bodies. For the two changes or reactions above-mentioned are expressed by the equations, KdCy + HCl = KdCl + HCy; and KdCy + KO = KdO + KCy; and these equations are exactly similar to those which occur most frequently in inorganic chemistry.

The facts already ascertained with regard to those compound organic radicals, whose existence has been either established, or rendered highly probable, entitle us to conclude that all organic compounds contain one or more organic radicals, combined either with each other, or with elementary radicals. In studying, therefore, any organic product, one chief object is to determine what organic radical or radicals it contains, since the knowledge of these at once gives us a means of classification.

Thus alcohol, on the theory of compound radicals, is considered as the hydrated oxide of ethyle; ethyle being an organic radical, C_4H_5. So that alcohol, $C_4H_6O_2$ is more accurately represented as $(C_4H_5)\,O + HO$; or, if we represent ethyle, C_4H_5, by Ae, then alcohol becomes AeO,HO, hydrated oxide of ethyle; perfectly analogous to KO,HO, hydrated oxide of potassium, or caustic potash.

Again, benzoic ether, $C_{18}H_{10}O_4$, is viewed as benzoate of oxide of ethyle, $C_4H_5O + C_{14}H_5O_3$: or, more briefly, AeO + BzO. Here we have the basic oxide of one radical united with the acid oxide of another.

It is very often by means of thus tracing the different organic radicals, that we are enabled to explain the very numerous cases of isomerism, which occur in organic chemistry. Thus, the following compounds have the same composition in 100 parts:—

Aldehyde . . .	$C_4H_4O_2$
Acetic Ether . . .	$C_8H_8O_4$
Butyric Acid . . .	$C_8H_8O_4$

Now, aldehyde is considered to be the hydrated protoxide of acetyle, $(C_4H_3)\,O$

+ HO; or, abbreviated, AcO,HO. Again, acetic ether is acetate of oxide of ethule, $C_4H_5O + (C_4H_3)O_3$; or, shortly, AeO,AcO_3; the dry acetic acid, $AcO_3 = (C_4H_3)O_3$, being a peroxide of the same radical, acetyle, ($C_4H_3 = Ac$) of which aldehyde is the protoxide. Lastly, butyric acid is considered (on the older view of acids,) as a hydrated acid, a compound of water with dry butyric acid: thus $HO + C_8H_7O_3$. It is true, that in the latter case, we are not yet acquainted with the true radical of butyric acid; but, we cannot doubt that, like acetic acid, it does contain a radical. These three compounds, therefore, may now be represented and distinguished as follows:—

	Empirical Formula.	Rational Formula.
Aldehyde	$C_4H_4O_2$	$= (C_4H_3)O + HO$
Acetic Ether	$C_8H_8O_4$	$= (C_4H_5)O + (C_4H_3)O_3$
Butyric Acid	$C_8H_8O_4$	$= C_8H_7O_3 + HO$

Even in those cases in which the composition of the radical is not known, or not known with certainty, we can often trace the radical with much probability. Thus, dry oxalic acid, C_2O_3, and dry mellitic acid, C_4O_3, may be viewed as different compounds of the simple radical carbon, the latter containing just twice the proportion of carbon to the same quantity of oxygen that the former does. This is merely stated by way of illustration; for, it is at least equally probable that the true radical of oxalic acid is C_2O_2.

But in the following four acids we may trace, theoretically, the same compound radical, namely, formyle, $= C_2H$, in combination with different proportions of oxygen. Here C_2H is also represented by Fo.

Formic Acid	(C_2H)	$+ O_3 = Fo\,O_3$
Succinic Acid	$C_4H_2O_3 = 2(C_2H)$	$+ O_3 = Fo_2O_3$
Malic Acid	$C_4H_2O_4 = 2(C_2H)$	$+ O_4 = Fo_2O_4$
Racemic Acid	$C_4H_2O_5 = 2(C_2H)$	$+ O_5 = FO_2O_5$

These relations, although as yet only to be traced in the formulæ, are yet not without interest, and may, at all events, serve to aid the memory.

In like manner, it may be observed, that the following acids all contain, as hydrates, 4 eq. of oxygen; and all likewise the same number of eqs. of carbon as of hydrogen.

Acetic Acid	$=$	$C_4\ H_4\ O_4$
Butyric Acid	$=$	$C_8\ H_8\ O_4$
Valerianic Acid	$=$	$C_{10}\ H_{10}\ O_4$
Œnanthic Acid	$=$	$C_{14}\ H_{14}\ O_4$
Lauric Acid	$=$	$C_{24}\ H_{24}\ O_4$
Cocinic Acid	$=$	$C_{26}\ H_{26}\ O_4$
Ethalic Acid	$=$	$C_{32}\ H_{32}\ O_4$
Margaric Acid	$=$	$C_{34}\ H_{34}\ O_4$

Here we may suppose the radical of the first acid to have been changed by the successive additions of 4, 6, 10, or 20 eqs. of carbon and hydrogen, the oxygen remaining unchanged. Or we may as readily suppose one of these acids, by losing oxygen, to pass into another. Thus we may either conceive butyric acid to be formed from acetic acid by the addition of C_4H_4; or acetic acid to give rise to butyric acid, by losing half its oxygen; for $2(C_4H_4O_4) = C_8H_8O_8$; and $C_8H_8O_8 - O_4 = C_8H_8O_4$.

When compound organic radicals, or their compounds, are subjected to powerful decomposing agents, they tend to produce new and less complex radicals. Thus, when alcohol, the hydrated oxide of ethule, is oxidized, it gives rise to aldehyde and acetic acid, which are compounds of acetyle, C_4H_3, a less complex radical than ethyle, C_4H_5. Further, when organic compounds are decomposed by a strong heat, they tend to produce compounds of simple radicals, such as carbon or hydrogen, or, at most, of the least complex radicals, such as cyanogen, C_2N, and amidogen, NH_2. These are principles of very general application.

It may here be observed, that while, in such cases as the supposed conversion of acetic into butyric acid, by the loss of half its oxygen, the change is from a less complex to a more complex organic compound, and while we can hardly doubt the possibility of such a result, yet the oxidation of a compound radical, that is, the addition of oxygen, appears always to produce less complex radicals or compounds.

It is often urged, as an argument against the doctrine of compound radicals, that these supposed radicals are entirely imaginary, and cannot be produced. Now, it is true, that a large proportion of those, whose existence is best attested, have not yet been obtained in the uncombined state; and it is even probable that some of them are only capable of existing, or rather of being preserved, when combined. But the argument founded on this fact has no cogency; for, in the first place, some organic radicals, such as cyanogen and kakodyle, are well known in the separate state. Now cyanogen and kakodyle are, in all their relations, exactly analogous, the former to chlorine, the latter to a metal; and, if we were unable to demonstrate their compound nature, their chemical relations would compel us to classify cyanogen as an element along with chlorine, and kakodyle along with the metals; and when we see whole series of organic compounds, in all respects analogous to those of cyanogen and kakodyle, we are entitled logically to draw the conclusion that these compounds contain similar compound radicals, even although we cannot isolate them. Secondly, in every chemical theory yet broached, many substances are admitted whose existence cannot be directly proved. Thus, the so-called anhydrous organic acids are, almost without exception, unknown in the separate state; they are equally imaginary with the radicals whose existence is doubted. Nay, many inorganic acids are equally hypothetical. Anhydrous nitric acid has never been seen; and, although there are reasons for doubting its existence, yet no one doubts the existence of hyposulphurous acid, which yet has never been separated, either as a hydrate, or in the anhydrous state.

We conclude, therefore, that organic compound radicals exist, and generally play the part of elements; and we shall avail ourselves of their existence, as far as it is established, to facilitate the study, the classification, and the retention in the memory, of organic compounds.

THEORY OF CHEMICAL TYPES.—DOCTRINE OF SUBSTITUTION.

The original and ingenious researches of Laurent have led to the adoption of what is called the Theory of Types and the Law or Doctrine of Substitution, which have been supported, and in a great measure established, by Dumas and other distinguished experimenters of the French school. The views of Laurent and of Dumas were, for a time, vehemently opposed by some chemists, especially

by Berzelius and Liebig; but although they have in some points been modified and restricted, the progress of discovery has gradually led to their general reception, so that recently some of the most striking illustrations and proofs of the law of substitution have been discovered by Dr. Hoffman, assistant to Professor Liebig, and working under his eye.

As the subject, therefore, is no longer purely controversial, it would be wrong to omit it from an elementary work, more especially as the doctrine has now taken such a form as to facilitate very much the study of organic compounds and of their metamorphoses.

It is not easy to define a chemical type; but in inorganic chemistry we may say, for example, that hydrochloric acid, HCl, is the type of a very numerous class of acids, the character of which is that they contain hydrogen united to a salt radical.

If for chlorine we substitute iodine, bromine, &c., or even cyanogen, the type remains unchanged, the compound is still an acid, analogous to that which was selected as the type.

Again, common salt, NaCl, is the type of a very large series of salts, in which a metal is united with a salt radical; and if we substitute potassium, lead, or silver for the sodium, the type is unaltered; we obtain a different salt, but still a salt of the type represented by NaCl.

Here, then, we have the simplest types and the most obvious cases of substitution; when iodine or cyanogen is substituted for chlorine in the acid type; or when potassium, lead, or silver is substituted for sodium in the salt type; in both cases without the loss of the type.

Nay in the salt type, represented by NaCl, we may not only replace sodium by other metals, but we may also substitute iodine, bromine, &c., or cyanogen for the chlorine, and still the type will remain unchanged. Iodide of sodium, NaI, bromide of magnesium, MgBr, and cyanide of silver, AgCy, are all as good examples of the salt type represented by NaCl, as common salt itself is.

It has been proposed, with great propriety, by Baudrimont, to employ certain Greek characters as symbols in representing the formulæ of extensive types or of types in general. I shall, therefore, express the above salt type by the formula ΔX, in which Δ stands for any metal or body acting as a metal, and X for chlorine or any other radical of analogous power, such as cyanogen. As hydrogen appears to stand alone in the power of forming acids with bodies of the type X, the acid type above alluded to becomes, in its most general form, XH.

But while it is very easy to understand the extensive substitutions which may be effected in the case of both elements of the type ΔX, yet we observe that in these substitutions the electrical character of the elements is retained; and that as Δ is the positive, and X is the negative element, so they are only replaced, Δ by positive and X by negative elements respectively.

So far as inorganic chemistry is concerned, the study of types would serve generally to confirm and establish the electro-chemical theory. At all events, we are not as yet acquainted with many exceptions to it; we do not usually find oxygen or chlorine occupying the place of Δ in a compound, or a metal playing the part of X. Even in inorganic chemistry, however, there are some examples of such interchanges. Manganese in manganic acid, MnO_3, and chromium in chromic acid, CrO_3, obviously represent the sulphur in sulphuric acid; and the manganese in hypermanganic acid, Mn_2O_7 represents the chlorine in perchloric acid, ClO_7; while, in its other compounds, manganese acts as a metal.

But the researches of Laurent and Dumas have shown that in organic chemistry the substitution of one element for another, even where the type is retained, is not limited by the electrical character of the elements. Thus, in acetic acid, HO, $C_4H_3O_3$, the 3 eq. of hydrogen in the anhydrous acid may be replaced by chlorine, giving rise to the compound HO, $C_4Cl_3O_3$, in which the type is so little affected, that this substance, chloracetic acid, has properties highly analogous to those of acetic acid. Here it is evident that the chlorine performs the same function as the hydrogen, which it replaces, did; and not, as in hydrochloric acid, an opposite function.

Again, in aldehyde, $(C_4H_3)O + HO$, the 3 eq. of hydrogen in the radical C_4H_3 may be replaced by 3 eq. of chlorine, and we then have chloral, $(C_4Cl_3)O + HO$, a body of the same type as aldehyde.

Such cases of substitution of chlorine (iodine, bromine, &c.,) for hydrogen, and even of oxygen for hydrogen, without change of type, are very frequent; and it is this kind of substitution, so adverse to the electro-chemical theory, which is included in the theory of substitutions of Laurent. Those more usual substitutions, where one body is replaced by another of similar electric character, may be viewed as so many examples of the doctrine of equivalents, the replacing body being equivalent to that for which it is substituted, on the electro-chemical theory.

Adopting, then, the views of Laurent, we are compelled to admit that the electro-chemical theory fails when applied to cases of substitution of chlorine for hydrogen, &c., where the type remains unaltered. This is clearly the case in acetic and chloracetic acids; and Hoffman has recently shown that in certain basic organic compounds hydrogen may be replaced by chlorine, while the new compound retains the basic type and characters. Aldehyde and chloral furnish an example of the same, in a body neither acid nor basic.

Here, then, is a fact of very general occurrence, which not only proves that the electro-chemical theory of combination is inapplicable, at all events in many cases, but also tends to establish a very different view: namely, that the electric character of an element is no permanent or essential property; and that the type or character, or general properties of a compound, depend, not on the *nature*, but solely on the *arrangement* of its elementary atoms; on the way in which they are grouped to form the compound molecule.

The reader will remember that, in the section on Isomorphism, the principle was laid down that the crystalline form of certain types of salts, such as the alum type, as well as many other properties of the compounds having those types, were the result of the *similar grouping* of *analogous elements*. We now see that, according to the law of substitution, as deduced from numerous careful observations, similarity of properties, or identity of type, are the result of similarity of grouping, even of elements not analogous, nay, of elements electrically opposed to each other. It is evident, therefore, that the arrangement of the elementary molecules to form the compound molecule is the circumstance on which depend almost exclusively the properties of the compound, or in other words, the character of the type.

Substitution may be either complete or partial. In chloracetic acid, and in chloral, the substitution of chlorine for the hydrogen of the radical acetyle C_4H_3 is complete. But when ether $(C_4H_5)O$ is acted on by chlorine, the substitution takes place by successive steps, one equivalent of hydrogen being replaced

at a time, after the oxygen has also been replaced by chlorine. Thus we have, first—

Ether or oxide of ethyle $=(C_4H_5)+O$

then, chloride of ethyle $=(C_4H_5)+Cl$

then, successively, $C_4\left\{\begin{matrix}H_4\\Cl\end{matrix}\right.+Cl$

$C_4\left\{\begin{matrix}H_3\\Cl_2\end{matrix}\right.+Cl$

$C_4\left\{\begin{matrix}H_2\\Cl_3\end{matrix}\right.+Cl$

$C_4\left\{\begin{matrix}H\\Cl_4\end{matrix}\right.+Cl$

and lastly, $(C_4Cl_5)+Cl$

We thus obtain the series of compounds here indicated, in which the hydrogen is gradually replaced by chlorine, until at last we obtain the compound $(C_4\ Cl_5)+Cl=C_4\ Cl_6=2C_2\ Cl_3$, which is the perchloride of carbon. Most of these compounds have actually been obtained; and it is obvious that they may all be referred to one type. Such a series is called a series of mechanical examples of the type in question, or rather of subtypes retaining the original character although modified.

In some cases, hydrogen has been replaced partly by chlorine and partly by bromine. Laurent has described two compounds derived from naphthaline by substitution, the empirical formula for both of which is the following:—$C_{20}\ H_4\ Cl_3\ Br$. Yet the properties of these two compounds are quite distinct, and it is certain that this difference of properties must depend on a difference in the arrangement of the elements. Now, in the formation of these two compounds we have a very beautiful proof of the existence of a difference in the arrangement: for one is produced when chlorine acts on the compound called by Laurent bronaphtése, $C_{20}\ H_6\ Br_2$; while the other is formed when bromine is made to act on chlonaphtise, $C_{20}\ H_5\ Cl_3$. It is obvious that in the first case 2 eq. of hydrogen and 1 eq. of bromine are replaced by chlorine; while in the second, 1 eq. of hydrogen is replaced by bromine. While, therefore, all four compounds may be deduced from the type $C_{20}\ H_8$, and while both the bromine and chlorine play the part of hydrogen, it is impossible to doubt that each of the 8 eq. of hydrogen has its special place in the compound molecule of the type, and that, in the two empirically identical formulæ above given, the 1 eq. of bromine does not replace the same eq. of hydrogen, and consequently the bromine occupies in the two compounds different positions. The same remark applies to the 3 eq. of chlorine.

We may illustrate our meaning as follows:—Let $C_{20}\ H_8$ be the type, and let each of the eqs. of hydrogen have a number attached indicating its place in the typical molecule. We shall then have

$$C_{20}\left\{\begin{matrix}H_1\ H_2\ H_3\ H_4\\H_5\ H_6\ H_7\ H_8\end{matrix}\right\}.$$

Now if we represent the two compounds above mentioned in the following manner, we can then conceive the influence of arrangement on the properties of two compounds having the same empirial formula. The first may be

$$C_{20}\left\{\begin{matrix}H_1\ H_2\ H_3\ H_4\\Cl_5\ Cl_6\ Cl_7\ Br_8\end{matrix}\right\},$$

and the second may be

$$C_{20}\left\{\begin{matrix}H_1\ H_2\ H_3\ Br_4\\Cl_5\ Cl_6\ Cl_7\ H_8\end{matrix}\right\}$$

It is only on this principle that we can explain the facts observed by Laurent; and it is easy to see that the above type, $C_{20} H_8$, will admit of innumerable modifications: for even the subtype $C_{20} H_4 Cl_3 Br$. is capable of yielding many more than the two above given; and the change of 1 eq. produces a new subtype, equally fertile in new forms.

In fact, Laurent has actually obtained, as will be shown further on, a very large number of what we have called subtypes from the type $C_{20} H_8$, which is naphthaline, and has established the same law in reference to many other types.

The preceding observations will, I trust, be found sufficient to convey a clear general notion of the prevalent doctrines of chemical types and of substitution, as applied to organic chemistry.

THE DECOMPOSITIONS AND METAMORPHOSES OF ORGANIC COMPOUNDS.

Organic compounds, whether actual organized tissues, unorganized products of animal and vegetable life, or new substances artificially produced, are generally characterized by a great proneness to undergo decomposition or metamorphosis. This instability is especially marked in those compounds which contain nitrogen, not only, because, containing four elements (in most cases, they are exposed to more numerous causes of change than such bodies as contain only three (carbon, hydrogen, and oxygen), but also because nitrogen is, in its relations to those three elements, the most remarkable element we know. According to the circumstances under which a change is induced, nitrogen may separate uncombined, as in the ultimate analysis of organic substances by combustion with oxide of copper or chromate of lead; or it may combine with oxygen, yielding nitric acid, as in nitrification; or with carbon, yielding the compound radical cyanogen, as when nitrogenized organic matter is ignited with carbonate of potash; or with hydrogen, yielding ammonia, as when nitrogenized organic matter is ignited with hydrated alkalies.

It is easy to see, therefore, that while all organic matter is prone to change, this is especially the case with nitrogenized compounds. In fact, many of these compounds cannot be kept more than a few hours without the commencement of decomposition or metamorphosis, in the shape of putrefaction or fermentation. This kind of metamorphosis will be separately considered hereafter: in the meantime it is important to observe, that when such a compound has entered into a state of decomposition, it acquires the properties of a ferment, that is, it is capable of inducing a similar metamorphosis in another compound, if placed in contact with it.

The true explanation of this fact appears to be, that the particles or molecules of the exciting body or ferment, being in a condition of change, and therefore in motion, communicate to the molecules of the body placed in contact with them an amount of motion sufficient to destroy the balance of the existing affinities; which in organic compounds is easily done, the chemical equilibrium being very unstable; and thus gives rise to a new play of affinities and the production of new compounds, as when sugar by contact with yeast is resolved into alcohol and carbonic acid.

But in addition to metamorphoses of the kind just alluded to, which, in the various ferments at least, commence spontaneously, air (at all events, at the commencement), moisture, and a certain temperature being the usual conditions, organic substances undergo very well marked decompositions when exposed to

the action of heat and of some powerful reagents; and it seems advisable here to give also a general account of such decompositions, as they admit of being classified under certain heads or rules generally applicable.

We shall here, therefore, briefly describe the changes produced on organic compounds: 1, by oxidation; 2, by the action of acids; 3, by the action of bases; 4, by the action of heat in close vessels, or the destructive distillation; and 5, by the contact of ferments.

1. *Oxidation: a. direct.*—The direct oxidation of organic compounds takes two distinct forms. The first is the familiar one of combustion, in which the action of the atmospheric oxygen is aided by a high temperature. The results differ according to the supply of oxygen. If there be an excess of air, or of oxygen, from any source, the whole of the carbon and hydrogen is converted into carbonic acid and water, which, along with uncombined nitrogen, are the ultimate products of the action of oxygen on organic matters. But if the supply of air be deficient, the hydrogen is oxidized in preference to the carbon, which is deposited as smoke, soot, or lampblack.

The second form of direct oxidation is that which is commonly called decay, but which Liebig proposes to call Eremacausis (*i. e.* slow combustion), and which takes place when organic matter is exposed to air and moisture. In dry air it does not occur.

One of the most familiar examples of this kind of oxidation is that decay of wood by which it is slowly converted into a dark brown powder—ulmine. In this process, as De Saussure has shown, the wood absorbs oxygen, and produces an equal volume of carbonic acid along with water, and the residue—ulmine. As, in combustion, the oxygen combines by preference with hydrogen, so also in eremacausis there is every reason to believe that the absorbed oxygen combines with the hydrogen of the wood, and that an equivalent quantity of oxygen, also derived from the wood, is given off in the form of carbonic acid. Now, since wood may be represented as composed of carbon and the elements of water, and as water and carbonic acid are two of the products of eremacausis, it might be supposed that the water was ready formed in the wood, and that the absorbed oxygen had combined with the carbon. But it has been shown that, in presence of hydrogen, carbon does not at the ordinary temperature combine with oxygen, for which its affinity is less powerful; and besides, in the decay of wood, the proportion of carbon in the residue (the ulmine) is constantly greater than in the wood. Thus oak wood, $C_{36} H_{22} O_{22}$ yields in one stage of decay, ulmine, the composition of which agrees with the formula $C_{35} H_{20} O_{20}$; and in a more advanced stage, an ulmine of the formula $C_{34} H_{18} O_{18}$. Here we see that for every 2 eqs. of hydrogen oxidized by the air, 1 eq. of carbon and 2 eqs. of oxygen have been separated; so that the per centage of carbon in the residue constantly increases, and the final result of eremacausis would be a residue of carbon; were it not that, as the proportion of carbon in the ulmine increases, its affinity for the other elements, strengthened by its mass, becomes too powerful to be overcome by the oxygen of the air without the aid of heat.

Other examples of eremacausis are, the acetification of alcohol, and the process of nitrification in which ammonia undergoes eremacausis. These, as well as other instances, will be considered in their proper place.

Eremacausis is greatly promoted by heat and by the presence of alkalies. It is, on the contrary, arrested or retarded by cold, dryness, acids, and many salts, such as corrosive sublimate, which has been used to prevent the decay of wood.

There is one circumstance connected with eremacausis, or decay, as above described, which is worthy of special attention. It is, that a substance, in a state of eremacausis, if placed in contact with another, which is capable of undergoing this change, speedily causes the latter to enter into the same condition of change. This effect of contact may be compared, in one sense, to that of a body in combustion, which sets fire to other bodies; but in ordinary combustion the high temperature plays an important part, while in eremacausis the effect appears to be due to the communication of motion from the particles of the decaying body to those of the other substance, which motion, as in the case of fermentation, overturns the existing balance of affinities, unstable as it is in organic compounds, and gives rise to the formation of new products.

The process of eremacausis, or slow oxidation in the atmosphere, is one of very great practical importance, inasmuch as, by this means, the elements of dead organic matter are made to assume those forms—namely, the forms of carbonic acid, water, and ammonia—in which they are capable of contributing to the nutrition of new or growing vegetables.

A peculiar species of eremacausis is observed in the case of the simultaneous action of oxygen and ammonia on certain colourless vegetable products, which, absorbing these gases greedily, are thus converted into nitrogenized compounds of very fine blue or purple colours. Of this we have examples in orcine, erythrine, and phloridzine; and there is good reason to attribute the formation of indigo, from a juice devoid of blue colour, to an action of this kind, since both oxygen and ammonia appear to be necessary to its production. The transformation of alloxantine or of uramile into murexide also depends on the simultaneous action of ammonia and oxygen.

b. Indirect Oxidation. The indirect oxidation of organic compounds may be effected in a variety of ways, as, for example, by nitric acid, the action of which we shall presently describe along with that of other acids; by certain salts, as by permanganate of potassa, which converts sugar, for example, into oxalic acid; or by the employment of a mixture of bichromate of potash and diluted sulphuric acid, by which means salicine may be made to yield the hyduret of salicyle (oil of spiræa): or, finally, by the combined action of heat and hydrated alkalies, as when indigo, heated with potash, gives rise to anthranilic acid, hydrogen being given off; or acetates, heated with baryta, yield marsh gas and carbonates.

2. *Action of Acids on Organic Compounds.* This action is very various; the two acids most frequently employed are the nitric and sulphuric acids, and, as might be expected, the former acts more as an oxidizing agent than the latter.

When sugar, for example, is heated with nitric acid, the latter loses oxygen, for nitrous acid is given off in enormous quantity; while the elements of the sugar, by the action of the oxygen are made to combine so as to produce compounds of less complex radicals than that of sugar probably is. Among the products are water, carbonic acid, oxalic acid, and saccharic acid, besides others not yet investigated; but the three first sufficiently show the tendency of oxidation to promote the formation of less complex radicals.

When nitric acid acts on organic matters, there is generally found one acid, if not more, among the products, and in this way a large number of acids have been discovered. Examples of this are, mucic acid from gum; indigotic and carbazotic acids from indigo; margaric acid from stearic acid; suberic and succinic acids from oily acids, besides many others. It frequently happens that compounds, whether acid or neutral, formed by the action of nitric acid on organic

matter, contain hyponitrous acid as a constituent, apparently substituted for some element. This is the case with nitrobenzide from benzine, and with nitronaphthalase, and a whole series of compounds discovered by Laurent in his study of the action of nitric acid on naphthaline. The carbazotic or nitropicric acid also appears to contain a compound of nitrogen and oxygen. Some organic bases, as morphia and brucia, strike a deep red colour with nitric acid.

When sulphuric acid is made to act on organic compounds, it chars a considerable proportion of them by virtue of its attraction for oxygen and hydrogen in the form of water. But in many cases it produces very different effects. Thus, by boiling with sulphuric acid and water, starch and lignine are converted into grape sugar. In other cases, the sulphuric acid seems to lose so much oxygen as to produce hyposulphuric acid, which enters into combination with an organic compound, forming a new acid, as when sulphuric acid acts on naphthaline, and forms sulpho-naphthalic acid; or on benzoic acid, forming hyposulphobenzoic acid; or on alcohol under certain circumstances, when an acid is produced containing the elements of hyposulphuric acid and of a carbo-hydrogen. In other cases, the sulphuric acid combines unchanged with the organic compound, as in sulphovinic acid, which is a bisulphate of oxide of ethyle; sulphomethylic acid, and others.

Many organic compounds, heated with excess of sulphuric acid, are entirely decomposed, yielding water which combines with the acid, and other products which are disengaged. Thus oxalic acid is resolved into water, carbonic acid, and carbonic oxide; formic acid into water and carbonic oxide; alcohol into water, olefiant gas, and other products.

Several organic compounds are dissolved by sulphuric acid with the production of a fine red or purple colour. Salicine strikes a red colour with the acid, and cedriret, one of the constituents of tar, dissolves in it with a deep blue colour, as does also naphthalase.

Phosphoric acid may be employed in some cases to remove water from organic compounds, as it does not char them. Like sulphuric acid, it forms with oxide of ethyle an acid salt, known as phosphovinic acid.

Hydrochloric acid and its congeners have no very extensive action on organic substances. With alcohol, hydrochloric acid gas yields chloride of ethyle; and a current of this gas, passed through an alcoholic solution of a fatty acid, gives rise to the compound of the fatty acid with oxide of ethyle, which would otherwise be obtained with difficulty. With oil of turpentine, oil of lemons, and some other essential oils composed of carbon and hydrogen, hydrochloric acid gas combines, forming solids resembling camphor. Pyroxanthine, a substance contained in tar, dissolves in strong hydrochloric acid with a fine and deep purple colour.

3. *Action of Bases on Organic Compounds.* Hydrated bases unite, of course, with organic acids; and when heated with neutral substances, they generally give rise to the formation of acids, such as acetic and oxalic acids, or even carbonic acid, oxygen being taken from the water of the base, and hydrogen being disengaged, or, (if the organic body contain nitrogen,) hydrogen and ammonia. This property of hydrated bases is employed as a means of converting all the nitrogen of organic compounds into ammonia, and in this form determining its quantity.

The presence of bases greatly promotes the absorption of atmospheric oxygen

by organic substances. This is the reason why alkalies assist eremacausis. The same effect is very conspicuous in the change which the salts of gallic acid (and some other acids) undergo when exposed to the air. A solution of an alkaline gallate absorbs oxygen very rapidly, and becomes very dark in colour, being oxidized in a far shorter time than if the acid had been uncombined.

4. *Action of Heat on Organic Compounds in close vessels.* This action is known under the name of the *destructive distillation.* It must be considered as a combustion with a very limited supply of oxygen, that namely afforded by the substance itself. A very great variety of compounds is produced, many of them very interesting and useful. The destructive distillation may be considered as it affects substances containing nitrogen, and substances devoid of that element. Many products are common to both cases, but many also are confined to one case, especially to that of nitrogenized substances.

The destructive distillation of non-nitrogenized substances has been chiefly studied in the case of wood, which, when heated in close vessels, yields a great variety of products: some, binary compounds, such as paraffine, naphthaline, eupione, water, carbonic oxide, carbonic acid, marsh gas, and olefiant gas: others ternary, such as acetic acid, $C_4H_3O_3$; hydrated oxide of methyle or pyroxylic spirit, (C_2H_3) O,HO; lignone, xylite, mesite, and other volatile etherial liquids, composed of the same elements as pyroxylic spirit, and very similar to it in properties; creosote; picamar; capnomore; cedriret; pittacal, and pyroxanthine, besides many others, not yet properly investigated.

When fatty or resinous bodies are subjected to the destructive distillation, there are obtained, besides other compounds, two solid carbo-hydrogens; chrysene, C_3H, and pyrene, $C_{10}H_2$; which also occur among the products of the distillation of coal.

This latter distillation may serve as an example, the best known, of the action of heat on nitrogenized organic bodies; for coal contains a certain although small proportion of nitrogen. The products, besides creosote, paraffine, naphthaline, and probably several others of those obtained from wood, include much ammonia, hydrocyanic acid: some peculiar non-nitrogenized acids, as carbolic acid, $C_{12}H_5$ O,HO, (a remarkable compound, having an odour resembling that of creosote, and yielding, when subjected to various re-agents, an extensive series of new compounds [Runge, Laurent];) rosolic and brunolic acids; and two very remarkable nitrogenized bases, containing no oxygen, namely, kyanol (*aniline, crystalline,*) $C_{12}H_7N$, and leukol, $C_{18}H_8N$; besides a third, not yet fully investigated, pyrrol; finally, paranaphthaline, or anthracene, $C_{30}H_{12}$, and coal tar naphtha, which is used as a solvent for caoutchouc.

The distillation of animal matter, such as hoofs, horns, or bones, yields analogous results, but is characterized by the very large amount of ammonia which is obtained, animal matter being richer in nitrogen than coal is. This ammonia appears as carbonate, which salt is thus manufactured, and hence was and occasionally still is, called salt of hartshorn.

Many organic acids, when heated in close vessels to a certain temperature, short of the destructive distillation, undergo a remarkable decomposition; carbonic acid is given off, and there remains a new acid, which is called a pyrogenous acid, or pyro-acid. Thus meconic acid, at a certain temperature, yields carbonic acid and komenic acid: while komenic acid, if heated in its turn, yields carbonic acid and pyromeconic acid. We have also pyromucic, pyrotartaric, or

pyroracemic and pyrocitric acids; citric acid yielding three pyro-acids, aconitic, (equisetic), itaconic and citraconic acids, and malic acid also yielding two, maleic and paramaleic or fumaric acids.

From the above statements, it is obvious, that the action of heat on organic compounds gives rise to a very large number of important products, of which only the most remarkable have been named. All will be described in their proper places.

5. *Action of Ferments on Organic Compounds.* Of this action the best known and most important example is the fermentation of sugar, by which it is resolved into alcohol and carbonic acid.

The circumstances under which this metamorphosis occurs are these: the sugar must be dissolved, the solution must have a certain temperature, and there must be present a ferment, such as yeast or some analogous body. In the juice of the grape a ferment, the fibrinous or caseous constituent of the juice is naturally present; and Gay-Lussac showed that the contact of atmospherical air was necessary to commence the fermentation, but that this contact with the atmosphere might be only for a very brief period, after which air was no longer necessary. It is obvious that the air acts by inducing a state of change in the ferment, for if any ferment, previously exposed to the air, be added to a pure solution of sugar, fermentation will take place without the mixture being exposed to the air after the ferment has been added.

Berzelius and others conceive that the ferment acts by contact in some way not very clearly defined, by catalysis, as it is called, as they conceive sulphuric acid to do in the formation of ether from alcohol. But Liebig has proved that in this latter case the acid first combines with ether (oxide of ethyle), forming sulphovinic acid (bisulphate of oxide of ethyle), and that this compound at a temperature rather higher than that at which it is formed, is decomposed into hydrated sulphuric acid and ether which distils over. The same chemist has pointed out many other instances of the effect of contact, even in inorganic chemistry: such as the action of oxide of silver on peroxide of hydrogen, where the former compound, by contact with the latter, not only decomposes it, causing oxygen to be rapidly given off, but is itself decomposed, losing all its oxygen; the solution in nitric acid of an alloy of platinum and silver, while platinum alone is insoluble in that acid; or the action of carbonate of silver on certain organic acids, which cause a disengagement of carbonic acid, this disengagement being attended with a partial reduction of the oxide of silver.

These, and many other, more familiar cases, particularly those where a compound is decomposed with detonation in consequence of a slight touch, or gentle friction, a moderate elevation of temperature, or the contact of another substance (*e. g.* chloride of nitrogen with oil) all tend, according to Liebig, to establish the doctrine that in certain compounds the balance of affinities is unstable, and therefore easily overturned, either by chemical or by mechanical influences.

The compounds which are capable of fermentation or any similar metamorphosis, are all of them bodies in which such an unstable equilibrium exists: they are all, in point of fact, easily decomposed by many different agencies, such as heat, acids, bases, oxygen, chlorine, &c. &c. Now, we can offer no other explanation of these facts of fermentation than this, that when a body in a state of progressive change, the particles of which are consequently in a state of motion, is placed in contact with another body, the particles of which are in a state of unstable equilibrium, the amount of motion mechanically communicated

to the particles of the latter from those of the former, is sufficient to overturn the existing equilibrium, and by the formation of a new compound establish a new equilibrium more stable under the given circumstances.

There is nothing unphilosophical in this explanation, and it is to be considered as the best theory of fermentation yet attempted. According to the view of Liebig, a ferment is merely a compound in a state of decomposition, capable of setting in motion, and thereby bringing also into a state of decomposition, the particles of another compound, the existence of which depends on a nice balance of affinities.

On the other hand the view adopted by Berzelius, according to which fermentation, and all the other phenomena of chemical change produced by contact are the results of a peculiar unknown force, the catalytic force, coming into action when certain bodies are placed in contact, appears unphilosophical, as, in the first place, assuming the existence of a new force where known forces would suffice to explain the facts; and, secondly, as furnishing no real explanation, but merely acknowledging, indirectly, our inability to offer any such explanation. When we ascribe an effect to catalysis, we are only saying, in other words, that we cannot account for it; catalysis is thus merely a convenient term for all that we do not understand. And to the use of the word in this sense, namely, as a name for the agent which produces certain effects, the agent itself being unknown, there would be no objection, were it not that catalysis has been employed to account for phenomena not only different from each other, but actually of an opposite kind. For example, platinum, in causing *the combination* of oxygen and hydrogen, is said to act catalytically, and the action of oxide of manganese, or oxide of silver in decomposing peroxide of hydrogen, that is, in causing *the separation of* oxygen and hydrogen, is also called catalytic. This example proves how loosely the word has been employed, and how vague are the views which have led to its introduction.

A variety of important and interesting processes come under the head of actions caused by ferments; the production of alcohol from sugar, of oil of bitter almonds from amygdaline, and of lactic acid from sugar of milk, are all examples of this; and in each of these cases, the ferment is peculiar. In the case of sugar it is yeast, or gluten undergoing eremacausis and putrefaction; in the case of amygdaline it is emulsine, a peculiar modification of albumen; and in the case of sugar of milk it is caseine, the nitrogenized constituent of the milk.

The access of air is required at first to yield oxygen to the gluten, &c., which then entering into eremacausis, or if air be excluded, into putrefaction, are capable of acting as ferments.

In the actions induced by ferments, we are to distinguish those in which some external element or elements are added to those of the compound, which cases resemble ordinary decompositions, from those in which the elements of the decomposed body merely transpose themselves, producing new compounds. The latter are properly and strictly termed metamorphoses. Fermentations, in which oxygen is absorbed, are examples of eremacausis, and it has already been mentioned that a body in a state of eremacausis acts on other bodies as an excitant of the same change, that is, as a ferment.

Indeed, most ferments, whether they induce eremacausis, or a more pure metamorphosis in other bodies, are themselves in a state of eremacausis, at all events in the commencement of the change.

The subject of fermentation and ferments will be hereafter more especially

considered, in connexion with fermentescible compounds: here the subject is merely treated in a general way.

Putrefaction, under ordinary circumstances, partakes largely of eremacausis, and differs from the ordinary kind only in the offensive odour of some of the products, chiefly compounds of sulphur and phosphorus, as sulphuretted and phosphuretted hydrogen. When air is excluded, putrefaction goes on, provided moisture be present, and it is then a metamorphosis, giving rise, in the case of vegetable matter putrefying under water, or in the strata of mines, to gaseous products, such as marsh gas and olefiant gas, constituting with air the fire-damp, and carbonic acid, which is the choke-damp, of the miner.

Animal matter, in a state of putrefaction, as putrid flesh, blood, cheese, or wine acts as a ferment, and is capable of causing the metamorphosis of sugar into alcohol and carbonic acid, as well as of inducing eremacausis, and also propagating a putrefactive decomposition analogous to its own. Thus, it is well-known that fresh cheese, if inoculated with decaying cheese, soon passes into decay, spreading from the seat of the inoculation.

We shall, hereafter, see that it is probable that some poisons and miasmata act as ferments on the blood. The singular sausage poison of Wurtemburg is animal matter in a peculiar state of decay, and does not contain any poisonous *compound*, only a poisonous *state* or *condition*; and the same principle may hereafter be found to furnish the true explanation of contagions.

Fermentation, putrefaction, and eremacausis are all promoted by the same circumstances, and arrested by the same influences. Antiseptics are substances which by combining with the ferment, or a part of it, or even with the body to be fermented, prevent the continuance either of the decomposition in the ferment, or of the fermentation itself. Corrosive sublimate and arsenic, which are powerful antiseptics, combine with animal matter, and form with it stable compounds; creosote combines energetically with albumen, &c., &c.

In fermentation, properly so called, the elements of the ferment take no chemical share in the metamorphosis of the body acted on by the mechanical agency above explained. That body is resolved into two or more new compounds of less complex radicals. The elements of water may or may not take part in the change; when they do, as in the case of sugar, the weight of the products, in this case alcohol and carbonic acid, is equal to that of the sugar, *plus* a certain weight of water. As, when the water is passed in vapour over carbon at a white heat, the carbon is shared between the oxygen and hydrogen, producing carbonic acid (or oxide), and carburetted hydrogen, so in the metamorphosis of sugar, and other analogous cases, we have on the one hand an oxidized compound, (in the case of sugar represented by carbonic acid), and on the other a compound in which part of the carbon is united to all the hydrogen (in the case of sugar, the alcohol). Similar results are obtained when alcohol or acetic acid are metamorphosed by heat, and this may be viewed as a general character of the metamorphosis of non-nitrogenized bodies: namely, that the carbon is divided between the oxygen and hydrogen.

In putrefaction, again, the ferment plays a chemical part in the change, and two or more compounds, the ferment and the putrefying body or bodies, combine to give rise to new compounds, with or without the elements of water. Putrefaction is generally the characteristic transformation of nitrogenized compounds, and the very great tendency of such compounds to undergo transformations is well illustrated by the spontaneous metamorphosis of a solution of cyanogen in

water. Such a solution contains the four principal elements of organic bodies; and its transformations may be said to be the only case of putrefaction which has been as yet carefully studied.

The solution after a time becomes brown and turbid, and deposits a dark matter, containing ammonia, united to a compound formed of the elements of cyanogen along with those of water. This matter being insoluble, undergoes no further change. Such a compound might arise from the reaction between 2 eq. cyanogen, and 4 eq. water: thus, $2C_2N + 4HO = NH_3 + (C_4HNO_4)$; according to some, the brown matter contains no ammonia, and is $C_4N_2HO = 2C_2N + HO$.

Another change is that in which water is decomposed, each of its elements uniting with cyanogen, and producing cyanic and hydrocyanic acids; thus: $2HO + 2C_2N = (C_2N,O + HO) + H,C_2N$.

Another metamorphosis gives rise to oxalic acid and ammonia. In this case, 1 eq. cyanogen acts on 3 eq. water; thus: $C_2N + 3HO = NH_3 + C_2O_3$.

But cyanic acid cannot exist in contact with water and other acids: it is instantly metamorphosed into bicarbonate of ammonia; thus; $C_2NO + 3HO = NH_3 + 2CO_2$.

Towards the end of the process, when ammonia has become predominant, the cyanic acid produced undergoes a different metamorphosis. It now unites with water and ammonia, and may possibly for a time exist as hydrated cyanate of ammonia; but at all events that salt, if formed at all, is soon transformed into urea. $NH_3 + C_2NO + HO = C_2H_4N_2O_2 =$ urea.

Again, the hydrocyanic acid gives rise to another brown solid body containing cyanogen or paracyanogen (possibly mellone also), and hydrogen; and, along with this, oxalic acid, urea, and carbonic acid, by metamorphoses already described.

Lastly the hydrocyanic acid in contact with water, and an acid or an alkali (here oxalic acid or ammonia), undergoes another metamorphosis, and is transformed into formic acid and ammonia; thus: $H,C_2N + 4HO = NH_3 + C_2HO_3, HO$.

Thus cyanogen, a binary compound, along with water, another binary compound, gives rise to no less than eight different compounds; 1st, the black compound, containing the elements of cyanogen and those of water, possibly C_4HN_2O: 2nd, ammonia, NH_3: 3rd, cyanic acid, HOC_2NO. 4th, hydrocyanic acid, H,C_2N. 5th, oxalic acid, C_2O_3: 6th, carbonic acid: 7th, a brown solid, containing cyanogen (paracyanogen) and hydrogen: 8th, formic acid, C_2HO_3,HO: and in addition to these, three bodies, formed by the combination of two of the above eight, and containing all the four elements; namely, 9th, oxalate of ammonia: 10th, bicarbonate of ammonia: 11th, urea.

This striking example is well adapted to give a clear idea of the immense variety attainable, when, instead of two binary compounds, two ternary or two quaternary compounds, along with water, are concerned; and of the slight modifications of external circumstances which are required to produce results so varied, all the above substances being produced in a liquid at the usual temperature.

It is hoped that the above sketch of the doctrine of the chemical changes and metamorphoses of organic compounds will suffice to enable the student to follow the individual processes and reactions, to be hereafter mentioned, which, owing to our limited space, we must treat with great brevity. We shall now conclude

our introductory matter by some general observations on the doctrines now held by many chemists on the subject of the organic acids; after which we shall enter on the study of the known organic radicals.

ORGANIC ACIDS.

The acids met with in organic chemistry are principally compounds of carbon, hydrogen, and oxygen, although some do contain also nitrogen. They are distinguished from inorganic acids by their high atomic weight, and by the action of heat, which decomposes them all. As, in many of them, the oxygen they contain is a multiple by a whole number of the oxygen of the bases which neutralize them, so they are viewed as oxygen acids by those who consider true sulphuric acid to be an oxygen acid, SO_3, and oil of vitriol to be its hydrate, HO,SO_3. In the case of acetic acid, for example, the formula of which is $(C_4H_3)\,O_3HO$, the compound $(C_4H_3)\,O_3$, unknown in a separate form, is called dry acetic acid, and the strong acetic acid is considered as its hydrate; and the analogy is supposed to be fortified by the fact that dry acetic acid, like dry sulphuric acid, contains 3 eq. oxygen, and neutralizes 1 eq. of base, MO, containing 1 eq. of oxygen.

But a careful study of the organic acids leads us to apply to them the same theory which we have already adopted for the inorganic acids, and to consider them as compounds of hydrogen, with compound radicals, usually consisting of carbon, hydrogen, and oxygen. On this view, as oil of vitriol is H,SO_4, the strongest acetic acid is $H,(C_4H_3)\,O_4$. It is true that this radical, $(C_4H_3)\,O_4$, does not exist, or is not known in the separate form; but the same remark applies to dry acetic acid, $(C_4H_3)\,O_3$, which on the old view is supposed to be combined with water, for it also is unknown in the separate state.

The existence of compound radicals in organic acids is not more difficult to imagine than that of SO_4 the compound radical of sulphuric acid, for $(C_4H_3)O_4$ only differs from it in containing three elements instead of two; indeed, as some ternary organic radicals are known in the separate form, we actually derive an argument from organic acids in favour of the existence of compound radicals in inorganic acids. Thus, the radical or organic metal, kakodyle, forms kakodylic acid.

But we find, among organic acids, a much larger proportion which are bibasic, tribasic, in short polybasic, than occurs among inorganic acids. Referring to what was said of the monobasic, bibasic, and tribasic phosphoric acids, it will be easily understood that while acetic acid, for example, is monobasic, tartaric acid, malic acid, komenic acid, alloxanic acid, and others are bibasic; that citric acid and mekonic acid are tribasic, and that saccharic acid is quinquebasic. And as the three modifications of phosphoric acid are described on the old view as monohydrated, bihydrated, and terhydrated, and on the new view, as containing, respectively, 1, 2, and 3 eqs. of hydrogen, replaceable by metals, so tartaric acid may be either $C_8H_4O_{10},2HO$ or $C_8H_4O_{12},H_2$; malic acid may be $C_8H_4O_8,2HO$ or $C_8H_4O_{10},H_2$; and so on; while citric acid may be either $C_{12}H_5O_{11},3HO$ or $C_{12}H_5O_{14},H_3$, and meconic acid, $C_{14}HO_{11},3HO$, or $C_{14}HO_{14},H_3$; and lastly, saccharic acid may be $C_{12}H_5O_{11},5HO$; or $C_{12}H_5O_{16},H_5$.

In such polybasic acids, there is always some hydrogen in the radical, of which it is a constituent, and some combined with the radical, and replaceable

by its equivalent of metals. It is only this latter hydrogen, the amount of which affects the neutralizing power of the acid.

Now, among the phenomena of the action of bases on organic acids, we have some facts which seem almost to demonstrate the existence of this replaceable hydrogen, as such, and thus to establish the new theory of acids. Thus, meconic acid, which is tribasic, forms, like tribasic phosphoric acid, three series of salts, in which 1, 2, or 3 eqs. of hydrogen are replaced by metal. But while the meconic acid, as well as the tribasic phosphoric acid, readily forms with the oxide of silver, the salt in which all the hydrogen is replaced by silver; it cannot form, or forms with difficulty, a similar salt with potash, with which it forms very easily salts with 1 and 2 eqs. of metal, and 2 or 1 eqs. of hydrogen. Here we have the apparent contradiction of a weak base, oxide of silver, neutralizing the acid easily and completely; while a strong base, potash, leaves it imperfectly neutralized. This cannot, I think, be accounted for on the old view, and many similar cases might be mentioned. On the new view, such apparent anomalies disappear: for since the neutralizing depends on the replacement of hydrogen by a metal, it is evident that an oxide which is easily reduced, or deprived of its oxygen by hydrogen, like oxide of silver, will most easily neutralize acid, while a difficultly reducible oxide, such as potash, cannot be so far reduced as to yield 3 eqs. of metal, so as to form the neutral salt.

There are other kinds of organic acids which are what may be called coupled acids; that is to say they contain an acid coupled with another body, which does not neutralize the acid, but accompanies it in all its combinations. Thus, in hyposulpho-naphthalic acid, $C_{20} H_8 S_2 O_5$, HO, we have hyposulphuric acid $S_2 O_5$, coupled with naphthaline, $C_{20} H_8$, and the coupled acid neutralizes exactly as much base as the hyposulphuric acid alone would do. Again, formobenzoilic acid $C_{16} H_7 O_5$, HO, may be viewed as a coupled acid, consisting of formic acid $C_2 HO_3$, HO and oil of bitter almonds (hyduret of benzoyle) $C_{14} H_6 O_2$, which neutralizes just as much base as the formic acid alone. Those coupled acids which contain hyposulphuric acid, as is often the case, are formed by the action of oil of vitriol, or of anhydrous sulphuric acid, on organic bodies, when 2 eqs. of acid, losing 1 eq. of oxygen, form hyposulphuric acid; which commonly unites with the organic matter *minus* 1 eq. of hydrogen, that hydrogen having combined with the oxygen derived from the sulphuric acid.

ORGANIC RADICALS.

In the following pages we shall adopt the arrangement of Liebig, which has the advantage of uniting those substances which are naturally allied in composition. It proceeds, in the first place, on the principle of describing, under each known or admitted organic radical, all the compounds derived from or closely connected with it. After having gone through these, it takes up the consideration of the best known organic acids, including the oily acids; then the neutral oils, fat and essential; the resins; the non-nitrogenous colouring matters, bitter and extractive principles, nitrogenized colouring matters and their congeners; the organic bases; starch; gum; woody fibre; destructive distillation of wood, of lignite, of coal; nitrogenized and sulphurized vegetable principles, albumen, &c., the modifications of these in the animal kingdom; bile; nervous matter; gastric juice; saliva; excrements; urine; blood; lymph, &c. And the whole is wound up with considerations on the nutrition of plants and animals.

This arrangement is not a scientific one, and in the present state of our knowledge such an arrangement is, I fear, unattainable. But it is very convenient, and, by judicious grouping, very much facilitates the learning and the retaining in the memory of the immense mass of facts which at present constitute organic chemistry.

We proceed, therefore, to consider those organic radicals which are admitted by the best authorities, although they are not always known in the separate state. The first compound radicals that attract our attention are certain binary ones, already mentioned as binary compounds, but not in their character of radicals, in the second Part of this work; these are amide or amidogen, cyanogen, and carbonic oxide.

I. Amide. NH_2=Ad=16·19.

Syn. *Amidogen.*—It has already been mentioned that certain compounds exist, in which we can hardly doubt that this substance is present. Thus, potassium or sodium, heated in dry ammoniacal gas, disengages 1 eq. of hydrogen, forming the compound KNH_2 or $NaNH_2$. When these are put into water, potash or soda is formed, while ammonia is set free: $K,NH_2+HO=KO+NH_3$. Again, when oxalate of ammonia, NH_3, HO, C_2O_3 is heated, there are formed, water which distils over, and the compound $NH_2C_2O_2$ which remains behind: thus, $NH_3,HO,C_2O_3=2HO+NH_2C_2O_2$. The latter compound is called *oxamide*, and is a sparingly soluble white powder, neutral or indifferent in itself, but yielding, when digested with an alkali ammonia, which escapes, and oxalic acid, which combines with the alkali. Or if oxamide be heated with diluted sulphuric acid, it yields ammonia which combines with the acid, and oxalic acid which crystallizes in cooling. In both cases water is decomposed: thus $NH_2C_2O_2+2HO=NH_3,HO+C_2O_3$.

Now oxamide is interesting, as being the type of a class of compounds, all of which, when heated with an alkali or an acid, yield ammonia and an acid, the ammonia and the anhydrous acid together containing just 1 eq. of water more than the compound which, with the aid of water, has yielded them. If we consider oxamide as $NH_2+C_2O_2$; that is, as composed of amide (or ammonia *minus* hydrogen NH_2), and the radical carbonic oxide (or oxalic acid *minus* oxygen C_2O_2), then all its congeners are likewise compounds of amide, on the one hand, and an anhydrous organic acid, *minus* oxygen, on the other. On this view benzamide is benzoate of ammonia, *minus* water, $(NH_3+C_{14}H_5O_3,HO)-2HO=NH_2+C_{14}H_5O_2$; or it is amide *plus* benzoyle (the radical of benzoic acid, $C_{14}H_5O_2$). Therefore, when benzamide is acted on by potash, ammonia is given off, and benzoate of potash is left; and when it is heated with an acid, a salt of that acid with ammonia is obtained, while benzoic acid crystallizes. There are a good many similar compounds which are called amides, and are viewed as compounds of amide.

It is obvious that the distinctive characters of amide, which is not known in the separate form, are its powerful affinity for hydrogen, and its equally strong tendency to combine with radicals which have a very great affinity for oxygen, such as those already mentioned, potassium, sodium, the radical C_2O_2, and the radical benzoyle.

With hydrogen amide forms two compounds, ammonia, Ad H, and ammo-

nium, Ad H_2. The former may be called, in this view, hydramide. The latter, as has been already explained, is considered to be a compound metal.

It is very remarkable, that when ammonia or hydramide combines with an acid, the resulting compound is not a salt, unless the acid contain hydrogen. Thus, hydramide, with dry sulphuric acid, SO_3, forms a compound which is not sulphate of ammonia, and is not a salt at all. But if, instead of SO_3, we employ oil of vitriol, HO, SO_3, or HO, SO_4, sulphate of ammonia, a true salt, is obtained.

Here we may conclude that Ad H, in contact with H, SO_4, takes the hydrogen, forming ammonium, and that the resulting salt is composed of Ad H_2 + SO_4; that is, a metal combined with the sulphuric acid radical, just as sulphate of potash is K, SO_4. In all the true salts of ammonia, therefore, Ad H_2 = Am (Ammonium) occupies the place of a metal, and may be replaced by a metal; and even if we consider sulphate of potash to be KO, SO_3, we have only to view the sulphate of ammonia as NH_4 O, SO_3 = Ad H_2 O, SO_3 = Am O, SO_3, that is, sulphate of oxide of ammonium.

It must be borne in mind, however, that although all the chemical relations of these compounds confirm the ammonium theory, yet neither ammonium nor its oxide are capable of existing uncombined; for ammonium, when separated, is resolved into ammonia and hydrogen; and oxide of ammonium, when separated, assumes the forms of ammonia and water.

Of the chief compounds of amide, ammonia or hydramide has been previously described. It remains for us to direct attention to this substance as constantly present in the atmosphere in minute quantity, from whence it descends in the rain, being an absolutely indispensable agent in vegetation. We have already seen that the putrefaction and eremacausis of nitrogenized compounds yields carbonate of ammonia as a product. Its presence in the air is therefore certain, *à priori*, even although we cannot detect it until it is condensed and accumulated in rain. It is, however, absorbed from the air by almost all minerals and soils, especially aluminous and ferruginous soils; hence a trace of ammonia is often found where it is not looked for, and where it has been erroneously believed to have been formed by the direct union of hydrogen and nitrogen. This is the true explanation of the very remarkable and accurate experiments of Faraday, which have lately been confirmed by Will and Varrentrapp.

As an ingredient of manures, ammonia is most valuable. Its action on growing vegetables will be hereafter explained.

Ammonia forms a large number of compounds with the oxides of metals, the chlorides of metals, of sulphur and of phosphorus, and finally with salts in general. These belong rather to inorganic chemistry, and the limited size of this work forbids us to describe them in detail.

But it is proper here briefly to notice the compounds formed by amide with metals, inasmuch as amide is here viewed as an organic radical, and some of these compounds are very important in reference to organic chemistry.

Amide then forms compounds with potassium, sodium, mercury, copper, silver, and platinum. The two former are of a greenish olive colour, and their action on water has been described above. The amide or amidide of mercury Hg Ad, is not known in a separate state, but forms with bichloride of mercury the salt called white precipitate, HgAd + $HgCl_2$.

This salt is prepared by adding ammonia to a solution of bichloride of mer-

cury. When boiled with potash, it yields another salt, $HgAd + HgCl_2 + HgO_2$. The amidide of mercury also combines with the basic sulphate, and the basic nitrates of the same metal, forming, with the basic protonitrate, the soluble mercury of Hahnemann.

The amidide of copper, AdCu, is only known in combination with the hyposulphate and with the nitrate of ammonia.

The amidide of silver, AgAd, is known in combination with the nitrate, sulphate, seleniate and chromate of ammonia.

But it is the amidide of platinum which offers the greatest interest, as it gives rise to several very singular compounds, exhibiting the characters of very powerful bases. These remarkable substances have been studied by Gros, Reiset, and very recently by Peyrone, but are yet far from being understood. We shall endeavour briefly to state what is known of them.

When bichloride of platinum, $PtCl_2$, is heated for some time to nearly the melting point of tin, it loses half its chlorine, and is converted into protochloride, PtCl, which forms a powder of a dirty brownish green colour, insoluble in water. By continued digestion in ammonia, with the acid of heat, the protochloride is first changed into a green crystalline compound, which finally dissolves entirely, forming a yellowish solution, which on evaporation deposits yellowish white prismatic crystals. The green crystalline compound, discovered by Magnus, contains the elements of protochloride of platinum and those of ammonia, $PtCl\,NH_3$; the yellowish white crystals, discovered by Reiset, contain twice as much ammonia and the elements of water, $PtCl, 2NH_3 + aq.$

These two compounds are very remarkable; neither of them contains ammonia as such; both are insoluble in hydrochloric and dilute sulphuric acids. But the green compound of Magnus dissolves in nitric acid, with evolution of nitrous acid, and the solution on cooling deposits white crystalline scales, while the liquid contains no ammonia. These white scales, discovered by Gros, are the nitrate of a new base, $PtCl\,N_2H_6O$; which may be derived from 2 eq. of the insoluble compound of Magnus, $Pt_2Cl_2N_2H_6$, by the loss of 1 eq. of protochloride of platinum and the addition of 1 eq. of oxygen. This base acts exactly like the basic oxide of a metal, or like oxide of ammonium, NH_4O, combining with acids and forming neutral salts. It not only forms salts with nitric and sulphuric acids and the like, but with hydrochloric acid it yields a heavy crystalline powder, which is a chloride, bearing the same relation to the base as chloride of ammonium, NH_4Cl (sal ammoniac) does to oxide of ammonium. This chloride, therefore, is $PtClN_2H_6Cl$, and the radical of the oxide or base and of the chloride, will be $PtClN_2H_6$, corresponding to ammonium, NH_4. Although Gros did not isolate either the radical or its oxide, yet from the characters and composition of its salts, there can be no doubt of its existence. If we represent this radical, $PtClN_2H_6$ by R, then we have

RO = oxide, the base of the salts, analogous to KO or NH_4O.
$RO + SO_3 = R + SO_4$ = sulphate, analogous to KSO_4
$RO + NO_5 = R + NO_6$ = nitrate, analogous to KNO_6
RCl = chloride, analogous to KCl or NH_4Cl

The soluble crystalline compound of Reiset, $PtClN_2H_6 + aq.$ when heated to 212°, becomes anhydrous, and is then $PtClN_2H_6$, that is, it has the same composition as the radical of the base and salts of Gros. But it is not this radical;

on the contrary, it is the chloride of a different radical, PtN_2H_6, and its true formula is $PtN_2H_6 + Cl$.

This new radical is also perfectly analogous to ammonium, as may be exhibited in a tabular form as follows.

	Chlorine Compound.	Sulphate.	Nitrate.	Double Chloride with Platinum.
Ammonium $NH_4 = Am$	AmCl	$AmSO_4$	$AmNO_6$	$AmCl + PtCl_2$
Radical of Reiset $PtN_2H_6 = R'$	R'Cl	$R'SO_4$	$R'NO_6$	$R'Cl + PtCl_2$

In the case of ammonium, we cannot isolate the oxide $AmO = NH_4O$, as it instantly resolves itself into ammonia and water, $NH_3 + HO$. But the oxide of Reiset's platinum radical, $R'O, = PtN_2H_6O$, or rather its hydrate PtN_2H_6O + aq. is easily obtained from the sulphate by adding just so much baryta as will remove the sulphuric acid, and evaporating the filtered solution in vacuo, when the hydrated oxide crystrallizes in colourless needles. This compound is strikingly analogous to hydrate of potash: it is a powerful caustic, attracts carbonic acid from the air as strongly as potash, and exhibits all the chemical characters of one of the strongest alkalies. Few compounds are so remarkable as this base. We shall call it the base *a*.

This singular compound may be viewed as containing the elements of protoxide of platinum, ammonia and water, $PtO,2NH_3,HO$. When heated to 212°, it loses its water and half its ammonia, leaving a compound $PtNH_3O$ or PtO, NH_3, which appears to be another new base, *b*, combining with acids and forming salts which detonate when heated. This last compound, when heated in the air, burns like tinder, and leaves metallic platinum. It is the oxide of a third radical, $b, = PtNH_3$.

With hydrochloric acid the base *a* of Reiset yields water and the original chlorine compound, thus: $PtN_2H_6,O + HCl = PtN_2H_6,Cl + HO$. When this chloride is heated to from 265° to 290°, it loses ammonia, and there is left a yellow powder discovered by Peyrone, which dissolves easily in hot water, and has the composition of the green insoluble crystalline compound of Magnus, $PtClNH_3$, of which it is an isomeric modification. Indeed, the compound of Magnus, (although insoluble in hot water,) if boiled with a saturated solution of sulphate or nitrate of ammonia, dissolves and is deposited on cooling in yellow crystals. The yellow ammoniated protochloride of platinum of Peyrone readily dissolves in ammonia, and the solution yields fine colourless prisms of the original chlorine compound of Reiset, but apparently not containing 1 eq. of water of crystallization, which is said to be present in the white scales obtained by Reiset from the green compound of Magnus.

When the yellow compound of Peyrone is acted on by nitrate of silver, it yields chloride of silver, and two new compounds containing nitric acid and platinum, one of which forms yellow octohedrons.

If the sulphate of Reiset's base, $PtN_2H_6 + SO_4$ be acted on by iodide of barium, BaI, there is formed sulphate of baryta, $BaSO_4$, and a protoiodide of Reiset's radical, *a*, PtN_2H_6,I. This iodide is soluble and crystallizable, and when boiled with water, loses ammonia, while a new iodine compound is precipi-

tated, $PtNH_3I$, corresponding to the chlorine compound of Peyrone and to that of Magnus, both of which are $PtNH_3Cl$.

This new iodine compound seems to be the iodide of the third radical, *b*, $PtNH_3$; for when acted on by nitrate or sulphate of silver, it yields iodide of silver, and a nitrate or sulphate of this new radical or of its oxide, $PtNH_3,I + Ag, So_4 = PtNH_3,SO_4 + AgI$; and $PtNH_3,I + Ag, NO_6 = PtNH_3, NO_6 + AgI$. These new salts may of course be represented as $PtNH_3,O + SO_3$, and $PtNH_3, O + NO_5$. With ammonia, these salts yield the nitrate and sulphate of Reiset's base *a*; and with hydrochloric acid they yield the yellow compound of Peyrone. This would indicate that the latter compound is $PtNH_3,Cl$, the chloride of the radical $PtNH_3$, while the green salt of Magnus may be the ammoniated protochloride of platinum $PtCl + NH_3$, or probably $PtCl,NH_3 + aq$.

Here we have, at all events, three very remarkable compounds, which contain platinum and the elements of ammonia. There is, first, the radical *b* last described, $PtNH_3$; secondly, the radical of Reiset's base, *a*, PtN_2H_6; and thirdly, the radicals of Gros's base, $PtClN_2H_6$.

Now we have given the history of these compounds somewhat minutely, because their existence throws much light on the nature of a numerous and important class of bodies, namely, the vegetable bases or alkaloids.

It will be observed, then, that the three new radicals above described all contain nitrogen, indeed, all contain the elements of ammonia, and are in their chemical relations entirely analogous to ammonium. Thus we have

	Radical.	Oxide.	Chloride.	Sulphate.
Ammonium.	NH_4	$NH_4 + O$	$NH_4 + Cl$	$NH^4 + SO^4$
Radical of Reiset's base *b*	$PtNH_3$	$PtNH_3 + O$	$PtNH_3 + Cl$	$PtNH_3 + SO_4$
Radical of Reiset's base *a*	PtN_2H_6	$PtN_2H_6 + O$	$PtN_2H_6 + Cl$	$PtN_2H_6 + SO_4$
Radical of Gros's base	$PtClN_2H_6$	$PtClN_2H_6 + O$	$PtClN_2H_6 + Cl$	$PtClN_2H_6 + SO_4$

That the above formulæ represent in some respects truly the relation of these new bases to one another, is rendered probable by the fact that, while the radical and base *b* of Reiset differ from his radical and base *a* by containing 1 eq. of ammonia less, and these last from those of Gros by containing 1 eq. of chlorine less, we can actually transform the salts of Reiset's base *b* into those of his base *a*, by the addition of ammonia; and the nitrate of Reiset's base *a*, by the addition of chlorine, yields a salt having the properties of the nitrate of Gros's base.

Now we have seen that ammonium may be viewed as a compound of amide, as $NH_2 + H_2 = AdH_2$. May we not therefore suppose the new radicals to be also compounds of amide? May not Reiset's radical *b* be ammonium, in which 1 eq. of hydrogen has been replaced by 1 eq. of platinum, $Ad \begin{cases} H \\ Pt? \end{cases}$ Again, just as we have seen in acids, viewed as hydrogen compounds, analogous elements added to the radical without affecting the neutralizing power of the acid, which remains the same as long as the *replaceable* hydrogen continues unchanged, we can suppose amide to be a basic radical, forming with hydrogen the base ammonia, but capable of taking up into the radical analogous elements without

affecting the basic character of the ammonia, because we have now the hydrogen compound of an analogous, but more complex, basic radical. On this view, Reiset's radical *b*, may be the hydrogen compound of a basic radical, more complex than amide; in fact, amidide of platinum. Its formula would then be Ad Pt + H, and, although on this view it should correspond to ammonia, rather than ammonium, we cannot speak positively, as this is the least known of the three.

The other two radicals may be readily viewed as hydrogen compounds of complex amidides, as ammonium is the hydrogen compound of amidide of hydrogen.

Amide, NH_2 = Ad, with hydrogen, forms ammonia AdH, and ammonium AdH + H. In like manner, in the radical *a* of Reiset's salts, we have a complex amide, composed of amide and amidide of platinum, Ad + PtAd = $PtAd_2$, which, with 1 eq. hydrogen, may be supposed to form a compound analogous to ammonia, $PtAd_2$,H, and with two eq. of hydrogen, actually does form the radical *a* of Reiset, $PtAd_2H$ + H, exactly analogous to ammonium. So the radical of Gros may be derived from the complex amide PtClAd + Ad = $PtClAd_2$, which may form $PtClAd_2$ + H and $PtClAd_2H$ + H, the latter being the actual composition of the radical of Gros, corresponding to ammonium.

It may also be mentioned, that just as we may view ammoniacal salts as containing ammonia and water rather than ammonium and oxygen, so, the base *b* of Reiset may be, NH_3 + PtO, analogous to NH_3 + HO in the salts of ammonia. If sulphate of ammonia be NH_3,HO + SO_3 the sulphate of Reiset's base *b* will then be NH_3,PtO + SO_3, the protoxide of platinum here playing the part of water, or in other words, platinum playing the part of hydrogen, a substitution far from unnatural or improbable. Again, if we consider the ammoniaco-sulphate of copper to be $\left.\begin{matrix}2NH_3\\CuO\end{matrix}\right\}$ + SO_3, then the sulphate of Reiset's base *a* will be $\left.\begin{matrix}2NH_3\\PtO\end{matrix}\right\}$ + SO_3 where platinum replaces copper, also a not improbable substitution. Reiset is disposed to adopt this view.

The chloride of Gros's radical, $PtClN_2H_6$ + Cl, may be viewed as a compound of bichloride of platinum with ammonia, $PtCl_2$ + $2NH_3$, and there is even reason to think that compounds of that radical may be obtained from the solution of bichloride of platinum in ammonia.

From the above remarks it will appear that every probable view which can be taken of these very interesting bases connects them with amide, ammonia, or ammonium, and it is for this reason that they have been treated of in this section. Many pages might be filled with details concerning them: but we have here only indicated those points which will help to elucidate the constitution of the vegetable alkalies.

That important class of compounds not only contains nitrogen, as an essential element, but exhibits the same analogy with ammonia which we have seen to exist in the compound platinum bases. Moreover, like these bases, the alkaloids do not contain ammonia *as such*; and the probability is very great that their constitution is analogous to that of the bases now described.

II. Carbonic Oxide (as a Radical); C_2O_2=28·106.

Syn.: *Oxalyle.*—There is good reason to believe that the radical of oxalic acid is formed of 2 eq. of carbonic oxide. It has long been known that carbonic

oxide, in the sun's light, combines with chlorine to form phosgene gas or chlorocarbonic acid, CO,Cl or C_2O_2,Cl_2. This compound may be viewed as the chloride of the radical C_2O_2, or as carbonic acid, in which 1 eq. of oxygen is replaced by chlorine, $C \begin{cases} O \\ Cl, \end{cases}$ corresponding to $C \begin{cases} O \\ O \end{cases}$ or CO_2. But the existence of this radical is more securely inferred from the combinations it forms with oxygen, potassium, and amide.

CARBONIC OXIDE AND OXYGEN.

1. Oxalic Acid (C_2O_2) O + HO, or C_2O_4,H=44·132.

This acid occurs in nature, generally in the form of an acid oxalate of potash in certain vegetable juices, such as that of oxalis acetosella, also as oxalate of lime in many lichens. It is formed artificially by the action of nitric acid on sugar, starch, and many other organic compounds; also by the action of hypermanganate of potash on sugar, &c.

To prepare it, one part of pure starch is gently heated with 8 parts of nitric acid, sp. gr. 1·20 or 1·25. A very energetic reaction ensues, and much nitrous acid is disengaged; when this slackens, heat is applied, and continued till no more red vapours appear, when the liquid, if sufficiently evaporated, deposits, on cooling, a large quantity of crystals of hydrated oxalic acid. These are dried on a porous tile, to remove the mother liquor which contains much free nitric acid, saccharic acid, and other products. The dried crystals being dissolved in a little hot water, the solution, on cooling, deposits pure oxalic acid in four-sided prisms, which are colourless, very acid, very soluble in hot water, moderately so in cold water. These crystals contain 3 eq. of water of crystallization, $C_2O_3,HO + 3$ aq. When sharply heated, a part sublimes as dry acid, C_2O_3, HO. Oxalic acid is destroyed by heat without blackening, which seems to distinguish it from most other organic acids.

It is very poisonous, and is the cause of many fatal accidents from its similarity to Epsom salts, from which, however, it is easily distinguished by its very sour taste. The best antidote is prepared chalk administered in water, which forms the insoluble and inert oxalate of lime. It is easily detected by forming with lime water, or a soluble salt of lime, if no free acid be present, the very insoluble oxalate of lime, which when dried and heated to low redness is converted, without blackening, into carbonate of lime.

When oxalic acid, or any of its salts, is heated with oil of vitriol in excess, a brisk effervescence takes place, and the gas given off is a mixture of equal volumes of carbonic acid and carbonic oxide. This character furnishes another good means of recognizing oxalic acid. The reaction is very simple, for C_2O_3, $HO + HO,SO_3 = (SO_3 + 2HO) + CO + CO_2$. The sulphuric acid seizes the whole of the water, and the anhydrous oxalic acid, C_2O_3, cannot exist in the separate state.

When the oxalates of certain protoxides, as those of cobalt and nickel, are heated in close vessels, the metal is left; carbonic acid being given off; $CoO, C_2O_3 = Co + 2CO_2$. Other oxalates, as that of manganese, give off carbonic acid and carbonic oxide, leaving the protoxide of the metal, $MnO,C_2O_3 = MnO + CO + CO_2$.

Oxalic acid forms salts with bases, many of which are insoluble. The insolubility of the oxalate of lime renders oxalic acid useful as a test for lime, and as a means of separating it, and determining its quantity, in analysis. As a test, it is commonly used in the form of oxalate of ammonia. It can only detect lime in neutral or alkaline fluids, the oxalate of lime being soluble in free acids.

The formation of oxalic acid by the action of oxidizing agents on organic matters, is a partial oxidation of their carbon; when that oxidation is complete, carbonic acid is the result. The action of nitric acid on starch or sugar is complicated, and not so well understood as to admit of being expressed in the form of an equation; but the oxidation of sugar by permanganate of potash is very simple, and is thus represented, $C_{12}H_{10}O_{10} + 6\ (KO,Mn_2O_7) = 6\ (KO,C_2O_3) + 10HO + 12MnO_2$; that is, 1 eq. of anhydrous sugar, with 6 eq. of the permanganate, produces 6 eq. of oxalate of patash, 10 eq. of water, and 12 eq. of peroxide of manganese.

The most important oxalates are those of potash, lime and ammonia. There are three oxalates of potash; the neutral oxalate, $KO,C_2O_3 + aq.$; the binoxalate, $KO,C_2O_3 + HO,C_2O_3 + 2$ aq.; and the quadroxalate, $KO,C_2O_3 + 3\ (HO,C_2O_3) + 4$ aq. The oxalate of lime is $CaO,C_2O_3 + 2$ aq. The oxalate of silver AgO,C_2O_3, detonates when heated, yielding, like several other oxalates of the noble metals, carbonic acid, and the metal. The oxalate of ammonia, $NH_4O,C_2O_3 + aq.$ is much used as a test. It crystallizes very readily. When heated, it gives rise to a very remarkable compound, namely, *oxamide*, which is the type of a class. We shall here consider it.

Oxamide, $C_2H_2NO_2 = C_2O + NH_2 = 44{\cdot}296$.

When oxalate of ammonia is heated in a retort, it gives rise to a variety of products, and among these, to a white crystalline powder, insoluble in cold water, which is oxamide. It may be formed far more abundantly by the action of ammonia in solution on oxalate of oxide of ethyle, or oxalic ether. (See oxalate of oxide of ethyle.)

The remarkable character of oxamide is, that while itself neutral, and certainly containing neither oxalic acid nor ammonia, it is easily converted into oxalic acid and ammonia by boiling it either with strong acids or strong alkalies. In this reaction, the elements of 1 eq. of water are shared between the constituents of oxamide, that is, between the radical C_2O_2 and the radical amide, NH_2; for oxamide is nothing more than oxalate of ammonia, NH_4O,C_2O_3, minus 2 eq. of water, or NH_2,C_2O_2. A very small portion of an acid, for example, is sufficient to produce this effect on a large quantity of oxamide; for if the acid we add be neutralized by the ammonia produced, a corresponding quantity of oxalic acid is set free, and acts as any other acid would do. A minute proportion of an acid, therefore, here, appears to exert its influence on an unlimited portion of oxamide, but this is only in appearance. The fact, however, that the presence of a little oxalic acid enables oxamide to decompose water and to produce ammonia and oxalic acid, is very important, and tends to throw light on many similar changes in the organic kingdom, where the agency is not so apparent.

But oxamide is not the only product of the action of heat on oxalate of ammonia; for, besides carbonic acid, carbonic oxide, hydrocyanic acid, water, ammonia, and oxamide, all of which are or may be formed, there is produced, when the heat is so regulated that a honey yellow residue remains in the retort,

a new acid, called oxamic acid, which constitutes that residue. It is mixed with a little oxamide, which is, however, left undissolved by hot water, in which the oxamic acid dissolves.

Oxamic acid forms soluble and crystallizable salts with lime, baryta, ammonia and oxide of silver. Acids precipitate it from the saturated solution of its compound with ammonia, as a white sparingly soluble powder, the composition of which is $C_4H_2NO_5$+aq. Although an acid, this compound exhibits all the relations of a compound of amide or amidogen, being converted by the action of alkalies at a high temperature into oxalic acid and ammonia. It differs, however, from oxamide in yielding 2 eq. oxalic acid and 1 eq. ammonia; for 1 eq. of oxamic acid, *plus* 3 eq. of water, contains the elements of binoxalate of ammonia. $C_4O_5,NH_2+3HO=(HO,C_2O_3)+(NH_4O,C_2O_3)$. This also explains its production;—

for 2 eq. of Oxalate of Ammonia 2 (NH_4O, C_2O_3)	$=C_4H_8N_2O_8$
when acted on by heat,	
Yield 1 eq. ammonia	$= H_3N$
3 eq. water	$= H_3O_3$
1 eq. anhydrous oxamic acid	$=C_4H_2NO_5$
Together . . .	$C_4H_8N_2O_8$

Oxamic acid is certainly a very remarkable compound, being an acid amidide, or at least admitting of being so regarded, C_4O_5,NH_2. There are a few other examples of acid amidides, and we shall soon come to one, namely, *euchronic acid*, which is highly analogous to oxamic acid: being formed by the action of heat on mellitate of ammonia, along with a neutral amidide, *paramide*, similar to oxamide; and as oxamic acid yields acid oxalate, so euchronic acid yields acid mellitate of ammonia when long boiled with water. Cyanic acid may also be considered as, in some sense, an acid amidide; for $C_2NO,HO=C_2O_2,NH$; and $C_2O_2,NH+2HO=NH_3,2CO_2$; or, as is well known, cyanic acid, in contact with water, produces bicarbonate of ammonia.

Oxamic acid may further be viewed as a coupled oxalic acid, the adjunct in which is oxamide: for $C_4O_5NH_2$ is equal to $C_2O_3+C_2O_2,NH_2$. Berzelius adopts this view, and is, generally speaking, favourable to the idea of coupled acids.

By the action of chlorocarbonic acid on alcohol, an ether is formed, which, with ammonia, yields a very beautifully crystallizable compound, long known as oxamethan, which is nothing else than oxamate of oxide of ethyle (see salts of oxide of ethyle). Its composition is $C_8H_7NO_6=(C_4H_5)O+C_4H_2NO_5$. A similar compound exists with oxide of methyle, and was formerly called oxamethylan.

2. Carbonic Acid. $CO_2=22$.

This acid has been already described, and it is introduced here merely because it is formed by the complete oxidation of carbonic oxide; $C_2O_2+O_2=2CO_2$.

CARBONIC ACID AND CHLORINE.

Chlorocarbonic Acid. $C\begin{cases}O\\Cl\end{cases}$ or $CO+Cl=49{\cdot}5$

Syn. *Phosgene gas.* When equal volumes of chlorine and carbonic oxide are

mixed and exposed to the sun's rays, they combine to form a colourless gas, of a pungent disagreeable smell, which acts strongly on the eyes. Sp. gr. of the gas 3·399. When dissolved in water it decomposes it, producing carbonic and hydrochloric acids. With alcohol and pyroxilic spirit it produces very remarkable compound ethers, to be hereafter described.

With ammonia, this acid forms sal-ammoniac, and a white volatile crystalline substance, which is carbamide, CO,NH_2, produced as follows:—$CO,Cl+2NH_3=NH_4,Cl+CO,NH_2$.

Under the influence of the mineral acids, carbamide yields ammonia and carbonic acid, $CO,NH_2+HO=CO_2+NH_3$.

The chlorocarbonic acid may be considered as carbonic acid $C+\begin{cases}O\\O,\end{cases}$ in which half the oxygen has been replaced by its equivalent of chlorine, $C+\begin{cases}O\\Cl.\end{cases}$

CARBONIC OXIDE WITH POTASSIUM.

Oxycarburet of Potassium: Rhodizonic Acid.

When potassium is heated in carbonic oxide gas, combination takes place, and a dark olive powder is formed, composed of carbonic oxide and potassium, in the proportion of $C_7O_7+K_3$, or $7CO+3K$. This substance is formed in large quantity in the preparation of potassium from carbonate of potash and charcoal, and is the source of great loss as well as inconvenience. No such compound is formed with sodium, for which reason that metal may be more cheaply prepared than potassium.

The oxycarburet of potassium, if heated in the air, takes fire, but if exposed to moist air, or placed in water, it is converted into the potash salt of a new acid, rhodizonic acid, hydrogen being disengaged, $C_7O_7K_3+3HO=C_7O_7,3KO+H_3$. As this hydrogen, however, is not pure, but contains carbon, the reaction is probably more complicated.

All the salts of rhodizonic acid are deep red, and when in crystals, reflect a green light. The rhodizonate of potash, when heated in solution in water, undergoes a very remarkable change, yielding free potash, oxalate of potash and croconate of potash, the latter being the salt of another new acid containing the same elements as rhodizonic acid in different proportions; this salt is C_5O_4,KO or C_5O_5K. The composition of rhodizonate of potash explains this reaction perfectly, for $C_7O_7+3KO=KO+KO,C_2O_3+KO,C_5O_4$.

Croconic Acid. C_5O_4,HO? or C_5O_5,H.

This acid is named from the yellow colour of its salts. It is obtained from the croconate of potash, prepared as above, by the action of fluosilicic acid, which separates the potash. The acid is yellow, soluble in water and alcohol, and crystallizes easily. All its salts are likewise yellow.

The rhodizonic acid, $C_7O_7,3HO$, may be viewed as a tribasic hydrogen acid, C_7O_{10},H_3; the croconic acid may also be viewed both as a hydrated oxygen acid, C_5O_4,HO, and as a hydrogen acid, C_5O_5,H. In this last form it connects itself with carbonic oxide, as it may be $5CO+H$. The same remark applies to another remarkable acid, containing the same elements, namely the mellitic acid.

Mellitic Acid. C_4O_3,HO or C_4O_4H.

This acid occurs, combined with alumina, in a very rare mineral, probably of organic origin, the mellite or honey stone. The acid is soluble, very sour, and permanent, not being altered by boiling nitric or sulphuric acids, nor by a heat of nearly 580°. The general formula of its salts, when dried at 212°, is MO,C_4O_4H, or HO,C_4O_4M. The salt of silver, however, at 212°, loses 1 eq. of water, and is left as C_4O_3,AgO, or C_4O_4,Ag. According to the latter formula, the radical in this salt, heated to 212°, is a form of carbonic oxide, $C_4O_4=4CO$.

The crystallized acid C_4O_3,HO, or C_4O_4H, appears to unite with most bases without the separation of water, generally observed when salts are formed. And although the silver salt would seem to contain a different radical, yet it yields, when decomposed, the original mellitic acid.

The mellitate of silver may also be looked on as oxalate of silver AgO,C_2O_3, plus 2 eq. of carbon in the acid AgO,C_4O_3.

The mellitate of ammonia, NH_4O,C_4H_3, when heated in a retort, yields several new and remarkable products. When this salt, $NH_3,HO,C_4O_3=C_4H_4NO_4$ is heated to 320°, it gives off ammonia and water, and there remains a mixture of two new compounds; a soluble one which contains *euchronic acid*, in combination with ammonia, and an insoluble one which is called *paramide*.

Paramide is a yellow solid, like clay. Its most remarkable character is that, when long boiled with water, it is converted into bimellitate of ammonia. This is the character of an amide, hence its name. The composition of paramide is $CHNO_4$, which readily explains, both its formation, and its conversion into bimellitate of ammonia.

If from bimellitate of ammonia, $NH_4O,C_3O_3,+HO,C_4O_3=C_8H_5NO_8$	
we subtract 4 eq. of water	$H_4\ O_4$
there will remain	Paramide$=C_8H\ NO_4$

and of course, when reconverted into bimellitate of ammonia by long boiling, it merely takes up again these 4 eq. of water.

The soluble compound, euchronate of ammonia, when its solution is acted on by hydrochloric acid, deposits a white crystalline powder, which is euchronic acid, $C_{12}NO_6$, 2HO. Its formation is easily explained, for

if from 3 eq. of mellitate of ammonia$=3(C_4H_4NO_4)=$	$C_{12}H_{12}N_3O_{12}$
we subtract 6 eq. of water and 2 eq. of ammonia $=$	$H_{12}N_2O_6$
there will remain anhydrous euchronic acid $=$	$C_{12}\ N\ O_6$

We can now see that the action of heat on 7 eq. of mellitate of ammonia gives rise to the following substances :—

2 eq. Paramide	$=$	$C_{16}H_2\ N_2O_8$
1 eq. Euchronic Acid$=$		$C_{12}\ N\ O_6$
4 eq. Ammonia	$=$	$H_{12}N_4$
14 eq. Water	$=$	$H_{14}\ O_{14}$
7 eq. mellitate of ammonia	$=$	$C_{28}H_{28}N_7O_{28}$

When euchronic acid is boiled with water, it is dissolved and converted into an acid mellitate of ammonia.

1 eq. Euchronic Acid	=	$C_{12}\ NO_6$
and 6 eq. Water	=	$H_6\ O_6$
Together		$C_{12}H_6NO_{12}$
3 eq. Mellitic Acid	=	$C_{12}H_3\ O_{12}$
and 1 eq. Ammonia	=	H_3N
Together		$C_{12}H_6NO_{12}$

Euchronic acid is deoxidized by a plate of zinc, yielding a powder of a fine deep blue colour, which dissolves in ammonia or potash, with a splendid tint of purple. The blue powder is an inferior oxide of the same nitrogenized radical, which, combined with more oxygen, forms euchronic acid. The whole subject of mellitic acid and euchronic acid is most interesting, but mellitic acid is so rare that it is very difficult to find material for the investigation. As mellitic acid, like succinic acid, is of organic origin, and contains only 1 eq. of hydrogen less, and 1 eq. of oxygen more than succinic acid, we may hope to be enabled to obtain it artificially.

III. Cyanogen. C_2N=Cy=26·23.

This very important compound has already been mentioned as a compound of carbon and nitrogen; but we have now to consider it in its far more important character of a compound radical. In fact, it was the first compound radical discovered, and the discovery of cyanogen by Gay-Lussac has proved more fertile in results than any other discovery yet made in Organic Chemistry. As cyanogen acts exactly like an element, we shall represent it by the symbol Cy, rather than by C_2N; using the latter only where the elements of cyanogen, and not itself, enter into changes and reactions.

Cyanogen is formed when animal matter is ignited along with carbonate of potash in close or covered iron vessels. The cyanogen being a gas, and combustible, would be dissipated, and in open vessels burned, were it not that it enters into combination with potassium derived from the carbonate, forming cyanide of potassium, KCy, a salt not altered by a red-heat in close vessels. As this salt, however, is decomposed by the action of water, yielding carbonate of potash and of ammonia, hydrogen being set free, ($K,C_2N + 5HO = KO,CO_2 + NH_3,HO,CO_2 + H$), it is necessary to convert the cyanide of potassium into a more stable compound. This is effected by the addition of iron, or of sulphuret of iron, the latter of which is formed by the mutual action of the sulphate of potash (always present in potashes), carbon, and the iron of the vessel. The iron, or its sulphuret, is readily dissolved by the aqueous solution of cyanide of potassium, yielding cyanide of iron, FeCy, and sulphuret of potassium KS, for $KCy + FeS = FeCy + KS$. The elements of the cyanide of iron then form, with cyanide of potassium, the very permanent double cyanide, well-known as prussiate of potash, properly ferrocyanide of potassium, which forms large and pure, transparent, yellow crystals. From this compound, all the other compounds of cyanogen, and cyanogen itself, are prepared. Its empirical formula is $FeCy,2KCy + 3HO$, or $FeK_2Cy_3 + 3HO$. At 212° it loses all the water, and then contains only iron, potassium, and cyanogen $Fe + K_2 + Cy_3$. It may be conveniently viewed as a compound of cyanide of iron with cyanide of potassium; but we shall see hereafter that its rational formula is probably very dif-

ferent, and that it is a compound of potassium with a new radical, ferrocyanogen.

Cyanogen gas is best prepared by heating dried bicyanide of mercury, when the gas is given off, a part however, assuming the solid form, and remaining behind as a black matter, paracyanogen, isomeric with cyanogen; or by heating a mixture of 6 parts dried ferrocyanide of potassium, and 9 parts bichloride of mercury, when chloride of potassium is formed by the action of the bichloride on the cyanide of potassium of the ferrocyanide, and the cyanide of mercury, if formed, is at once decomposed by the heat. $FeCy,2KCy + HgCl_2 = FeCy, 2KCl + Hg + Cy_2$. The cyanide of iron is not altered. The gas may be collected over mercury, but is absorbed by water, with which it produces the various changes which have been minutely explained at p. 540. It has a very pungent and peculiar smell, is colourless and transparent; and may be liquefied by a pressure of about 4 atmospheres. It is combustible and burns with a beautiful pink or purplish flame.

Cyanogen forms with hydrogen an acid, the hydrocyanic, HCy; with oxygen and the elements of water, three acids, CyO,HO; $Cy_2O_2,2HO$: and Cy_3O_3, $3HO$; of which the first is cyanic, the second fulminic, and the third is cyanuric acid. With chlorine, &c. it combines; with sulphur it forms a new radical CyS_2, sulphocyanogen; and with metals it forms salts, perfectly analogous with chlorides, such as $KCy,FeCy,AgCy,HgCy_2$, &c. In short it plays exactly the part of a simple radical, and were it not easily decomposable, we should at once class it with chlorine as an element.

TABLE OF COMPOUNDS.

Hydrocyanic Acid	CyH.
Cyanic Acid	CyO,HO.
Urea	CyO,HO,NH_3.
Fulminic Acid	$Cy_2O_2,2HO$.
Cyanuric Acid	$Cy_3O_3,3HO$.
Mellone	Cy_3N.
Chloride of Cyanogen, (gaseous)	CyCl.
Chloride " *(solid)*	Cy_3Cl_3
Bromide "	CyBr.
Iodide "	CyI.
Bisulphuret "	CyS_2.
Cyanide of Potassium	CyK. &c., &c.

CYANOGEN AND HYDROGEN.

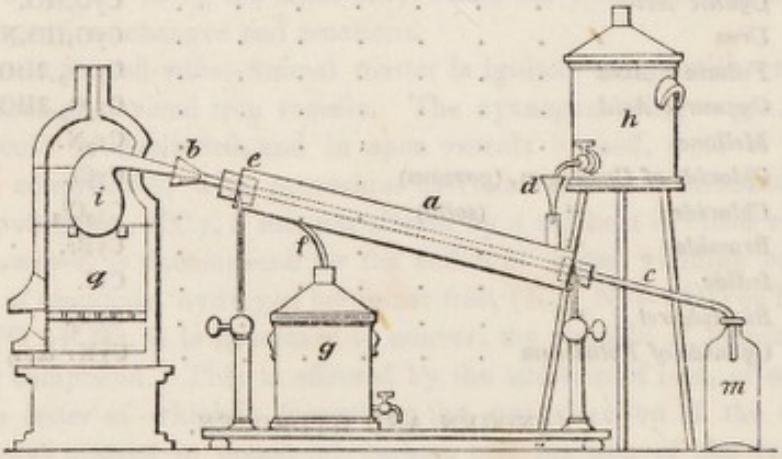
Hydrocyanic or Prussic Acid. HCy = 27·23

This acid may be obtained by a great variety of processes; but the easiest, most economical, and most certain, is to act on the ferrocyanide of potassium with diluted sulphuric acid. The process requires to be slightly modified, according as our object is to prepare the dry or anhydrous acid, or the diluted aqueous solution of it used in medicine.

1. *Anhydrous Acid.*—To prepare this acid, 15 parts of powdered ferrocyanide are to be distilled at a gentle heat with a mixture of 9 parts of oil of vitriol, and 9 of water, and the product is to be received in a convenient receiver placed in a freezing mixture, and containing 5 parts of chloride of calcium in small lumps.

As soon as liquid enough has distilled to cover the chloride, the distillation is stopped, and the hydrocyanic acid, deprived of water by the chloride of calcium, is to be decanted into a dry and well-stopped bottle. It may also be obtained by distilling, under similar circumstances, cyanide of potassium with dilute sulphuric acid. In both cases, the acid is formed by the reaction of sulphuric acid on cyanide of potassium, or its elements. $KCy + H,SO_4 = K,SO_4 + HCy$. Dry hydrocyanic acid is a limpid and colourless liquid, of sp. gr. 0·6967 at 66°; at 59° it becomes a fibrous mass, in consequence of the presence of a trace of water; and at 80° it boils; the density of its vapour is 0·9476. It is inflammable, and has a very peculiar and disagreeable smell and taste. It is the most energetic poison known, one drop introduced into the mouth being sufficient to destroy an animal of considerable size. When pure it is soon spontaneously decomposed, depositing a dark brown solid; a trace of sulphuric acid causes it to keep perfectly. When in contact with the strong mineral acids and water, it is decomposed, being converted into ammonia and formic acid; $H,C_2N + 4HO = NH_3,HO + C_2HO_3$.

2. *Medicinal or diluted Hydrocyanic Acid.*—This may be prepared by simply diluting the anhydrous acid with the required proportion of water, adding, for example, 97 grains of water to 3 of the acid, to obtain an acid of 3 per cent.; which is about the average strength used in medicine. In round numbers, to 1 part, *by weight*, of dry acid, $32\frac{1}{3}$ parts of water, by weight, are to be added; or, to 1 *volume* of anhydrous acid, $22\frac{1}{2}$ volumes of water. But as it is troublesome to prepare the anhydrous acid, it is best to distil 2 parts of ferrocyanide, with 1 of sulphuric acid and 2 of water, to dryness in a chloride of calcium bath, condensing in a Liebig's apparatus,



in the receiver of which 2 more parts of water are placed. By this means we obtain $4\frac{1}{2}$ parts of an acid, not anhydrous, but far too strong for use, containing from 15 to 20 per cent. of dry acid. Its precise strength is ascertained, and it is reduced to the standard strength, in the following simple manner:—

Any convenient quantity, say 50 or 100 grains, is weighed out, being added to a counterpoised vessel containing about 2 drachms of nitrate of silver, dissolved in 2 or 3 ounces of water. Let us suppose that we have dropped into this vessel 70 grains of our acid. This will be entirely converted into cyanide of silver, but we make sure by testing with a drop of nitrate of silver. The precipitate is then collected on a filter, well washed, dried at 212° on a weighed

filter, and the increase in weight of the filter gives the weight of the cyanide of silver formed. Now this cyanide is formed as follows; $HCy + (AgO,NO_5) = AgCy + (HO,NO_5)$. Therefore, 1 eq. of hydrocyanic acid, $HCy = 27{\cdot}23$ produces 1 eq. cyanide of silver $AgCy = 134{\cdot}54$; or 1 grain of anhydrous hydrocyanic acid will yield almost exactly 5 grains of cyanide of silver; for 27·23 : 134·54 : : 1 : 4·94. We may, therefore, safely assume that the weight of the cyanide of silver, divided by 5, gives the weight of anhydrous acid present with sufficient accuracy for all practical purposes. Now, we have used 70 grains of our dilute acid, the strength of which we wish to know. Let us suppose that our filter weighs, when empty, 20 grains, and with the cyanide of silver, dried at 212° till it ceases to lose weight, 100 grains. The difference, or 80 grains, is the weight of cyanide of silver obtained from 70 grains of our acid. Dividing this by 5, we have 16 grains as the weight of anhydrous acid contained in the 70 grains, and consequently combined with 54 of water.

Now, if we wish to state the per centage of this acid, we obtain it by the calculation, 70 : 16 : : 100 : x, and $x = \frac{16 \times 100}{70} = 22{\cdot}85$, so that our acid contains 22·85 per cent. of anhydrous acid. But if our only object be to reduce the acid to a standard strength, say that of 3 per cent., this last calculation is unnecessary, and we can proceed as follows: acid of 3 per cent. contains 3 grs. of dry acid and 97 of water; therefore, to find how much water is to be added to 16 grs. of anhydrous acid, 3 : 97 : : 16 : x, and $x = \frac{97 \times 16}{3} = 517{\cdot}3$ grains of water, which must be added to 16 grs. of anhydrous acid, to bring it to the same strength. But our 70 grains of acid contain already, with the 16 of anhydrous acid, 54 grains of water, consequently we have only to add to these 70 grains 517·3 — 54 = 463·3 grains of water, and the same quantity of water for every 70 grains of the same acid. Of course, it is easy to calculate the water necessary for 1 or more ounces of the acid, when we have once found it for any given quantity. I have here supposed 70 grains, but with 50 or 100 the calcution is easier, and with a drachm by weight (60 grains), we have simple data for calculating how much water is required for any number of ounces or drachms of acid.

This beautiful and simple method of preparing the medicinal hydrocyanic acid, and ascertaining its precise strength, has been minutely described, because of its practical importance. It is so simple an operation, that any one may very soon learn to ascertain the strength of hydrocyanic acid, and it is very exact. Besides, no other method of obtaining a medicinal acid of uniform strength ought to be trusted to; and we ought never to attempt to obtain the acid of the standard strength by distillation, although many methods are given for this. I have never seen any one of these yield twice the same result; whereas by the above method we can prepare acid of exactly the same strength any number of times, and the acid prepared from the ferrocyanide, by sulphuric acid, keeps perfectly well. Of course, when we have added the calculated quantity of water to reduce the acid, it is proper to ascertain its strength once more, to make sure that we have made no error in our calculation. If it be acid of 3 per cent., it will yield 15 grains of cyanide of silver from 100 of acid.

There are two other methods which deserve to be mentioned, as, with pure materials and careful manipulation, they yield, in a few minutes, a standard acid. The first is that of Dr. Clarke, who adds to 1 eq. cyanide of potassium dissolved

in water, 2 eq. tartaric acid, which separates the potassium as cream of tartar, while diluted hydrocyanic acid remains dissolved. For every 100 grs. of water, $7\frac{1}{3}$ grs. of cyanide of potassium and $16\frac{1}{2}$ of crystallized tartaric acid, are required. This is an excellent extemporaneous process, if we have pure cyanide of potassium, but that salt does not keep well, and even in its preparation it is apt to be decomposed, at least, partially. It is, besides, an expensive salt. The other is the process of Everett, who suspends cyanide of silver in water, and adds an equivalent of hydrochloric acid. $AgCy + HCl = AgCl + HCy$. This is also a good extemporaneous process, 15 grs. of AgCy being used for every 100 of water, and 4 grs. of dry HCl, that is, about 12 grs. of acid sp. gr. 1·21, being added. This process is also expensive, although the silver is not lost; but the chief objection is, that it is difficult to add the precise amount of hydrochloric acid which is necessary, and that an excess causes, *pro tanto*, a conversion of the hydrocyanic acid into formic acid and ammonia.

The medicinal acid has the smell and taste of the anhydrous, and is very poisonous, the average dose safe for an adult being 1 to 2 drops in a glass of water. It is as much used as a sedative and anodyne, but, unless its strength and dose be perfectly known, it is a dangerous remedy. Fatal accidents have occurred from prescriptions, found, after experience, to act favourably, being made up in another place, or by the same druggist with a fresh stock; this fresh stock being exactly of the standard strength, while the previous acid had lost so much by keeping that the dose has been of necessity increased. There, danger actually arose from a too weak acid being used. Hence the necessity for the great exactness, for which rules are given above. In cases of poisoning by this acid, now unfortunately of very frequent occurrence, there is seldom time to administer an antidote; but when life is not extinct, we may confidently rely on the antidotes we possess. The best is the administration of two solutions, one of mixed sulphate of protoxide and peroxide of iron, and the other of carbonate of potash, as recommended by Messrs. Smith, Edinburgh,* by which the acid still in the stomach is rendered insoluble, being converted into Prussian blue. The symptoms already produced are best combated by ammonia inspired from a sponge, or taken, diluted, internally, and by other diffusible stimulants; also by the cold affusion.

Hydrocyanic acid is very easily recognized by its smell, and by its forming Prussian blue if acted on, in solution, successively, by proto-persulphate of iron, by potash, and by an excess of hydrochloric acid. The first two tests form the Prussian blue, the last, dissolving the excess of oxide of iron, brings the blue into view. Any liquid, suspected to contain hydrocyanic acid, ought first to be distilled with the addition of a little dilute sulphuric acid, and the tests applied to the first ounce that comes over. Nitrate of silver produces a white cloud of cyanide of silver, exactly like the chloride in appearance.

Hydrocyanic acid, with metallic oxides, gives rise to water and metallic cyanides. $HCy + MO = HO + MCy$: or $2HCy + MO_2 = 2HO + MCy_2$.

CYANOGEN AND OXYGEN.

1. Cyanic Acid. $CyO,HO = CyO_2,H = 43{\cdot}25$.

A monobasic acid; is formed when dry cyanide of potassium is heated in the

* See *Lancet* for 1844, vol. ii. p. 41.

air, when oxygen is absorbed, and cyanate of potash is produced. $KCy + O_2 = KO,CyO$ or K,CyO_2.

When a stronger acid is added to this salt, the cyanic acid is set free, but immediately decomposes with water, producing ammonia which unites with the strong acid used, and carbonic acid which escapes as gas. $C_2NO,HO + 2HO = NH_3 + 2CO_3$. The carbonic acid carries with it a little cyanic acid, which forms dense white vapours, and has a pungent acid smell like that of strong acetic acid. Under all circumstances, free cyanic acid, in contact with water, is instantly destroyed.

It may, however, be obtained in the anhydrous state, according to the formula $CyO_2 + H$, or as monohydrated acid, if viewed as CyO,HO, by distilling cyanuric acid, $Cy_3O_6 + H_3$, or $Cy_3O_3 + 3HO$. This acid is isomeric with cyanic acid, and, when heated, 1 eq. cyanuric acid splits up into 3 eq. cyanic acid, which appears in the receiver as a volatile, pungent, very corrosive acid liquid. This acid only keeps for a very short time, even in the freezing mixture in which it is condensed. If removed from the cold, it soon becomes turbid, then hot, boils violently and with violent shocks, and is converted into a solid dense white body, like porcelain, quite insoluble and indifferent.

This is *Cyamelide*, another isomeric compound, containing the same elements in the same proportions, but differently arranged, possibly $C_2O_2 + NH$; for it yields, under the influence of water and strong acids, carbonic acid and ammonia, ($C_2O_2,NH + 2HO = 2CO_2 + NH_2$) just as cyanic acid does. When distilled, it is reconverted into cyanic acid, another proof that it is isomeric with that acid.

CYANATES.

The salts of cyanic acid are all distinguished by the action on them of strong acids, which cause disengagement of carbonic acid, while ammonia may now be detected in the liquid. The cyanates of potash, ammonia, &c. are soluble, those of lead, silver, &c., insoluble.

Cyanate of Potash is best formed by the oxidation of Liebig's cyanide of potassium,* which may easily be effected by adding litharge in proper quantity to the melted salt, $KCy + 2PbO = K,CyO_2 + Pb_2$. The cooled mass is powdered and boiled with alcohol of 80 per cent., which on cooling deposits pure crystals of cyanate of potash, very similar to chlorate of potash. Or dried ferrocyanide of potassium, mixed with half its weight of peroxide of manganese, may be gently heated, spread out on an iron plate, when it burns like tinder, partly at the expense of the oxide of manganese, partly in the oxygen of the air. It is well stirred till every part has glowed, and the cold mass is treated with alcohol as above.

Cyanate of potash must be kept in sealed tubes, for in phials occasionally opened it is soon changed into bicarbonate of potash, ammonia being given off. $K,C_2NO_2 + 3HO = (KO_1 2CO_2) + NH_3$: Triturated with dried oxalic acid, this salt yields oxalate of potash and cyamelide. When acetic acid is added to a concentrated freshly made solution of cyanate of potash, the latter being in excess, there is deposited the acid cyanurate of potash,

$$Cy_3O_6 \begin{cases} K \\ H_2 \end{cases} \text{ or } Cy_3O_3 \begin{cases} KO \\ 2HO \end{cases}$$

* The formation of this salt will be described below.

a. *basic.* When dry ammonia and the vapour of cyanic acid are mixed, they form a light white solid, which is a cyanate of ammonia, containing more ammonia than is required for a neutral salt. This salt gives off ammonia when treated with alkalies, and cyanic acid when treated with sulphuric acid. But if dissolved in water, and the solution digested and evaporated, it yields crystals, which, although containing the elements of cyanic acid, ammonia, and water, exhibit neither of these characters of a cyanate, but are found to possess all the properties of *urea*, a product of the animal system.

b. *anomalous cyanate of ammonia*, or urea, $C_2H_4N_2O_2=(C_2NO,HO,NH_3)$. This remarkable compound exists in large proportion in healthy urine, and is extracted from it by evaporating at about 200° to a thin syrup, and adding about an equal volume of colourless nitric acid, sp. gr. 1·35, quite free from nitrous acid, which forms a very copious crystallization of nitrate of urea, while the colouring matter is destroyed with brisk effervescence. If cold be applied, the colouring matter resists, and the nitrate is then very dark and very difficult to purify; cold ought therefore, not to be used, and the nitrate of urea is deposited nearly white, having only a clear yellow tint. It is dissolved in water, after being recrystallized, and neutralized by potash or baryta. The whole is then gently evaporated to dryness, after separating as much nitrate of potash or of baryta as possible, and the dry mass digested in alcohol, which dissolves only the urea, and by spontaneous evaporation yields it in large transparent prismatic crystals. Should these not be colourless, the digestion of their aqueous solution with a little permanganate of potash, which has no action on urea, destroys the colouring matter entirely. Should an excess of that salt be added, a few drops of alcohol will instantly destroy it, and the filtered liquor will yield snow-white crystals of urea.

But although urea may thus be obtained (or by the action of oxalic acid on the urine, which forms a sparingly soluble oxalate of urea) in any quantity from urine, it is found much easier to prepare it artificially from cyanate of ammonia. Liebig recommends the following process, which I have found to succeed perfectly. 28 parts of dried ferrocyanide of potassium, and 14 of peroxide of manganese are mixed in powder and calcined, as above described, on a flat iron plate at a very low red heat, sufficient to keep up the glow which takes place. When this is over, the cold mass, powdered, is acted on by a moderate quantity of cold water, which dissolves the cyanate of potash. This is filtered off, and set aside. A fresh portion of cold water being added to the powder, to wash it, is also filtered, and in this liquid are now dissolved 20½ parts of sulphate of ammonia, and the solution is added to the first filtered solution of the cyanate. A large quantity of sulphate of potash is deposited, which is strained off, and the filtered liquid now containing, with some sulphate of potash, all the cyanate of ammonia, is evaporated to dryness, during which process the cyanate of ammonia is transformed into urea. The dry mass is digested in alcohol, which dissolves only the urea, and yields it from the first chemically pure and in any quantity, if the operation be carefully performed. Urea thus obtained is far cheaper than that extracted from urine.

The artificial production of urea from cyanate of ammonia was discovered by Wöhler. It was the first example of an organic product artificially formed, although many other cases are now known.

Urea forms four-sided prisms, resembling nitre in appearance, and also in their taste, which is saline and cooling, exactly like that of nitre. It is soluble both in water and alcohol. When heated, it melts, gives off much ammonia, and finally solidifies, being in a great measure converted into ammonia and cyanuric acid.

Urea belongs to the class of organic bases, for it forms crystallizable compounds with several acids, such as nitric, oxalic, and acetic acids.

The nitrate, when impure, crystallizes in scales of a high lustre; when pure, it forms opaque prisms, or a crystalline powder. It is sparingly soluble in cold water, but very soluble in hot water. Formula, ($C_2H_4N_2O_2$,HO,NO_5.)

The oxalate forms long transparent prisms, very sparingly soluble. Formula, ($C_2H_4N_2O_2$,HO,C_2O_3)=$C_4H_5N_2O_6$.

The acetate I have obtained as a mass of prismatic crystals, exceedingly soluble in water. Formula, probably ($C_2H_4N_2O_2$,HO,$C_4H_3O_3$)=$C_6H_8N_2O_6$.

Although urea combines with pure nitric acid, it is instantaneously decomposed by hyponitrous acid, yielding ammonia, water, and equal volumes of carbonic acid and nitrogen gases. $C_2H_4N_2O_2+NO_5=NH_3+HO+2CO_2+N_2$. When acted on by strong acids, or alkalies, with the aid of heat, urea takes up the elements of water, and forms carbonate of ammonia, $C_2H_4N_2O_2+2HO=2(NH_3, CO_2)$. When urine is left in contact with the mucus usually suspended in it, the mucus entering into decomposition excites in the urea such a reaction with the elements of water, as very soon to convert the whole urea into carbonate of ammonia. Hence the reason why urine soon becomes alkaline, even if acid when voided. But if filtered from the mucus as soon as passed, it keeps unchanged, in clean vessels, for a long period.

2. Fulminic Acid. Cy_2O_2, 2HO=Cy_2O_4,H_2=86·5.

A bibasic acid, unknown in the separate form. It is obtained in combination with oxide of mercury, or oxide of silver, by treating alcohol with the nitrates of these metals, and free nitric acid. A violent effervescence takes place, dense white vapours are disengaged, and a crystalline powder is deposited, which is fulminate of mercury or of silver. Both detonate powerfully by heat, friction, or percussion.

In the above reaction there are first formed, on the one hand, hyponitrous acid; on the other, aldehyde, and formic and oxalic acids. The fulminic acid is the result of a reaction between oxide of ethyle (ether) and hyponitrous acid, in presence of oxide of mercury or oxide of silver. $2NO_3+C_4H_5)O=C_4N_2O_2+5HO$ $=Cy_2O_2$, 2HO+3HO.

This acid cannot be isolated, being instantly decomposed when deprived of a fixed base. It forms two series of salts: neutral, with 2 eq. of fixed base, Cy_2O_2, 2MO; and acid, with 1 eq. of fixed base and 1 of water $Cy_2O_2 \left\{ \begin{matrix} HO \\ MO. \end{matrix} \right.$ It also forms salts with 1 eq. of two different bases, of which one is always easily reducible, as oxide of silver, mercury and copper, while the other may be difficult to reduce, such as baryta, potash, &c.

The fulminates of silver and mercury, Cy_2O_2, 2AgO, and Cy_2O_2, 2HgO, are examples of the first class. The acid fulminate of zinc $Cy_2O_2 \left\{ \begin{matrix} HO \\ ZnO, \end{matrix} \right.$ formerly supposed to be the fulminic acid, is an example of the second; and the double

fulminates of copper and silver, and of potash and silver, $Cy_2O_2 \begin{cases} CuO \\ AgO, \end{cases}$ and $Cy_2O_2 \begin{cases} KO \\ AgO \end{cases}$ are examples of the third. No neutral fulminates exist with 2 eq. of a difficultly reducible oxide, such as potassa, soda, baryta, &c.; nor do any acid fulminates occur with such bases. These very remarkable facts evidently point to some relation, not yet understood, between the oxygen of the base in a salt and the acid of that salt. Of course all the above formulæ may be written according to the theory of compound radicals and hydrogen acids.

To prepare the fulminate of mercury, which is much used for percussion caps, 1 part of mercury is dissolved in 12 parts of nitric acid, sp. gr. 1·36; 11 parts of alcohol at 80 per cent. are added, and the whole is warmed. A brisk reaction soon ensues, very thick white vapours are given off, and the salt is deposited in crystalline grains, mixed with a little metallic mercury. This salt explodes by friction, by percussion, or by heat, and it is a dangerous product, exploding occasionally without apparent cause. An explosion of this nature, not long since, destroyed the distinguished chemist, Mr. Hennell, who was preparing a large quantity in the open air. The fulminate of silver is prepared in the same way, only with 10 parts of nitric acid and 20 of alcohol. Caustic alkalies precipitate from its solution half the silver, forming double fulminates; and chlorides also only precipitate half the silver. Nitric acid, added to the solution, causes a deposit of acid fulminate of silver,

$$Cy_2O_2 \begin{cases} H\ O \\ AgO \end{cases} \text{ or } Cy_2O_4 \begin{cases} H \\ Ag \end{cases}$$

Hydrochloric acid added to fulminate of silver, gives rise to water, chloride of silver, hydrocyanic acid, and a new acid, chlorohydrocyanic acid C_2NCl_5,H_2. Thus—

$$C_4N_2O_2,\ 2AgO + 7HCl = 4HO + 2AgCl + C_2NH + C_2NCl_5,H_2.$$

3. Cyanuric Acid. $Cy_3O_3,\ 3HO = Cy_3O_6,H_3 = 126{\cdot}75$.

A tribasic acid discovered among the products of the distillation of uric acid. It is formed when solid chloride of cyanogen Cy_3Cl_3 acts on water: $Cy_3Cl_3 + 6HO = 3HCl + Cy_3O_6,H_3$. It is also formed when urea is heated so as to expel its ammonia. According to what has been stated of the composition of urea, it ought to yield cyanic acid when deprived of its ammonia; but at that temperature 3 eq. of cyanic acid, 3CyO,HO, coalesce to form 1 eq. of cyanuric acid, $Cy_3O_3,3HO$. When, again, acetic acid is added to cyanate of potash, in quantity insufficient to decompose the whole, there is deposited a salt which is an acid cyanurate of potash, $Cy_3O_3 \begin{cases} KO \\ 2HO. \end{cases}$

Finally, cyanuric acid is obtained by dissolving melame, ammeline, ammelide and melamine (see those substances) in sulphuric acid, and diluting and heating the solution, until it yields no precipitate with ammonia. On evaporation and cooling, the acid forms prismatic crystals, which are $Cy_3O_3,3HO + 4$ aq. When dissolved in hot nitric or hydrochloric acid, it is deposited, on cooling, in anhydrous octahedrons. When it has been prepared by heating urea, it is purified by dissolving it in oil of vitriol, and adding nitric acid, drop by drop, till the

colour is entirely destroyed. An equal bulk of water is then added, and on cooling, pure cyanuric acid is obtained in crystals.

Cyanuric acid has a weak acid taste, and is sparingly soluble in cold water, more soluble in hot water. Unlike cyanic and fulminic acids, it is very permanent in the uncombined state. When heated in close vessels, it is entirely volatilized in the form of cyanic acid, of which 3 eq. are exactly equal to 1 eq. of cyanuric acid.

As cyanuric acid is formed when urea (cyanate of ammonia) is decomposed by heat, and when cyanate of potass is acted on by acetic acid, and as cyanuric acid, when heated, is resolved into cyanic acid, we have every reason to think that in the former cases, 3 eqs. of cyanic acid coalesce to form one of cyanuric acid, and that, in the latter case, 1 eq. of cyanuric acid is broken up into 3 eqs. of cyanic acid. $3(CyO,HO)=Cy_3O_3,3HO$.

Like other tribasic acids, cyanuric acid forms three series of salts, according to the formulæ :—

Hydrated Acid.	Salt with 1 eq. of fixed base.	Salt with 2 eq. of fixed base.	Salt with 3 eq. of fixed base.
Cy_3O_3, 3HO	Cy_3O_3 { MO, 2HO	Cy_3O_3 {2MO, HO	Cy_3O_3, 3MO

The salts with 1 and 2 eqs. of fixed base are acid; that with 3 eqs. is neutral. With potash and other similar oxides, only the two acid salts are known: with oxide of silver, the salts with 2 and 3 eqs. of oxide.

The three following salts, namely,

Cyanate of Silver.	Fulminate of Silver.	Cyanurate of Silver.
CyO, AgO;	Cy_2O_2, 2AgO;	Cy_3O_3, 3AgO.

have exactly the same composition in 100 parts; and yet they are in properties entirely dissimilar; this can only be accounted for by some such difference in their formulæ, as is exhibited above. The acids of these salts are all mutually convertible: for when fulminate of silver is decomposed by a salt of ammonia, the fulminate of ammonia is transformed, like the cyanate, into urea; urea when heated yields cyanuric acid; and cyanuric acid when distilled is transformed into cyanic acid. All these circumstances favour the belief that all three are compounds of cyanogen, and that they differ in the absolute number of equivalents of their elements.

Cyamelide; $C_2O_2 + NH$?

But this is not the end of these transformations: for when cyanic acid is left to itself it becomes turbid and hot, and is soon converted with great heat, into an opaque white solid body, cyamelide, which has no acid properties; and which is also obtained as a white insoluble powder, when fused cyanate of potash is triturated with dried oxalic acid, in which case oxalate of potash is formed, and the cyanic acid, at the moment of being set free, is transformed into cyamelide. Cyamelide is neutral and insoluble in water and acids. It dissolves in aqua potassæ, ammonia being evolved, and the solution yields cyanurate of potash. Heated by itself it yields cyanic acid, which again passes into cyamelide; and when heated with strong sulphuric acid it forms sulphate of ammonia, while carbonic acid escapes; this action is identical with that which occurs when cyanic acid is acted on by water and by acids. All these observations prove that cyame-

lide is another isomeric modification of cyanic, fulminic, or cyanuric acid. Its probable formula is $C_2O_2 + NH$, and this, with 2 eqs. HO, yields bicarbonate of ammonia, just as cyanic acid, the formula of which is the same, does. The action of potash is probably this. $4(C_2O_2NH) + 3HO + 4KO = C_6N_3O_6$, $\left\{\begin{matrix} 2KO \\ HO \end{matrix}\right. + 2KO,CO_2 + NH_3$; that is: 4 eqs. cyamelide, 3 eqs. water, and 4 eqs. potash, yield 1 eq. cyanurate of potash, 2 eqs. carbonate of potash, and 1 eq. ammonia.

The three oxygen acids of cyanogen may be fitly compared with the three phosphoric acids; and as we have hitherto made use of the older view of these acids, that which makes them hydrated oxygen acid, we shall, in this comparison, adopt the other theory, and speak of them as hydrogen acids.

	Monobasic.	Bibasic.	Tribasic.
Acids of Cyanogen . .	$CyO_2 + H$	$Cy_2O_4 + H_2$	$Cy_3O_6 + H^3$
Acids of Phosphorus . .	$P_2O_6 + H$	$P_2O_7 + H_2$	$P_2O_8 + H_3$

In the cyanic acids, both the radical and the replaceable hydrogen being doubled and trebled, the capacity of saturation increases in the same ratio. In the phosphoric acids, the capacity of saturation also increases with the replaceable hydrogen, but a great addition to the radical has no corresponding effect in increasing either the replaceable hydrogen or the neutralizing power. Thus, if to tribasic phosphoric acid $P_2O_8 + H$, we add 2 eqs. of $P_2O_5 = P_4O_{10}$ we obtain $P_6O_{18} + H_3 = 3(P_2O_6 + H)$; that is, the acid becomes monobasic, but the quantity of base neutralized is the same after that addition as before. Notwithstanding this difference, however, the analogy between the monobasic, bibasic, and tribasic acids of cyanogen and phosphorus, as well as that between their salts, is most interesting and worthy of attention. As we believe that the phosphoric acids contain three different radicals, P_2O_6, P_2O_7, and P_2O_8, so we may admit that the three cyanic acids have each a distinct radical; only in this case the three radicals are alike in composition, and differ in their relative weight: the first being $C_2N = Cy$; the second $C_4N_2 = Cy_2$; and the third $C_6N_3 = Cy_3$; or, in other words, these radicals are three different cyanogens. The relations of chlorine to cyanogen countenance this idea.

CYANOGEN AND NITROGEN.

Mellone $= Cy_3N = C_6N_4 = Me = 93$.

Cyanogen, when it combines with nitrogen in the proportion of 3 eq. Cy to 1 eq. $N = C_6N_4$, produces a very remarkable compound, discovered by Liebig, and called mellone, which being itself a well marked compound radical, will be described as such, and not as a compound of cyanogen and nitrogen.

CYANOGEN AND CHLORINE.

Cyanogen forms two chlorides: one gaseous, but compressible, obtained by the action of chlorine gas on dry hydrocyanic acid; the other solid, formed by a spontaneous transformation of the former when kept in the liquid form in sealed tubes. Both are volatile and both contain cyanogen and chlorine, equivalent for equivalent. But the vapour of the solid chloride is three times denser than that of the other; and, moreover, the solid chloride, in contact with water, produces

hydrochloric and cyanuric acids: while the gaseous chloride, under the same circumstances, gives rise to hydrochloric acid, and cyanic acid, the latter with water, at once passing into bicarbonate of ammonia, so that the final result is sal ammoniac and carbonic acid.

These considerations prove that the two chlorides are isomeric: that the first or gaseous chloride is CyCl; and that the solid chloride is Cy_3Cl_3, and is formed by the junction of 3 eq. of the other; and we are consequently justified in extending this view to cyanic and cyanuric acids, and in supposing the vapour of the latter to be three times more condensed than the vapour of cyanic acid: and the cyanogen of cyanuric acid to be the cyanogen of the solid chloride, and three times denser than ordinary cyanogen.

CYANOGEN WITH BROMINE AND IODINE.

With these elements cyanogen readily combines when cyanide of mercury is distilled with bromine or iodine. The bromide and iodide are both volatile, and crystallizable, pungent and poisonous.

To judge by the density of their vapours, these compounds are CyBr and CyI, corresponding to the liquid chloride, which is also very pungent and irritating to the eyes.

CYANOGEN AND SULPHUR.

Bisulphuret of Cyanogen. $CyS_2 = 58{\cdot}5$.

When sulphocyanide of potassium, (see that salt) is acted on by chlorine or by dilute nitric acid, there is obtained an orange-yellow powder, which contains sulphur and cyanogen, and which is supposed by some to be bisulphuret of cyanogen, by others to contain hydrogen. This question will be considered hereafter, for whether this be so or not, there is a compound, possibly that compound of sulphur and cyanogen, which acts as a radical, and is hence called sulphocyanogen. It will be described separately, since it is far more important as a radical than as a compound of cyanogen.

CYANOGEN AND METALS.

With metals, cyanogen forms compounds which in many cases are analogous to the chlorides of the same metal. When the metal is easily reducible, such as silver, mercury or palladium, the cyanide is formed by the action of hydrocyanic acid on the oxide, or its salts: $MO + HCy = HO + MCy$. In the case of difficultly reducible metals, such as potassium, hydrocyanic acid seems to combine with the oxide, not being able to reduce it, until another cyanide is added, which tends to form a double cyanide.

Cyanide of Potassium, = KCy is best formed by heating to whiteness in close vessels the ferrocyanide of potassium, a salt which may be viewed as containing cyanide of iron and cyanide of potassium. The former is converted into insoluble carburet of iron; the latter remains unchanged, and may be mechanically picked out, or dissolved by hot alcohol of 60 p. c., which deposits it on cooling. Or, an alcoholic solution of pure and dry hydrocyanic acid is added to an alcoholic solution of potash; or, lastly, the vapours of hydrocyanic acid, formed on the process given at p. 556, are conducted into an alcoholic solution of potassa, kept cool, when the salt is deposited.

It is white, and crystallizable in cubes. It has no smell when pure, but when exposed to moist air, smells of hydrocyanic acid. It is very poisonous. When heated it fuses easily, and is not altered by heat in close vessels. Heated in the air it absorbs oxygen and is converted into cyanate of potash $KCy + O_2 = KO.CyO$. It is very soluble and deliquescent, and its solution, attracting carbonic acid from the air, gives off hydrocyanic acid: hence its smell.

Cyanide of Sodium is analogous to the preceding salt.

Cyanide of Zinc, ZnCy is obtained by adding hydrocyanic acid to acetate of zinc. It is a snow-white insoluble powder, which is used in medicine.

Cyanide of Iron.—Protocyanide of iron, FeCy, has not been isolated. There appears to exist a percyanide, also not yet isolated, Fe_2Cy_3; and, according to Pelouze, there may be obtained an intermediate cyanide, Fe_3Cy_4, analogous to the magnetic oxide of iron, as a green powder.

But although the cyanides of iron are little known, there are some very important compounds, especially those of two radicals, which contain those elements, namely, cyanogen and iron, along with hydrogen and with metals. These will be described after we have gone over the simple cyanides of the metals.

Cyanide of Cobalt, CoCy, is obtained as a brownish-white precipitate, by adding hydrocyanic acid to the acetate of cobalt. Cobalt also forms compounds analogous to those of iron above alluded to, with cyanogen, &c.

Bicyanide of Mercury, $HgCy_2$, is easily obtained by dissolving red oxide of mercury in very dilute hydrocyanic acid, till the smell of the acid is destroyed. The liquid, rendered neutral, if necessary, by a few drops of hydrocyanic acid, yields fine crystals, on evaporation and cooling. Or it may be made by the action of three parts of persulphate of mercury on two of ferrocyanide of potassium dissolved in fifteen of hot water, which is boiled and filtered, and the filtered liquid on cooling deposits the bicyanide.

It forms regular prismatic crystals, permanent in the air, of a horrible metallic taste, soluble in water and alcohol. It is used for making cyanogen, also to prepare hydrocyanic acid by one process, and to yield the bromide and iodide of cyanogen.

Cyanide of Silver. AgCy.—Formed by the action of hydrocyanic acid or cyanide of potassium on nitrate of silver. It is exactly similar to the chloride, white, curdy, insoluble in water or acids, soluble in ammonia. It is decomposed by hydrochloric acid, yielding hydrocyanic acid.

Cyanide of Palladium, PdCy.—The affinity of cyanogen for palladium is most powerful, and hydrocyanic acid, or a soluble cyanide, when added to a salt of oxide of palladium, precipitate the cyanide as a grey powder. This property serves for separating palladium from other metals.

Cyanides of Gold.—The protocyanide, AuCy, is formed by adding cyanide of potassium in excess to protochloride of gold, till a clear solution is formed, and then adding hydrochloric acid, which precipitates the protocyanide as a bright-yellow powder, very permanent, and soluble in cyanide of potassium.

The tercyanide, $AnCy_3$, is formed by the action of cyanide of potassium on terchloride of gold, and appears as whitish-yellow precipitate, soluble in cyanide of potassium, insoluble in acids.

DOUBLE CYANIDES OF THE METALS.

The insoluble metallic cyanides, such as those of iron, cobalt, copper, silver, gold, platinum, and others, dissolve readily in cyanide of potassium, or sodium, forming crystallizable double cyanides, which are not affected by soluble carbonates nor by chlorides, but are generally decomposed by acids, which precipitate the insoluble cyanide. If these double cyanides, which may be $2KCy + mCy$ (mCy being an insoluble metallic cyanide) are added to the solution of the oxide of another metal forming also an insoluble cyanide, this latter metal takes the place of the potassium, and a new double insoluble cyanide is the result. Thus $(2\,KCy + mCy) + 2MO = 2KO + (2MCy + mCy)$. (Here m may be iron and M copper or lead.) Now, as these double cyanides, thus precipitated, are of various and often characteristic colours, the ferrocyanide of potassium, $2KCy + FeCy$, is extensively used as a test for metals.

The protocyanide of iron, the percyanide of iron, the percyanide of cobalt, and perhaps some others, not only form double salts with the elements of cyanide of potassium, but also produce very remarkable acids, by combining with the elements of hydrocyanic acid, that is, with hydrogen replacing the potassium of the double salt. Thus ferrocyanic acid is $2HCy + FeCy$, and so on. In these compounds the hydrocyanic acid is no longer poisonous, and it is therefore highly probable that these acids, and their corresponding salts, really contain new and very peculiar radicals. The assumption of these radicals will alone enable us to classify or remember these compounds.

IV. Ferrocyanogen. $Cy_3Fe = Cfy = 105{\cdot}87$.

We assume, then, the existence of this radical as the basis of ferrocyanide of potassium, or prussiate of potash. It is bibasic, combining with 2 eq. of hydrogen or of metals. The following formulæ expresses the composition of ferrocyanic acid, and of ferrocyanide of potassium, &c.

Ferrocyanic Acid	$= Cfy,H_2$	$= Cy_3Fe,H_2$	$= 2HCy + FeCy.$
Ferrocyanide of Potassium	$= Cfy,K_2$	$= Cy_3Fe,K_2$	$= 2KCy + FeCy.$
—— Iron	$= 3Cfy,Fe_4$	$= 3Cy_3Fe,Fe_4$	$= 9Cy + 7Fe.$

It will be seen, by the two first compounds, that we may consider them either as compounds of the radical Cfy with hydrogen or metals, or as double cyanides. In the third, which is the formulæ of Prussian blue, we see that the iron exists in two different states, in one of which it cannot be detected by the usual tests. That form is the radical Cfy, which exists also in the two preceding compounds.

Ferrocyanic Acid. $Cfy,H_2 = 107{\cdot}87$.

This very interesting compound is obtained by mixing a cold saturated solution of ferrocyanide of potassium with one quarter its volume of strong hydrochloric acid, and, agitating the mixture with half its bulk of pure ether, the ether rises to the surface, carrying with it, suspended, a white crystalline substance, which when washed with ether and dried, is ferrocyanic acid. It is soluble in water and alcohol, has a decidedly acid taste and reaction, and decomposes the alkaline carbonates, forming, with carbonate of potash, the ferrocyanide of potassium. The production of this compound by the action of hydrochloric acid on

ferrocyanide of potassium is very easily explained. $Cfy,K_2 + 2HCl = Cfy,H_2 + 2KCl$.

Although this compound may be represented as a combination of cyanide of iron with hydrocyanic acid, $FeCy + 2HCy$, there is every reason to believe that it contains no hydrocyanic acid, as such. For not only is it far more strongly acid, (and protocyanide of iron cannot be supposed to give acid properties to hydrocyanic acid,) but it is totally destitute of all poisonous properties, for both it and its salts may be taken internally without further effect than the laxative action common to most neutral salts.

Ferrocyanic acid, being bibasic, forms two kinds of salts: in the first the 2 eq. of hydrogen are replaced by 2 eq. of potassium, sodium, &c.; &c., in the second, they are replaced by equivalents of two different metals: such as potassium and barium. An example of the first class is, $Cfy + K_2$; of the second, $Cfy \left\{ \begin{matrix} K \\ Ba \end{matrix} \right.$. Of all these compounds, by far the most important is the ferrocyanide of potassium, or prussiate of potash, from which all the compounds of cyanogen may be prepared, and which is manufactured on the large scale, being also used in the arts.

Ferrocyanide of Potassium. Syn. Prussiate of Potash. Anhydrous, $CfyK_2$, 184·17. Crystallized, it is $Cfy,K_2 + 3HO = 211·2$.—This valuable salt is prepared by fusing animal matter, such as dried blood, hoofs, hair, horns, &c., or the animal charcoal remaining after such matters have been distilled to obtain carbonate of ammonia, with potashes or pearlash, in iron vessels, as long as gas is disengaged. The melted mass is then withdrawn from the fire, and when cold, lixiviated with water, the solution digested with the insoluble part, filtered and evaporated, when it deposits, on cooling, yellow crystals; which by a second solution and crystallization become quite pure.

The essential points of this process are, first, the presence of as much nitrogen as possible in the animal matter: hence fresh, dried uncalcined animal matter is far preferable to animal charcoal: secondly, the presence of metallic iron or sulphuret of iron: the former is either directly derived from the vessels, which are rapidly corroded, or added as filings; the latter is formed from the iron of the vessels by the action of bisulphuret of potassium, which arises from the decomposition, by charcoal at a red heat, of the sulphate of potash contained in the potashes or pearlash; hence pure carbonate of potash is not adapted to this process. Thirdly, the exclusion of the air as far as possible, in order to prevent the oxidation and destruction of the cyanide of potassium formed.

The explanation of the process is very simple and beautiful, and we are indebted for it to the researches of Liebig. When animal matter is heated along with potash, cyanogen is formed, and combining with the potassium (set free at the same time by the action of carbon on potash) produces cyanide of potassium, a salt which is not decomposed by a red heat in closed vessels. At the same time, metallic iron and sulphuret of iron are present in the mixture, but not a trace of the ferrocyanide, previous to the action of water, for the very obvious reason, that the ferrocyanide is decomposed by a red heat, into cyanide of potassium and carburet of iron, nitrogen being disengaged.

If the cooled mass be now digested in water, the cyanide of potassium dissolves, either the metallic iron with disengagement of hydrogen, or the sulphuret of iron, and the filtered liquid now contains the ferrocyanide.

Direct experiments have shown that cyanide of potassium dissolves either

iron, oxide of iron, or sulphuret of iron, producing the ferrocyanide; $3KCy + Fe + HO = (2KCy + FeCy) + KO + H$. Or, $3KCy + FeS = (2KCy + FeCy) + KS$. And it has also been shown by Liebig that if the fused mass be lixiviated with alcohol, the residue, when treated with water, yields no ferrocyanide, while the alcohol contains none, but only cyanide of potassium.

Taking these facts into consideration, perhaps the best method would be to use pure carbonate of potash, free from sulphate, by which means no sulphuret of potassium would be formed, and the iron vessels would not suffer as they now do. The cyanide of potassium, being dissolved in water and filtered, should then be placed in contact with iron turnings in flat open vessels, when, the third part of the potassium being oxidized by the air, the iron is rapidly dissolved, and a quantity of ferrocyanide obtained equal to that indicated by the cyanide of potassium present.

The ferrocyanide of potassium forms large honey-yellow, transparent, flat, quadrangular prisms, derived from a rhombic octahedron. It is very soluble in water, and forms precipitates in almost all metallic solutions, many of which are characteristic. Thus, with solutions of zinc and lead, it gives a white precipitate, with those of copper a chesnut brown, with those of peroxide of iron a deep blue, with protoxide of iron a pale blue, with those of barium and calcium whitish-yellow crystalline precipitates. The lead precipitate is Cfy,Pb_2; that of copper Cfy,Cu_2; those of barium and calcium $Cfy \left\{ \begin{matrix} K \\ Ba \end{matrix} \right.$ and $Cfy \left\{ \begin{matrix} K \\ Ca \end{matrix} \right.$; and that of zinc, $2Cfy + \left\{ \begin{matrix} Zn_3 \\ K \end{matrix} \right. + 6\ aq. = Cfy,Zn_2 + Cfy \left\{ \begin{matrix} Zn \\ K \end{matrix} \right. + 6\ aq.$ That of protoxide of iron is $2Cfy \left\{ \begin{matrix} Fe_3 \\ K \end{matrix} \right. = Cfy,Fe_2 + Cfy \left\{ \begin{matrix} Fe \\ K \end{matrix} \right.$. All of these formulæ are easily referred to the general formula of the ferrocyanides, Cfy,M_2.

Ferrocyanide of Iron.—But the most remarkable of all these compounds is that formed with persalts of iron, namely prussian blue. It is produced when ferrocyanide of potassium comes in contact with perchloride, or any salt of peroxide of iron. Now as ferrocyanogen is a bibasic radical, 1 eq. of it corresponds to 2 eq. of potassium, hydrogen, oxygen, chlorine, &c.; and as perchloride of iron, Fe_2Cl_3, contains 3 eq. of chlorine, $1\frac{1}{2}$ eq. of ferrocyanide of potassium will be required to decompose 1 eq. of it, or, to avoid fractions, 3 eq. of ferrocyanide $Cfy_3K_6 = 3Cfy,K_2$, are required for 2 eq. perchloride of iron, $Fe_4Cl_6 = 2Fe_2Cl_3$. The result is, $Cfy_3K_6 + Fe_4Cl_6 = 6KCl + Cfy_3Fe_4$; and this last is the true formula of prussian blue, although, from its tendency to combine both with ferrocyanide of potassium and with oxide of iron, its analysis offers great difficulties. The formula Cfy_3Fe_4 or Fe_4Cfy_3 shows that prussian blue corresponds to peroxide and perchloride (sesquioxide and sesquichloride) of iron, Fe_2O_3 and Fe_2Cl_3, for Cfy being bibasic is equivalent to Cl_2 or O_2, and consequently Fe_4Cy_3 is equivalent to Fe_4Cl_6 or Fe_4O_6, that is, to $2Fe_2Cl_3$ and $2Fe_2O_3$. It must be admitted to be a very strong argument in favour of the existence of ferrocyanogen, as a bibasic radical, according to the theory of Liebig, that prussian blue, on all other theories the most complex and anomalous compound in the whole range of chemistry, becomes quite normal and one of a series.

Ferrocyanide of potassium is employed to yield cyanogen and all its compounds. We have already seen how cyanogen, hydrocyanic acid, cyanide of potassium, cyanate of potash, urea, cyanic and cyanuric acids, and ferrocyanic acid are obtained from it. Cyanide of potassium, for testing, and to be used as a flux and

in analysis, is best prepared, according to Liebig, by heating 8 parts of the dry ferrocyanide with 3 of pure carbonate of potash in an iron vessel till the fused mass is colourless. It is then poured off from the sponge of reduced iron, and kept in well-stoppered bottles. This very useful preparation, known as Liebig's cyanide of potassium, is not quite pure, containing a little cyanate of potash: but this does not interfere with its use. But another very remarkable compound is produced by the action of a current of chlorine gas on the solution of ferrocyanide, if transmitted until the solution ceases to produce prussian blue with perchloride of iron, yielding only a brownish-green colour, but no precipitate. The liquid now gives, on evaporation, beautiful deep hyacinth red crystals of a new salt, the ferridcyanide of potassium, discovered by Gmelin. This salt contains a new radical, ferridcyanogen.

V. FERRIDCYANOGEN. Cy_6Fe_2=Cfdy=211·74.

This radical has not yet been isolated. It is formed by the coalescence of 2 eq. of ferrocyanogen, and is tribasic. It forms an acid with hydrogen, and salts with metals.

Ferridcyanic Acid. $(2Cfy+H_3)$=$Cfdy,H_3$=214·74.

This acid is obtained from the lead salt $Cfdy,Pb_3$, by the action of sulphuric acid. It is soluble in water, and by the action of sulphuretted hydrogen, is converted into ferrocyanic acid: $2Cfy,H_3+HS=2(Cfy,H_2)+S$. With bases it forms salts; as with potash the ferridcyanide of potassium.

Ferridcyanide of Potassium. SYN. Red prussiate of potash. Its preparation has been described above. Its formula is $2Cfy+K_3=Cfdy,K_3$; and it is quite anhydrous. Like the yellow prussiate, it forms precipitates with most metallic solutions, many of which are characteristic. With salts of peroxide or with perchloride of iron, it only strikes a brown or green colour, but with protochloride or salts of protoxide, it forms prussian blue. As the radical is tribasic, 1 eq. of it ought to be equivalent to 3 eq. of oxygen, chlorine, &c., and if we suppose the potassium in the ferridcyanide replaced by its equivalent of iron, we should have $Cfdy,Fe_3=Fe_5Cy_6$; for $K_3Cfy_2+3FeO=Fe_3Cfy_2+3KO$; and $Fe_3Cfy_2=Fe_5Cy_6$. But, instead of this compound, there is formed prussian blue, the same we have above described as being formed by the action of yellow prussiate or peroxide of iron. In fact, when the red prussiate is added to a solution of a salt of protoxide, or to protochloride of iron, yellow prussiate is formed along with prussian blue and a salt of potash. Bearing in mind, as in all the above explanations, that 1 eq. ferridcyanogen Cfdy is equal to 2 eq. ferrocyanogen Cfy, and that, consequently, the red prussiate, $Cfdy,K_3$ may be equally well represented as $2Cfy,K_3$, then we have $2(2Cfy,K_3)+4(FeO,SO_3)=(3Cfy+Fe_4+(Cfy,K_2)+4(KO,SO_3)$.

The ferridcyanide of potassium may be viewed as ferrocyanide of potassium, *plus* a certain amount of ferrocyanogen; $2(Cfdy,K_3)=3(Cfy,K_2)+Cfy$.

With salts of lead, ferridcyanide of potassium forms the ferridcyanide of lead, $Cfdy,Pb_3$.

VI. COBALTOCYANOGEN. Cy_6Co_2=Cky=216·52.

Not yet isolated, but known in combination with hydrogen, potassium, &c. It is analogous to ferridcyanogen in constitution, and like it, is tribasic.

Cobaltocyanic acid $CkyH_3$=219·52.—Obtained by the action of sulphuric acid

on cobaltocyanide of lead Cky,Pb_3. It forms silky filaments, which are deliquescent and strongly acid.

Cobaltocyanide of Potassium, Cky,K.—Is obtained by acting on a salt of oxide of cobalt with solution of cyanide of potassium and hydrocyanic acid, when hydrogen is given off and the new salt is obtained in crystals. The protocyanide of cobalt, precipitated on the first addition of cyanide of potassium, redissolves in an excess of that salt, forming a compound, $2CoCy+KCy$, or $2CoCy+3KCy$. At all events there is enough of cyanide of potassium present to form the latter compound. The hydrocyanic acid, being now added, yields 1 eq. of cyanogen, converting the 2 eq. of protocyanide into 1 eq. of sesquicyanide of cobalt, while hydrogen is given off: $2CoCy+HCy=Co_2Cy_3+H$. Lastly, the sesquicyanide Co_2Cy_3, with the 3 eq. of cyanide of potassium, $3KCy$, produces the cobaltocyanide of potassium, $Cy_6Co_2+K_3=Cky,K_3$. The crystals are isomorphous with those of the red prussiate of potash; they are yellow, soluble; their solution is not altered by acids, and gives, in solution of protoxide of cobalt, a beautiful rose-coloured precipitate, analogous probably to prussian blue; possibly, however, it may be Cky,Co_3. It precipitates many other metallic solutions, such as those of lead and silver.

Cobaltocyanide of potassium is a singularly permanent salt, resisting the action of the strongest acids; which is, in itself, a sufficient proof that it cannot contain cyanide of potassium as such. With the salts of nickel it forms a green precipitate, Cky,Ni_3, which is insoluble in boiling dilute acids. This property has been applied by Liebig to the separation of cobalt from nickel in analysis. All other metals being removed, an excess of potash is first added, and then hydrocyanic acid till the precipitate at first formed is dissolved, and the whole is then boiled. Hydrochloric acid is now added, and if no nickel be present, it produces no change, because it has no action on cobaltocyanide of potassium. But if nickel be present (of course by this time as cyanide) it is converted into chloride, and this is instantly precipitated by the cobaltocyanide of potassium as cobaltocyanide of nickel. Should there be more cobalt than nickel present, the whole nickel is precipitated, and the precipitate, acted on by potash, leaves the nickel as peroxide, while the cobalt is dissolved as cobaltocyanide, and may be determined along with the portion not precipitated for want of nickel. If, on the other hand, there be more nickel than cobalt, all the cobalt is contained in the green precipitate of cobaltocyanide of nickel, and may be dissolved by potash, and its quantity determined, while the nickel left by the potash as peroxide may be added to that left in the liquid for want of cobalt. Such is an outline of this very beautiful and refined method, which gives most accurate results.

VII. Chromocyanogen. $Cy_6Cr_2=Cry$.

This radical is little known. It is analogous to the two preceding, forming with hydrogen an acid, Cry,H_3, and with potassium a yellow crystallizable salt, Cry,K_3, which precipitates metallic solutions.

VIII. Platinocyanogen. $PtCy_2=Cpy=151{\cdot}38$.

This radical is not known in the separate state. It forms with hydrogen a crystallizable acid of a gold or copper colour and metallic lustre, Cpy,H_2, which is very soluble and deliquescent. This acid is powerful, decomposes the carbonates, and produces platinocyanides. Platinocyanide of potassium, Cpy,K_2,

is obtained by heating spongy platinum to low redness with dried ferrocyanide of potassium, and lixiviating with water; or by dissolving protochloride of platinum in hot solution of cyanide of potassium. It forms crystals yellow and metallic by transmitted, blue by reflected light. By the action of this salt on protonitrate of mercury, a cobalt-blue precipitate is formed, which, when heated in the fluid, becomes white, and is then pure platinocyanide of mercury, Cpy, Hg(?) This salt, acted on by sulphuretted hydrogen, yields the platinocyanic acid. A solution of platinocyanide of potassium acted on by chlorine, yields beautiful copper-like crystals of a new salt, which is either a double cyanide, $2KCy + Pt_2Cy_3 + 5HO$; or the potassium salt of a new radical, $Pt_2Cy_5,K_2 + 5HO$. (Knop.)

The platinocyanides of barium, strontium, and calcium, are easily obtained by the action of platinocyanic acid on these bases, and crystallize readily in beautiful greenish yellow colour, or in some cases green and red with metallic lustre.

IX. Iridiocyanogen. Cy_3Ir=Ciy.

This radical has not been isolated—it forms with hydrogen, iridiocyanic acid Cy_3Ir,H_2, which is obtained by the action of sulphuretted hydrogen on iridiocyanide of lead Cy_3Ir, Pb_3.

Iridiocyanide of Potassium, Cy_3Ir,K_2, is obtained by the action of protochloride of iridium on cyanide of potassium. It forms colourless crystals; its solution gives, with salts of peroxide of iron, a deep indigo colour.

There appears to be a series of similar compounds formed by cyanide of palladium. The palladiocyanide of potassium corresponds to the platinocyanide, and its formula is Cy_2PdK.

There is also reason to believe that manganese forms a manganocyanogen, corresponding to ferridcyanogen, Cy_6Mn_2=Cmy. The manganocyanide of potassium is probably $Cy_6Mn_2 + K_3$=Cmy,C_3.

From what has been stated in the preceding pages, it will be seen that cyanogen has a very great tendency to form cyanides containing 2 or 3 metals, and likewise cyanides containing one of these metals and hydrogen in the place of the other. As these latter compounds are very powerful acids, we are naturally led to consider them as hydrogen acids, in which the hydrogen is combined with radicals. This view has been adopted above, and we have seen reason to admit the following radicals:—

Platinocyanogen	Cpy = Cy_2Pt
Palladiocyanogen	Cpdy = Cy_2Pd
Ferrocyanogen	Cfy = Cy_3Fe
Iridiocyanogen	Ciy = Cy_3Ir
Ferridcyanogen	= Cfdy = Cy_6Fe_2
Cobaltocyanogen	= Cky = Cy_6Co_2
Chromocyanogen	= Cry = Cy_6Cr_2
Manganocyanogen	= Cmy = Cy_6Mn_2

It will be observed that there are three different formulæ among these radicals, namely, Cy_2M; Cy_3,M; and Cy_6M_2; the first monobasic, the second bibasic, the third tribasic. No other view can at present be given of these compounds, of their acids, and of their salts, which is at once so satisfactory, so consistent,

and so advantageous for the learner, as being adapted to assist the memory. It is true that the acids may be viewed as compounds of cyanide of a metal with cyanide of hydrogen (hydrocyanic acid), and their salts as compounds of two metallic cyanides. Thus, ferrocyanic acid, $Cy_3Fe + H_2$, may be said to be 2H Cy + FeCy, and ferrocyanide of potassium, 2KCy + FeCy. Again, ferridcyanic acid may be 3HCy + Fe_2Cy_3 and its potassium salt 3KCy + Fe_2Cy_3; while platinocyanic acid and its potassium salt may be HCy + PtCy and KCy + PtCy.

But the strong acid properties and inert nature of these acids, and the remarkable permanence, both of the acids and of the salts, are entirely inconsistent with the presence of so weak an acid and so frightful a poison as hydrocyanic acid, or of bodies so easily decomposed as hydrocyanic acid and cyanide of potassium. Besides, there are numerous double cyanides, such as KCy,ZnCy; KCy,CdCy; KCy,Cu_2Cy, &c. &c. &c., which act as such; being easily decomposed, and exhibiting no indications of containing radicals like those above described. We shall therefore not dwell on any other view, and merely allude here to the true double cyanides, as belonging more to the history of the metals, and less to that of the organic radicals.

PARACYANOGEN.

As an appendix to the metallic cyanides, we may here mention this compound, which is left behind as a dark-brown powder, when cyanide of mercury is heated in a retort. As cyanogen and mercury alone are given off, we should expect the salt to be dissipated by heat entirely; but this not being the case, it is evident that the residue, if it contain no mercury, must have the same composition as cyanogen, and be, in short, an isomeric modification of it—a solid cyanogen. Again, when cyanide of silver is heated, it gives off part of its cyanogen; it then glows, and, if soon removed from the fire, yields a peculiar residue, which is only partly dissolved by nitric acid. The insoluble residue appears to contain silver and cyanogen in the proportion $AgCy_3$, and it is probable that the cyanogen here is in the solid modification, of which 1 eq. is supposed to be formed by 3 eq. of cyanogen.

Whether, therefore, we admit paracyanogen as a separate radical or not, the two residues just mentioned contain carbon and nitrogen in the proportions to form cyanogen. It is also possible that some such compound may exist in cast iron and steel, which appear to contain nitrogen as well as carbon.

In treating of mellone, we shall see that doubts may be entertained of the existence of paracyanogen, and that the proportions of carbonic acid and nitrogen gases obtained in analyzing the supposed paracyanogen may be derived from a mixture of mellone and carbon.

CYANOGEN AND SULPHUR.

X. Sulphocyanogen. $CyS_2 = Csy$.

Syn. *Bisulphuret of Cyanogen.*—When ferrocyanide of potassium is heated with sulphur, there is formed a new salt, the formula of which is $CyS_2 + K$. This is sulphocyanide of potassium, which appears to contain the radical CyS_2, or Csy. We cannot say that this radical is known in the free state, but by the action of chlorine on sulphocyanide of potassium there is formed a bright orange

powder, which contains sulphocyanogen, mixed with some other bodies. Like the preceding radicals, sulphocyanogen, with hydrogen, forms a peculiar acid, the sulphocyanic or hydrosulphocyanic acid.

Hydrosulphocyanic Acid—$CyS_2,H = CsyH$—is obtained by passing sulphuretted hydrogen gas through sulphocyanide of lead, Csy,Pb, suspended in water. The solution thus formed is highly acid, and has the odour of acetic acid. It strikes a blood-red colour with salts of peroxide of iron, and this property is found in all soluble sulphocyanides. The formula of this acid corresponds to that of cyanic acid, CyO_2,H; and it may be viewed as cyanic acid, the oxygen of which has been replaced by sulphur. With metallic oxides, it forms the sulphocyanides of the metals; $CyS_2,H + MO = CyS_2,M + HO$.

Sulphocyanide of Potassium—$CyS_2,K = Csy,K$. The best process for obtaining this salt is to melt at a gentle heat (only raised at the end to low redness) 46 parts of dried ferrocyanide of potassium, 32 of sulphur, and 17 of pure carbonate of potash. The mass when cold is boiled with water, and the solution, being filtered and evaporated, deposits striated prismatic crystals of the salt, very similar in appearance, and in taste also, to nitre.

If not quite pure, it is purified by solution in alcohol and recrystallization. In this process, the whole cyanogen of the ferrocyanide is first converted into cyanide of potassium, and then, by the taking up of sulphur, into sulphocyanide; while the iron is converted into sulphuret. As 1 eq. ferrocyanide contains 3 eq. of cyanogen and 2 of potassium, 1 eq. of carbonate of potash is added, and the 3 eq. of cyanide of potassium thus obtained take up 6 eq. of sulphur to form the new salt. $3KCy + S_6 = 3(CyS_2,K)$.

Sulphocyanide of potassium causes precipitates in some metallic solutions, but as many metallic sulphocyanides are soluble, the greater number of metals are not precipitated by this salt. With salts of peroxide of iron it strikes an intense blood-red colour, but causes no precipitate. With acetate of lead it gives yellow crystals, and with subacetate a white precipitate, and with salts of suboxide of copper also an insoluble white subsulphocyanide of copper. Sulphocyanide of silver is precipitated as a curdy white solid, when sulphocyanide of potassium is added to nitrate of silver. The other sulphocyanides are soluble.

When sulphocyanic acid is set free from its salts, by diluted acids, and exposed to heat, it is resolved, with the aid of the elements of water, into carbonic acid, bisulphuret of carbon, and ammonia. $C_2NS_2,H + H_2O_2 = \left.\begin{matrix} CS_2 \\ CO_2 \end{matrix}\right\} + NH_3$. Compare this with the spontaneous decomposition of cyanic acid when set free from its salts: $C_2NO_2,H + H_2O_2 = \left.\begin{matrix} CO_2 \\ CO_2 \end{matrix}\right\} + NH_3$. This shows that the view which considers sulphocyanic acid as cyanic acid, the oxygen of which has been replaced by sulphur, is confirmed by the similarity in the decomposition of these two acids; which, in this point of view, may be said to belong to the same type.

When sulphocyanide of potassium is mixed with 6 or 8 volumes of strong hydrochloric acid, hydrocyanic acid is given off, and a new crystalline acid is deposited, which contains more sulphur, and may be called (hydro) persulphocyanic acid. $3(CyS_2,H)$, that is 3 eq. of sulphocyanic acid lose CyH, 1 eq. of hydrocyanic acid, and there remain 2 eq. of the compound CyS_3,H, or persulphocyanic acid. The formula of its salts is CyS_3,M. When the acid is dissolved in ammonia, it soon deposits sulphur, and the liquid retains a new

compound Cy_2S_5,H_2 ($=2CyS_3,H-S$) combined with ammonia: on adding an acid, persulphocyanic is reproduced and deposited, while sulphocyanic acid remains in the solution: $Cy_2S_5,H_2 = \begin{cases} CyS_3,H \\ CyS_2,H \end{cases}$

When solution of sulphocyanide of potassium is acted on by chlorine, or by nitric acid, a bright orange-yellow powder is deposited, which was long supposed to be sulphocyanogen; but it now appears to be a compound or mixture of sulphocyanogen, sulphocyanic acid, and water, in the proportions $3CyS_2 + CyS_2, H + HO = C_6N_3S_6 + (C_2NS_2,H) + HO = C_8N_4S_8H_2O$. This yellow compound undergoes a very remarkable change when heated: it gives off bisulphuret of carbon, sulphur, and a little persulphocyanic acid, and there is left in the retort a grayish yellow powder, containing no sulphur, oxygen, nor hydrogen, and not decomposed by a low red heat. By a strong red heat it is dissipated, yielding a mixture of 3 vol. cyanogen to 1 vol. nitrogen.

This residue may be viewed as a cyanide of nitrogen $NCy_3 = C_6N_4$, and as it plays the part of a radical, analogous to cyanogen, it is called mellone, and has the symbol Me. Its production from sulphocyanogen is easily explained: $4(C_2NS_2) = 2CS_2 + S_4 + C_6N_4$. If the orange-yellow compound which yields it be thrown into melted sulphocyanide of potassium the mellone actually seizes the potassium, expelling the sulphocyanogen, which is resolved into bisulphuret of carbon, sulphur, cyanogen, and nitrogen, all of which escape with effervescence. This is because mellone is not only a powerful radical, but also capable of resisting a strong heat.

XI. Mellone. $Me = C_6N_4 = 92{\cdot}94$.

The preparation of this radical by the action of heat on impure sulphocyanogen, has been described above. It may also be obtained by heating to low redness the sulphocyanide of ammonium, as will be explained below. It appears as a grayish-yellow powder, which is capable of combining directly with potassium when heated with it, and of decomposing sulphocyanide of potassium, as beforementioned. In both cases it forms a fusible, soluble, crystallizable salt, mellonide of potassium. When to the solution of this salt an acid is added, it causes a white gelatinous precipitate, which is an acid, sparingly soluble in water, the hydromellonic acid.

TABLE OF COMPOUNDS.

Hydromellonic Acid . . .	C_6N_4,H
Melam	$2C_6N_4 + CNH_3$
Melamine	$C_6N_4 + 2NH_3$
Ammeline	$C_6N_4 + NH_3 + 2HO$
Ammelide	$2C_6N_4 + NH_3 + 6HO$

Hydromellonic Acid—$MeH = C_6N_4,H$—is best formed by mixing a hot solution of mellonide of potassium with strong hydrochloric acid, when, on cooling, hydromellonic acid is deposited as a snow-white powder. It is somewhat soluble in hot water, sparingly so in cold; it is a strong acid, and with acetate of potash, produces mellonide of potassium, displacing the acetic acid. If, however, a saturated hot solution of the mellonide be mixed with acetic acid, half the potash is removed, and on cooling, crystals of an acid salt are deposited, which, in the case of a hydrogen acid, is very unusual. It is possible, however,

that hydromellonic acid may be bibasic, which would account for the fact of its forming an acid salt.

Mellonide of Potassium.—Me,K = C_6N_4,K—occurs as an accidental product in the making of sulphocyanide of potassium. It is best obtained by fusing at a low red heat, in a covered iron crucible, dried ferrocyanide of potassium, with about half its weight of sulphur, and adding, towards the end of the fusion, about 5 per cent. of dried carbonate of potash. The cooled mass is boiled with water, and the filtered solution concentrated, till, on cooling, it forms a semi-solid mass of minute needles, which are purified from sulphocyanide by washing with alcohol, in which the mellonide is insoluble. The mellonide may also be obtained by adding mellone to fused sulphocyanide of potassium, when, by the decomposition of the sulphocyanogen, an additional quantity of mellone is formed. In the first process, also, a portion of mellone is formed by the action of heat on the sulphocyanide of iron, produced at the commencement of the fusion; and this mellone acts, as in the second process, on the sulphocyanide of potassium, giving rise, in so doing, to an additional amount of mellone: hence, the advantage of adding some carbonate of potash, to prevent any loss of mellone. Finally, mellonide of potassium may also be prepared by adding 2 parts of dry subsulphocyanide of copper to 3 of fused sulphocyanide of potassium.

Mellonide of potassium is soluble in water, insoluble in alcohol. It has a bitter taste, and its crystals contain 5 eq. of water, of which 4 eqs. are expelled at 212°. When acted on by hydrochloric acid, it yields hydromellonic acid; when, by acetic acid, it gives the acid salt above-mentioned. By the action of mellonide of potassium on the salts of baryta, strontia, lime or magnesia, the mellonides of barium, &c. are obtained as sparingly soluble salts, which crystallize in fine needles.

By boiling mellonide of potassium with excess of potash, ammonia is given off, and a new salt is formed. This decomposed by acetic acid, yields a white crystalline precipitate, containing no potash, probably a new acid. When dilute solution of mellonide of potassium is acted on by strong hydrochloric acid, and boiled till the hydromellonic acid is re-dissolved, the liquid, on cooling, deposits cyanuric acid, and contains sal ammoniac. Hydromellonic acid Cy_3NH, with 3 eq. of water H_3O_3, and 1 eq. oxygen, yields dry cyanuric acid, Cy_3O_3, and oxide of ammonium, NH_4O. The equivalent of oxygen is probably derived from the atmosphere; but this decomposition, as well as the preceding, requires minute investigation.

PRODUCTS OF THE DISTILLATION OF SULPHOCYANIDE OF AMMONIA.

As an appendix to sulphocyanogen and its derivative mellone, we may consider the remarkable results of the action of heat on sulphocyanide of ammonium, NH_4,C_2NS_2.

When this salt is heated in a retort, there are given off as gases or vapours, bisulphuret of carbon, ammonia, and sulphuretted hydrogen, the two latter partly combined as sulphuret of ammonium:

4 eq. Sulphocyanide of Ammonium . .	$= C_8\ N_8\ S_8\ H_{16}$
may yield	
2 eq. Bisulphuret of Carbon	$= C_2\ S_4$
4 eq. Ammonia	$= N_4\ H_{12}$
4 eq. Sulphuretted Hydrogen	$= S_4\ H_4$
1 eq. Mellone	$= C_6\ N_4$
	$C_8\ N_8\ S_8\ H_{16}$

Such is, in fact, the result of the action of a strong heat on the salt, mellone alone remaining in the retort. But if a more moderate heat be employed, a gray residue is left, containing the elements of mellone with those of ammonia. If this crude residue be dissolved in boiling potash, and the solution quickly filtered, there is deposited, on cooling, a heavy white powder, which is the chief product of the distillation of the sulphocyanide, in a state of purity. It has been called *Melam*, and its formula is $C_{12}N_{11}H_9 = 2C_6N_4 + 3NH_3$, or 2 eq. mellone and 3 eq. ammonia.

When the crude melam is acted on by oil of vitriol it dissolves with the aid of a gentle heat, and if water be added, and the whole boiled till the addition of carbonate of ammonia causes no further precipitate, the liquid, on cooling, deposits a large quantity of cyanuric acid, and is found to contain sulphate of ammonia. Now, as mellone, by the action of acids or alkalies, yields cyanuric acid and ammonia, it is easy to see that melam should do the same, $C_{12}N_{11}H_9$; that is, melam is equal to 2 eq. mellone $C_{12}N_8$, and 3 eq. ammonia N_3H_9; and if we represent mellone by Cy_3N, melam will be $2\,Cy_3N + 3NH_3$. Now let us add 12 eq. of water, and $2Cy_3N + H_{12}O_{12} = 2\,(Cy_3O_6,H_3) + 2NH_3$, and adding the 3 eq. of ammonia already present in melam, we have 2 eq. hydrated cyanuric acid, $2\,(Cy_3O_6,H_3)$, and 5 eq. ammonia, $5NH_3$, as the final results from 1 eq. melam and 12 eq. water, under the influence of acids and heat.

When melam is acted on by boiling with potash, a series of new compounds is obtained. The first is *melamine*, which is deposited in crystals when the alkaline solution cools. Melamine contains no oxygen, but is an artificial organic base, neutralizing acids, and forming salts. Its formula is $C_6N_6H_6 = C_6N_4 + N_2H_6$; that is, it contains the elements of 1 eq. mellone, and 2 eq. ammonia.

The second new body is obtained as a white powder, when the alkaline solution which has deposited melamine, is supersaturated with acetic acid. It is called ammeline, and is also a base, although weaker than melamine. Its formula is $C_6N_5H_5O_2 = C_6N_4 + NH_3 + 2HO$, or 1 eq. mellone, 1 eq. ammonia, and 2 eq. water. It forms a crystallizable salt with nitric acid.

It may here be observed, that melam, $C_{12}N_{11}H_9$, with 2 eq. water, H_2O_2, contains the elements of 1 eq. melamine, $C_6N_6H_6$, and 1 eq. ammeline, $C_6N_5H_5O_2$.

When either melamine or ammeline is dissolved in strong sulphuric acid, or melam in nitric acid, and the solution mixed first with two vol of water, and then with four of alcohol, a white powder is obtained, resembling ammeline, but having the formula $C_{12}N_9H_9O_6 = 2C_6N_4 + NH_3 + 6HO$, or 2 eq. mellone, 1 eq. ammonia, and 6 eq. water. It is called ammelide, and has rather the characters of an acid than of a base.

Melamine, by the action of hydrochloric acid, aided by heat, is transformed into ammeline, giving off ammonia, while water is taken up. $C_6N_6H_6 + H_2O_2 = C_6N_6H_8O_2$, and $C_6N_6H_8O_2 - NH_3 = C_6N_5H_5O_2$.

Melam also, when treated in the same way, yields ammeline and ammonia. $C_{12}N_{11}H_9 + H_4O_4 = C_{12}N_{11}H_{13}O_4$; and $C_{12}N_{11}H_{13}O_4 - NH_3 = C_{12}N_{10}H_{10}O_4 = 2\,(C_6N_5H_5O_2)$.

All these substances may be resolved, by the action of acids, into cyanuric acid and ammonia. It appears that they are all, that is, melam, melamine, and ammeline, first converted into ammelide, and that ammelide is the source of the cyanuric acid and ammonia.

It is obvious that they are all closely related to each other, and to cyanuric acid. That they are also related to mellone is probable, because when heated

they leave a yellow residue, which is converted by a stronger heat into cyanogen and nitrogen; which, in short, is mellone. All these compounds may be represented as tribasic cyanurate of ammonia, minus water, or water and ammonia. Thus,

1 eq. anhydrous cyanurate of ammonia, $Cy_3O_3,3NH_3$	$= C_6 N_6 H_9 O_3$
Minus 3 eq. water	$= H_3 O_3$
Yields 1 eq. melamine	$= C_6 N_6 H_6$
1 eq. anhydrous cyanurate of ammonia . .	$= C_6 N_6 H_9 O_3$
Minus 1 eq. water $= HO$, " 1 eq. ammonia $= H_3N$ $\}$ NH_4O . .	$= N\ H_4\ O$
Yields 1 eq. ammeline	$= C^6 N_5 H_5 O_2$
2 eq. anhydrous cyanurate of ammonia . .	$= C_{12}N_{12}H_{18}O_6$
Minus 1 eq. ammonia $= NH_3$, " 6 eq. water $= H_6O_6$ $\}$ . . .	$= N\ H_9\ O_6$
Yields 1 eq. melam	$= C_{12}N_{11}H_9$
2 eq. anhydrous cyanurate of ammonia . .	$= C_{12}N_{12}H_{18}O_6$
Minus 3 eq. ammonia	$= N_3\ H_9$
Yield 1 eq. ammelide	$= C_{12}N_9\ H_9\ O^6$

When the mass remaining in the retort in which urea is heated, and formerly believed to be cyanuric acid or cyanurate of ammonia, is acted on by acids, it yields cyanuric acid, and ammonia is found in the solution; but if it be boiled with water, an insoluble snow-white powder is obtained, which agrees with ammelide in almost all its properties. Its formula, however, is $C_6N_4H_4O_4$, and it may also be derived from cyanurate of ammonia, as follows:—

1 eq. anhydrous tribasic cyanurate of ammonia $Cy_3O_3,3NH_3$ $\}$	$= C_6N_6H_9O_3$
Minus 2 eq. ammonia	$= N_2H_6$
and	$= C_6N_4H_3O_3$
Plus 1 eq. water	$= H\ O$
Yields 1 eq. of the new product from urea	$= C_6N_4H_4O_4$

This product, therefore, is intermediate between ammelide and cyanuric acid. To be transformed into hydrated cyanuric acid it has only to lose 1 eq. ammonia, and to gain 2 eq. water. Its formation from urea is very easily understood; for 4 eq. urea, minus 2 eq. carbonic acid and 4 eq. ammonia, will give this compound:—

4 eq. urea	$C_8N_8H_{16}O_8$
Minus 2 eq. carbonic acid C_2O_4, " 4 eq. ammonia N_4H_{12} $\}$	$= C_2N_4H_{12}O^4$
1 eq. of the new compound	$C_6N_4H_4\ O_4$

In order to render still more obvious the relation of these compounds, melam excepted, to cyanuric acid and among each other, let us express the hypothetical compounds NH by M_2, M, therefore, standing for $\frac{1}{2}$ eq. NH. We then have—

Melamine, $C_6N_6H_6$ . . . . . $= Cy_3\ M_6 + H_3$

Ammeline, $C_6N_5H_5O_2$ . . . . $= Cy_3 \begin{cases} M_4 \\ O_2 \end{cases} + H_3$

Ammelide, $C_6N_4\frac{1}{3}H_4\frac{1}{3}O_3$ . . . $= Cy_3 \begin{cases} M_3 \\ O_3 \end{cases} + H_3$

The new compound from urea, $C_6N_4H_4O_4$ $= Cy_3 \begin{cases} M_2 \\ O_4 \end{cases} + H_3$

And cyanuric acid . . . . . $= Cy_3\ O_6 + H_3$

Here we see the change in properties accompanying the gradual substitution of M for O. At one end of the series is melamine, a base, containing no oxygen; at the other cyanuric acid, a highly oxygenized acid; while ammeline is a weak base, and the remaining two are neutral, or have a tendency, but a very slight one, to acid properties.

Before quitting these compounds, it is proper to point out that as sulphocyanic acid corresponds to cyanic acid, sulphur being substituted for oxygen, so sulphocyanide of ammonium corresponds precisely in the same way to urea; for urea is $C_2N_2H_4O_2$, and sulphocyanide of ammonium is (see above) $C_2N_2H_4S_2$. That this analogy is not imaginary we have seen in the similarity of the action of heat on both.

In the case of urea, 4 eq. . . . . $= C_8N_8H_{16}O_8$

yield 2 eq. carbonic acid, C_2O_4 } and 4 eq. ammonia, N_4H_{12} } . . . $= C_2N_4H_{12}O_4$

Leaving 1 eq. of the new body . . . . $= C_6N_4H_4O_4$

In the case of sulphocyanide of ammonium, 4 eq. . $= C_8N_8H_{16}S_8$

yield 2 eq. bisulphuret of carbon, C_2S_4 } and 4 eq. ammonia, N_4H_{12} } . . $= C_2N_4H_{12}S_4$

Leaving 1 eq. mellone + 4 eq. sulphuretted hydrogen . $= C_6N_4 + H_4S_4$

The analogy only fails here in the fact, that the elements $C_6N_4H_4S_4$, instead of uniting, as $C_6N_4H_4O_4$ do, to form one compound, are resolved into two, namely, mellone and sulphuretted hydrogen. Of course the substance from urea may be viewed as compound of 1 eq. mellone and 4 of water; and it may possibly hereafter be resolved into those substances.

When mellone is boiled with nitric acid a new acid is formed, crystallizing in octohedrons, which, when redissolved in water, form pearly scales. Liebig, who alone has studied it, found its formula and all its reactions exactly like those of cyanuric acid, and called it cyanilic acid: 1 eq. mellone and 6 eq. water, $C_6N_4 + H_6O_6$, are equal to 1 eq. cyanilic (or cyanuric) acid, and 1 eq. ammonia ($C_6N_3O_6,H_3 + NH_3$.) Further experiments are required to establish cyanilic acid as an independent acid.

Having now concluded our sketch of the compounds derived from that of sulphur and cyanogen, it only remains to mention, that cyanogen forms one or two compounds with sulphuretted hydrogen, and that sulphocyanic acid forms a compound with the same gas. These compounds, however, are as yet too little known to permit of their being clearly laid down.

Cyanogen does not form any compound of importance with phosphorus or the remaining metalloids. But there is a very interesting and important series of

compounds, in which we may conceive, with some probability, a radical to exist, formed of the elements of cyanogen and those of oxalyle, or carbonic oxide, C_2O_2. This is the series of compounds derived from uric acid, and consequently closely connected with urea, which we have seen to be derived from cyanate of ammonia, and, through cyanic acid, from cyanuric acid, which connects it again with mellone, melam, and sulphocyanogen.

We shall first briefly describe uric acid itself, as the starting point of an extensive series of products. The radical supposed to exist in these compounds will be better understood if described after we have become acquainted with them.

CYANOGEN WITH CARBONIC OXIDE.

XII. Uryle.

1. Uric Acid. $C_{10}N_4H_4O_6=C_{10}N_4H_3O_5+HO$.

Syn. *Urilic Acid.*—*Lithic Acid.*—Occurs in small quantity in the healthy urine of man and quadrupeds, and in much larger quantity in the urine of birds, whether carnivorous or herbivorous, as in the pigeon and hawk tribes. In the urine of birds it forms the white part, in the form of urate of ammonia, and it is still found as such in guano—a substance produced by the long-continued action of the air on the urine (or excrement, for they are voided together) of sea-fowl. The only excrement of serpents, as, for example, of the boa constrictor, is a white semi-solid mass, which soon dries, and is pure urate of ammonia. In serpents, which are all carnivorous, it is very remarkable that the whole excreta (except occasionally hair and feathers, which pass undigested), should take the form of urate of ammonia. In diseased urine, uric acid is often deposited on cooling, and generally of a reddish colour; it also constitutes the most frequent form of gravel and of calculus, when deposited within the bladder. Urate of soda is found in the chalk stones of gouty patients; and it is well known that gout is a disease closely allied to calculus of this kind.

It is best obtained from the excrement (or urine) of the boa, which is powdered, and dissolved in 40 parts of boiling water by the gradual addition of caustic potash, till the liquid is decidedly alkaline. The uric acid forms urate of potash, which dissolves, while the ammonia escapes. The hot liquid, being filtered to separate impurities (and with the above proportion of water it filters rapidly, while with less it crystallizes on the filter and chokes it up), is mixed with a decided excess of hydrochloric acid, when the uric acid is set free, and being insoluble, is deposited, at first as a very bulky gelatinous hydrate, which in a few minutes spontaneously loses water and shrinks into a crystalline heavy precipitate. This is well washed with cold water and dried in the air, when it forms a shining powder, composed of distinct but minute crystals. If made from a cold saturated solution of urate of potassa, the crystals are much larger, but contain 17·5 per cent.; in this case 4 eq. of water are expelled at 212°, leaving the same substance as that precipitated from a hot solution, which, when dried in the air, loses no weight at 212°. The latter is $C_{10}N_4H_3O_5+HO=\overline{Ur}+HO$; the large crystals are a hydrate, $\overline{Ur},HO+4$ aq.

If pure white fragments of the urine of the boa have been used, the above simple process yields uric acid chemically pure, even when the solution in potash has had a decided yellow colour. This uric acid is snow white, and is entirely dis-

sipated by heat, leaving no trace of ashes. But if the boa's urine have been impure, or if calculi have been employed to yield uric acid, in both of which cases the alkaline solution is brown, often very dark, and yields a coloured uric acid, or again if we wish to extract uric acid from guano, we must first purify the urate of potash by evaporating the alkaline solution till it crystallizes in a mass, or passing carbonic acid through it to neutralize the free potash, when the urate of potash is deposited, and is washed on a filter with cold water, in which it is very sparingly soluble, till it is quite white. It is then dissolved in boiling water, and decomposed by hydrochloric acid as before. I have described thus minutely the preparation of pure and colourless uric acid, because none of the very interesting products derived from it can be obtained if we employ uric acid with even a very slight tinge of colour. The presence of a mere trace of the colouring matter of urine I have found to exert a most remarkable influence on the oxidation of uric acid by nitric acid, an influence which I can only compare to that of a ferment in causing a peculiar decomposition to take place.

Uric acid requires 15000 parts of cold and nearly 2000 of hot water for solution, and its solution reddens litmus. It forms salts with bases, especially with the alkalies and alkaline earths, all of which are insoluble or sparingly soluble. Urate of potash, the most soluble of them, requires 85 parts of boiling water, but less if free potash be added. The urate of soda is still less soluble, requiring 124 parts of hot water. The urate of ammonia, a frequent form of calculus, is very sparingly soluble, requiring 243 parts of hot and 1727 of cold water. These are the only urates of any importance.

PRODUCTS OF THE OXIDATION OF URIC ACID.

Uric acid is very permanent under ordinary circumstances, but is readily oxidized by powerful oxidizing agents, such as peroxide of lead, peroxide of manganese, permanganate of potash, and nitric acid.

1. *Oxidation of uric acid by peroxide of lead.* If uric acid be mixed with twenty parts of boiling water, and peroxide of lead added in small portions to the liquid kept boiling, the brown colour of the oxide disappears, and a heavy white powder is formed. When we have added about two parts of the oxide for one of uric acid, or, at all events, when the oxide begins not to lose its brown colour, the hot liquid is to be filtered, and on cooling it deposits a number of hard brilliant white crystals, of which more are obtained on evaporation. The mother liquid at last crystallizes in a mass of very soluble prismatic crystals. These last are pure urea; the first crystals are Allantoine, and the powder is oxalate of lead, mixed with a little carbonate, and with the excess of peroxide. Hence, the products of this oxidation are, Urea, Allantoine, and Oxalic Acid. After describing allantoine, we shall be able to explain the reaction.

Allantoine.—$C_4N_2H_3O_3$.—Syn. *Allantoic Acid.*—This body was first observed in the allantoic fluid of the fetal calf, which is, in fact, the urine of the fetal animal. When this fluid is evaporated, it deposits crystals of allantoine, formerly called allantoic acid, which, however, is not an acid. Its occurrence in the allantoic fluid, that is, as an ingredient in urine; and its artificial production from uric acid by a process of oxidation, are facts of very great interest when viewed in connection. It is best obtained from uric acid, as above described. It is a very indifferent, or neutral substance, and forms few compounds; only one,

with oxide of silver, has been described, the formula of which is $C_8N_4H_5O_5$ + AgO=2 eq. allantoine, minus 1 eq. water, and plus 1 eq. oxide of silver.

When boiled with alkalies, it is resolved into ammonia which escapes, and oxalic acid which combines with the alkali. In fact, both allantoine, $C_4N_2 + H_3O_3$, and oxalate of ammonia, $C_2O_3 + NH_3$, may be represented as formed of cyanogen and water, and it is obvious that the addition of 3 eq. of water, to 1 eq. of allantoine gives $C_4N_2 + H_6O_6 = 2(C_2NH_3O_3)$.

We can now explain the formation of allantoine.

1 eq. Uric acid			$= C_{10}N_4H_4O_6$
Plus 2 eq. oxygen (from 2 eq. PbO_2)	$= O_2$	H_3O_5	$=$ H_3O_5
and 3 eq. water . . .	H_3O_3		
Together			$= C_{10}N_4H_7O_{11}$
Are equal to 1 eq. urea			$= C_2N_2H_4O_2$
2 eq. oxalic acid			$= C_4 \quad O_6$
1 eq. allantoine			$= C_4N_2H_3O_3$
Together			$= C_{10}N_4H_7O_{11}$

Or in the form of an equation,

$$C_{10}N_4H_4O_6 + O_2 + H_3O_3 = C_2N_2H_4O_2 + 2C_2O_3 + C_4N_2H_3O_3$$

That allantoine is closely related to uric acid and urea further appears from the fact, that 1 eq. uric acid, 1 eq. urea, and 1 eq. water, added together, are exactly equal to the sum of 3 eq. allantoine. $C_{10}N_4H_4O_6 + C_2N_2H_4O_2 + HO = C_{12}N_6H_9O_9 = 3(C_4N_2H_3O_3)$.

2. *Oxidation of uric acid by peroxide of manganese.* This is performed much as the preceding, and there appear to be produced compounds, partly the same as those from peroxide of lead, partly different. Of the latter, one at least is crystallizable, but has not been sufficiently examined. The subject requires investigation.

3. *By permanganate of potash.* In this oxidation also, some products appear, which are obtained by peroxide of lead; such as urea, and, in some forms of the experiment at all events, oxalic acid; but I have also observed the formation of a new acid, containing nitrogen, the precise nature and composition of which is not yet ascertained.

4. *By nitric acid.* This mode of oxidation of uric acid has been minutely studied by Liebig and Wöhler, and they have shown that it yields a very large number of new and important products, among which is again found urea, and also, under certain circumstances, oxalic acid. The changes are best traced when colourless nitric acid of a moderate concentration, of sp. gr. 1·3 or 1·25 for example, is employed.

1. *Alloxan.* When uric acid is added, in small portions, to this acid, it is dissolved with a gentle and uniform effervescence, due to the escape of pure carbonic acid and nitrogen gases, without any trace of the red vapours of nitrous acid. Heat is also developed, so that no external heat is required, and it may even be necessary to moderate the reaction by placing the vessel in cold water. If too much uric acid be added at once, or if the mixture be allowed to get too hot, a violent reaction ensues, accompanied by copious red fumes, after which the experiment cannot succeed, and must be recommenced with fresh materials. The presence of a trace of the colouring matter of the urine infallibly causes

this violent reaction, even with a much weaker nitric acid, and thus prevents us from obtaining the desired result, even to a small extent. In all these cases, the whole seems to be converted into oxalate and carbonate of ammonia. When the operation is properly managed, and a little practice makes it quite easy, there appear, in the warm liquid, after a certain quantity of uric acid has been dissolved, granular crystals of the new compound, alloxan. If a little more uric acid be added, it is still dissolved, and when the warm liquid (at about 120°) contains a good many crystals, it is allowed to cool, when the quantity of crystals greatly increases. They are now thrown on a filter stopped with asbestus, and when they have drained, the acid liquor still in their pores is displaced by a little ice-cold water, which is added till the droppings altogether, with the liquid first filtered, have exactly the original bulk of liquid. (This liquid is again treated as before with uric acid, the crystals again collected and washed with a little cold water, and this operation may be repeated always four, occasionally five times, with the same acid, yielding five crops of crystals, and preserving the mother liquor, of which hereafter.) The crystals are now dissolved on the funnel with water at 120°, and the filtered solution evaporated at that or even a lower temperature, till, on being set aside, it deposits large transparent crystals of hydrated alloxan, which are chemically pure. The mother liquid of these crystals, being gently evaporated, yields more, and the final mother liquid, which is now rather acid, from nitric acid, is added to the original acid mother liquor, to be used for other purposes. By the above process, I have constantly obtained, without difficulty, upwards of 90 parts of hydrated alloxan, quite pure, from 100 of uric acid, besides what remains in the mother liquid, and cannot be extracted in that form.

The crystals of hydrated alloxan, when heated to 212° lose about 27 per cent. of water, = 6 eq. The dry or anhydrous alloxan, which may also be obtained in crystals when a saturated solution is evaporated in a warm place, is composed of $C_8N_2H_4O_{10}$, which explains its formation from uric acid; for $C_{10}N_4H_4O_6 + O_2 + H_4O_4 = C_8N_2H_4O_{10} + C_2N_2H_4O_2$: that is, uric acid, *plus* 2 eq. oxygen and 4 eq. water, yields 1 eq. alloxan and 1 eq. urea.

The urea, when formed, is in contact with hyponitrous acid (derived from nitric acid by the separation of 2 eq. oxygen), and is immediately decomposed by it, yielding oxide of ammonium, which combines with some free nitric acid, carbonic acid, and nitrogen, which two last escape as gases. $C_2N_2H_4O_2 + NO_3 = NH_4O + 2CO_2 + N_2$. At the end of the operation, therefore, the acid liquid, which has deposited crystals of alloxan, contains nothing but alloxan, nitrate of ammonia, and free nitric acid. We may therefore express the final result as follows: $C_{10}N_4H_4O_6 + 2(HO,NO_5) + 2HO = C_8N_2H_4O_{10} + (NH_4O,NO_5) + 2CO_2 + N_2$.

Alloxan is very soluble in water, also in alcohol. Its solution stains the skin pink, and gives to it a heavy sickly odour. Its taste is peculiar and almost acidulous; but, although it reddens litmus, it has not the chemical characters of an acid. It is a very remarkable substance, from the numerous transformations which it undergoes, when subjected to the action of different re-agents.

By the action of soluble fixed alkalies, it is converted into a powerful acid, *alloxanic acid*; by the action of ammonia it yields another acid, *mykomelinic acid*; boiled with peroxide of lead, it is converted into *urea* and *carbonic acid*; by boiling with nitric acid it is changed into a new and powerful acid, *parabanic acid*; by the action of sulphuretted hydrogen and other deoxidizing agents, it

yields a new compound *alloxantine*; with hydrosulphuret of ammonia it gives a new salt called *dialurate of ammonia*; with sulphurous acid it combines, forming a compound acid, *alloxano-sulphurous* acid: and with sulphite of ammonia it forms another new salt called *thionurate of ammonia*. Such are the compounds formed by the direct action of re-agents on alloxan; but many others are produced by the action of re-agents on these, singly or jointly. Thus, when alloxan or alloxantine are both present in a hot solution, ammonia causes the developement of a deep purple colour, and the deposition, on cooling, of the gold green crystals of *murexide*; acids acting on thionurate of ammonia produce *thionuric acid*, *uramile*, and *uramilic acid*; acids acting on murexide, produce *murexan*; acids acting on dialurate of ammonia separate *dialuric acid*; ammonia, acting on parabanic acid, converts it into a new acid, *oxaluric acid*; and by the action of heat on alloxanate of baryta another new acid, *mesoxalic acid*, is produced. We shall endeavour briefly to trace the formation and the relations of these remarkable products.

2. *Alloxanic Acid.* Its formula $C_8N_2H_2O_8 + 2HO$. It is therefore isomeric with alloxan, and differs from it in this, that 2 eq. water have become basic, and replaceable by metallic oxides. It is a bibasic acid. It is formed when solution of alloxan is mixed with barytic water, as long as the white precipitate first formed redissolves with a gentle heat. When it begins to be permanent, a drop or two of alloxan is added to clear all up; and on cooling, alloxanate of baryta is deposited in small white crystals. From this salt the acid is obtained by adding sulphuric acid, so as to separate all the baryta. The acid solution on evaporating yields crystals of alloxanic acid. The acid, when neutralized by ammonia, forms, with nitrate of silver, a white precipitate, which, when boiled, becomes yellow, and is reduced with effervescence. When the solutions of its salts, with baryta, lime, and strontia, are boiled, they become turbid, depositing carbonates, while urea and a mesoxalate remain dissolved. The formula of the alloxanates is $C_8N_2H_2O_8,2MO$ + aq.

3. *Mesoxalic Acid.* Obtained, in combination with baryta, by boiling alloxanate of baryta; or combined with oxide of lead, by adding alloxan in solution, to a boiling solution of acetate of lead. The baryta salt is pale yellow, and sparingly soluble; the lead salt white and insoluble. The former is $C_3O_4 \left\{ \begin{matrix} BaO \\ H\ O, \end{matrix} \right.$ the latter $C_3O_4,2PbO$. The acid may be obtained from either of these salts; it crystallizes, is very sour, and is probably bibasic, and has, also probably, the formula $C_3O_4,2HO$. In that case, the anhydrous acid is very remarkable as a new compound of carbon and oxygen, of the same class as mellitic and oxalic acids; hence the name. It is characterized by forming, when neutralized by ammonia with nitrate of silver, a yellow precipitate, which, when heated, is reduced with brisk effervescence. This is evidently the cause of the reaction of alloxanic acid, above mentioned, with nitrate of silver. Mesoxalic acid deserves and requires a very careful investigation. Its formation from alloxan or alloxanic acid, if its formula be C_3O_4, is very easily explained: for 1 eq. alloxan, *minus* 1 eq. urea, gives 2 eq. mesoxalic acid. $C_8N_2H_4O_{10} - C_2N_2H_4O_2 = C_6O_8 = 2C_3O_4$.

4. *Mykomelinic Acid.* $C_8N_4H_5O_5$. Is formed when ammonia acts on solution of alloxan; when a yellowish gelatinous precipitate of mykomelinate of ammonia soon appears. This, boiled with dilute sulphuric acid yields a similar yellowish precipitate, which, when dry, forms a powder sparingly soluble in cold,

more readily in hot, water. It is decidedly acid. It is formed of the acid by the reaction of 2 eq. of ammonia on 1 eq. alloxan. $C_8N_2H_4O_{10} + 2NH_3 = C_8N_4H_5O_5 + 5HO$. It would appear to differ from allantoine, only by 1 eq. of water: for eq. of allantoine are $C_8N_4H_6O_6$.

5. *Parabanic acid.* $C_6N_2O_4+2HO$. Is formed when alloxan or uric acid is heated with an excess of nitric acid, and the solution concentrated until on cooling it forms a soft crystalline mass. This is dried on a tile, and the dry crystals are purified by solution in hot water, filtration, and recrystallization. A large quantity of parabanic acid may easily be obtained from the acid mother liquors of alloxan. When pure, the acid is beautifully white and crystallized, very acid, and very soluble. It is characterized by its great permanence in the free state, for it may be boiled with nitric acid, as its preparation shows, and at the same time by its extreme proneness to change in contact with bases. Thus, if neutralized with ammonia in the warm solution, it deposits, on cooling, a crystallized salt, which is oxalurate of ammonia. The same change takes place with all bases except oxide of silver, so that the parabanate of silver is the only salt of this very powerful and remarkable acid which can be obtained. To be converted into oxaluric acid, parabanic acid only requires 3 eq. of water. The production of parabanic acid is very simple. 1. From uric acid. $C_{10}N_4H_4O_6+O_4+H_2O_2 = C_2N_2H_4O_2 + 2CO_2 + C_6N_2O_4,2HO$. 2. From alloxan. $C_8N_2H_4O_{10} + O_2 = 2CO_2+2HO+C_6N_2O_4,2HO$.

6. *Oxaluric acid.* $C_6N_2H_3O_7+HO$. Formed by the action of bases on parabanic acid. $C_6N_2O_4 + KO + 3HO = C_6N_2H_3O_7,KO$. The acid is obtained by adding dilute sulphuric acid to a hot saturated solution of oxalurate of ammonia, prepared by the action of ammonia on parabanic acid. On cooling, the oxaluric acid is deposited as a heavy white powder. When long boiled in water, it is decomposed into oxalate of urea and free oxalic acid. In fact, it contains the elements of 2 eq. oxalic acid and 1 eq. urea. $2C_2O_3+C_2N_2H_4O_2=C_6N_2H_3O_7$, HO. It is also characterized by forming with oxide of silver a white salt, which dissolves in hot water, and crystallizes beautifully on cooling.

The *oxalurate of ammonia*, $NH_4O+C_6N_2H_3O_7$, is formed whenever a solution of alloxan, or alloxantine in water, or of uric acid in nitric acid, is evaporated with excess of ammonia, and where colouring matter is present, as when ammonia is made to act on the acid in the mother liquors of alloxan, the oxalurate is often deposited in radiated hemispherical concretions, which sometimes attain the size of an inch or two in diameter, and are very hard. When declorized by animal charcoal, it forms small, soft, flexible needles. I have found that this salt, when exposed to heat in a retort, yields ammonia, hydrocyanic acid, and much oxamide, besides water, and perhaps other products, while a dark residue is left.

7. *Thionuric Acid*, $C_8N_3H_7S_2O_{14}=(C_8N_3H_5O_8,2SO_2)+2HO$, is formed when sulphite of ammonia, with excess of base, is added to solution of alloxan, and the whole boiled for a few minutes, or until crystals appear in the hot liquid. On cooling it forms a semi-solid mass, from the separation of a large quantity of thionurate of ammonia in beautiful silvery crystals, which are to be washed with cold water, and dried on a tile. From this salt thionurate of lead is prepared, and this, being decomposed by sulphuric acid, yields thionuric acid. The acid is crystallizable, but very soluble. It is bibasic, and contains the elements of 1 eq. alloxan, 1 eq. ammonia, and 2 eq. sulphurous acid, not, however, as such, for the elements of 2 eq. water have assumed the basic form.

Its most striking character is, that when its solution is heated it becomes turbid from the deposition of a new compound, uramile, and in the liquid *sulphuric* acid may now be found, which was not previously present. $C_8N_3H_5O_8+2SO_2=C_8N_3H_5O_6+2SO_3$; so that the sulphurous acid obtains oxygen from the rest of the acid, and becomes sulphuric acid, leaving uramile, $C_8N_3H_5O_6$.

Thionurate of Ammonia, $(C_8N_3H_5O_8,2SO_2)+2NH_4O+2aq.$ is formed as above described. When its solution is mixed with 1 eq. of hydrochloric acid, half the ammonia is removed, and by evaporation we obtain *acid thionurate of ammonia* in minute silky needles. But when the hot solution of thionurate of ammonia is mixed with an excess of acid, the thionuric acid is set free and instantly decomposed, uramile being deposited. Little is known of the other thionurates.

8. *Uramile*; $C_8N_3H_5O_6$; its formation has been described above. It occurs either as a crystalline powder, or in dendritic or feathery crystallizations, of very beautiful aspect. It dissolves in ammonia and potash, and the solution absorbs oxygen; becoming purple, and depositing green crystals of murexide, or of potassium-murexide. When boiled with peroxide of mercury, and a very little ammonia, it is also converted into murexide. Boiled with caustic potash, or with dilute acids, it is said to yield uramilic acid. Nitric acid reconverts it into alloxan.

9. *Uramilic Acid.* Obtained, by Liebig and Wöhler, by evaporating acid thionurate of ammonia, or uramile, with dilute sulphuric acid; also, it is said, by boiling uramile with potash. It appeared to these chemists as fine prisms, very soluble in water, and its analysis indicated the formula $C_{16}N_5H_{10}O_{15}$; which might be derived from 2 eq. uramile by the loss of 1 eq. ammonia, and the addition of 3 eq. water. $2(C_8N_3H_5O_6)+2HO-NH_3=C_{16}N_5H_{10}O_{15}$. But this acid has not been again obtained, and its existence is still doubtful.

10. *Alloxantine*; $C_8N_2H_5O_{10}$; obtained in large quantity by diluting the acid mother liquid of alloxan with 3 or 4 parts of water, and passing a current of sulphuretted hydrogen through it. In a short time sulphur is deposited, and then white crystals of alloxantine. When a large quantity has formed, it is collected with the sulphur, on a filter, washed with a little cold water, and the filter with its contents then boiled with a large quantity of water. The solution filtered while hot, and with the addition of a few drops of hydrochloric acid, deposits, on cooling, a large crop of pure crystals of alloxantine. The acid liquid, filtered from the first deposit, often, on standing a day or two, deposits a large additional quantity of alloxantine. This always happens, if too much sulphuretted hydrogen has been used; for that converts the alloxantine partially into dialuric acid, which is more soluble, but by absorbing oxygen from the air is reconverted into alloxantine, and thus deposited.

Alloxantine may also be obtained by deoxidizing a pure solution of alloxan, either by sulphuretted hydrogen, or by other deoxidizing agents; or by heating a solution of alloxan to the boiling point, either by itself or with the addition of dilute mineral acids, when alloxantine is formed and deposited on cooling. But the process above given for converting into alloxantine the alloxan of the acid mother liquor, which cannot be purified by crystallization, is so productive, and yields alloxantine so pure, that, if we have to prepare alloxan, we need never be at a loss for alloxantine.

The formation of alloxantine from alloxan by sulphuretted hydrogen is easily explained, for these compounds only differ by 1 eq. hydrogen, which the alloxan takes from sulphuretted hydrogen. Oxidizing agents, by converting this hydro-

gen into water, readily reconvert alloxantine into alloxan. $C_8N_2H_5O_{10} + O = HO + C_8N_2H_4O_{10}$.

Alloxantine forms white, hard, brilliant crystals, which never exceed a certain small size. It is very sparingly soluble in cold water, much more so in hot water. Its solution is characterized by giving with solution of baryta a deep violet precipitate, which with excess of baryta, changes to white; and by instantly reducing nitrate of silver, forming a black powder of silver, the alloxantine passing into alloxan, or oxaluric acid. The crystals of alloxantine, heated to 300°, lose 3 eq. of water.

In the preparation of alloxan, it is necessary, as has been stated, to be very careful that the first solution of the crystals formed in the nitric acid should not be heated too strongly, because, as this solution contains free nitric acid, alloxantine is formed at a certain temperature; and, besides, even a pure solution of alloxan, if boiled, is partly converted into alloxantine. The action of diluted nitric and other mineral acids on alloxan is to produce, from 2 eq. alloxan, 1 eq. alloxantine, 3 eq. oxalic acid, 1 eq. ammonia, and 1 eq. cyanic acid, the latter, with 3 eq. water, producing bicarbonate of ammonia. When solution of alloxan is boiled alone, it is converted into alloxantine, parabanic acid, and carbonic acid. $3(C_8N_2H_4O_{10}) = (C_8N_2H_5O_{10}) + C_6N_2H_2O_6 + 2CO_2$.

In all these, or in similar cases, the presence and the relative proportion of alloxantine contained in alloxan at any period, may be judged of by the colour of the precipitate formed in baryta. If pure white, no alloxantine is present: if slightly pink, it is present in small quantity; if deep violet, all, or nearly all, the alloxan has been converted into alloxantine.

It is when both alloxan and alloxantine are present, that the addition of ammonia produces the deep purple colour, and the green crystals, of murexide. When ammonia acts on alloxantine alone, it gives rise to uramile, and, finally, to oxalurate of ammonia.

The most remarkable change which alloxantine undergoes is that caused by the further action of sulphuretted hydrogen. If that gas be passed through a hot solution of alloxantine sulphur is precipitated, and an acid liquid is obtained, which, if neutralized by carbonate of ammonia, forms a salt in soft white silky crystals, the dialurate of ammonia. Alloxantine, by the action of hydrogen, which removes 1 eq. oxygen, is converted into dialuric acid.

11. *Dialuric Acid.* $C_8N_2H_3O_7 + HO = C_8N_2H_4O_8$. Produced by the action of sulphuretted hydrogen on alloxantine. $C_8N_2H_5O_{10} + HS = S + 2HO + C_8N_2H_4O_8$. It is best obtained, in combination with ammonia, by adding a slight excess of hydrosulphuret of ammonia to a solution of alloxan or alloxantine, when a copious crystalline precipitate appears. This, when boiled, dissolves in the liquid, and on cooling is deposited in minute silky prisms, which are white, but in drying become pink, or even deep red. They should be washed on the filter, first with diluted hydrosulphuret of ammonia, then with alcohol, to which a little hydrosulphuret has been added; and lastly, with pure alcohol; and dried by pressure in blotting paper, and in the vacuum of the air-pump. They may thus be obtained white, or very nearly so; and when once quite dry they are permanent. When this salt is dissolved in hot and moderately strong hydrochloric acid, crystals of dialuric acid are deposited on cooling. These crystals resemble somewhat those of alloxantine, but are larger, and not so brilliant. Their solution, and the crystals themselves under water, absorb oxygen, and are soon changed

into alloxantine, from which dialuric acid only differs by 1 eq. oxygen, and 1 eq. water.

Dialuric acid is a powerful acid. Its salts are insoluble or sparingly soluble, and only permanent in the dry state. The dialurate of ammonia, above described, is the most interesting.

12. *Murexide.* Syn. *Purpurate of ammonia.* Formed, as already mentioned, when ammonia acts on a solution containing both alloxan and alloxantine, which explains its production when ammonia is added to the solution of uric acid in dilute nitric acid, after evaporation to a certain extent: also, when uramile or murexan is boiled, with red oxide of mercury or oxide of silver, in water, with a few drops of ammonia, or when uramile or murexan is dissolved in ammonia and exposed to the atmosphere; and in a great variety of circumstances from all the preceding compounds, or nearly all of them.

On the small scale, 4 grains of alloxantine and 7 grains of hydrated alloxan, are dissolved together in $\frac{1}{2}$ oz. by measure of water by boiling, and the hot solution added to $\frac{1}{6}$ oz. by measure of a saturated or nearly saturated solution of carbonate of ammonia, the latter being cold. This mixture has exactly the proper temperature for the formation of murexide; and it does not, owing to its small bulk, remain too long hot. It instantly becomes intensely purple, while carbonic acid is expelled; and as soon as it begins to cool, the beautiful green and metallic-looking crystals of murexide appear. As soon as the liquid is cold, these may be collected, washed with a little cold water, and dried on filtering-paper. I have obtained them, by the above process, and on this small scale, of from 2 to 3 lines in length. When made with larger quantities, the crystals are always smaller, owing, probably, to some effect of the slower cooling of the larger mass of liquid, as continued heat is not favourable to their formation. If we do not care about having the finest crystals, we may prepare murexide in large quantity by adding solution of alloxan to a boiling solution of alloxantine, and cautiously adding cold solution of carbonate of ammonia, till the mixture has become nearly black, and the green crystals begin to appear. The vessel being removed from the fire, deposits a very large quantity of murexide. In these processes, the residual liquid is still coloured, and is alkaline from excess of ammonia: if kept, it loses the red colour, becomes yellowish, and if evaporated, yields much alloxanate of ammonia in crystals.

Murexide is one of the most beautiful products of chemistry; the crystals are metallic green by reflected light, like the cantharides fly or the gold beetle, and deep red by transmitted light. Their solution is deep purplish red, and they dissolve in potash with the most splendid purplish blue colour that can be imagined; this, however, soon disappears. When their solution is acted on by a dilute mineral acid, it is decolorized, and deposits a shining scaly crystalline powder, of a pale yellow colour, which is murexan. The same compound is obtained when acids are added to the solution of murexide in potash, after the purple tint has disappeared on digestion in a gentle heat.

The composition of murexide is uncertain, and there are different views of its constitution. According to some it is a salt of ammonia; and this view is supported by the fact that, with salts of baryta and oxides of lead and silver, it yields purple salts, which, according to Fritzsche, contain the same acid that in murexide is combined with ammonia, and which may be called purpuric acid. But murexide is not a compound of ammonia with the purpuric acid of Prout, for when that body (murexan) is dissolved in ammonia, it only forms murexide

by absorbing oxygen from the air, and yields other compounds at the same time. Again, the action of sulphuretted hydrogen is inconsistent with the view of murexide being a salt of ammonia, and in many of its relations it more resembles a neutral body—such as a compound of amide. Its products of decomposition are very numerous, and altogether the subject is one of much difficulty. Possibly there may be two substances similar in appearance, but distinct in consitution; one a salt of ammonia, the other an indifferent body, or an amidide. The great discrepancy in the results of analysis, is obtained by Liebig and Wöhler on the one hand, and Fritzsche on the other, as well as some differences in the properties ascribed to it by different chemists, lead to some such conclusion. The formula considered by Liebig and Wöhler the most probable, all things considered, but not established, is $C_{12}N_5H_6O_8$; another, somewhat less probable, is $C_{20}N_8H_{10}O_{14}$. Both of these will enable us to account for its production in different circumstances. The formula of Fritzsche, which agrees with his analysis, is $C_{16}N_6H_8O_{11} = NH_3 + C_{16}N_5H_5O_{11}$. The salt formed with nitrate of silver is, $C_{16}N_5H_5O_{11} + AgO$, which would exhibit the unusual phenomenon of ammonia, instead of oxide of ammonium, being replaced by oxide of silver; and the baryta compound is $C_{16}N_5H_5O_{11} + HO + BaO$. Admitting the formulæ of Fritzsche for the silver and barium compounds to be correct, these are not demonstrated to be salts of purpuric acid: but besides this, his formula for murexide does not enable us to explain its production in any case. In these circumstances, we shall not attempt to explain the formation of murexide, further than to point out, that it appears to require the presence of a compound intermediate between alloxan and alloxantine (the former losing oxygen, the latter gaining it), and of ammonia; and that it is not the only product.

13. *Murexan.* Syn. *Purpuric Acid.* $C_6N_2H_4O_5$? Formed by the action of acids on murexide, but along with several other products. It appears as a shining powder, composed of scales, generally pale yellow, sometimes pale brown, never quite white. It is insoluble in water or nearly so, but the liquid filtered from it has always a peculiar opalescent aspect and play of colours. It dissolves in potash and ammonia, and the solutions become purple, by absorbing rapidly oxygen from the air, and finally deposit green crystals. When boiled with peroxide of mercury, water, and a little ammonia, it yields murexide. It dissolves in oil of vitriol, and is precipitated unchanged by water. In all these characters, except in its external aspect, it coincides entirely with uramile, and it is not impossible that it may be hereafter found to be uramile, disguised by the presence of a foreign substance. For the present, however, its analysis compels us to distinguish it from uramile.

Having now described the numerous products of the oxidation of uric acid by nitric acid, we are prepared to understand the nature of the radical supposed to be common to most of these compounds.

Uryle. Ul. $= C_8N_2O_4 = 4CO + 2C_2N$.

Syn. *Cyanoxalic Acid.* This radical is unknown in the separate form. It contains the elements of four eq. carbonic oxide or 2 eq. oxalyle (C_2O_2), and 2 eq. cyanogen. Hence the name cyanoxalic acid. Assuming it to exist, we have the following series.

Rational formulæ.	Names.	Empirical formulæ.
Ul + 1 eq. urea	= Uric acid	= $C_{10}N_4$ H_4 O_6
Ul + O + 5HO	= Alloxantine	= C_8 N_2 H_5 O_{10}
Ul + O_2 + 4HO	= Alloxan	= C_8 N_2 H_4 O_{10}
Ul + 4HO	= Dialuric acid	= C_8 N_2 H_4 O_8
Ul + NH_3 + 2HO	= Uramile	= C_8 N_3 H_5 O_6
Ul + O_2 + 4HO + NH^3 + $2SO_2$	= Thionuric acid	= C_8 $N_3H_7O_{14}S_2$

The ready conversion of these compounds one into another is a strong argument for the existence of the radical Uryle. But the rational formulæ above given do not represent what we suppose to be the actual arrangement; they only point out by what simple means, as the addition or removal of oxygen, or ammonia, or water, the elements of the new compounds might be supplied. The other derivatives of uric acid are probably compounds of different radicals: thus, parabanic and oxaluric acids each contain only 6 eq. of carbon, and cannot therefore be compounds of uryle.

APPENDIX TO URIC ACID.

1. *Uric or Xanthic oxide.* This is a very rare ingredient of urinary calculi. Its formula is $C_5N_2H_2O_2$, which, taken double, differs from uric acid only by 2 eq. oxygen. Hence its name of uric oxide. It is soluble in potash and precipitated by acids as a white powder. It dissolves in nitric acid, and the solution evaporated to dryness leaves a yellow residue; hence the name of xanthic oxide. It is said to occur in small quantities in some kinds of guano.

2. *Cystic oxide.* $C_6NH_6O_4S_2$. Another very rare form of calculus. It dissolves both in acids and alkalies, and has the characters of an organic base, forming crystalline compounds with acids. It is remarkable from the large quantity of sulphur it contains.

XIII. Benzoyle. Bz = $C_{14}H_5O_2$.

This is the radical of Benzoic Acid, of oil of bitter almonds, and of an extensive series of compounds. The radical is not yet known with certainty in the separate form, although a compound exists, having the same composition. (See Benzile.) We shall describe first the benzoic acid, and afterwards the other compounds derived from, or connected with it.

TABLE OF COMPOUNDS.

Benzoic acid	$C^{14}H^5O^3$,HO = BzO,HO
Hyduret of Benzoyle	= Bz,H
Chloride "	= BzCl + HCl
Benzamide	= BzAd
Formobenzoilic acid	= Fo_3,BzH + HO
Benzoate of Hyduret of Benzoyle . .	= BzO,HO + 2BrH
Hippuric acid	= $C^{18}NHsO^5$ + HO.

1. Benzoic Acid. $C_{14}H_5O_3$,HO = BzO,HO, or BzO_2,H.

This acid is found in gum benzoin, mixed with some resins; and it also occurs in the urine of herbivorous animals, under certain circumstances. It is also formed by the oxidation of the oil of bitter almonds. It may be obtained from benzoin by sublimation, the powdered gum being gently heated on an iron

plate forming the bottom of a broad and short cylinder, the top of which is covered with bibulous paper pasted tightly down to the sides, while another cylinder slides over the upper end of the first, to prevent the escape of the acid. The vapours of the acid, which is very volatile, pass through the paper, and forming crystals, are there retained, falling on its upper surface. The following method, however, is far more productive, as in the process of sublimation some of the acid is always decomposed. Benzoin is dissolved in strong alcohol, and to the hot solution there is added hydrochloric acid in quantity sufficient to precipitate the resin: the whole is then distilled. The benzoic acid passes over under the form of benzoic ether (benzoate of oxide of ethyle); and when the greater part of the liquid has been distilled off, water is added to the residue, and distilled as long as any other passes over with it. When this ceases, the hot water remaining in the retort is filtered, and on cooling deposits part of the benzoic acid in crystals. The benzoic ether and all the distilled liquors are now treated with caustic potash, until all the ether is decomposed, and the solution, now containing benzoate of potash, is heated to boiling, and supersaturated with hydrochloric acid. On cooling it deposits the benzoic acid in crystals. By this means the whole benzoic acid of the benzoin is obtained.

Benzoic acid forms fine light prismatic crystals, or flexible pearly scales. When pure, it has no smell, but by heat it acquires the odour of benzoin or of vanilla, and as commonly prepared it has a very pleasant odour derived from the presence of some foreign compound which accompanies the acid, and is not easily separated from it. It is very fusible and volatile, and its vapours are very irritating, provoking cough. It is inflammable, burning with smoke. It is sparingly soluble in cold water,more so in boiling water; it dissolves also in alcohol and ether.

With bases it forms salts, many of which are crystallizable. Their general formula is BzO,MO, or BzO_2,M. When the alkaline and earthy benzonates are heated in close vessels, they yield carbonates, while new products distil over, such as benzone, benzole, naphthaline, &c. The benzonate of peroxide of iron, $3BzO + Fe_2O_3$, has a reddish white colour, and is insoluble. Benzoic acid, in the form of benzoate of ammonia, is therefore, sometimes used as a means of separating peroxide of iron from some other bases. But its use requires many precautions, and it is quite inapplicable if alumina, glucina, yttria, or zirconia be present. Benzoate of silver, BzO,AgO, is sparingly soluble, and when formed in hot solutions crystallizes on cooling.

2. Hyduret of Benzoyle. $C_{14}H_6O_2 = BzH$.

Syn. *Essential oil of bitter almonds.* When bitter almonds, after being macerated with water for a day or two, are distilled with the water, there is obtained a fragrant oily liquid, heavier than water, which contains, besides hyduret of benzoyle, benzoic acid, hydrocyanic acid, and benzoine, a solid compound isomeric with the hyduret of benzoyle. To purify it, this oily liquid is distilled along with a mixture of protochloride of iron and slaked lime, which retain the two acids, and the benzoine remaining behind, the pure hyduret passes over.

It is a colourless transparent liquid, of a high refractive power. It has a peculiar and very powerful smell, and it is on this account that the crude oil is so much used in perfumery. Its odour has been compared to that of hydrocyanic acid, but this has arisen from the fact that the crude oil contains both; for on comparing the two, no similarity can be perceived. It ought, however, to be

borne in mind that the commercial oil is highly poisonous, not only because it contains hydrocyanic acid, but because the hyduret of benzoyle is poisonous. Hyduret of benzoyle boils at 356°.

When exposed to the air, it absorbs 2 eq. of oxygen, and is converted into pure crystallized benzoic acid. $BzH + O_2 = BzO,HO$. Heated with caustic potash in close vessels, it yields benzoate of potash and hydrogen gas which is disengaged. $KO,HO + BzH = KO,BzO + H$. It is still more easily converted into benzoate of potash by an alcoholic solution of potash; the alcohol here swims above the salt, and holds in solution an oily matter not yet examined.

When hyduret of benzoyle is mixed with a little hydrocyanic acid, and placed in contact with aqua potassæ, lime water, or baryta water, it is gradually converted into the solid crystalline compound, isomeric with itself, which is called benzoyne. When mixed with aqua ammoniæ, and gently heated, it produces a new compound, hydrobenzamide. With chlorine and bromine, if dry, it yields chloride and bromide of benzoyle, with hydrochloric and hydrobromic acids; if water be present, benzoic acid is likewise formed, part of which combines with some unchanged hyduret of benzoyle.

3. *Chloride of benzoyle*, formed by the action of dry chlorine on the hyduret, is a colourless liquid, of a strong disagreeable odour. It is formed as follows: $BzH + Cl_2 = BzCl + HCl$. With the alkalies it yields benzoate of the alkali, and chloride of the metal: $BzCl + 2KO = KO,BzO + KCl$. With dry ammonia it yields *benzamide*; with alcohol it produces benzoic ether and hydrochloric acid. $AeO,HO + BzCl = AeO,BzO + HCl$. When acted on by metallic bromides, iodides, sulphurets, or cyanides, it produces metallic chlorides, and bromide, iodide, sulphuret or cyanide of benzoyle. The *bromide of benzoyle* is a crystalline solid, in other respects analogous to the chloride. The *iodide* and *sulphuret* of benzoyle are also crystallizable: the cyanide is a liquid having an odour like that of cinnamon.

4. Benzamide. $C_{14}NH_7O_2 = C_{14}H_5O_2 + NH_2 = BzAd$.

This compound is formed when dry ammonia acts on chloride of benzoyle, $BzCl + NH_2,H = Bz,NH_2 + HCl$: also when hippuric acid (which see), is boiled with peroxide of lead. When prepared from the chloride, it is accompanied by sal ammoniac, formed by the hydrochloric acid produced, with the excess of ammonia. This is removed by cold water; and the benzamide, being dissolved in hot water, crystallizes on cooling. It forms fine soft needles or pearly scales, very fusible and volatile. Like other amidides, it yields ammonia when boiled with alkalies, while a benzoate is formed.

5. Formobenzoilic Acid. $\left\{\begin{matrix} C_2HO_3 + C_{14}H_6O_2 + HO = FoO_3, \\ BzH + HO. \end{matrix}\right.$

This compound is obtained by adding to distilled water some crude oil of bitter almonds, which always contains hydrocyanic acid (see amygdaline,) and evaporating to dryness along with some hydrochloric acid. From the dry mass, ether dissolves the new acid, which it deposits as a crystalline powder by evaporation. In this process, the hydrocyanic acid, under the influence of hydrochloric acid, is converted, along with the elements of water, into formic acid and ammonia. The latter combines with the hydrocyanic acid, the former with the hyduret of benzoile, yielding formobenzoilic acid. With bases, this acid forms salts, in which the quantity of base neutralized is exactly that which

would be neutralized by the formic acid alone. Their formula is $MO + FoO_3$, BzH; by which it is seen that the hyduret of benzoyle has entered into the radical of the acid, without altering its power of saturation; and perhaps the rational formula of the acid ought rather to be, $(FoO_4, BzH) + H$; and that of the salts, $(FoO_4, BzH) + M$; which exhibits this view still more clearly.

6. Benzoate of Hyduret of Benzoyle. $C_{42}H_8O_{18} = BzO,HO + 2BzH$.

This compound is formed when moist chlorine is passed through the oil of bitter almonds. Hydrated benzoic aid is formed, which unites with the unchanged hyduret. The action of moist chlorine in producing hydrated benzoic acid is as follows: $BzH + 2HO + Cl_2 = 2HCl + BzO,HO$. The new compound is crystalline, insoluble in water, soluble in alcohol and ether. It is volatile without decomposition. An alcoholic solution of potash dissolves it, and converts it into benzoate of potash.

7. Hippuric Acid. $C_{18}NH_8O_5 + HO$.

This acid is found in very considerable quantity in the urine of herbvivorous animals, such as the horse and cow, more especially when stall-fed. It has also been lately discovered by Liebig in human urine. It is easily obtained by evaporating gently to a small bulk the fresh urine of the horse or cow, and acidulating with hydrochloric acid. On standing, the liquid deposits brown crystals of hippuric acid, which may be decolorized by a little bleaching liquor and hydrochloric acid.

The pure acid forms pretty large semi-opaque four-sided prisms, sparingly soluble in cold water, very soluble in hot water and in alcohol. When heated, it melts, and gives off benzoic acid, benzoate of ammonia, and an oily matter, which has a very fragrant odour like that of the tonka bean. By nitric acid it is converted into benzoic acid. Heated with peroxide of manganese and sulphuric acid, it yields ammonia, carbonic acid, and benzoic acid; boiled with peroxide of lead, it yields benzamide and carbonic acid.

With bases it forms salts, most of which are soluble and crystallizable.

Hippuric acid may be viewed in two ways; first, as a compound of benzamide with an acid, C_4HO_3 (fumaric or aconitic acid?); secondly, as composed of hyduret of benzoyle, hydrocyanic acid, and formic acid. Either view readily accounts for its easy decomposition into benzoic acid and other products. As an ingredient of the urine, this acid is important; and we shall hereafter see that benzoic acid, taken into the system, appears in the urine as hippuric acid.

PRODUCTS OF THE DECOMPOSITION OF THE COMPOUNDS OF BENZOYLE.

1. Hyposulphobenzoic Acid. $C_{14}H_4O_3 + S_2O_5 + 2HO$.

A bibasic acid. Formed when anhydrous sulphuric acid acts on crystallized benzoic acid. $C_{14}H_5O_3,HO + 2SO_3 = C_{14}H_4O_3 + S_2O_5 + 2HO$. The acid is soluble and crystallizable, and forms with baryta a soluble and crystallizable salt, from which the acid may be obtained by the action of sulphuric acid. It forms two series of salts, one with 2 eq. of fixed base, the other with 1 eq. of fixed base and 1 eq. of water.

2. Bromobenzoic Acid. $C_{28}H_9BrO_8 + 2HO$.

A bibasic acid. When the vapour of bromine is allowed to act on benzoate

of silver at the ordinary temperature, there is produced this acid, along with bromide of silver and hydrobromic acid. 2 eq. of benzoate of silver and 4 eq. of bromine yield 1 eq. bromobenzoic acid, 1 eq. hydrobromic acid, and 2 eq. bromide of silver. $2(C_{14}H_5O_3AgO) + Br_4 = C_{28}H_9BrO_8 + HBr + 2AgBr$. Ether dissolves the acid and deposits it on evaporation, in a confused mass of crystals, very sparingly soluble in water. When the acid crystallizes, it takes up 2 eq. of water. With bases it forms salts, which are generally soluble and crystallizable. Their general formula is $C_{28}H_9BrO_8,2MO$.

3. Benzole. $C_{12}H_6$.

Syn. *Benzine. Benzène. Phène.*—Occurs in the volatile liquids condensed from oil gas; but is best obtained in a state of purity by distilling 1 part of crystallized benzoic acid with 3 of slaked lime. It is a limpid, colourless liquid, of an agreeable etherial odour. Its sp. gr. is 0·85; it boils at 186°, and at 32° it becomes solid. It is insoluble in water, soluble in alcohol and ether. In its formation, 1 eq. of benzoic acid yields 2 eq. carbonic acid and 1 eq. benzole, the carbonic acid uniting with the lime. $C_{14}H_5O_3,HO = C_{12}H_6 + 2CO_2$.

4. *Sulphobenzide.* $C_{12}H_5SO_2$. When anhydrous sulphuric acid acts on benzole, a viscid mass is formed, from which, by the addition of water, is separated a new compound, which may be dissolved and crystallized by means of ether. $C_{12}H_6 + SO_3 = HO + C_{12}H_5,SO_2$. Sulphobenzide is quite neutral. 5. *Hyposulphobenzidic Acid.*—This acid is found in the liquid from which the preceding compound has been deposited. Its formula is $C_{12}H_5,S_2O_5 + HO$. It may be viewed as formed by the action of 2 eq. of dry sulphuric acid on 1 eq. of benzole, $C_{12}H_6 + 2SO_3 = C_{12}H_5,S_2O_5,HO$; or as formed by the combination of sulphobenzide with oil of vitriol; $C_{12}H_5,SO_2 + HO,SO_3$. Either view readily explains its formation. The acid is best obtained pure from its salt with oxide of copper (which crystallizes very easily), by the action of sulphuretted hydrogen. It is very soluble, and may be crystallized. It has a very acid taste, and neutralizes bases, forming crystallizable salts. 6. *Nitrobenzide.* $C_{12}H_5NO_4$.—Formed when benzole is dissolved to saturation in fuming nitric acid, and water added to the hot solution. On cooling, the nitrobenzide falls to the bottom as a heavy oil. It is, at 60°, a yellow liquid, very sweet to the taste, with an odour like that of cinnamon; it boils at 434°, and solidifies at 37°. Its sp. gr. is 1·209. It is insoluble in water, soluble in alcohol and ether. It is formed from 1 eq. benzole and 1 eq. nitric acid. $C_{12}H_6 + NO_5 = HO + C_{12}H_5,NO_4$. 7. *Azobenzide.* $C_{12}H_5N$.—This compound is formed when an alcoholic solution of nitrobenzide is distilled with dry hydrate of potash. After the alcohol has distilled, the azobenzide volatilizes, forming large red crystals, fusible at 150°, boiling at 380°. The production of this compound is not yet explained; and its formula requires confirmation. 8. *Chloride of benzole.* $C_{12}H_6Cl_6$.—Formed when chlorine gas and benzole are exposed to the sun's rays. It is a colourless crystalline solid. 9. *Chlorobenzine.* $C_{12}H_3Cl_3$.—Obtained by distilling the preceding compound with hydrate of lime, as a colourless oily liquid.—Bromine forms with benzole analogous compounds.

10. Benzone. $C_{13}H_5O$.

One of the products of the distillation of neutral benzoate of lime. When purified from benzole and naphthaline, it is an oily viscid colourless liquid, hea-

vier than water. It differs from 1 eq. of anhydrous benzoic acid by 1 eq. of carbonic acid. $C_{14}H_5O_3 = C_{13}H_5O + CO_2$.

11. Hydrobenzamide. $C_{42}H_{18}N_2$.

When 1 vol. hyduret of benzoyle and 20 vol. of strong aqua ammoniæ are exposed in an hermetically sealed vessel to a temperatare of from 105° to 120°, it is converted after a time into a crystalline mass, which is to be washed with ether. The residue dissolved in alcohol, yields, by spontaneous evaporation, regular crystals of hydrobenzamide. In its formation, 3 eq. hyduret of benzole, and 2 eq. ammonia, produce 1 eq. hydrobenzamide and 6 eq. water. $3(C_{14}H_6O_2) + 2NH_3 = C_{42}H_{18}N_2 + 6HO$. If, in preparing this substance, we employ the crude oil of bitter almonds, we obtain a yellow resinous mass, which is a mixture of *hydrobenzamide*, *benzhydramide*, *azobenzoyle*, and *azotide of benzoyle*, all of them discovered by Laurent. 12. *Benzhydramide* is isomeric with hydrobenzamide, but is not converted, like the former, into hyduret of benzoyle, and sal-ammoniac by the action of hydrochloric acid. 13. *Azobenzoyle*. $C_{42}H_{15}N_2$, is much less soluble in alcohol than the preceding. It is derived from benzoyle as follows:— $3(C_{14}H_5O_2) + 2NH_3 = C_{42}H_{15}N_2 + 6HO$. 14. *Azotide of benzoyle*, $C_{14}H_5N$, is quite insoluble in boiling alcohol. It may be derived from anhydrous benzoic acid as follows: $C_{14}H_5O_3 + NH_3 = C_{14}H_5N + 3HO$.

15. Benzimide. $C_{28}NH_{11}O_4$.

According to Laurent, this compound is found in the crude oil of bitter almonds. It is crystallizable, and appears to be decomposed by acids into benzoic acid and ammonia. It may be derived from anhydrous bibenzoate of ammonia by the separation of 2 eq. water. $C_{28}H_{10}O_6 + NH_3 = C_{28}H_{11}NO_4 + 2HO$. But this is not probable. A compound precisely similar is obtained when an alcoholic solution of potash is added to a mixture of hyduret of benzoyle and strong hydrocyanic acid; but this compound yields with acids ammonia and hyduret of benzoyle.

16. Benzoine. $C_{14}H_6O_2$.

Isomeric with hyduret of benzoyle. It is formed when an alcoholic solution of potash or sulphuret, or cyanide of potassium, act on the crude oil of bitter almonds, containing hydrocyanic acid. It separates in a congeries of small crystals, insoluble in water, soluble in alcohol. It may be volatilized without change. Sulphuric acid dissolves it with a violet colour. Hydrate of potash, melted with it, forms benzoate of potash, with disengagement of hydrogen. It dissolves with a violet colour in a hot alcoholic solution of potash, and is converted by boiling with it into benzilic acid. When its vapour is passed through a red-hot tube, it is converted into hyduret of benzoyle, or at least into an oil smelling like that compound, and passing into benzoic acid on exposure to the air. By the action of chlorine it loses hydrogen, and is converted into *Benzile*, a compound having the composition of the radical benzoyle.

The action of hydrocyanic acid in promoting the formation of benzoine is not yet explained; but it is certain that from pure hyduret of benzoyle we cannot procure it, while the addition of hydrocyanic acid ensures its formation.

17. Hydrobenzoinamide.

Syn. *Benzoniamide*. Isomeric with hydrobenzamide. It is formed by ex-

posing a mixture of benzoine and ammonia to a moderate heat; and appears as a white tasteless powder, volatile without decomposition.

18. Benzile. $C_{14}H_5O_2$.

Syn. *Benzoyle.* It is formed by the action of chlorine gas on melted benzoine. When cold the mass is boiled with alcohol, which on cooling deposits benzile in crystals which are yellow six-sided prisms; insoluble in water, soluble in alcohol and ether, melting at 195° and volatile without decomposition. An alcoholic solution of potash dissolves it with a violet colour, and converts it into benzilic acid.

19. Benzilic Acid. $C_{28}H^{11}O_5 + HO$.

Formed when benzile is dissolved in a hot alcoholic solution of potash, and boiled until the violet colour at first produced has disappeared, and is no longer restored by a fresh portion of potash. To the boiling solution of benzilate of potash hydrochloric acid is added in excess, and on cooling the benzilic acid is deposited in colourless brilliant crystals, fusible at 248°, not volatile, but yielding, when heated, benzoic acid, and purple vapours. Sulphuric acid dissolves it with a bright crimson colour. Its formation is explained as follows:—2 eq. of benzile take up 2 eq. of water, one of which is incorporated in the acid; while the other is replaceable by bases. $2(C_{14}H_5O_2) + 2HO = C_{28}H_{11}O_5 + HO$. *Benzilate of potash* forms large transparent crystals, soluble in water and alcohol.

20. *Azobenzoide.*—$C_{84}H_{33}N_5$? Obtained by adding ammonia to the oil produced when bitter almonds are distilled per descensum, and dissolving away by means of ether all other products. A white powder, decomposed by heat. Its formula is doubtful.

21. *Cyanobenzile.* Formed when an alcoholic solution of benzile is warmed with $\frac{1}{3}$ of its volume of concentrated hydrocyanic acid. It is deposited in large transparent crystals, the composition of which is not yet known.

21. Hyduret of Sulphobenzoyle. $C_{14}H_5S_2,H$.

One vol. of crude essence of bitter almonds is dissolved in 8 or 10 of alcohol, and gradually mixed with one vol. of hydrosulphuret of ammonia. After a time, the mixture deposits a fine white powder, formed of grains smaller than those of starch, which give to the fingers a very persistent odour of garlic. It is insoluble in water and alcohol. Ether liquefies it, but a few drops of alcohol restore its solid form. It may be considered as the hyduret of a new radical, in which the oxygen of benzoyle has been replaced by sulphur. When heated, it melts, and if now allowed to cool, forms first a transparent plastic mass, and afterwards a brittle glass. If kept melted for some time, it crystallizes, but is now altered.

22. Stilbene. $C_{28}H_{12}$.

When the preceding compound is strongly heated, it gives off a large quantity of sulphuretted hydrogen, and a little of a liquid, apparently bisulphuret of carbon. Continuing the heat, there distil over, first a substance crystallizing in pearly scales, *stilbene*; and later, a compound crystallizing in needles, called by Laurent, the discoverer, *sulphessale*. To obtain the stilbene pure, the first crystals are dissolved in boiling alcohol, which leaves undissolved the other body,

and on cooling deposits stilbene in tables. These being dissolved in hot ether, form, by slow evaporation, remarkably fine crystals, with the pearly lustre of stilbite, hence the name. It is fusible and volatile, and combines with chlorine and bromine. Nitric acid decomposes it, giving rise to several new products. Strong chromic acid attacks it with violence, and reproduces hyduret of benzoyle.

Chloride of stilbene is formed when chlorine is passed through melted stilbene.

It appears in two isomeric modifications, *a* and *b*, both of which have the formula $C_{28}H_{12},Cl_2$, but crystallize in different forms. By the action of a boiling alcoholic solution of potash, each loses 1 eq. of hydrochloric acid (or its elements), and thus they produce two isomeric modifications of a new compound $C_{28}\left\{\begin{matrix}H_{11}\\Cl,\end{matrix}\right.$ which Laurent calls Chlostilbase; and in which 1 eq. of hydrogen of stilbene is replaced by chlorine. One of these is called Chlostilbase *a*, the other Chlostilbase *b*. Both are oily liquids, but they are distinguished by the action of bromine, which combines with both, producing again two isomeric compounds, both crystallizable, but in entirely different forms. Their formulæ are,

$a\ C_{28}\left\{\begin{matrix}H_{11}\\Cl\end{matrix}\right. + Br_2$ and $b\ C_{28}\left\{\begin{matrix}H_{11}\\Cl\end{matrix}\right. + Br_2$.

Along with chloride of stilbene is formed another compound, chloride of chlostilbase, analogous to these bromides of chlostilbase. It is a crystallizable solid: formula, $C_{28}\left\{\begin{matrix}H_{11}\\Cl\end{matrix}\right. + Cl_2$.

Bromide combines with stilbene, forming the bromide of stilbene, $C_{28}H_{12},Br_2$, which is a white powder.

When stilbene is boiled with nitric acid, it forms several compounds not yet fully examined. Among these are Nitrostilbase, Nitrostilbèse, and Nitrostilbic acid. The latter, according to Laurent, is $C_{28}H_{11}NO_{14}$.

23. *Hyduret of Sulphazobenzoyle*, $(C_{14}H_5S\frac{4}{3}N\frac{2}{3})\ H$, is generally formed along with hyduret of sulphobenzoyle. It seems to be hyduret of benzoyle, in which the 2 eq. oxygen of the benzoyle are replaced partly by sulphur, partly by nitrogen. Besides these compounds Laurent has described a hydrosulphuret of azobenzoyle, with the strange formula $C_{14}H_6SN\frac{3}{4}$. Ought it not rather to be $C_{14}H_6SN$?

By the action of ammonia on the crude essence, he has obtained two other compounds, *Azobenzoidine*, $C_{14}H_6N\frac{5}{3}$(?); and *Azobenzoilide*, isomeric with it; also two which he calls *hyduret of azobenzoyline* and *hyduret of benzoyline*, the former $C_{14}H_6N\frac{4}{3}$: the latter isomeric with the crude essence.

All these compounds are interesting, but the most recent researches of Laurent go to prove that the formula of the last-named compound should be trebled, $C_{42}H_{18}N_5$, and that it is a base, which he calls *amarine*.

24. Nitrobenzoic Acid. $C_{14}H_4NO_7HO$.

Formed when nitric acid acts on benzoic acid. It is a crystalline volatile acid, and contains the elements of benzoic acid, in which 1 eq. hyponitric or nitrous acid has been substituted for 1 eq. hydrogen. $C_{14}H_5O_3 - H + NO_4 = C_{14}\left\{\begin{matrix}H_4\\NO_4\end{matrix}\right. O_3$; and the basic water of the benzoic acid unites with the new acid as with the old.

25. Bromide of Benzole. $C_{12}H_6Br_6$.

This compound is formed as a white insoluble powder, when bromine acts on benzole. An alcoholic solution of potash removes hydrobromic acid (or its elements), and causes the separation of a white crystalline body, $C_{12}\left\{\begin{matrix}H_3\\Br_3\end{matrix}\right.$, which Laurent calls *bromobenzinise;* and which is formed by substitution of bromine for half the hydrogen of benzole. The bromide of benzole may, therefore, be $C_{12}\left\{\begin{matrix}H_3\\Br_3\end{matrix}\right.+3HBr$.

26. *Hydrocyanate of benzoine.* $C_{46}N_2H_{18}O_4$, is formed as a light crystalline matter, when oil of bitter almonds is mixed with one-fourth its volume of dry hydrocyanic acid, and warmed with its own volume of aqua potassæ, sp. gr. 1·25, diluted with six parts of alcohol. It arises from the action of 3 eq. hyduret of benzoyle and 2 eq. hydrocyanic acid: $3(C_{14}H_6O_2)+2(C_2NH)+C_{46}N_2H_{18}O_4+2HO$.

27. *Hydrocyanate of benzile*, $C_{14}H_5O_2+C_2NH=C_{16}NH_6O_2$, is formed by direct combination when a hot alcoholic solution of benzile is mixed with an equal bulk of anhydrous hydrocyanic acid. It forms large colourless crystals.

APPENDIX TO BENZOYLE.

1. Amygdaline. $C_{40}NH_{27}O_{22}$

Is found in bitter almonds, in the leaves of the cherry laurel, and probably in the kernels of all the bitter species of amygdalus and prunus as the peach and plum. To obtain it, bitter almonds are pounded and forcibly pressed between warm iron plates to remove the fat oil (oil of almonds). The marc or residue is boiled with alcohol of 94 per cent., and the tinctures distilled off in the water-bath to the consistence of syrup. This liquid, which contains amygdaline and sugar, is diluted with water, mixed with yeast, and set aside. When the fermentation is over, the whole is filtered and again evaporated to a syrup, which being mixed with a large excess of cold alcohol (of 94 per cent.) deposits the amygdaline as a white crystalline powder. This is pressed in folds of bibulous paper, and finally purified by repeated crystallization from boiling alcohol. It forms crystalline scales, very soluble in water, very sparingly soluble in cold alcohol, but more soluble in hot alcohol. It has a bitter taste. When heated it emits an odour like that of May blossom, and leaves a bulky coal.

When distilled with nitric acid, or other oxidizing agents, it is resolved into ammonia, hyduret of benzoyle, benzoic acid, formic acid, and carbonic acid. Caustic alkalies convert it into ammonia and amygdalinic acid; permanganate of potash converts it into cyanate and benzoate of potash.

2. Amygdalinic Acid. $C_{40}H_{26}O_{21}+HO$.

Prepared by boiling amygdaline with baryta as long as ammonia is given off, and then removing the baryta from the soluble amygdalinate of that base by sulphuric acid. By evaporation it yields a transparent amorphous mass, which has a very pleasant acid taste. Nitric acid, and other oxidizing agents, convert it into hyduret of benzoyle, with formic and benzoic acid. Its salts are almost all soluble: their formula is $C_{40}H_{26}O_{24}+MO$.

3. Distilled Water of Bitter Almonds.

Expressed bitter almonds are made into a thin cream with water, and this distilled in the heat of a chloride of calcium bath, till a quantity of water has passed over equal in weight to the almonds before being pressed. The distilled water is milky from suspended oil of bitter almonds, and smells both of hyduret of benzoyle and of hydrocyanic acid. When freshly prepared, it contains little more than 1 grain of hydrocyanic acid per ounce; but its strength diminishes by keeping, and as it is difficult to obtain it of uniform strength even when fresh, it is not a good form of administering hydrocyanic acid. It is remarkable, that nitrate of silver does not detect the hydrocyanic acid, unless ammonia is added with the nitrate, and after a time neutralized by nitric acid. It is used in medicine, especially on the Continent, and is poisonous.

4. Laurel Water.

Obtained by distilling two parts of fresh leaves of *prunus laurocerasus* with water till three parts have passed over. It exactly resembles the preceding water, and is equally uncertain, and equally poisonous.

THEORY OF THE FORMATION OF HYDURET OF BENZOYLE FROM BITTER ALMONDS.

Bitter almonds contain, like sweet almonds, a large quantity of an albuminous or caseous matter, called *emulsine* or *synaptase*, along with abundance of a mild fat oil, the oil of almonds, very similar to olive oil. But in addition to these, the bitter almonds contain 4 or 5 per cent. of amygdaline, which is not present in sweet almonds.

Now, if the amygdaline be removed by boiling alcohol, the residue, when distilled with water, does not yield a trace of the volatile oil of bitter almonds. Again, if the residue of the bitter almonds, after the fat oil has been pressed out, be heated to such a point as to coagulate the emulsine, before water is added, the distillation also yields no volatile oil, even although the amygdaline be present.

These facts prove that the production of the volatile oil of bitter almonds depends on the presence, first, of amygdaline, secondly of soluble emulsine; and that is the result of the mutual action of these bodies on each other. This is further demonstrated by the fact that if amygdaline be placed in contact with the emulsine or synaptase of *sweet almonds*, and water, distillation of the mixture now yields the oil abundantly.

When the solution of 10 parts of amygdaline in 100 of water is added to a solution of 1 part of synaptase in 10 of water, mutual decomposition at once takes place: the liquid acquires the odour of hyduret of benzoyle and of hydrocyanic acid, and when distilled, yields the crude oil of bitter almonds, which is a mixture of these two compounds. The residue of the distillation contains sugar in such quantity, that it is probable the elements of the synaptase have contributed to form it; and when this sugar is destroyed by fermentation, a fixed acid is found. If the synaptase has been coagulated, it has not the slightest action on amygdaline.

When the expressed bitter almonds are moistened with water, the very same reaction occurs; and if enough water be present to dissolve the oil as it is formed, the whole amygdaline disappears in a short time. But if the expressed

almonds be thrown into boiling water, the synaptase coagulates, and can then produce no change in the amygdaline. To obtain the full proportion of oil, 1 part of expressed almonds should be macerated for 24 hours with 20 parts of water at about 102°, and then distilled.

100 parts of amygdaline produce 47 of crude oil, and these 47 parts of crude oil contain almost exactly 6 of anhydrous hydrocyanic acid; so that 17 grains of amygdaline, dissolved in 1 oz. of emulsion of *sweet* almonds, yields a mixture containing 1 grain of dry hydrocyanic acid, and consequently of the same strength as the distilled water professes to be. This mixture has, besides, the advantage of containing the hyduret of benzoyle present in the distilled water, to which is perhaps owing the superiority of the distilled water of bitter almonds on laurel leaves over mere diluted hydrocyanic acid, a superiority which, according to the Continental physicians, is very decided and obvious. The above simple recipe, given by Liebig and Wöhler, is admirably adapted for extemporaneous use, and the mixture ought never to be made in larger quantity at a time, as, like the distilled water, it alters by keeping.

In the above remarkable decomposition, we have a very beautiful example of a metamorphosis in which the elements of two bodies take a share; but as the whole of the products are not yet exactly known, and even the composition of the emulsine or synaptase is uncertain, we cannot explain the whole change with precision. We know, however, that from 1 eq. amygdaline, $C_{40}NH_{27}O_{22}$, the following compounds may be derived:—

1 eq. hydrocyanic acid	$C_2\,NH$
2 eq. hyduret of benzoyle	$C_{28}\,H_{12}O_4$
½ eq. sugar	$C_6\,H_5\,O_5$
2 eq. formic acid	$C_4\,H_2\,O_6$
7 eq. water	$H_7\,O_7$
1 eq. amygdaline	$C_{40}N\,H_{27}O_{22}$

Also, 1 eq. amygdalinic acid, $C_{40}H_{26}O_{24}$, may yield

3 eq. formic acid	$C_6\,H_3\,O_9$
2 eq. hyduret of benzoyle	$C_{28}H_{12}O_4$
½ eq. sugar	$C_6\,H_5\,O_5$
6 eq. water	$H_6\,O_6$
1 eq. amygdalinic acid	$C_{40}H_{26}O_{24}$

Now, we can trace all these products among the results of this transformation; and it is probable, not only that there is more sugar than can be accounted for by the amygdaline, but also that other products, not yet known, are formed: as, for example, the fixed acid above alluded to. The emulsine or synaptase, which produces this remarkable change in amygdaline, in which it itself participates, contains nitrogen, is soluble in water, coagulable by heat, and in short very analogous both to albumen and caseine, along with which we shall again notice it. In the almond it appears to be accompanied by albumen.

We have seen, above, that the assumption of the existence of the radical benzoyle brings a number of compounds into a more easily understood form, and very materially aids the memory by enabling us to classify these compounds as analogous to others better known. Other views may be taken of this series of

compounds: for example, according to Dumas, hyduret of benzoyle may be represented as a compound of benzoic acid with a carbo-hydrogen: $2C_{14}H_5O_3 + (C_{14}H_5)H_3$: benzoic acid being the teroxide and the carbo-hydrogen the terhyduret of the body, $C_{14}H_5$: for $2(C_{14}H_5)O_3 + (C_{14}H_5)H_3 = C_{42}H_{18}O_6 = 3(C_{14}H_6O_2) = 3BzH$. The same view might be extended to some of the other compounds of benzoyle, but it is complex, and cannot well be applied to benzamide, hydrobenzamide, and several others. Again, according to Mitscherlich, benzoic acid is $C_{12}H_6 + 2CO_2$; that is, benzole plus 2 eq. carbonic acid; while a dry benzoate would contain, united to the base, the hypothetical body *benzide*, $C_{12}H_5$, and the equally hypothetical anhydrous oxalic acid, C_2O_3. These views appear both to be in all respects inferior to that which we have adopted, and which must be retained, until a better shall be proposed.

XIV. Salicyle. $C_{14}H^5O_4 = Sa$.

This is the hypothetical radical of a remarkable series of compounds; and, as such, belongs to the same group as benzoyle. Its most interesting compound is the hyduret of salicyle, which we shall therefore first consider.

TABLE OF COMPOUNDS.

Hyduret of Salicyle	$C_{14}H_5O_4$, H
Salicylic acid	$(C_{14}H_5O_4)$ O,HO
Chlorosalicylic acid	$C_{14}H_5O_4$, Cl
Nitrosalicylic acid	$C_{14}H_5O_4$, NO_4
Salicine	$C_{42}H_{22}O_{16} + 6HO$
Phloridzine	$C_{42}H_{23}O_{18} + 6HO$

1. Hyduret of Salicyle. $C_{14}H_5O_4,H = SaH$.

Syn. *Salicylous acid.* This compound is found as the chief ingredient in the essence of meadowsweet, that is the essential oil obtained by distilling the flowers of *spiræa ulmaria* with water. It is probable that, like the essence of bitter almonds, it is formed by the metamorphosis of a compound or compounds present in the flowers. The crude essence is distilled with aqua potassæ, which combines with the hyduret, and an oil distils over which seems to be a carbohydrogen. The salt of potash being now redistilled with a slight excess of dilute sulphuric acid, yields the pure hyduret of salicyle.

It may also be obtained by distilling one part of salicine, one part of bichromate of potash, two and a half of oil of vitriol, and twenty of water, together. The salicine is dissolved in part of the water, and the acid diluted with the rest. The mixture is then made in a retort, and after the effervescence which takes place is over, the whole is distilled, and yields the hyduret, to the amount of one-fourth of the salicine employed.

Hyduret of salicyle is an oily colourless liquid having a fragrant aromatic odour, and a burning taste. Its sp. gr. is 1·1731, and it boils about 380°. With chlorine and bromine it forms new compounds. With bases it forms salicylurets, water being separated. $HSa + MO = HO + MSa$, so that it has the characters of an acid.

Salicyluret of ammonium. Sa,NH_4, is formed when concentrated ammonia is poured upon hyduret of salicyle. It is a yellow solid, having a faint odour of roses. When moist, this salt is decomposed spontaneously, becoming black,

and giving off ammonia and an odour like that of roses. With dry ammoniacal gas, hyduret of salicyle forms the compound $3SaH + 2NH_3$.

Salicylimide, $C_{42}N_2H_{18}O_6$, is formed when caustic ammonia is added, drop by drop, to a solution of 1 vol. hyduret of salicyle in 3 vol. alcohol, and the small yellow crystals which first formed are dissolved by a gentle heat. On standing, salicylimide appears in the form of golden yellow brilliant prisms. It is formed from 3 eq. hyduret of salicyle and 2 eq. of ammonia, by the separation of 6 eq. water, $3\ (C_{14}H_6O_4) + 2NH_3 - 6HO = C_{42}N_2H_{18}O_6$. As it is no longer soluble in the liquid from which it was first deposited, it is probable that the yellow salt first formed, which dissolved in the alcohol by aid of a gentle heat, was salicyluret of ammonium, which by excess of ammonia, was converted into salicylimide.

The salts of the hyduret of salicyle or hydrosalicylic acid, are constituted, for the most part, according to the formula SaM. The potassium salt, SaK, when exposed to the air in a moist state, becomes first green, then black. When the change is complete, water dissolves acetate of potash, and leaves a black matter, *melanic acid*, $C_{10}H_4O_5$: 1 eq. of salicyluret of potassium, 2 eq. water, and 3 eq. oxygen, contain the elements of 1 eq. acetate of potash, and 1 eq. melanic acid, $C_{14}H_5O_4,K + 2HO + O_3 = C_4H_3O_4,K + C_{10}H_4O_5$. Melanic acid combines with bases.

2. Salicylic Acid. $(C_{14}H_5O_4)\ O,HO = SaO,HO = SaO_2H$.

Formed when hyduret of salicyle is heated with hydrate of potash till the mass loses its brown colour. Hydrogen is given off, and salicylate of potash is formed. Hydrochloric acid, added to the solution of this salt, causes the deposition of crystals of salicylic acid.

The same acid is formed when coumarine, the stearoptene or camphor of the tonka bean, is acted on by caustic potash. Moreover the essential oil of wintergreen, or *Gaultheria procumbens*, appears, by the researches of Cahours and Gerhard, to be the salicylate of oxyde of methyle.

Salicylic acid crystallizes in tufts of slender prisms, very like benzoic acid. It may be sublimed without decomposition. The formation of this acid from hyduret of salicyle is very simple: $C_{14}H_5O_4,H + KO,HO = C_{14}H_5O_5,KO + H_2$. When the salicylate of potash is decomposed by an acid, the salicylic acid takes up 1 eq. of basic water, and separates as $C_{14}H_5O_5,HO$, or $C_{14}H_5O_6,H$. The decompositions of this acid are very interesting, connecting it with several other series of organic compounds.

When it is acted on by nitric acid, it is first converted into indigotic acid, or anilic acid, $C_{14}H_4NO_9,HO$, along with other products; and by the continued action of nitric acid, there is finally produced the remarkably bitter acid, called carbazotic, or nitropicric acid, $C_{12}H_2N_8O_{13},HO$. Both these acids are formed from indigo by the action of nitric acid.

When salicylic acid is distilled with caustic baryta, it yields carbonate of baryta, and a heavy oily liquid, which is the acid known as carbolic acid (Runge), and hydrate of phenyle (Laurent), the formula of which is $C_{12}H_6O_2 = C_{12}H_5,O,HO$. The production of carbolic acid from salicylic acid is easily understood: it is in fact analogous to that of benzine from benzoic acid. $C_{14}H_5O_5,HO + 2BaO = 2\ (BaO,CO_2) + C_{12}H_6O_2$. As the action with baryta is so violent as to destroy a great part of the acid, it is found better to heat rapidly

salicylic acid mixed with powdered glass, when it is resolved into carbolic and carbonic acids.

Now it is very remarkable, that carbolic acid, which is one of the chief ingredients of the oil of coal tar, a product, therefore, of the destructive distillation, is also converted by the action of nitric acid into nitropicric acid. This would indicate that when salicylic acid is acted on by nitric acid, it yields, first, some compound containing the same radical as carbolic and nitropicric acid, and that this is further oxidized into the latter acid. We shall hereafter see that the probable radical of carbolic acid is *phéne*, $C_{12}O_6$, from which, by substitution and oxidation, carbolic and nitropicric acids, and a whole series of compounds, may be formed.

On the whole, from its relation to hyduret of salicyle and to salicine (from which it may also be formed by the action of caustic potash), from its analogy in formation, constitution, and properties to benzoic acid, from its occurrence in nature in the first compound of methyle not artificially produced, and from its ready convertibility into indigotic acid, carbolic acid, and nitropicric acid, salicylic acid is a compound of very great interest.

The salts of salicylic acid have the general formula $C_{14}H_5O_5,MO$ or $C_{14}H_5O_6$, M. The salicylate of oxide of methyle $C_2O_3,O + C_{14}H_5O_5$, occurs in the essential oil of *Gaultheria procumbens*, and is much used in perfumery. It gives rise to a number of remarkable products, when subjected to the action of nitric acid, chlorine, bromine, alkalies, &c.; but all these things will be treated of in their proper places.

3. Chlorosalicylic Acid. $C_{14}H_5\left\{\begin{matrix}O_4\\Cl\end{matrix}\right.$ or $C_{14}H_5O_4,Cl$.

When dry chlorine is made to act on dry hyduret of salicyle, this compound is formed, along with hydrochloric acid; it crystallizes readily, and may be sublimed unchanged. Its formation is entirely analogous to that of chloride of benzoyle, and it might be viewed as chloride of salicyle, $C_{14}H_5O_4,Cl = Sa\,Cl$. But its properties are those of an acid, and hence we are compelled to consider it as salicylic acid, $C_{14}H_5O_5$, in which 1 eq. oxygen has been replaced by 1 eq. chlorine, the type remaining unchanged. Hence after this substitution, it is still an acid, and its true formula is $C_{14}H_5\left\{\begin{matrix}O_4\\Cl\end{matrix}\right.$ an acid of the type of anhydrous salicylic acid.

With ammonia, it forms a new compound, *chlorosalicylimide*. As in the action of ammonia on hyduret of salicyle, so in this case 2 eq. ammonia act on 3 of the acid, and 6 of water are separated. The formula of chlorosalicylimide, which is a yellow, insoluble solid, is $C_{42}H_{15}N_2Cl_3O_6$; for $3\,(C_{14}H_5ClO_4) + 2\,NH_3 = 6\,HO + C_{42}H_{15}Cl_3N_2O_6$. It is, in fact, salicylimide in which 3 eq. chlorine have been substituted for 3 eq. hydrogen.

With bromine and iodine, hyduret of salicyle yields the two analogous compounds bromosalicylic acid, and iodosalicylic acid; $C_{14}H_5\left\{\begin{matrix}O_4\\Br\end{matrix}\right.$ and $C_{14}H_5\left\}\begin{matrix}O_4\\I\end{matrix}\right.$.

4. Nitrosalicylic Acid, $C_{14}H_5NO_8 = C_{14}H_5\left\{\begin{matrix}O_4\\NO_4\end{matrix}\right.$.

This acid is formed by the action of nitric acid on hyduret of salicyle. It

forms yellow prisms, and with bases, yields yellow detonating salts. Ammonia colours it blood-red, and perchloride of iron cherry-red. It would appear, according to the above formula, derived from the analysis of Piria, to be salicylic acid, in which 1 eq. nitrous (hyponitric) acid is substituted for 1 eq. oxygen. But its characters, and those of its salts, are such as to lead to the suspicion that it is identical with the nitrophenesic acid of Laurent (derived from carbolic acid by the action of nitric acid), the formula of which is $C_{12}H_3N_2O_9$, HO. The subject requires further investigation. It is not improbable that this acid may ultimately be found identical with indigotic acid, $C_{14}H_4NO_9$, HO.

APPENDIX TO SALICYLE.

5. Salicine. $C_{42}H_{29}O_{22} = C_{42}H_{23}O_{16} + 6HO$.

This compound occurs in the bark of all such willows as are bitter, such as *Salix helix*, *S. amygdalina*, &c. It is extracted by boiling with water, decolorizing the decoction with litharge, removing the lead dissolved by sulphuric acid and sulphuret of barium, and evaporating to a syrup. The salicine crystallizes on standing, in fine scales of a silky lustre, which have a very pure bitter taste, and are highly febrifuge. It is neutral, soluble in water and alcohol, insoluble in ether. Oil of vitriol colours it blood-red. When a mixture of acetate of lead with ammonia is added to a solution of salicine, there is formed a precipitate, which appears to be $C_{42}H_{23}O_{16} + 6PbO$. Distilled with bichromate of potash and sulphuric, it yields formic and carbonic acids, hyduret of salicyle, and a resinous matter.

Saliretine. $C_{30}H_{15}O_7 + HO$. When salicine is boiled with diluted sulphuric or hydrochloric acid, it deposits a yellowish white powder, which has the characters of a resin. This is saliretine. It is insoluble in water and ammonia, soluble in alcohol. Oil of vitriol colours it blood-red; heated with nitric acid, it yields nitropicric acid. Its formation is accompanied by the production or separation of grape sugar. In fact, salicine, plus 1 eq. hydrogen, contains the elements of saliretine and of grape sugar. $C_{42}H_{29}O_{22} + H = C_{30}H_{15}O_7$, HO + $C_{12}H_{14}O_{14}$.

Chlorosalicine. When chlorine is made to act on a solution of salicine, there is obtained a powder, $C_{42}H_{25}Cl_4O_{22}$. This is chlorosalicine, which is salicine, having 4 eq. of chlorine substituted for 4 eq. hydrogen. If heat be applied during the operation, a red liquid is formed, which is $C_{42}H_{18}Cl_7O_{18}$. It appears to be formed from salicine, *minus* 4 eq. water, $C_{42}H_{25}O_{18}$, by the substitution of 7 eq. chlorine for 7 eq. hydrogen.

Rutiline is the name given to the red compound formed by the action of oil of vitriol on salicine. When pure it is of a deep reddish-brown colour; acids change it to a bright red, alkalies to a deep violet.

6. Phloridzine. $C_{42}H_{29}O_{24} = C_{42}H_{23}O_{18} + 6HO$.

This is a substance, very analogous to salicine, which occurs in the bark of the roots of the apple, pear, plum, &c. It is extracted in the same way as salicine, and resembles it much; forming small scales, soluble in hot water, and in alcohol, very bitter and powerfully febrifuge. It may be viewed as salicine, *plus* 2 eq. oxygen, or as a higher oxide of the same radical. When boiled with dilute sulphuric acid, it yields a resinous compound, *phloretine*, analogous to sali-

retine, along with grape sugar. Phloretine is $C_{30}H_{15}O_{10} = C_{30}N_{14}O_9$, HO; and $C_{30}H_{15}O_{10} + C_{12}H_{14}O_{14} = C_{42}H_{29}O_{24}$. According to Stas, however, Phloretine is $C_6H_3O_2$, or double or quadruple of this. The compound of phloretine with oxide of lead he found to be $C_{12}H_5O_3$, 2PbO; which would indicate, for hydrated phloretine, $C_{12}H_5O_3$, $2HO = C_{12}H_6O_4$, $HO = C_{12}H_7O_5$.

By the action of nitric acid on phloridzine, there is formed a puce-coloured acid, nitrophloretic acid, which, according to Piria, is $C_{30}H_{12}NO_{15}$; according to Stas, $C_{24}H_{10}NO_{12}$.

Phloridzéine. $C_{42}H_{20}N_2O_{26}$. When moist phloridzine is exposed to air and ammonia, it is transformed into a deep red compound, which dissolves in ammonia, and may be precipitated by acids. It is equal to phloridzine, *plus* 8 eq. oxygen and 2 eq. ammonia. When dissolved in ammonia, and dried in vacuo, it leaves a purple mass, with coppery lustre, which communicates to water a splendid blue colour. This is a compound of phloridzéine and 1 eq. ammonia. The formation of this blue pigment is a very good example of that kind of eremacausis with the aid of ammonia, by which indigo, litmus, orchil, &c. are produced from colourless bodies.

XV. Cinnamyle. $C_{18}H_8O_2$ = Ci.

The radical of essence of cinnamon, but unknown in a separate form.

TABLE OF COMPOUNDS.

Hyduret of Cinnamyle, . . .	$C_{18}H_8O_2$, H.
Cinnamic Acid, ...	$C_{18}H_8O_4$

1. Hyduret of Cinnamyle. CiH = $C_{18}H_8O_2$, H.

This is the purified essence, or oil of cinnamon. The oil of commerce contains, besides, cinnamic acid and two resins, all of which have been produced from the original oil, $C_{20}H_{11}O_2$ by the additions to 3 eq. of it, of 8 eq. oxygen. $3(C_{20}H_{11}O_2) + O_8 = C_{18}H_8O_4$ (cinnamic acid + $C_{12}H_5O$ (a resin); + $C_{30}H_{15}O_4$ (another reain), + 5HO. With less oxygen, hyduret of cinnamyle, $C_{18}H_8O_2$, is formed, along with the resins, so that the oil of commerce contains, besides the original oil, all the compounds above mentioned.

The hyduret of cinnamyle, CiH, is a fragrant oil. It forms, with nitric acid, a crystalline compound, CiH + NO_5, which, when mixed with water is resolved into its constituents, hyduret of cinnamyle and nitric acid. When the hyduret is exposed to the air, it absorbs oxygen, producing cinnamic acid, CiO, HO = $C_{18}H_8O_3$, HO.

The fresh oil of cinnamon is, as has been stated, $C_{20}H_{11}O_2$. With 6 eq. oxygen from the air, it yields hyduret of cinnamyle and the two resins: with 2 eq. more, the hyduret passes into cinnamic acid. With oil of vitriol, 3 eq. of the fresh oil = $C_{60}H_{33}O_6$, lose 3 eq. water, and form two resins, one = $C_{30}H_{15}O$; the other $C_{30}H_{15}O_2$. With hydrochloric acid, it yields an oil and two resins; one, $C_{20}H_8O$; the other $C_{14}H_6O$.

2. Cinnamic Acid. $C_{18}H^7O^3 + HO = CiO, HO$.

Formed by exposing oil of cinnamon to the air. It is most easily obtained by dissolving the oil of balsam of Peru in an alcoholic solution of potash, evaporating to dryness, dissolving in hot water, and adding to the solution of cinna-

mate of potash an excess of hydrochloric acid. It crystallizes very readily, and may be sublimed. By the action of nitric acid, cinnamic acid is converted into hyduret of benzoyle, and into an acid very similar to benzoic acid, if not identical with it. When cinnamic acid is added to cold nitric acid, it forms an acid, $C_{18}H_7NO_8 = C_{18}H_8O_4 - H + NO_4$; that is, cinnamic acid, in which 1 eq. of nitrous acid is substituted for 1 of hydrogen; $C_{18}\begin{cases}H_6\\NO_4\end{cases}O_3$, HO. This is *nitrocinnamic acid*. Its salts detonate when heated. With oxide of ethyle, it forms a crystallizable ether, AeO, $C_{18}H_6NO_7$.

When oil of cinnamon is acted on by nitric acid with the aid of heat, it yields benzoic and nitrobenzoic acids. By the action of chlorine, oil of cinnamon is converted into several new products, one of which is *chlorocinnose*, $C_{18}\begin{cases}H_4\\Cl_4\end{cases}O_2$. It is hyduret of cinnamyle in which 4 eq. of chlorine are substituted for 4 eq. of hydrogen.

Balsam of Peru contains compounds connected with cinnamyle. The principal is an oil, *cinnameine*, which, when boiled with alkalies, yields cinnamic acid and a neutral oily body, *peruvine*, $C_{18}H_{12}O_2$. Cinnamine, heated with dry potassa, yields hydrogen gas and pure cinnamate of potassa. When exposed to cold, cinnameine deposits crystals, which have the same composition as hyduret of cinnamyle, and are therefore an isomeric modification, analogous to benzoine.

According to Richter, balsam of Peru contains two distinct oils, *myroxiline*, insoluble in alcohol, *myriospermine*, soluble in alcohol. With an alcoholic solution of potassa, myriospermine yields an acid resembling cinnamic acid, but different from it, *myriospermic acid*. Balsam of Tolu resembles Balsam of Peru in its constituents. These substances require further investigation.

In the preceding pages we have considered a large number of compound radicals, constituting chiefly the group of radicals analogous in their relations to chlorine: namely, cyanogen; ferrocyanogen and its numerous congeners; sulphocyanogen; and mellone. We have only described one radical, *amide*, which has a tendency to produce basic compounds, such as *ammonia*, *ammonium*, and the *platinised bases*; and one, *carbonic oxide* or *oxalyle*, the chief tendency of which is to form acid compounds, such as *oxalic*, *carbonic*, *rhodizonic*, *croconic*, and *mellitic* acids. Finally, we have studied three: namely, *benzoyle*, *salicyle*, and *cinnamyle*, whose characteristic is to form essences or fragrant volatile compounds with hydrogen, acids with oxygen, and peculiar compounds with chlorine, iodine, &c. This last group would appear to have a strong tendency to form acid compounds: for not only is an acid formed by the union of salicyle and oxygen, but the hyduret of salicyle is a decided acid, forming salicylous acid, $C_{14}H_5O_3$,HO, isomeric with benzoic acid; instead of hyduret of salicyle, $C_{14}H_5O_4$. Further, the chloride, bromide, and iodide of salicyle, although they contain salicyle, *plus* those elements, are all strong acids, and appear to be in fact *salicylic acid* with 1 eq. of chlorine, &c. substituted for 1 eq. of hydrogen. It is evident that this group of radicals, so well characterized by their hydrogen compounds, does not correspond exactly to any simple radical, but has characters common to different groups of elementary radicals, being, however, analogous in more points to carbon, sulphur, and phosphorus than to any other elements. In studying the decomposition of the compounds of salicyle, we have

met with the very remarkable fact of the production from that radical of a series of compounds: namely, anilic acid, nitropicric acid, carbonic acid, &c., probably derivatives of a totally different radical, phenyle; which radical is also met with in numerous other decompositions, and especially in the decomposition of indigo by nitric acid, by alkalies, and by heat, and in the destructive distillation of coal. This is an important consideration, as every day's experience tends to identify with each other the products of decomposition of different and apparently quite unconnected organic compounds, even in cases where these products have been described as different. Another very important fact which has come under our notice is the occurrence of salicylate of oxide of methyle as the chief ingredient in the oil of Gaultheria. Not only is the occurrence of salicylic acid interesting, since this acid was only known before as an artificial product, but the existence, in this oil, of oxide of methyle, hitherto only known as a product of destructive distillation, goes far to confirm the theory which admits this radical, methyle, and others similar to it. All the properties of the oil of Gaultheria entirely agree with the doctrine of its containing two radicals, methyle and salicyle, the former oxidized, as a base; the latter, also oxidized, as an acid.

We now proceed to consider that group of radicals to which methyle belongs, and which are analogous, in their relations, to metals, more than to any other class of elements; forming, like metals, bases with oxygen. This group contains Ethyle, Methyle, Amyle, Glyceryle, Cetyle, and Cacodyle; besides several radicals, derived from the decomposition of these: as, Acetyle from Ethyle, and Formyle from Methyle. These latter, however, belong to that group which are analogous to the combustible metalloids, and form acids with oxygen, instead of bases, like the radicals from which they are derived, and in connection with which they shall be described.

XVI. Ethyle. C_4H_5=Ae.

Unknown hitherto in a separate form; but very well known as anhydrous oxide, or ether, and hydrated oxide, or alcohol. These compounds have not yet been found as natural products of vegetable life, although it is probable that the fragrance of certain fruits, such as pine-apples, melons, apples, is derived from compounds of ethyle. The compounds of ethyle, especially alcohol, are, however, very abundantly produced by the fermentation of saccharine vegetable juices, such as that of the grape. The alcoholic or vinous fermentation of sugar is a metamorphosis, induced in the sugar by contact with yeast or ferment, which is gluten or fibrine in a state of decomposition. In this metamorphosis, the particles of the ferment only act in communicating mechanical motion to those of the sugar; they do not join the elements of the sugar in producing new compounds, but are decomposed separately; while the elements of the sugar, *plus* a small proportion of the elements of water, form two compounds, alcohol and carbonic acid. $C_{12}H_{11}O_{11}+HO=2(C_4H_5,O+HO)+4CO_2$.

TABLE OF COMPOUNDS.

Oxide of Ethyle	C_4H_5O
Hydrate Oxide of Ethyle	C_4H_5O,HO
Chloride " "	C_4H_5,Cl
Bromide " "	C_4H_5,Br
Iodide " "	C_4H_5,I
Sulphuret " "	C_4H_5,S
Mercaptan " "	$C_4H_6,S+HS$.

1. Oxide of Ethyle. $AeO=C_4H_5,O$.

Syn. *Ether. Sulphuric Ether.*—This compound is obtained from alcohol, its hydrate, by heating it gently along with sulphuric or phosphoric acid, which removes the water, or at all events causes the separation of the ether from the water. The best process is as follows: 5 parts of alcohol, of at least 90 per cent., are mixed with 9 of sulphuric acid, and the mixture introduced into a retort, where it is rapidly heated to the boiling point, and kept at that point, while by means of a bent tube passing through the cork which stops the tubulure of the retort, and furnished with a stop-cock, fresh alcohol is allowed to enter the retort so as to keep the liquid constantly at the original level, flowing in exactly as fast as the ether, &c. distils over. The products are condensed in a powerful refrigeratory, such as Liebig's, figured at p. 556; they consist chiefly of ether, with water in such proportion as would convert the ether into alcohol; and a very little alcohol, sometimes none at all. The operation may be advantageously continued until 31 parts of alcohol, at 90 per cent., have flowed into the retort, and of course an equal volume of ether and water has distilled over.

This process, as to its final result, may be thus expressed. $AeO,HO+2(HO,SO_3)=2HO,SO_3+HO+AeO$. That is, the action of heat and of oil of vitriol has caused the separation of the ether and the water, which, together, constitute alcohol. And it is to this view of the change, which he considers one of decomposition by contact, that Berzelius applies his theory of a catalytic force. But in reality, the process consists of two stages: the first is the formation of bisulphate of oxide of ethyle (sulphovinic acid) $AeO,HO,2SO_3$; and the second is the decomposition of this by heat into AeO and $HO,2SO_3$. The bisulphate is formed when a mixture of 2 eq. oil of vitriol, 1 eq. alcohol, and from 1 to 3 eq. of water, is heated to about 285°; and at almost precisely the same temperature, the bisulphate is decomposed, especially if the liquid be kept in steady ebullition. Now, the bisulphate contains anhydrous sulphuric acid, ether, and water, $2SO_3+AeO+HO$; and when decomposed the sulphuric acid seizes the water, thus preventing the ether from uniting with it to reproduce alcohol. The ether, therefore, distils over; but as, when the bisulphate was formed, ether, AeO, displaced water, HO, from half the oil of vitriol, so now, when the bisulphate is decomposed, and while its water is retained by the 2 eq. of anhydrous acid, the vapours of ether traverse a liquid containing oil of vitriol diluted, both with the water displaced from the other part of it by the ether, and with the water of the alcohol (which at 90 per cent. amounts to 2 eq. for 1 of ether, one combined with the ether to form the alcohol, the other serving to dilute it). Now, a sulphuric acid, thus far diluted, and heated to a temperature even short of 285°, gives off water, and therefore the vapour of ether in passing through this acid, becomes saturated with the vapour of water, without combining with it, and thus ether and water distil over together. At the surface of the boiling, or effervescing liquid, however, the ether produced by the decomposition of the bisulphate is brought into contact with water in the nascent state, also derived from that decomposition, and in this manner, according to Liebig, a little alcohol is reproduced, and distils over with the ether, the ether being produced in the body of the liquid, the alcohol only at the surface. It is certain that a little alcohol generally accompanies the ether, even in the most successful operation; but it is not easy to see how, according to the above explanation, the sulphuric acid which, in the body of the liquid, is able to prevent the ether from combining with water,

should fail to do so at the surface. The ether and water, it would appear, are equally in the nascent state in both situations. While, therefore, we admit Liebig's very beautiful explanation of the facts connected with the production of ether, we cannot feel the same certainty in regard to his explanation of the simultaneous occurrence of alcohol. It will now be seen how little necessity there is for resorting to the mysterious agency of catalysis; for the change is not one due to contact alone, but, on the contrary, one depending on strong affinities very nicely balanced, and influenced to a very great extent by the degree of heat employed. The idea that the contact of oil of vitriol caused the ether and water of alcohol to separate, arose from the circumstance that the formation of the bisulphate of ethyle takes place at a temperature quite close to that at which it is decomposed, and that the formation of the bisulphate in this process had been overlooked.

The crude ether is mixed with an alcoholic solution of potash, so as to render it alkaline, and distilled in the vapour-bath, as long as the sp. gr. of the product does not exceed 0·725 at 80°. The ether is then digested for a few days with chloride of calcium, or quicklime, and rectified once more with one of these substances. When pure, oxide of ethyle is a colourless, very mobile, highly refracting liquid, of sp. gr. 0·725 at 60°. It is very volatile, boiling at 76°, and producing intense cold by its evaporation. It has a pungent, cooling, aromatic taste; and a penetrating, agreeable odour. It is very combustible, and its vapour is apt to form dangerous explosive mixtures with air. When oxidized slowly, it yields aldehyde, aldehydic acid, acetic and formic acids.

Ether is used in medicine as a diffusible stimulant, and in chemistry as a solvent, especially of organic matters: such as fats, fat oils, essential oils, resins, some acids, and some bases.

In its relations to other bodies it exhibits the characters of a base, neutralizing acids, and forming compounds which are subject to the laws of double decomposition, like salts of inorganic bases. These salts of oxide of ethyle are, commonly, ethereal liquids; many of them crystallizing at low temperatures, and a good many being solid and crystalline at ordinary temperatures. They are often called ethers, with the name of the acid; as acetic ether, benzoic ether, &c. Those ethers which contain organic acids are for the most part fragrant. The formula for the salts of oxide of ethyle corresponds to that for the salts of potash, &c. Thus, as $KO,\bar{A}$ represents acetate, and $KO,\overline{Bz}$ benzoate of potash, so $AeO,\bar{A}$ or AeO,AcO_3, and $AeO,\overline{Bz}$ or AeO,BzO represent the acetate and benzoate of oxide of ethyle.

The analogy between ether and metallic protoxides is further shown in the action of both on hydrochloric acid and its congeners; for while KO, with HCl yields HO and KCl; so $AeO + HCl = HO + AeCl$: that is, ether, with hydrochloric acid, yields water and chloride of ethyle. The same is true of the bromide, iodide, &c., and by proper means both the cyanide of ethyle, $Ae\dot{C}y$, and the sulphuret of ethyle, AeS, may be obtained. In short, we cannot better connect and classify the numerous facts now known in regard to ether, than by adopting the view which considers it as the basic oxide of ethyle, a compound radical, very analogous to a metal.

2. *Hydrate of oxide of ethyle.* $AeO,HO = C_4H_5O,HO$. Syn. *Alcohol.* This compound is formed when ether and water meet in the nascent state, as we shall see occurs when some of the acid salts of ethyle are heated, or otherwise decom-

posed. But, practically, it is produced entirely from sugar by fermentation. The juice of the grape, or any other saccharine juice, or an infusion of malt, when exposed to the air for a short time, and then from a temperature of from 40° to 85°, soon enters into fermentation, and a large quantity of carbonic acid is given off, while the sugar totally disappears, and alcohol is found in its place. A pure solution of sugar in water does not ferment, but on the addition of yeast it does so. The juice of the grape and the infusion of malt both contain, besides sugar, some body which plays the part of yeast, or ferment. This is, in the grape juice, fibrine, and in the malt, gluten, both of which readily enter into putrefaction when exposed to air and moisture, and being in this state, their particles in motion, this motion is communicated to the particles of sugar, and the existing equilibrium of affinities being thereby disturbed, new compounds are formed, in this case alcohol and carbonic acid. The subject of fermentation will be afterwards fully discussed: in the mean time, it is to be observed that any similar substance, in a state of putrefaction, will induce the fermentation of sugar; as, for example, putrefying flesh, blood, milk, cheese, white of egg, urine, &c. &c., and that none of these ferments contributes to the production of the alcohol, or carbonic acid, but yield ammonia and other products. Crystallized cane sugar, $C_{12}H_{11}O_{11}$, requires the elements of 1 eq. of water to yield 2 eq. alcohol $C_8H_{12}O_4$ and 4 eq. carbonic acid $4CO_2 = C_4O_8$; and grape sugar, $C_{12}H_{14}O_{14}$, produces, besides the alcohol and carbonic acid, 2 eq. of water. Thus we have $C_{12}H_{11}O_{11} + HO = 2(C_4H_6O_2) + 4CO_2$; and $C_{12}H_{14}O_{14} = 2(C_4H_6O_2) + 4CO_2 + 2HO$.

From the fermented liquid, which, in the case of the grape juice, is wine, in that of malt, beer, ale, or wort, the alcohol is separated by distillation, and being more volatile than water, it predominates in the first portions distilled. These constitute, when from wine, brandy; when from a fermented infusion of malt, whiskey; and when from fermented solution of molasses, rum. In these forms it still contains 30, 40, or more per cent. of water, and a little volatile odoriferous oil. It is again rectified, and the first portions distilled are colourless, and go by the name of spirits of wine. After another rectification they are called rectified spirits of wine. They now contain only alcohol, with from 10 to 20 per cent of water, which is removed by digesting the spirit with quicklime, and distilling: or by rectifying over dried carbonate of potash, or chloride of calcium.

Pure or absolute alcohol is a colourless, mobile fluid of sp. gr. 0·795 at 60°, and boiling at 173°. It has a burning taste, and a pleasant fruity smell. Rectified spirit of wine, that of 90 per cent. is very similar to it, having the sp. gr. 0·825 to 0·836; ordinary spirit of wine, at 70 per cent., has the sp. gr. 0·880. Pure alcohol has never been frozen. It is very combustible, and produces, in burning, a very intense heat. Hence spirit of wine is much used for lamps for chemical purposes. Alcohol has a strong attraction for water, and on this account acts as an antiseptic, preserving animal and vegetable substances from putrefaction. The strength of alcohol is ascertained by its specific gravity; and all chemical works contain tables of the relation between the density of the spirit and the per centage.

Alcohol is a powerful diffusible stimulant, and has intoxicating properties. It is much used as a solvent, for many, indeed most vegetable acids and bases, for volatile oils, for resins, and for many salts, even inorganic. Most deliquescent salts are soluble in alcohol, as are the caustic alkalies and iodine. Acids act on

alcohol, producing the compound ethers. Solutions made with proof spirit (a mixture of equal volumes of rectified spirit of wine and of water, sp. gr. 0·960), are called tinctures.

3. *Chloride of ethyle*, $AeCl = C_4H_5,Cl$, is prepared by saturating alcohol with hydrochloric acid gas, and distilling the mixture in the vapour-bath, collecting the product in a well cooled receiver. It is formed as follows: $AeO,HO + HCl = AeCl + 2HO$. It is dried by digestion with chloride of calcium. It is a colourless liquid, sp. gr. 0·874, boiling at 52°, of an aromatic odour, slightly alliaceous. When exposed to the combined action of chlorine and the sun's rays, it yields by substitution a whole series of chlorinized ethers, of which series one extremity is ether $(C_4H_5)O$; and the other, perchloride of carbon $(C_4Cl_5)Cl = 2C_2Cl_3$. With an alcoholic solution of protosulphuret of potassium KS, it gives chloride of potassium and sulphuret of ethyle. $AeCl + KS = AeS + KCl$. With hydrosulphuret of sulphuret of potassium, it yields *mercaptan*, which is alcohol, in which all the oxygen has been replaced by sulphur. $AeCl + KS,HS = KCl + AeS,HS$; the latter, mercaptan, being analogous to AeO,HO.

4. *Bromide of ethyle*, formed by distilling bromine with alcohol and phosphorus. These are first formed, when the materials are mixed, phosphorous and hydrobromic acids, and the latter when heated with the alcohol, decomposes it, yielding AeBr, which resembles the chloride.

5. *Iodide of ethyle*, AeI, formed by a similar process, is analogous to the two preceding compounds.

6. *Sulphuret of ethyle*, AeS, is prepared, as above stated, from the chloride by sulphuret of potassium. It is a colourless liquid, boiling at 167°, of a strong offensive alliaceous smell.

7. *Hydrosulphuret of sulphuret of ethyle* or *mercaptan*, $AeS,HS = C_4H_6S_2$ or $C_4H_5,S + HS$. This very remarkable compound is formed when a solution of sulphate of lime and ethyle (sulphovinate of lime) of sp. gr. 1·28, is distilled with its own bulk of a solution of potash of the same density, previously saturated with sulphuretted hydrogen, and converted into KS,HS. The volatile product, after digesting it with a little oxide of mercury and chloride of calcium, to remove sulphuretted hydrogen and water, is mercaptan. Its formation is thus explained: $(CaO,SO_3 + AeOSO_3) + KS,HS = CaO,SO_3 + KO,SO_3 + AeS,HS$. Pure mercaptan is a colourless liquid, very mobile, boiling at 97°, of sp. gr. 0·842. It has a most penetrating and offensive odour of onions, as it were concentrated, which adheres obstinately to the hair or clothes, so that it is most unpleasant to experiment upon. As above mentioned, it is formed from alcohol by substitution of sulphur for oxygen; and as alcohol is the hydrate of oxide of ethyle, AeO,HO, mercaptan is the hydrosulphuret of the sulphuret of ethyle, AeS,HS. The sulphuret of ethyle, AeS, corresponds to the oxide, ether, AeO.

Mercaptan acts strongly on some metallic oxides, especially those of the noble metals, such as mercury, gold, platinum, &c. The metal takes the place of the hydrogen of the sulphuretted hydrogen in mercaptan; thus $MO + (AeS,HS) = HO + (AeS,MS)$. The red oxide of mercury is acted on by mercaptan, and converted into a white crystalline compound, called the mercaptide of mercury; oxide of gold forms a gelatinous white mercaptide; and oxide of lead yields lemon yellow crystals of mercaptide of lead, AeS,PbS.

Mercaptan may also be viewed as $H + AeS_2$, in which case the above metallic compounds will have the general formula $M + AeS_2$. Here the supposed radical,

the *mercaptum* of Zeise, is bisulphuret of ethyle; so that on either view mercaptan is connected with ethyle.

Zeise has described, under the name of thialic oil or ether, another very fetid compound, which seems to be AeS_3, or persulphuret of ethyle.

Seleniuret and cyanide of ethyle are both volatile alliaceous offensive liquids, formed when sulphate of ethyle and potassa is distilled with seleniuret or cyanide of potassium. Sulphocyanide of potassium, alcohol and sulphuric acid, when dissolved together, yield a most offensive volatile liquid, supposed to be, or at all events to contain, sulphocyanide of ethyle. It will be observed that all these compounds of sulphur with ethyle and similar bodies are characterized by odours resembling that of garlic, but so intense and penetrating as to be insupportable. This character is observed in all volatile organic compounds of sulphur, whether artificial, as the above, or natural, as oils of garlic, assafœtida, horseradish, &c.

7. Salts of Oxide of Ethyle.

Oxide of ethyle forms both neutral and acid salts. The neutral salts are not at ordinary temperatures decomposed by other salts, like inorganic saline compounds. Thus an alcoholic solution of chloride of calcium does not cause any precipitate in an alcohol solution of oxalate of oxide of ethyle or oxalic ether. But they are easily decomposed by contact with hydrated alkalies, the acid uniting with the alkali, while the oxide of ethyle separates as hydrate, that is, as alcohol. Thus oxalic ether C_2O_3,AeO, with hydrate of potash, KO,HO, yields oxalate of potash KO,C_2O_3, and hydrate of oxide of ethyle, AeO,HO.

Oxide of ethyle has a very great tendency to form double salts, in which there are 2 eq. of the acid, 1 eq. of a basic, and 1 eq. oxide of ethyle. In these salts, the acid, as in the neutral salts cannot be detected by the usual tests; and indeed they may be viewed as simple salts, containing a compound acid, of which oxide of ethyle is a constituent united to the inorganic base. Thus the double sulphate of ethyle and potash, $KO,SO_3 + AeO,SO_3$, may be viewed as sulphovinate of potash, $KO + AeO,2SO_3$; and sulphovinic acid is, on this view, when separated, $HO + AeO,2SO_3$.

The acid salts of ethyle are on one view double salts, as, for example, the double sulphate formed of sulphate of ethyle, AeO,SO_3, with sulphate of water, HO,SO_3. On the other view, they are compound or coupled acids, and the above example becomes, as mentioned in the last paragraph, sulphovinic acid, $HO + (AeO,2SO_3)$, the hydrate of a compound of anhydrous sulphuric acid with ether. These acid salts are decomposed, by boiling with water, into alcohol which distils over, and hydrated acids which remain behind. When distilled with the salts of volatile acids, they yield the ethers of those acids: formiate and acetate of ethyle may be thus obtained. When an acid salt of ethyle is heated with acids not volatile, it often happens that the ethers of these acids are obtained: this is the case with the fatty acids and with some others.

TABLE OF SALTS OF THE OXIDE OF ETHYLE.

Acid sulphate of the oxide of Ethyle . . .	$HO,SO_3 + AeOSO_3$
Acid phosphate " "	P_2O_5,AeO,2HO
Nitrate " "	AeO,NO_5
Hyponitrite " "	AeO,NO_3
Carbonate " "	AeO,CO_2

Double carbonate of ethyle and potash . . .	$KO,CO_2 + AeO,CO_2$
Oxalate of oxide of ethyle	AeO,C_2O_3
Oxamate " "	$AeO,C_2O_3 + Ad,C_2O_2$.
Sulphocarbonate and water	$AeO,HO,2CS_2$
Bicyanurate of oxide of Ethyle . . .	$Cy_3O_3,3AeO, + Cy_3O_3,3HO + 3Aq.$
Benzoate " "	AeO,BzO
Hippurate " "	$AeO, + C_{18}NH_8O_6$
Salicylate " "	$AeO + C_{14}H_5O_5$

8. *Acid sulphate of oxide of ethyle*, $HO,SO_3 + AeSO_3$, is also called *sulphovinic acid*, $HO + (AeO,2SO_3)$. Sulphuric acid forms no neutral compound with oxide of ethyle. The acid salt is formed when the vapour of ether is conducted into oil of vitriol, or when oil of vitriol is mixed with alcohol and heated to a certain point. To obtain it pure, the double sulphate of ethyle and baryta (sulphovinate of baryta) in solution, is decomposed by sulphuric acid, and the filtered liquid is a solution in water of the acid sulphate. It has a very sour taste, and cannot be concentrated by evaporation, whether at the ordinary temperature or with the aid of heat, without being decomposed into alcohol and sulphuric acid. It forms, with most bases, crystallizable double salts, which are all soluble, so that, for example, the addition of baryta causes no precipitate if the acid be pure. As the acid sulphate itself is called sulphovinic acid, so these double salts are called sulphovinates. It is because all these salts are soluble, that the usual tests cannot detect the sulphuric acid they contain. When, however, their solutions are boiled with a little hydrochloric acid, alcohol is given off, and then the sulphuric acid may be detected as usual. All these salts are decomposed by heat, yielding, according to the temperature, double sulphate of ethyle and etherole, alcohol, sulphurous acid, olefiant gas, and a sulphate as residue, mixed with charcoal. When heated with hydrated alkalies, they yield sulphates and alcohol. The *double sulphate of ethyle and potash* crystallizes in shining scales, which are the anhydrous salt, $KO,SO_3 + AeO,SO_3$. The *baryta salt* contains 2 eq. of water of crystallization, and forms beautiful tabular crystals, as do also the *salt of lime*, and the *salt of lead*, both of which likewise contain 2 eq. of water. These three salts are all composed according to the formula, $MO,SO_3 + AeO,SO_3 + 2$ eq.

9. *Acid phosphate of oxide of ethyle*, or phosphovinic acid, $P_2O_5 \left\{ \begin{matrix} AeO \\ 2HO, \end{matrix} \right.$ is formed in the same way as sulphovinic acid, and obtained pure from the double salt of baryta, $P_2O_5 \left\{ \begin{matrix} AeO \\ 2BaO \end{matrix} \right. + 12HO$. It is a tolerably permanent acid, decomposed only by a high temperature. With bases it forms double salts, in which the 2 eq. water of the acid are replaced by 2 eq. of a protoxide. The *baryta salt*, the formula of which is given above, crystallizes in pearly scales.

OXIDE OF ETHYLE WITH NITRIC ACID.

10. Nitrate of Oxide of Ethyle. AeO,NO_5.

When 2 fluid ounces of alcohol, and 1 fluid ounce of pure nitric acid, of sp. gr. 1·4, are distilled together, with the addition of 10 or 20 grains of urea, to destroy any nitrous or hyponitrous acid, the distillation proceeds calmly and smoothly, and the distilled liquor contains water, alcohol, and nitrate of ethyle,

which partly separates, towards the end of the process, as a heavy oily stratum, and is more completely separated by the addition of water. It is a colourless liquid, of sp. gr. 1·112; which boils at 185°, and is inflammable, burning with a bright white flame. It is quite insoluble in water, but very soluble in alcohol; and it possesses a pleasant smell and a sweet taste. An alcoholic solution of potash converts it into alcohol and pure nitrate of potash.

11. Hyponitrite of Oxide of Ethyle. AeO,NO_3.

Syn. *Nitrous ether.*—*Nitric ether.* This is best prepared in a state of purity when a current of hyponitrous acid vapours, derived from starch and nitric acid, is passed through weak alcohol, the product being condensed in Liebig's refrigeratory. The ether is washed with water, and dried by means of chloride of calcium. The whole apparatus must be kept cool, otherwise the action is too violent, and the results very complex. When nitrous ether is made by the usual processes, in which ordinary nitric acid is mixed with alcohol, the product always contains a large proportion of aldehyde, and in fact very little of the true ether. The action in this case is as follows, $2\,(C_4H_6O_2) + NO_5 = C_4H_3O$, HO (aldehyde), $+ 3HO + (C_4H_5O + NO_3)$. The pure hyponitrous ether, prepared by Liebig's process, given above, is a pale yellow liquid, boiling at 62°, of sp. gr. 0·947. It has a very agreeable odour of rennet-apples. With an alcoholic solution of potash, it yields alcohol, and pure hyponitrite of potash. The *sweet spirit of nitre* or *spiritus ætheris nitrosi* of the pharmacopœia, is a solution of the impure hyponitrous ether in alcohol.

12. Carbonate of Oxide of Ethyle. AeO,CO_2.

Syn. *Carbonic ether.* When oxalic ether is acted on by potassium, there are formed several products, one of which is this ether. When pure, it is an aromatic liquid, of sp. gr. 0·975, boiling at 260°. An alcoholic solution of potash converts it into alcohol and carbonate of potash. Chlorine acts on it, forming products to be described when we treat of the action of chlorine on ethers generally.

13. *Double carbonate of ethyle and potassa*, $KO,CO_2 + AeO,CO_2$, is formed when dry carbonic acid gas is passed through an alcoholic solution of fused potash. A saline mass is obtained, from which, after washing with ether, alcohol dissolves the double salt, leaving carbonate and bicarbonate of potash. The double salt forms pearly scales, which are decomposed by water into alcohol and bicarbonate of potash.

14. *Oxalate of oxide of ethyle.* AeO,C_2O_3.—Syn. Oxalic Ether.—This ether is formed by distilling 4 parts of superoxalate of potash, 5 of oil of vitriol and 4 of alcohol at 90 p. c., mixing the product with 4 times its bulk of water, and washing with water the ether which separates, until all free acid is removed. The ether is then rectified. It is a colourless liquid, of sp. gr. 1·093, boiling at 364°. It has an aromatic smell. If pure, it may be kept under water: but if a trace of alcohol or of oxalic acid be present, it is soon resolved into oxalic acid and alcohol when in contact with water. Fixed alkalies cause the same change. When an excess of ammonia is added to it, oxamide is formed: where the ether is in excess, there is formed a substance in beautiful pearly tables, formerly called oxamethane, but now proved to be oxamate of ethyle. These two reactions are easily explained. In the first case, $AeO,C_2O_3 + NH_3 = (AeO,HO)$

$= (C_2O_2,NH_2)$. In the second, half the ether undergoes the above change, and the other half combines with the oxamide formed. $AeO,C_2O_3 + C_2O_2,NH_2 = AeO,C_4NH_2O_5$. Chlorine acts on oxalic ether, giving rise to products which will be hereafter described along with the results of the action of chlorine on other ethers.

When to an alcoholic solution of oxalic ether there is added enough of an alcoholic solution of potassa or soda to decompose the half of the ether, double salts are obtained, of the formula $MO,C_2O_3 + AeO,C_2O_3$. When the alcoholic solution of the double oxalate of ethyle and potash is treated by fluosilicic acid, there is obtained the *acid oxalate of ethyle*, $HO,C_2O_3 + AeO,C_2O_3$, which is often called *oxalovinic acid*. The salt of potash, $KO,C_2O_3 + (AeO,C_2O_3)$ (*oxalovinate of potash*) forms crystalline scales; soluble in alcohol. The *oxalovinate of baryta* is extremely soluble, and may be used to furnish the other oxalovinates, by acting with it on the soluble sulphates of different bases.

15. *Oxamate of oxide of ethyle*, $C_8NH_7O = AeO,C_4NH_2O_5 = AeO,C_2O_3 + Ad,C_2O_2$, is formed, as above stated, when ammonia is cautiously added to an alcoholic solution of oxalic ether, until a white powder (oxamide) begins to appear. The liquid now yields fine pearly tabular crystals, formerly called oxamethane. It now appears to be oxamate of ethyle, but may also be viewed as oxalate of ethyle, *plus* oxamide. By an excess of ammonia, it is converted into alcohol and oxamide. The action of ammonia on oxalic ether has been explained above.

16. *Sulphocarbonate of ethyle and water.* $AeO,HO,2CS_2$.—When bisulphuret of carbon is added to a strong alcoholic solution of potash a salt is obtained, in colourless or yellow needles, which is a double sulphocarbonate of ethyle and potash, $KO,CS_2 + AeO,CS_2$. When this salt is acted on by diluted sulphuric or hydrochloric acid, there is obtained a heavy oily liquid. This is the acid compound in question, $HO,CS_2 + AeO,CS_2$, formerly called xanthic acid, from the yellow colour of its salts. With bases it gives rise to double salts, like that of potash just mentioned; which were called xanthates. The salt of protoxide (suboxide) of copper is lemon yellow.

17. *Bicyanurate of oxide of ethyle*, $(Cy_3O_3,3AeO + Cy_3O_3,3HO) + 3$ aq.: is formed when the vapours of hydrated cyanic acid are brought in contact with a mixture of ether and alcohol. It appears in the form of prismatic brilliant crystals, easily purified from cyamelide by boiling alcohol or even water, which dissolve it and deposit it on cooling.

18. *Benzoate of oxide of ethyle*, or *benzoic ether*, AeO,BzO, is best formed by distilling 4 parts of alcohol, 2 of benzoic acid, and 1 of strong hydrochloric acid. The ether distils over with alcohol, from which water separates it. When pure, it is an oily, colourless liquid, of a faint agreeable aromatic odour, and an acrid, spicy taste. Its sp. gr. is 1·054, and it boils at about 410°. Chlorine decomposes it, giving rise to several products, probably by substitution.

19. *Hippurate of oxide of ethyle*, or *hippuric ether*, $C_4H_5,O + C_{18}NH_8O_5$, is formed by passing a current of hydrochloric acid gas through a solution of hippuric acid in alcohol, and heating the mixture for some time near to its boiling point. The addition of water separates a thick, heavy oil, which when purified from alcohol and hydrochloric acid, and placed in vacuo, along with sulphuric acid, forms a solid crystalline mass, composed of silky needles. It is decomposed, like other ethers, by alkalies, and by boiling with water.

20. *Salicylate of oxide of ethyle*, $C_4H_5,O + C_{14}H_5O_5$, is obtained by distilling

2 parts of alcohol, $1\frac{1}{2}$ of salicylic acid, and 1 of sulphuric acid. When purified from alcohol, acid, and water, it is a colourless oily fluid, having a sweet smell like that of the corresponding compound of methyle, which occurs naturally in the oil of *Gaultheria procumbens*. It is heavier than water, and boils at 437°. Like the oil of Gaultheria, it plays the part of an acid, forming with bases crystallized soluble salts. When exposed to a high temperature with caustic baryta, it yields carbonic acid, and an oil analogous to that obtained from the methyle compound, probably $C_{18}H_{20}O_2$. When fuming nitric acid is added drop by drop to the salicylic ether, it dissolves it with a deep red colour: water now separates an oil, which soon concretes into a solid mass, which when dissolved in hot alcohol, yields on cooling, yellow silky needles. These are *indigotate or anilate of oxide of ethyle*, $C_4H_5,O + C_{14}NH_4O_9$. By the further action of nitric acid, carbazotic or nitropicric acid is obtained. The indigotic ether dissolves in potash and soda, apparently like the salicylic ether, playing the part of an acid. Indigotic ether does not dissolve in ammonia: left in contact within close vessels, it finally disappears: alcohol is reproduced, and there is formed a new product, *anilamide*, $C_{14}N_2H_6O_8$, which, when pure, forms brilliant yellow crystals. When boiled with potash, anilamide yields anilate (indigotate) of potash, and gives off ammonia; for, $C_{14}N_2H_6O_8 + 2HO = NH_3 + C_{14}H_4NO_9,HO$. Bromine acts on salicylic ether, producing two compounds: monobromuretted salicylic ether, $C_{18}H_9BrO_6 = C_4 \left\{ \begin{matrix} H_4 \\ Br \end{matrix} \right. O + C_{14}H_5O_5$: and bibromuretted salicylic ether, $C_{18}H_8Br_2O_6 = C_4 \left\{ \begin{matrix} H_3 \\ Br_2 \end{matrix} \right. O + C_{14}H_5O_5$. The former crystallizes in fine needles: the latter in large pearly scales, which, when melted, form on cooling a most beautiful crystallization, formed of large and perfect cubes, like those of bismuth.

COMPOUNDS OF ETHYLE OF UNCERTAIN CONSTITUTION.

1. *Chloro-carbonic ether*, $C_6H_5ClO_4 = C_4H_5,O + C_2 \left\{ \begin{matrix} O_3 \\ Cl \end{matrix} \right.$? Formed when absolute alcohol is placed in contact with chloro-carbonic acid gas. It appears as an oily liquid, of sp. gr. 1·133, boiling at 200°. It is formed as follows: 2 eq. of chloro-carbonic acid and 1 of alcohol, losing 1 eq. hydrochloric acid, yield 1 eq. of the new ether. $C_2O_2Cl_2 + C_4H_6O_2 = HCl + C_6H_5ClO_4$. It may be viewed as a compound of oxide of ethyle, with a peculiar acid $C_2 \left\{ \begin{matrix} O_3 \\ Cl \end{matrix} \right.$; or as carbonic ether $C_5H_5O_3$, *plus* 1 eq. chloro-carbonic acid, $C \left\{ \begin{matrix} O \\ Cl \end{matrix} \right.$.

2. *Urethane*, $C_6H_7NO_4$, is formed by the action of ammonia on the preceding compound, along with sal ammoniac, from which it is separated by being sublimed, or rather distilled, when it passes over at a gentle heat, as a liquid which crystallizes on cooling. It is very soluble in water and alcohol, and yields very large crystals. It may be viewed as chlorocarbonic ether, in which amide, NH_2 has been substituted for the chlorine: $C_4H_5,O + C_2 \left\{ \begin{matrix} O_3 \\ NH_2 \end{matrix} \right.$. It is formed as follows: $C_6H_5ClO_4 + 2NH_3 = (NH_3,HCl) + C_6H_7NO_4$. It may also be viewed as formed of 2 eq. carbonic ether and 1 eq. urea: for $2(C_5H_5O_3) + (C_2N_2H_4O_2) = 2(C_6H_7NO_4)$. Finally, it has the composition of dry lactate of

ammonia, $NH_3 + C_6H_4O_4$, or rather a compound of ammonia with sublimed lactic acid.

METAMORPHOSES OF THE COMPOUNDS OF ETHYLE.

When ether or alcohol is passed in vapour through a red hot tube, it yields aldehyde, water, olefiant gas, and marsh gas, $3(C_4H_5O) = C_4H_4O_2 + HO + 3C_2H_2 + C_2H_4$: or $2(C_4H_5O) = C_4H_4O_2 + C_2H_2 + C_2H_4$. By the action of chloride of zinc on alcohol, there are formed water, and two liquid carbo-hydrogens, C_8H_7 and C_8H_9, together $C_{16}H_{15}$, that is, olefiant gas, or an isomeric modification of it. Now ether and alcohol both contain the elements of water and of olefiant gas; for alcohol is $C_4H_6O_2 = 2HO + C_4H_4$; and ether is $C_4H_5O = HO + C_4H_4$.

In the manufacture of ether there occur two liquids, one of which is called *oil of wine*, which is $C_{16}H_{15}$, or very nearly the proportions of olefiant gas, according to the only analysis we have. The other is called the sweet or heavy oil of wine, and is a compound of sulphuric acid with ether, and a body having the same composition in 100 parts as olefiant gas. Sweet oil of wine is $2SO_3 + AeO + C_4H_4$; and as this body, C_4H_4, is called etherole, the compound is named the double sulphate of oxide of ethyle and of etherole. This latter is produced, along with sulphovinic acid, from the reaction of 4 eq. dry sulphuric acid and 3 eq. ether, $4SO_3 + 3AeO = (2SO_3,AeO,HO) + (2SO_3,AeO,C_4H_4)$. The same compound is formed when sulphovinate of lime is heated, but is accompanied by alcohol, sulphurous acid, olefiant gas, and a residue of sulphate of lime and charcoal, $2(CaO,AeO,2SO_3) = (2SO_3,AeO,C_4H_4) + HO + 2(CaO,SO_3)$; and again, $2(CaO,AeO,2SO_3) = 2(CaO,SO_3) + 2SO_2 + C_4H_6O_2 + C_2H_2 + C_2 + 2HO$.

The sweet oil of wine is an oily liquid, quite neutral. It boils at 536°, and has the sp. gr. 1·133. When heated with water it gives off etherole as an insoluble oil, while the liquid contains pure sulphovinic acid. When the etherole thus separated is exposed to cold, it deposits crystals of *etherine*, a compound isomeric with etherole and with olefiant gas.

ETHIONIC, ISETHIONIC, METHIONIC AND ALTHIONIC ACIDS.

These acids are formed by the action of sulphuric acid on ether and alcohol under various circumstances. When anhydrous acid, SO_3 acts on alcohol, or when olefiant gas is absorbed by that dry acid, there is formed a compound, $2SO_3 + C_4H_4$, in crystals, which, when put into cold water, produce ethionic acid, $2SO_3,C_4H_5O$. When this solution is heated, 2 eq. of sulphuric acid and 1 of alcohol separate from one half, and there is formed from the other half isethionic acid, $2SO_3,C_4H_5O$, or rather $S_2O_5,C_4H_5O_2$. Ethionate of baryta, formed by adding baryta to the acid before boiling, is $2SO_3,C_4H_5O,BaO$. From it all the other ethionates may be made. The salts of isethionic acid, like those of ethionic acid, have the same composition in 100 parts as the sulphovinates; but as they contain hyposulphuric acid, their formula is $S_2O_5,C_4H_5O_2 + MO$. They crystallize with remarkable facility. When, in acting on ether with anhydrous sulphuric acid, the mixture gets too hot, there is formed a new acid, *methionic acid*, the baryta salt of which is $S_2C_2H_3O_7,BaO$, or $S_2O_5,C_2H_3O_2 + BaO$. This acid apparently bears the same relation to oxide of methyle, C_2H_3O, as isethionic does to ether, C_4H_5O. When oil of vitriol in great excess, is heated with alcohol,

olefiant gas is given off, and the residue is found to contain an acid, the salts of which have the very same composition as the sulphovinates, but differ in crystalline form. This acid is called *althionic acid*. It is highly probable that the althionates are mixtures or compounds of sulphovinates with isethionates, just as the salts of ethionic acid appear to contain sulphovinates and isethionates or compounds isomeric with these. The two compounds which seem to be distinct and independent are sulphovinic acid, ($AeO,HO,2SO_3$) and isethionic acid, isomeric with it, but probably arranged as (HO,AeO_2,S_2O_4); the salts of the former being strictly double sulphates of ethyle and bases, ($MO,SO_3 + AeO,SO_3$); and those of the latter being $MO + (AeO_2,S_2O_5)$. Whatever explanation may be given of the fact, it is a fact, that the ethionic and althionic acids and their salts have the same empirical composition as these two acids and their salts, at least according to the best analyses we have.

PRODUCTS OF THE OXIDATION OF ETHYLE AND ITS DERIVATIVES.

The oxidation of alcohol and of ether may be effected in a great variety of ways, and the products are rather numerous, varying according to the amount of oxygen taken up. Thus we have, first aldehyde, then acetic acid, formic acid, oxalic acid, and finally carbonic acid and water. The first effect of oxidation is to destroy the radical ethyle, giving rise to a new and less complex radical, *acetyle* $= C_4H_3$. Afterwards we obtain compounds of the still less complex radical, *formyle*, $= C_2H_3$, and lastly, compounds of the simple radicals carbon and hydrogen.

We shall here consider, first, the radical acetyle and its compounds: bearing in mind that while derived from the basic radical ethyle, acetyle has no basic characters whatever, but is, on the contrary, a most distinctly acidifiable radical.

TABLE OF PRODUCTS.

Acetyle	$C_4H_3 = Ac$
Hydrated Oxide of Acetyle (Aldehyde) .	$(C_4H_3)O, + HO$
Acetal	$C_4H_3,O + C_4H_5O + HO$
Acetylous Acid	$(C_4H_3)O_2,HO$
Acetic Acid	$C_4H_3,O_3 + HO$

XVII. Acetyle. $C_4H_3 = Ac$.

Acetyle is unknown in a separate form, but is easily obtained in the form of a hydrated protoxide, or *aldehyde*, and hydrated peroxide, or *acetic acid*.

1. Hydrated Oxide of Acetyle, or Aldehyde. $(C_4H_3)O, HO. = AcO, HO$.

Aldehyde is formed when ether or alcohol is passed through a red-hot tube, or when ether or alcohol are oxidized by nitric acid, or by chlorine, &c. In these cases it is not pure; but it may be obtained quite pure by distilling 2 parts of the compound of aldehyde and ammonia dissolved in 2 parts of water, along with a mixture of 3 parts of oil of vitriol and 4 of water, and rectifying at a temperature of about 80°, over chloride of calcium.

It is a clear, colourless liquid, of a peculiar and powerful etherial odour, of sp. gr. 0·79 at 65°, and boiling at 70°. It mixes in all proportions with water, alcohol, and ether, and is neutral and inflammable. In contact with the atmosphere it rapidly absorbs oxygen, passing into hydrated acetic acid: for C_4H_3,O

+ HO, with O_2, at once produce $C_2H_3,O_3 + HO$; or $AcO,HO + O_2 = AcO_3$, HO.

When heated with caustic potash it is rapidly converted into the brown matter called resin of aldehyde. If gently heated with oxide of silver and water, part of the oxide is reduced without effervescence, coating the glass tube with a bright surface of silver, while the water is found to contain a salt of silver, the acid of which contains less oxygen than acetic acid: this is aldehydic or lampic acid, $C_4H_3O_2,HO$, or AcO_2,HO. The solution of aldehydate of silver, if filtered and heated to boiling, again deposits metallic silver, while the aldehydic acid becomes acetic.

When long kept, even in sealed tubes, aldehyde is transformed into two isomeric modifications, namely, *metaldehyde*, a hard crystalline, inodorous solid; and *elaldehyde*, which is liquid.

Aldehydite of ammonia. $C_4H_3,O + NH_3 + HO$. Aldehyde has no basic characters, and rather exhibits a tendency to the acid character, in combining with ammonia, as it does directly, to form a crystallized compound. To prepare it, as the substance from which aldehyde is obtained, 6 parts of oil of vitriol, 4 of water, 4 of alcohol, and 6 of peroxide of manganese, in fine powder, are distilled together. The crude product is twice rectified over chloride of calcium; it is now aldehyde, containing a little water, alcohol, and acetic and formic ethers; and this liquid, when mixed with ether, and saturated with ammoniacal gas, yields crystals of the new compound, which are washed with ether. These crystals become brown on being kept, even in close vessels, and acquire the smell of burnt feathers. They dissolve in water and alcohol, but hardly in ether. Nitrate of silver forms, in the concentrated solution, a precipitate, insoluble in alcohol, which, when heated, is reduced.

2. Acetal. $C_8H_9O_3 = C_4H_3,O + C_4H_5,O + HO = AcO + AcO + HO$.

It is formed by the action of the oxygen of the air on the vapours of alcohol, under the influence of the black powder of platinum. It is a colourless very mobile liquid, sp. gr. 0·825, boiling at 203°. It might, according to its composition, be a compound of 3 eq. oxide of ethyle, and 1 eq. acetic acid; for $3(C_4H_5,O) + C_4H_3O_3 = C_{16}H_{18}O_6 = 2(C_8H_9O_3)$. But the action of potash, which forms resin of aldehyde, and of oil of vitriol, which blackens and thickens it as it does aldehyde, indicate pretty certainly the presence of aldehyde; and we therefore prefer the formula above given, which makes acetal a compound of aldehyde and oxide of ethyle.

The resin of aldehyde, formed by the action of potash on aldehyde is little known. *Elaldehyde*, an isomeric form of aldehyde, which is liquid at ordinary temperatures, but solid at 32°, has a formula exactly triple that of aldehyde, $C_{12}H_{12}O_6$. *Metaldehyde*, the other isomeric modification, which, like the preceding, spontaneously forms in aldehyde, when kept, has no doubt a similar relation in its formula to that of aldehyde; but its precise formula is not yet known. The density of its vapour would settle the point. It forms very hard prisms, which sublime at 248° without melting. It is worthy of notice that aldehyde, like the corresponding chlorine compound, formed by substitution, *chloral*, $C_4Cl_3O + HO$, undergoes very easily, and even spontaneously, these very singular metamorphoses. This indicates a relation in the constitution of these bodies, which cannot be overlooked.

3. Acetylous Acid. $(C_4H_3)O_2,HO = AcO_2,HO$.

Syn. *Aldehydic acid. Lampic acid.* It has already been stated that this acid is obtained in combination with oxide of silver, when aldehyde is gently heated with excess of that oxide in water. The solution, when the silver has been separated by sulphuretted hydrogen, contains the acetylous acid very diluted. It is very easily decomposed, especially by heat, into acetic acid and a brown resin, like that of aldehyde. When the acetylite or aldehydate of silver is decomposed by baryta, so as to precipitate all the oxide of silver, and the acetylite of baryta is now heated with the precipitated oxide of silver, the metal is reduced, and *acetate* of baryta is now found in the solution. This demonstrates the relation of acetylous to acetic acid; for $BaO,AcO_2 + AgO = BaO,AcO_3 + Ag$. This acid is one chief ingredient of the acid produced by the slow combustion of ether in the lamp with a spiral of platinum wire on the wick, the platinum continuing red-hot, but no flame appearing, and which acid is called lampic acid.

Aldehyde is a constant ingredient of the nitrous ether of the pharmacopœias.

4. Acetic Acid. $C_4H_3,O_3 + HO = AcO_3,HO$.

Syn. *Acetylic acid.—Pyroligneous acid.—Vinegar.*—This important acid is formed in two principal ways: first, by the oxidation of alcohol: and, secondly, by the destructive distillation of wood. Wine, beer, and other fermented liquors, if exposed to the air, under certain circumstances, undergo what is erroneously termed the acetous fermentation; that is, they attract oxygen from the air, undergo eremacausis of the alcohol they contain, and, after a time, contain no alcohol, but in its place acetic acid; they are, in fact, converted into vinegar. The ultimate change is very simple: $C_4H_6O_2 + O_4 = C_4H_3O_3,3HO, = AcO_3,HO + 2$ aq. But we have already seen that there are intermediate steps in the process. The first effect of the oxygen is to remove from the alcohol, or rather from the ethyle in it, 2 eq. of hydrogen, thus leaving the radical acetyle, C_4H_3, in the place of the ethyle $(C_4H_5)O,HO + O_2 = (C_4H_3)O,HO + 2$ aq. In this stage, alcohol is simply converted into aldehyde, while 2 eq. of water are formed. In the next stage, the hydrated protoxide of acetyle (the aldehyde), or rather the radical C_4H_3, takes up two additional equivalents of water, and thereby becomes acetic or acetylic acid $(C_4H_3)O,HO + O_2 = (C_4H_3)O_3,HO$.

Such being the action of the oxygen of the air on alcohol, it is obvious that the process of acetification is no fermentation, but a case of eremacausis or slow combustion. But, as was formerly explained, the state of eremacausis is induced by contact of a body in that state or even in the state of fermentation or putrefaction, and the presence of a ferment is required to commence the process of eremacausis of alcohol. Pure alcohol, exposed to air alone, is not acetified: but if its vapour, mixed with air, come in contact with platinum powder, eremacausis is induced. Hence, if alcohol be placed in a flat basin under a bell jar, beside a small flat dish containing platinum black, the bell jar is, in a few seconds, filled with the pungent smell of aldehyde; and in an hour or two, the acetification is nearly complete. Here the platinum, by virtue of its singular power of causing gases or vapours to unite on its surface, acts as a ferment, or, as it may be called, an excitant, inducing the slow combustion, and acting as a carrier of oxygen from the air to the alcohol.

In wine or beer, there is present an actual ferment in the shape of gluten or fibrin, at least in all cases where the vinous fermentation has not decomposed

the whole of the ferment. In these cases, exposure to the air for a short time causes the decomposition of the gluten, &c. to recommence; and this state of decomposition, being mechanically communicated in the shape of motion to the particles of alcohol, slow combustion commences, and continues till every trace of alcohol has been acetified, when the process is arrested for want of fuel, that is, of alcohol. Where, in the fermentation of wine (as sherry), or of beer (as Bavarian beer), all ferment has been destroyed or removed, these liquors do not become sour when exposed to air: and if we wish to acetify them, we must add yeast or some other ferment. So, also, when we wish to make strong vinegar by the acetification of brandy or of whiskey, we have to add a ferment, such as yeast, and expose the mixture to a certain temperature in open vats. By carefully attending to all these principles, the process of acetification may be very much abridged. The following is the rapid process now followed on the Continent. There is made a mixture of 1 part of alcohol at 80 p. c., 4 to 6 parts of water, and $\frac{1}{1000}$ of a ferment such as vinegar, honey, or must of beer. A large, high barrel is packed with twigs or shavings of beech, previously soaked in strong vinegar; and holes are drilled in the middle and upper part of the barrel to admit a free circulation of air. The mixture is now warmed to from 75° to 80°, and made to trickle slowly upon the shavings and through the barrel, thus exposing an immense surface to the air. The temperature rises rapidly to 95° or 105°, and if a proper supply of air be given, continues at that point during the operation. When the mixture has been three or four times passed through the barrel, it is found perfectly acetified: this may take place in from 24 to 36 hours. Should the supply of fresh air, that is, of oxygen, be deficient, much aldehyde is produced, which, from its volatility, is carried off as vapour and lost. This was long a source of great loss to the makers, and the cause could not be traced, until Liebig, by the discovery of aldehyde, explained it, and showed how to avoid the loss, by giving a due supply of air. The manufacturer now obtains, as nearly as can be expected, the theoretical quantity of vinegar from his spirits. Any aromatic substance, or essential oil, or even a trace of wood vinegar (contaminated with kreosote, &c.) will arrest the progress of acetification.

The peculiar pleasant smell of good vinegar, in addition to that of pure diluted acetic acid, is owing to the presence of acetic ether. Distilled vinegar is a tolerably pure but weak acetic acid; but to obtain acetic acid pure and strong, we must have recourse to the salts of acetic acid, which, when distilled with moderately strong sulphuric acid, yield pure acetic acid, mixed with more or less water.

The pyroligneous acid is contaminated with pyroxylic spirit and with oil of tar. When combined with soda, lime, or oxide of lead, these salts may be easily purified by crystallization, and by heating them so far as to expel or destroy the oily impurities. The pure salts, distilled with sulphuric acid, yield acetic acid, identical with that from true vinegar.

Hydrated acetic acid, *radical vinegar*, or *crystallizable acetic acid*, AcO_3,HO, is obtained by distilling 3 parts of dry powdered acetate of soda with 9·7 of oil of vitriol, as pure and concentrated as possible: $\frac{1}{8}$ of the acid distils over by the heat spontaneously developed in the mixture; a gentle heat expels the rest. The product is rectified and exposed to a cold of 23° or 24°, when crystals of the hydrate are formed in a weaker liquid. The crystals are allowed to drain, and then melted, and again exposed to cold. The crystals of this second operation are generally free from all superfluous water. At temperatures below 60°, hy-

drated acetic acid is solid, at 62° or 63° it melts, forming a liquid which sometimes continues liquid at a much lower temperature, and then crystallizes from some very trifling cause. The sp. gr. of the liquid is 1·063; it boils at 248°; has a pungent, peculiar, but agreeable smell, and a burning acid taste. It raises a blister on the skin, and soon produces a painful sore, like a mineral acid. It is miscible in all proportions with water, alcohol, and ether. It dissolves camphor and essential oils, and the aromatic vinegar is a solution of camphor with a little oil of lemons and bergamot, &c. Strong acetic acid, in this form, is used as a diffusible stimulant, applied to the nostril in faintness or sickness. It may be used, also, externally as a very powerful rubefacient and epispastic. The hydrated acid is combustible. It is decomposed by anhydrous sulphuric acid, yielding a new acid, *sulphacetic acid*: also by chlorine, yielding by substitution *chloracetic acid*. The vapour of acetic acid, passed through a red-hot tube, yields carbonic acid and acetone, C_3H_3O: the same transformation occurs when acetic acid is heated with bases.

The salts of acetic acid are, almost without exception, soluble in water: the acetates of silver and protoxide of mercury are sparingly soluble. The formula for the neutral acetate is $MO,C_4H_3O_3$ or $M,C_4H_3O_4$. There are hardly any acid salts; but a considerable number of basic salts, as basic acetates of lead and copper.

Acetate of oxide of ethyle or *acetic ether*, AeO,AcO_3, is easily prepared by distilling 10 parts of acetate of soda, 16 of oil of vitriol, and 6 of alcohol. The product is rectified over lime and chloride of calcium. It may also be obtained by distilling any sulphovinate with strong acetic acid. In either case, acetic acid is brought in contact with nascent ether, and combines with it. Acetic ether is a colourless liquid of a refreshing odour, very combustible. It boils at 165°; its sp. gr. is 0·89. It is easily decomposed by alkalies, yielding an acetate and alcohol. Acids also decompose it. It is always present, in small quantity, in wine vinegar, which owes its flavour to this compound.

Acetate of ammonia. There is a well-known febrifuge and diaphoretic remedy called the *spirit of Mindererus*, which is a diluted solution of acetate of ammonia, formed by neutralizing distilled wine vinegar with carbonate of ammonia. A more uniform preparation, although stronger than that usually employed here, is made by neutralizing 6 parts of aqua ammoniæ, sp. gr. 0·96, with strong acetic acid, and adding enough water to make up 24 parts. This, being uniform, can easily be reduced if desirable. There is an acid acetate of ammonia, which forms deliquescent needles. *Acetate of potash*, KO,AcO_3, is obtained as a fibrous crystalline mass, very deliquescent, which has a warm saline taste. It is much used as a diuretic. When heated with arsenious acid, it yields oxide of cacodyle; a substance of most remarkable composition and characters, $C_4H_6As_2,O$. *Acetate of soda* NaO,AcO_3+6 aq. is formed from pyroligneous acid, and is the form in which the acid is brought in order to be purified from oil of tar. The salt is melted at a moderate heat, and roasted, then redissolved, filtered through charcoal, evaporated, again melted, and so on, until it becomes snow-white. 10 parts of the crystals of the salt after the first fusion, while still slightly coloured, being distilled with 6 of oil of vitriol, yield what is called wood vinegar, sufficiently pure for use, but requiring 7 waters to reduce it to the average strength of wine vinegar. Acetates of baryta, strontia and lime all crystallize readily. The first is used as a test; the last in the manufacture of acetic acid and all other acetates from pyroligneous acid. *Acetate of alumina*, $Al_2O_3,3AcO_3$, prepared by

mixing solutions of alum and acetate of lead (or of baryta) is very soluble. It is much used in the above form, containing sulphate of potash, as a most valuable mordant in dyeing and calico printing. When heated it deposits an insoluble basic salt, which adheres tenaciously to the cloth, and afterwards combines firmly with the colouring matter. The pure acetate of alumina, formed from sulphate of alumina and acetate of baryta, is not so decomposed by heat, but requires the presence of a neutral salt. *Acetate of manganese*, MnO,AcO_3, formed by acting on sulphate of manganese by acetate of lime, is much used in calico printing, as it gives with bleaching liquor a rich bronze brown. *Acetate of zinc*, $ZnO,AcO_3,+3$ aq. is used in medicine and pharmacy. *Acetate of protoxide of iron*, FeO,AcO_3, is used as a mordant. *Acetate of peroxide of iron*, $Fe_2O_3,3AcO_3$, is formed by precipitating acetate of lead with persulphate of iron. It has the same valuable properties as acetate of alumina, depositing a basic salt, when heated with neutral salts, and is much prized as a mordant. *Acetate of lead;* a. *neutral*, Syn. *Sugar of lead;* is best prepared by dissolving litharge in acetic acid, and crystallizing. It has a sweet astringent taste, and is much used as an astringent and styptic in diarrhœa, dysentery, and various hæmorrhages. It is poisonous, especially where it forms carbonate: it ought therefore never to be given without abundance of vinegar being taken by the patient. The crystals are PbO,AcO_3+3 aq. b. *sesquibasic*, $3PbO+2AcC_3$ soluble pearly scales. c. *tribasic* or *subacetate of lead* is formed in crystals by mixing 1 vol. of aqua ammoniæ with 5 of a cold saturated solution of the neutral salt, and setting it aside. It forms long needles. The solution, or Goulard's extract, is made by digesting 7 parts of litharge with 6 of sugar of lead and 30 of water, till the oxide, which is not dissolved, has become white. It is much used as a lotion, and to precipitate gum, organic acids, albumen, caseine, extractive matter, &c. from organic mixtures and solutions. Its formula is $3PbO + AcO_3$. d. *sexbasic*, formed by adding the last or any of the previous acetates of lead to an excess of ammonia. It forms a crystalline powder very sparingly soluble, which is $6PbO+AcO_3$. It usually exists in white lead, along with carbonate of lead.

Acetate of copper. a. *neutral;* appears in two forms: as dark green oblique rhombic prisms, becoming opaque in air: $CuO,AcO_3=5$ aq: and as dark blue transparent crystals of great beauty, $CuO,AcO_3 + 5$ aq. These latter, heated to 86°, lose 4 eq. of water, and fall to a powder of the green salt. b. *bibasic* or *verdigris*, $2CuO+AcO_3+6$ aq.$=CuO,AcO_3$, 5 aq.$+CuO,HO$. Verdigris is prepared by a tedious process, and is seldom pure, containing usually different basic acetates. c. *sesquibasic*, $3CuO,2AcO_3+6$ aq. d. *tribasic*, $6CuO,2AcO_3 +$ 3 aq. The two last occur in the verdigris of commerce. All these salts are poisonous.

Schweinfurt or Vienna green is a double salt, formed of acetate and arsenite of copper; $CuO,AcO_3+3(As_2O_3,CuO)$ is formed when 10 parts of verdigris, suspended in water, are left to digest for 24 hours, after mixing them with a hot solution of 8 parts of arsenious acid in 100 of water. A dirty green precipitate first appears, which on standing changes to a most beautiful green, much used as a paint.

Acetate of protoxide of mercury is obtained in sparingly soluble silvery scales by adding acetate of potash to protonitrate of mercury, both hot. It blackens when exposed to light. It is used in medicine, especially on the Continent.

Acetate of silver, AgO,AcO_3, very much resembles the preceding salt. It is occasionally used as a test. It is very sparingly soluble.

ACTION OF CHLORINE, BROMINE, ETC., ON ETHYLE, ACETYLE, AND THEIR DERIVATIVES.

1. Oxide of Ethyle and Chlorine.

When dry chlorine is made to act on ether, with the aid of the sun's rays, there are produced several compounds. The first is a heavy, oily liquid, oxychloride of acetyle, $C_4H_3\left\{\begin{matrix}O\\Cl_2\end{matrix}\right.$; which is dry acetic acid with 2 eq. of oxygen replaced by 2 eq. of chlorine. With water, it forms acetic and hydrochloric acids. When the action is pursued, there is obtained a compound C_4Cl_5O, which is ether, in which all the hydrogen is replaced by chlorine. The first compound may be connected with this one by being viewed as ether in which hydrogen is partially replaced by chlorine, $C_4\left\{\begin{matrix}H_3\\Cl_2\end{matrix}\right.O$. Finally there is obtained a crystallizable solid compound, C_4Cl_6, which may be represented as C_4Cl_5,Cl, showing that the oxygen of ether is also here replaced by chlorine. This last body is chloride of carbon, C_2Cl_3, for $C_4Cl_6=2C_2Cl_3$. Besides these compounds there are others formed at the same time, more difficult to separate, and which are doubtless the intermediate links of the chain of substitutions, beginning with ether, C_4H_5,O, and ending with *chloride of carbon*, C_4Cl_5,Cl. The other members of the series which are more easily obtained by the action of chlorine on *chloride of ethyle*, (see below, p. 625), are C_4H_5,Cl, chloride of ethyle: $C_4\left\{\begin{matrix}H_4\\Cl,\end{matrix}\right.Cl$: $C_4\left\{\begin{matrix}H_3\\Cl_2,\end{matrix}\right.Cl$: $C_4\left\{\begin{matrix}H_2\\Cl_3,\end{matrix}\right.Cl$: $C_4\left\{\begin{matrix}H\\Cl_4,\end{matrix}\right.Cl$; and as the compound C_4Cl_5O is formed, it is probable that there is another series, beginning with ether, and ending with C_4Cl_5,O, in which the oxygen remains unchanged. The above are not all cases of substitution with preservation of the type; for the compound $C_4\left\{\begin{matrix}H_3\\Cl_2,\end{matrix}\right.O$, may very likely be $C_4H_3\left\{\begin{matrix}O\\Cl_2\end{matrix}\right.$ belonging to the type of acetic acid, rather than that of ether. These compounds are as yet but little known: it is obvious that the simultaneous occurrence of so many similar compounds must render the study of them exceedingly complicated and difficult.

The body $C_4H_3\left\{\begin{matrix}O\\Cl_2,\end{matrix}\right.$ or oxychloride of acetyle, when acted on by sulphuretted hydrogen, yields two new compounds, in which its chlorine is partially or entirely replaced by sulphur. Both are crystalline: one, the oxysulphuret of acetyle, $C_4H_3\left\{\begin{matrix}O\\S_2\end{matrix}\right.$ forms large colourless prisms: the other, oxychlorosulphuret of acetyle, $C_4H_3\left\{\begin{matrix}O_5\\Cl,\end{matrix}\right.$ forms yellow tabular crystals.

2. Salts of Oxide of Ethyle with Chlorine.

When chlorine acts on these salts or ethers, their oxide of ethyle is acted on as if separate, but in many cases the acids remain combined with the new chlorinized compounds: or the acids also are acted on, and the products derived from them combine with those derived from the ether.

Acetic ether yields a compound $C_8H_6Cl_2O_4$, which may be viewed as C_4H_3

$\left\{\begin{matrix}O\\Cl_2\end{matrix}\right. + C_4H_3O_3$, that is, acetate of the oxychloride of acetyle. When the compound is further exposed to the action of chlorine at a high temperature, it yields a series of compounds, in which its hydrogen is gradually replaced by chlorine, till the compound $C_8Cl_8O_4$ is left, which is called perchloruretted acetic ether. Acetic ether is $C_8H_8O_4$; and we have the acetate of oxychloride of acetyle $C_8\left\{\begin{matrix}H_6\\Cl_2\end{matrix}\right. O_4$; then $C_8\left\{\begin{matrix}H_5\\Cl_3\end{matrix}\right. O_4$: $C_8\left\{\begin{matrix}H_4\\Cl_4\end{matrix}\right. O_4$: $C_8\left\{\begin{matrix}H_3\\Cl_5\end{matrix}\right. O_4$: $C_8\left\{\begin{matrix}H_2\\Cl_6\end{matrix}\right. O_4$: $C_8\left\{\begin{matrix}H\\Cl_7\end{matrix}\right. O_4$: and $C_8Cl_8O_4$. The two last can be obtained with certainty pure: the others, after $C_8\left\{\begin{matrix}H_6\\Cl_2\end{matrix}\right. O_4$, are so mixed that it is very difficult to obtain them pure enough for analysis.

When *benzoic ether*, AeO,BzO, is acted on by chlorine, it loses 2 eq. hydrogen, and 1 eq. oxygen, and takes up 3 eq. chlorine, producing a compound which may be viewed as containing chloride of benzoyle and oxychloride of acetyle, $BzCl + C_4H_3\left\{\begin{matrix}O\\Cl_2\end{matrix}\right. = C_{18}H_8Cl_3O_3$.

Oxalic ether, exposed to the action of chlorine under the influence of the direct rays of the sun, loses all its hydrogen, which is replaced by chlorine. $(C_4H_5)O,C_2O_3$, thus becomes $(C_4Cl_5)O,C_2O_3$. The latter is called *chloroxalic ether*. It is a crystallizable solid, fusible at 288°. Dry ammonia acts on it as on oxalic ether, producing *chloroxamethane*, a crystalline compound analogous to oxamethane. It was formerly stated that oxamethane, $C_8H_7NO_6$, has the composition of oxamate of oxide of ethyle $(C_4H_5)O + C_4H_2NO_5$; or of oxalic ether *plus* oxamide $(C_4H_5)O,C_2O_3 + NH_2,C_2O_2$. In like manner, chloroxamethane represents chloroxalic ether *plus* oxamide: $(C_4Cl_5)O,C_2O_3 + NH_2,C_2O_2 = C_8H_2Cl_5NO_6$. When chloroxamethane is left in contact with ammonia, it takes up 2 eq. of water, and forms a new salt, chloroxalovinate of ammonia, $C_4Cl_5O,NH_4O,2C_2O_3$, which is deliquescent. From the corresponding salt of soda the chloroxalovinic acid may be obtained, which may of course be viewed as an acid oxalate of the compound C_4Cl_5O. Its formula is $C_4Cl_5O,C_2O_3 + HO,C_2O_3$. By the action of alcohol on chloroxalic ether, there is formed a neutral oil, $C_8Cl_5O_7$, which contains the elements of anhydrous chloroxalovinic acid, C_4Cl_5O, $2C_2O_3$; and when dissolved in potash, yields chloroxalovinate of potash.

Carbonic ether, by the action of chlorine, yields two products: 1st. Bichloruretted carbonic ether, $C_4\left\{\begin{matrix}H_3\\Cl_2\end{matrix}\right. O,CO_2 = C_5H_3Cl_2O_3$; and 2nd. Perchloruretted carbonic ether, $C_4Cl_5O,CO_2 = C_5Cl_5O_3$. The former is an oily liquid; the latter crystallizable.

Chloride of ethyle $(C_4H_5)Cl$, when acted on by chlorine, yields a very remarkable series of products, in which the hydrogen is gradually replaced by chlorine, as mentioned at p. 624, to which I refer for the formulæ. I shall only here mention, that the compound there represented as $C_4\left\{\begin{matrix}H_4\\Cl_2\end{matrix}\right. Cl, = C_4H_4Cl_2$, corresponds to aldehyde, and is, therefore, probably $(C_4H_3)Cl + HCl$, just as aldehyde is $(C_4H_3)O + HO$. In like manner, the compound $C_4\left\{\begin{matrix}H_3\\Cl_2\end{matrix}\right., Cl = C_4H_3Cl_3$, corresponds to dry acetic acid, $C_4H_3O_3$. The action of potash on these

two compounds confirms this view, according to which they are protochloride and perchloride of acetyle.

When *alcohol*, the hydrated oxide of ethyle, is subjected to the long-continued action of chlorine, aided by the sun's rays, there is formed, after a very tedious operation, a remarkable compound called *chloral*, the empirical formula of which is $C_4HCl_3O_2 = C_4Cl_3O + HO$. This compound represents aldehyde or hydrated oxide of acetyle, in which the hydrogen of the acetyle has been replaced by chlorine. It is an oily liquid, boiling at 199°, of sp. gr. 1·502. Like aldehyde, chloral, when kept, is spontaneously converted into an insoluble solid compound which has the same composition as chloral itself. In contact with water, chloral is soon converted into a solid hydrate, which dissolves in a larger quantity of water. It contains 1 eq. chloral and 2 eq. water. When heated with caustic alkalies, chloral produces formiate of the alkali and perchloride of formyle, $C_4HCl_3O_2 + HO,KO = (C_2H)\,O_3,KO + (C_2H)\,Cl_3$. The perchloride of formyle, in contact with the alkali, is partly decomposed, yielding chloride of the metal.

Pure Acetic Acid, when acted on by chlorine and the sun's rays, is converted into a crystallizable acid, the chloracetic acid, $C_4Cl_3O_3,HO$. As acetic acid may be considered to be aldehyde *plus* 2 eq. oxygen, or hydrated peroxide of acetyle, so chloracetic acid is chloral *plus* 2 eq. oxygen, or hydrated peroxide of C_4Cl_3, which may be called *chloracetyle*. Chloracetic acid forms tabular crystals, fusible at 113°, boiling at 390°. The density of the liquefied acid at 113° is 1·617. When heated with excess of potash, it yields first carbonic acid and perchloride of formyle, $C_4Cl_3O_3,HO + 2KO = 2\,(KO,CO_2) + C_2HCl_3$. The perchloride of formyle is partly converted by another portion of potash, into formiate of potash and chloride of potassium, $C_2HCl_3 + 4KO = 3KCl + KO, C_2HO_3$.

With bases, chloracetic acid forms salts which are very analogous to the acetates; and it is very important here to observe, that both in chloral and chloracetic acid, the substitution of chlorine for all the hydrogen of the radical (acetyle) of aldehyde and acetic acid, has not affected the general chemical characters of the compounds; that, in other words, the original type has been retained. We have also seen, in the preceding pages, among the products of the action of chlorine on oxide of ethyle and on the salts of oxide of ethyle, that oxide of ethyle, C_4H_5O, is converted into oxide of chlorethyle, C_4Cl_5O, without the type being altered: the oxide of chlorethyle forming with the acids previously combined with oxide of ethyle, compounds perfectly analogous to the ethers from which they are obtained.

The *sulphuret of ethyle* is readily acted on by chlorine, and yields a yellow oily liquid, of sp. gr. 1·673, boiling at 320°, of a most fetid odour, the formula of which is $C_4\left\{\begin{matrix}H\\Cl_4\end{matrix}\right.S$. Here 4 eq. of hydrogen of the compound, C_4H_5S, are replaced by chlorine.

Heavy muriatic ether is an oily liquid, formed by the action of moist chlorine on alcohol. It is obviously a mixture, and probably contains aldehyde, chloride of ethyle, chloral, and products intermediate between aldehyde and chloral.

Bromal. C_4Br_3O,HO. This compound, analogous to chloral, is formed by the action of bromine on alcohol. It forms a hydrate with 3 eq. water. By caustic alkalies it is resolved into formic acid, which combines with the alkali, and perbromide of formyle.

Iodine does not, so far as is known, produce a compound corresponding to chloral and bromal; but a solution of iodine in alcohol, treated with an alcoholic solution of potash, yields formiate of potash and periodide of formyle, C_2HI_3.

By the action of chlorine on alcohol, holding in solution hydrocyanic acid or a metallic cyanide, there is produced a crystalline compound, the empirical formula of which appears to be $C_{16}H_{14}N_2Cl_2O_8$. This is equal to 3 eq. aldehyde, 2 eq. chloride of cyanogen, and 2 eq. water; but the true nature of this compound is unknown.

3. Compounds derived from Alcohol, but of uncertain constitution.

Olefiant Gas. Syn. *Hyduret of Acetyle.* $C_4H_4 = C_4H_3,Cl = AcH$. This well-known compound is generally present in coal gas, oil gas, and in general, in all gaseous mixtures produced by the action of heat on organic substances. It is best obtained pure by heating 1 part of alcohol with 6 or 7 of oil of vitriol. There is produced some ether, then sweet oil of wine, and lastly, a mixture of sulphurous acid and olefiant gases. By passing the gas through milk of lime, the sulphurous acid is removed, and by then passing it through oil of vitriol, the ether, alcohol, and water which may be present, are likewise separated. Pure olefiant gas has been already described (see p. 261, Part II.); here we shall attend to its combinations. It is absorbed by anhydrous sulphuric acid, forming the crystalline compound formerly mentioned, $2SO_3 + C_4H_4$, which, in contact with water, produces ethionic acid. When mixed with its own volume of chlorine, both gases are condensed into a liquid, the composition of which is $C_4H_4Cl_2$. This is the oily compound, from which the gas was called olefiant gas: the oil is often called the oil of the Dutch chemists; having been discovered by an association of chemists in Holland.

When mixed with 2 vol. of chlorine, and set fire to, the whole of the carbon of the gas is deposited in the solid form or as smoke, while all the hydrogen forms hydrochloric acid, $C_4H_4 + Cl_4 = 4HCl + C_4$.

The oil of olefiant gas, or of the Dutch chemists, C_4H_4,Cl_2, may be viewed as composed of hydrochloric acid, and a chloride of acetyle: $HCl + C_4H_3Cl$. When acted on by an alcohol solution of potassa, chloride of potassium and water are formed, and a new compound separates, which is the *protochloride of acetyle*, C_4H_3Cl. It is gaseous at ordinary temperatures, has an alliaceous smell and burns, like all similar chlorinized compounds, with a dark red flame edged with green. At 0° it condenses into a liquid.

When this protochloride of acetyle is acted on by perchloride of antimony, it yields, among other products, a liquid, boiling at 240°, which is $C_4H_3Cl_3$, and therefore has the same composition as perchloride of acetyle, formerly mentioned. But the action of potash dissolved in alcohol, proves that these two compounds are distinct, and that the one now under consideration is $C_4H_2Cl_2 + HCl$. At all events, it yields chloride of potassium, water, and a very volatile liquid, $C_4H_2Cl_2 = 2(C_2H,Cl)$, or in other words, protochloride of formyle.

By continuing the action of chlorine there is obtained a compound $C_4H_2Cl_4 = C_4HCl_3 + HCl$; which, with potash, yields the body C_4HCl_3; and the final result of this action is the protochloride of carbon, $C_4Cl_4 = 4CCl$; which, however, unites with chlorine to produce the sesquichloride, $C_4Cl_4 + Cl_2 = C_4Cl_6 = 2C_2Cl_3$.

The *perchloride of acetyle* has been already mentioned as a product of the action of chlorine on ether: it is $C_4H_3Cl_3 = AcCl_3$.

The oil of olefiant gas, $C_4H_4Cl_2$, which may be considered the hydrochlorate of chloride of acetyle, $C_4H_3,Cl + HCl$, is best prepared by passing olefiant gas into perchloride of antimony, as long as it is absorbed. The mixture, if distilled, yields the oil in question. It is purified by alternate distillation with water and sulphuric acid, and finally drying it with chloride of calcium. It is a very mobile liquid, of a pleasant etherial smell, and a very sweet taste; it boils at 180°, is insoluble in water, soluble in alcohol and ether.

When subjected to the action of chlorine, it yields hydrochloric acid, and products rich in chlorine. Among these are, the hydrochlorate of chloride of formyle, $C_2HCl + HCl$, which distils at 240°, and the bichloride of formyle, C_2H,Cl_2, which distils at 275°. This last is finally converted into sesquichloride of carbon; for $C_2H,Cl_2 + Cl_2 = C_2Cl_3 + HCl$.

Chloretheral is the name given by D'Arcet to a compound formed by the action of chlorine on olefiant gas, containing both alcohol and ether. Its empirical formula is C_4H_4ClO; so that it may be aldehyde, *plus* oil of olefiant gas; $C_4H_3O,HO + C_4H_3Cl,HCl = 2(C_4H_4ClO)$; or oxychloride of acetyle, *plus* oxide of ethyle: $C_4H_3\left\{\begin{matrix}O\\Cl_2\end{matrix}\right. + C_4H_5O = 2(C_4H_4ClO)$. The true nature of this compound is unknown.

Bromine forms, with olefiant gas, a liquid compound analogous to the oil of olefiant gas. Its formula is $C_4H_3,Br + HBr$. Iodine forms, with olefiant gas, a solid compound, which would appear to be $C_4H_3,H + I_2$ rather than $C_4H_3,I + HI$.

Anhydrous sulphuric acid absorbs olefiant gas, producing a white crystalline solid, $2SO_3 + C_4H_4H_4$; which, when dissolved in water, forms with 1 eq. of water, ethionic acid, $2SO_3 + C_4H_5O = C_4H_5O_2 + S_2O_5$. The original crystalline compound has been called sulphacetylic acid.

4. Action of bichloride of platinum on Alcohol.

This action is very complex, yielding aldehyde, chloride of ethyle, chloride of acetyle, and other volatile compounds, along with a salt, composed of chloride of platinum and chloride of acetyle. It is possible that 3 eq. of oxide of ethyle, with 4 eq. of bichloride of platinum, may yield 1 eq. aldehyde, 1 eq. water, 4 eq. hydrochloric acid, and 2 eq, of the new salt. $3(C_4H_5O) + 4PtCl_2 = CH_3O,HO + HO + 4HCl + 2(C_4H_3Cl + Pt_2Cl)$. Zeise considers the salt to be $C_4H_4 + 2PtCl$, which formula differs from the preceding in containing 1 eq. hydrogen more. Malaguti supposes it to be $C_4H_3O + 2PtCl$; but Zeise has shown that it contains no oxygen. It does not crystallize, but forms a gummy mass, spontaneously decomposing when kept.

When a solution of bichloride of platinum in alcohol is digested with a little hydrochloric acid, and chloride of potassium, the alcohol distilled off, and the residue neutralized by carbonate of potash, a yellow crystallizable salt is obtained, which contains the preceding compound, plus 1 eq. chloride of potassium, $C_4H_3Cl + Pt_2Cl + KCl$. Similar double salts are formed with chloride of sodium and chloride of ammonium.

These double salts form with ammonia a yellow precipitate, which is $C_4H_3Cl,PtCl + NH_3$.

5. Action of heat on acetic acid and the acetates.

Acetone. Syn. *Pyroacetic Spirit. Mesitic Alcohol.* Formula C_3H_3O. Is formed when acetic acid is passed through a tube heated to low redness, along with carbonic acid, carbonic oxide, and carburetted hydrogen: also when the acetate of an alkali or alkaline earth is exposed to heat, when a carbonate is left, and acetone distils over. It is best prepared by distilling a mixture of 2 parts of crystallized acetate of lead, and 1 part quicklime. Its formation is easily explained; for anhydrous acetic acid, $C_4H_3O_3$ contains the elements of 1 eq. carbonic acid, and 1 eq. acetone. $C_4H_3O_3 = CO_2 + C_3H_3O$. Acetone is also formed in the distillation of sugar, of citric acid, of tartaric acid, &c. It is purified by rectification, until its boiling point becomes constant at 100°. It is a clear and colourless liquid, of sp. gr. 0·7921, and has a peculiar smell and a pungent taste. It is miscible with water, alcohol, and ether, in all proportions; and is separated from water by the addition of caustic potassa, chloride of calcium, or other salts insoluble in acetone.

Heated with hydrochlorite of lime, it is converted into carbonic acid and perchloride of formyle. When prepared by the distillation of acetates, acetone is accompanied by an oily liquid $C_{10}H_8O$.

Acetone contains, in 3 eq., the elements of 1 eq. carbonic ether and 1 eq. olefiant gas (hyduret of acetyle). $C_4H_5O,CO_3 + C_4H_3,H = C_9H_9O_3 = 3(C_3H_3O)$; or, in 4 eq.; we have the elements of 1 eq. acetic ether, and 1 eq. hyduret of acetyle: $C_4H_5O,C_4H_3O_3 + C_4H_3,H = C_{12}H_{12}O_4 = 4(C_3H_3O)$. Kane considers acetone to be $C_6H_6O_2 = C_6H_5O,HO$; that is, the hydrated oxide of a radical C_6H_5, which he calls *mesityle*. In this view, acetone is analogous to alcohol, and C_6H_5O, the oxide of mesityle, to ether. But although Kane has obtained this compound C_6H_5O, and also another C_6H_5Cl, his chloride of mesityle, and although he has likewise formed double salts containing sulphuric acid and the elements C_6H_6O, yet the analogy is far from being established. It has not yet been found possible to reproduce acetone, the *alcohol*, from the supposed *ether* of the series, as we can reproduce alcohol from the salts of oxide of ethyle. Moreover, in these double salts, the body C_6H_5O, does not act as a base, but is only coupled with the acid, as naphthaline in sulphonaphthalic acid. We shall not, therefore, enter into minute details of the theoretical views alluded to. It is sufficient to enumerate the supposed radical *mesityle*, C_6H_5: its oxide C_6H_5O, oxide of mesityle; its hydrated oxide, C_6H_5O,HO (acetone); the chloride and iodide of mesityle, C_6H_5Cl and C_6H_5I; the acid sulphate of oxide of mesityle, $C_6H_5O,HO,2SO_3$ (sulphomesitylic acid); the double salts of this sulphate, the formula of which is $C_6H_5O,HO,2MO,2SO_3$; and a compound discovered by Zeise, containing oxide of mesityle with chloride of platinum, $C_6H_5O,PtCl$.

The action of nitric acid on acetone gives rise to a new product: *nitrite of oxide of pteleyle*, C_6H_3O,NO_3; phosphoric acid appears to form a compound acid with acetone; and when phosphorus, iodine, and acetone are distilled together, another acid is obtained, which appears to contain hypophosphorous acid.

When chlorine acts on acetone, it produces a liquid, $C_6H_4Cl_2O_2$, which is called *mesitic chloral.*

Mesitylene, C_6H_4. This compound is obtained when acetone is distilled with fuming sulphuric acid. It is an oily liquid, boiling about 300°. Acetone $2(C_3H_3O) = C_6H_4 + 2HO$; and this explains its production.

When mesitylene is acted on by nitric acid, it yields a liquid $C_6H_4O_2$, called

by Kane mesitic aldehyde. But when chlorine is passed through mesitylene, a crystalline solid is obtained, containing a new radical, pteleyle, combined with chlorine. $C_6H_4 + Cl_2 = C_6H_3Cl + HCl$. The compound C_6H_3Cl, is the chloride of the supposed new radical pteleyle, C_6H_3. Kane has described a compound in yellow scales, which he considers to be iodide of pteleyle. It is very desirable that the whole of the compounds derived from acetone should be again carefully examined, since their true constitution cannot be considered as established.

COMPOUNDS CONTAINING ARSENIC, DERIVED FROM ACETYLE.

When acetate of potash is heated along with arsenious acid, a very remarkable liquid is obtained, which is the oxide of a new radical. This liquid, which is spontaneously inflammable, and has a most offensive alliaceous smell, has been long known in an impure state, under the names of the liquor of Cadet, and *alcarsine*. Bunsen, by a long series of the most profound and persevering researches, established its true character as the oxide of the radical *kakodyle*. He has even succeeded in obtaining the radical itself in the separate state, and in establishing the most perfect analogy between that radical and a metal, in all its chemical relations.

XVIII. KAKODYLE. $C_4H_6As_2 = Kd$.

The radical is best obtained from the chloride of kakodyle, KdCl, by the action of zinc at 212°. Chloride of zinc is formed, and kakodyle is set free. It is rectified in an apparatus filled with carbonic acid gas, to prevent decomposition. It is a clear liquid, refracting light strongly. When cooled, it crystallizes in large square prisms, and acquires, when pure, the appearance of ice. Its smell is insupportably offensive, and its vapour is highly poisonous. The two latter characters belong to all the compounds of kakodyle, with hardly an exception. Kakodyle is spontaneously inflammable in the air: a rod moistened with it instantly takes fire when exposed to the air. It forms two distinct oxides: the protoxide KdO (alkarsine), and kakodyle acid, KdO_8.

TABLE OF COMPOUNDS.

Protoxide of Kakodyle	$C_4H_6As_2,O = KdO$
Kakodylic Acid	$= KdO_3$
Chloride of Kakodyle	KdCl

Protoxide of Kakodyle. $C_4H_6As_2,O = KdO$.

SYN. *Alkarsine.* This is the chief ingredient of the liquor of Cadet; it is purified by repeated rectifications in an atmosphere of carbonic acid, and is, when pure, a limpid etherial liquid, refracting light powerfully; it boils at about 300°, and at —9° it crystallizes in white scales of a satiny lustre. Its smell is most offensive, and its taste very nauseous. If placed on the skin, it causes violent itching, and if taken internally it is a most energetic poison. It is sparingly soluble in water, more soluble in alcohol and ether. Like kakodyle, it takes fire when exposed to the air. When left under water, it gradually disappears, being for the most part converted into kakodylic acid. The production of oxide of kakodyle is very simple: 2 eq. dry acetic acid and 1 eq. arsenious acid yield 4 eq. carbonic acid and 1 eq. oxide of kakodyle. $2(C_4H_3O_3) + As_2O_3 = 4CO_2 + C_4H_6As_2O$.

Kakodylic Acid. $KdO_3 = C_4H_6As_2,O_3$.

Syn. *Alcargene.* Formed by the gradual oxidation of the protoxide, under water. It forms oblique four-sided prisms, brittle, and of a glassy lustre. They have no smell, and are soluble in water and alcohol. Its salts do not crystallize. Many reducing agents convert it into the protoxide by removing 2 eq. of oxygen. It is not in the least poisonous.

There appears to be an intermediate oxide KdO_2; but it has not been obtained in a state of purity.

Chloride of Kakodyle, $KdCl = C_4H_6As_2,Cl_4 = KdCl$, is obtained by heating a compound of oxide of kakodyle and corrosive sublimate along with hydrochloric acid: $KdO,HgCl_2 + HCl + KdCl + HO + HgCl_2$. It is a volatile horribly fetid liquid, the vapour of which attacks strongly the lining membrane of the nose, and provokes a flow of tears. When exposed to the air it deposits crystals of an oxychloride of kakodyle $KdO + 3KdCl$. The iodide, bromide, and fluoride of kakodyle are in all points analogous to the chloride; and form, when exposed to the air, oxyiodide, oxybromide, &c.

Sulphur forms with kakodyle three compounds; the *protosulphuret*, KdS, is obtained by distilling chloride of kakodyle with hydrosulphuret of barium: $KdCl + BaS,HS = KdS + BaCl + HS$. It is a clear, volatile, very fetid liquid, heavier than water. It dissolves sulphur, forming the *bisulphuret* KdS_2, which is a very permanent compound. The *persulphuret*, KdS_3, is a sulphur acid, and forms sulphur salts which are very permanent, with the sulphurets of highly basic metals. The sulphur salt of kakodyle and lead, PbS,KdS_3 crystallizes beautifully.

Cyanide of Kakodyle, $KdCy = C_4H_6As_2,C_2N$, is formed by distilling bicyanide of mercury with water and oxide of kakodyle. When pure it forms large brilliant crystals, very fusible and volatile. The vapour of this compound is so poisonous as to be in the highest degree dangerous to the experimenter.

COMPOUNDS OF KAKODYLE CONTAINING PLATINUM.

Chloride of Kakoplatyle, $C_4H_7As_2PtO_2,Cl$. This compound is formed when an alcoholic solution of bichloride of platinum is added to a similar solution of chloride of kakodyle, when a reddish brown precipitate is formed, which, being boiled with water, gives a solution from which, on cooling, needles of the new compound are deposited. *Bromide of kakoplatyle and iodide of kakoplatyle* may be formed from the chloride, and are analogous to it. The former appears in large yellow crystals, the latter in golden micaceous scales.

When the chloride is acted on by sulphate of silver, there is obtained, along with chloride of silver, the sulphate of the oxide of kakoplatyle, $C_4H_7As_2PtO_3,SO_3$. It forms white crystalline grains.

The radical of these singular compounds, kakoplatyle, may be represented as composed of protoxide of platinum, water, and kakodyle; $PtO,HO,C_4H_6As_2$. We have, therefore, the following series, which, like those derived from the bases containing platinum formerly described, throws much light on the nature of the vegetable bases.

Radical, Kakoplatyle . .	$PtO + Kd = C_{14}H_6As_2PtO$.
Chloride of do., anhydrous . .	$PtO,Kd + Cl$
Chloride, hydrated . .	$PtO,Kd + Cl + HO$
Chloride, ammoniated . .	$PtO,Kd + Cl + NH_3$
Oxide, hydrated . .	$PtO,Kd + O + HO$
Sulphate, hydrated . . .	$(PtO,Kd$ [illegible] $+ SO_3$.

It is to be particularly borne in mind that this radical, whose basic character is quite obvious, contains two metals, arsenic and platinum, quite foreign, in general, to organic compounds.

The existence of kakodyle itself, and the perfect analogy which may be traced between it and the simple metals, in their relations to all other substances, render the results of the researches of Bunsen, which have been so very briefly described in this work, of the very highest importance to the theory of organic compounds, and especially to that of compound radicals.

APPENDIX TO ETHYLE AND ACETYLE.—SUGAR.

Sugar, as the substance from which alcohol and all the compounds of ethyle are exclusively obtained, comes properly to be considered here as an appendix to these compounds. There are several kinds of sugar, capable of undergoing fermentation and of producing alcohol. These are, cane sugar; grape sugar; (sugar of starch; of honey; diabetic sugar;) sugar of milk; and uncrystallizable sugar. The sugar of mushrooms has been found to be mannite, which is not fermentescible.

VARIETIES OF SUGAR.

Cane Sugar	$C_{12}H_9O_9+2HO$
Grape Sugar (Starch Sugar) . .	$C_{12}H_{14}O_{14}$
Sugar of Milk (lactine) . . .	$C_{24}H_{24}O_{24}$
Sugar of Mushrooms . . .	$C_{12}H_{13}O_{13}$

1. *Cane sugar*, $C_{12}H_9O_9+2HO$, occurs in great abundance in the sugar cane, the beet root, the maple, besides many other vegetables. It is extracted from the juice of these plants by crystallization, the evaporation being conducted at as low a temperature as possible. It crystallizes with great facility, either in small grains by rapid cooling of a strong syrup, as in loaf sugar; or in large distinct crystals by a slow process, as in sugar candy. The above formula represents the composition of pure crystallized sugar.

Sugar forms large transparent hard crystals, which melt at 302°, or according to Peligot at 356°, forming a viscid liquid, which on cooling forms a transparent amorphous mass, *barley sugar*. This, when kept, gradually becomes crystalline, opaque and friable. About 420° sugar is converted into caramel, losing 3 eq. of water.

Sugar dissolves in $\frac{1}{3}$ of its weight of cold, and in any quantity of boiling water; a solution saturated at 230° becomes a solid crystalline mass on cooling (tablet): a solution saturated in the cold is viscid, and is called syrup. Syrup, when long boiled, loses the property of crystallizing. The crystallization of sugar from syrup is also prevented by the addition of $\frac{1}{20}$ of oxalic, citric, or malic acids. When boiled with diluted sulphuric acid, cane sugar is converted into grape sugar. With strong sulphuric acid it produces a dark brown liquid, containing a new acid, sulphosaccharic acid. Nitric acid converts it into saccharic acid, oxalic acid, and carbonic acid.

When boiled with very diluted sulphuric acid, sugar absorbs oxygen from the air, and produces formic acid, and a brown matter identical with ulmine, formed by the decay of wood. Sugar prevents the precipitation of many metallic solutions by alkalies; and when mixed with oxide of copper and potash, the oxide of copper is dissolved, forming a purple solution, which on boiling, deposits red

suboxide of copper. It reduces partially the oxides of many metals, when boiled with their solutions.

Sugar forms crystallizable compounds with the alkalies, oxide of lead, and chloride of sodium. When in contact with the lining membrane of the stomach of a calf, or with the caseine of milk, sugar is transformed into lactic acid.

Sugar, if taken along with nitrogenized food, may be called nutritious: it would appear, however, to act chiefly in contributing to the support of respiration, and thus keeping up the animal heat. An animal, confined to sugar as food, soon dies from want of nitrogen, with the symptoms of starvation.

When a solution of sugar is examined by polarized light, it gives rise to a series of rings of the prismatic colours, when the plane of polarization is made to rotate from left to right.

SUGAR WITH BASES AND SALTS.

With lime sugar forms a sparingly soluble compound, $C_{12}H_9O_9 + \left\{ \begin{matrix} CaO. \\ HO \end{matrix} \right.$ With baryta, it forms a crystallizable compound, $C_{12}H_9O_9 \left\{ \begin{matrix} BaO \\ HO \end{matrix} \right.$. With oxide of lead it yields an insoluble compound, $C_{12}H_9O_9,2PbO$; and with common salt it yields a crystalline compound, $2C_{12}H_9O_9 + \left\{ \begin{matrix} 3HO \\ NaCl. \end{matrix} \right.$

2. *Grape Sugar.* Syn. *Glucose. Diabetic Sugar. Starch Sugar*, $C_{12}H_{14}O_{14}$. This sugar occurs in the juice of many fruits, and is besides a product of the metamorphoses of starch, cane sugar, woody fibre, sugar of milk, &c., when boiled with diluted acids. It may also be obtained from starch by the action of infusion of malt, or of diastase. It occurs in the urine of those affected with *diabetes mellitus*. The crystals which form in honey are likewise grape sugar.

It is best extracted from *dried grapes*, or honey, and is also prepared on the large scale from starch. 1 part of starch is boiled with 4 of water, and from $\frac{1}{100}$ to $\frac{1}{10}$ of sulphuric acid, during 36 or 40 hours; or an infusion of malt is added to jelly of starch, which soon becomes liquid, and, in a few hours is converted into sugar. When acid is used, it is neutralized by chalk, the solution of sugar filtered, and evaporated to a syrup, or, if required, to a dry mass. In this process, starch, $C_{12}H_{10}O_{10}$, takes up 4 eq. of water, and produces grape sugar, $C_{12}H_{14}O_{14}$; so that 100 parts of pure starch yield, or ought to yield, 122 of grape sugar. The same explanation, only varying the quantity of water, applies to the conversion into grape sugar of cane sugar, $C_{12}H_{11}O_{11}$; woody fibre, $C_{12}H_8O_8$; and sugar of milk $C_{12}H_{12}O_{12}$, these compounds requiring 3, 6, and 2 eq. of water respectively to form grape sugar.

The action of infusion of malt is not explained: all that we know is, that this infusion, or a solution of diastase, a substance contained in it, do actually cause starch to take the form of grape sugar. It is probable that the diastase is in a state of decomposition, and may act as a ferment. The action of the acid would seem to be equally obscure; but there is some reason to think that there is first formed, as in the case of ether, a coupled acid, or acid salt, which, like sulphovinic acid, is decomposed by boiling. According to De Saussure, sulphuric acid and starch actually form a crystallizable compound.

Grape sugar crystallizes from alcohol in square tables or cubes; a concentrated syrup of it yields only a mass formed of crystalline grains. It is much less

soluble, requiring 1½ part of cold water, and less sweet to the taste than cane sugar: in fact 1 part of cane sugar sweetens as much as 2½ of grape sugar. It is much more soluble in cold alcohol than cane sugar. At 212° grape sugar loses 2 eq. of water; when heated beyond 284° it becomes caramel. Hot water dissolves any quantity of grape sugar, but the syrup is not so nearly viscid as that of cane sugar. Solution of grape sugar exhibits the prismatic rays with polarized light when the plane of polarization is rotated from right to left, the colours being less brilliant. Now, as cane sugar, when fermenting, becomes first grape sugar, the coloured rings at first shown by it when the plane of polarization rotated from left to right disappear during fermentation; but reappear when rotation is made from right to left.

Grape sugar is easily distinguished from cane sugar by the action of acids and bases. Strong sulphuric acid dissolves without charring it, forming sulphosaccharic acid; and the alkalies or alkaline earths, which do not decompose cane sugar unless very concentrated, rapidly convert grape sugar into a brown matter. Peroxide of lead converts it, at 212°, into basic formiate of lead, carbonate of lead, and water.

With baryta and lime, and oxide of lead, grape sugar forms compounds which it is difficult to obtain pure. That with baryta appears to contain 3 eq. baryta for 2 eq. of sugar, and as the baryta replaces water in such compounds, it is probably $C_{24}H_{25}O_{25},3BaO = C_{24}H_{22}O_{22}\left\{\begin{matrix}3BaO\\3HO\end{matrix}\right.$. The compound with lime appears to be $C_{12}H_{12}O_{12},2CaO$; and that with lead, $C_{12}H_{11}O_{11},3PbO$. If we suppose the dry grape sugar to be $C_{12}H_{11}O_{11}$, and to combine with 3 eq. water and 3 eq. base, then we should have

Crystallized grape sugar	$C_{12}H_{11}O_{11}+3HO$
Compound with baryta	$\left\{\begin{matrix}C_{12}H_{11}O_{11}+3HO\\C_{12}H_{11}O_{11}+3BaO\end{matrix}\right.$
——— lime	$C_{12}H_{11}O_{11}+\left\{\begin{matrix}2CaO\\HO\end{matrix}\right.$
——— oxide of lead	$C_{12}H_{11}O_{11}+3PbO$

But the compound which grape sugar forms with common salt, and which crystallizes very readily, does not agree exactly with this view. The crystals are $2(C_{12}H_{12}O_{12})+NaCl+2HO$; and at 212° they lose the two equivalents of water.

The sulphosaccharic acid, above mentioned, as being formed when grape sugar is acted on by oil of vitriol, has not been fully examined. It forms a soluble salt with baryta.

With organic acids grape sugar forms compounds, the sugar in which cannot be brought to crystallize. Hence organic acids in vegetable juices act injuriously by first converting cane sugar into grape sugar, and then forming with it uncrystallizable compounds.

When sugar is boiled with hydrochloric acid, it yields different brown products, according to the strength of the acid. With equal parts of acid and water, it yields a body, $C_{24}H_{11}O_9$: with a weaker acid, two brown compounds; a soluble one, $C_{40}H_{14}O_{12}$, and an insoluble one, $C_{40}H_{16}O_{14}$. When boiled with diluted sulphuric acid, two substances are formed, which are nearly black; one, sacchulmine, insoluble, and the other sacchulmic acid, soluble in ammonia. The latter is $C_{35}H_{10}O_{15}$.

When boiled with alkalies, cane sugar is first converted into grape sugar, and then into formic acid, the two new acids, the glucic acid and the melassic acid. Glucic acid is very soluble, and its formula is either $C_{24}H_{15}O_{15},6HO$, or $C_{12}H_8O_8,3HO$. It is chiefly formed before the application of heat, which converts it into melassic acid. This latter acid is formed from sugar by the joint action of heat and alkalies. It has a very dark colour, and when separated by hydrochloric acid, appears as a black flocculent deposit. Its formula is $C_{24}H_{12}O_{10}$(?).

Caramel, the black matter formed by heating sugar to about 400°, has the formula of anhydrous cane sugar, $C_{12}H_9O_9$. It dissolves readily in water forming a solution like sepia, which is tasteless when pure. The caramel of commerce contains a good deal of undecomposed sugar.

When sugar is distilled with 3 parts of lime, it yields a liquid which is a mixture of acetone and metacetone. Metacetone is a colourless liquid, of an agreeable odour, boiling at 183°, and insoluble in water. Its formula is C_6H_5O; and it may be considered as 2 eq. acetone $C_6H_6O_2$, *minus* 1 eq. water.

1 eq. of anhydrous sugar	$C_{12}H_9O_9$
Contains—1 eq. acetone	$C_3\ H_3O$
1 eq. metacetone	$C_6\ H_5O$
3 eq. carbonic acid	$C_3\quad O_6$
1 eq. water	$H\ O$
Together	$C_{12}H_9O_9$

The formation of these products is therefore easily accounted for.

When sugar is heated with hydrate of potassa, several products are formed, but among them is an acid, $C_6H_5O_3,HO$, which is metacetonic acid, evidently derived from metacetone by oxidation at the expense of the hydrate. It is very similar to acetic acid.

ACTION OF NITRIC ACID ON SUGAR.

Saccharic Acid, $C_{12}H_{10}O_{11}5HO$?, or $C_6H_4O_7,HO$, is one of the products of the action of diluted nitric acid on cane or grape sugar. When stronger acid is used, oxalic and carbonic acids are the chief products. When sugar has been heated with 2 parts of nitric acid and 10 of water, the acid liquid gives, with basic acetate of lead, an insoluble saccharate of lead, which is decomposed by sulphuretted hydrogen, and the acid solution so far neutralized with potassa that on evaporation it yields crystals of the acid saccharate of potash. This salt is purified, again converted into saccharate of lead, and again the lead salt is decomposed by sulphuretted hydrogen. The acid this time is pure. It crystallizes with difficulty.

This acid has been supposed to be quintibasic, and to form 5 series of salts, but the latest researches of Heintz lead to the conclusion that it is either $C_6H_4O_7,HO$, or $C_{12}H_8O_{14},2HO$. Owing to the very discordant results of different experimenters, we shall not here enter into details which are uncertain. Saccharic acid forms a crystallizable acid salt with potassa, and definite salts with many other bases. It is isomeric with mucic acid: for $C_{12}H_8O_{14},2HO$ is the probable formula of mucic acid.

The saccharate of silver, when gently heated under water, is decomposed, the silver being reduced; and as this occurs without effervescence, the reduced metal adheres to the glass, and forms a bright mirror surface. The other saccharates are only interesting in respect to their composition. On the whole, saccharic acid is a compound of high theoretical interest, and the formation of two isomeric acids, saccharic and mucic, by the action of nitric acid on cane and grape sugar on the one hand, and on sugar of milk on the other, is a fact which may hereafter lead to a knowledge of the true constitution of the different kinds of sugar.

Notwithstanding the fact that cane sugar is easily converted into grape sugar, and that the formulæ differ only by 3 eq. water, it is evident that these two kinds of sugar differ more than if they were merely different kinds of hydrates of the same compound. Strong mineral acids instantly decompose cane sugar, but have little action on grape sugar; while alkalies, which combine with cane sugar to form crystalline compounds, rapidly convert grape sugar into dark compounds, glucic and melassic acids. And although both sugars agree in undergoing the same (vinous) fermentation, yet it is most probable that cane sugar, before fermenting, becomes grape sugar.

When vegetable juices containing cane sugar are evaporated, the presence of organic acids causes its conversion into grape sugar; and when lime is added, to clarify the juice, the action of the lime on grape sugar when evaporated, produces glucic and melassic acids; in other words, renders much sugar dark and uncrystallizable, converting it into molasses. A great part of the loss owing to this cause has of late years been avoided by carefully neutralizing with sulphuric acid as soon as the lime has effected the clarification.

3. *Sugar of milk, or lactine*, $C_{34}H_{19}O_{19}+5HO=C_{24}H_{24}O_{24}$, is obtained by evaporating clarified whey till it crystallizes. When pure it forms hard white crystals, soluble in 5 or 6 parts of cold and $2\frac{1}{2}$ of hot water. The taste of the crystals is feeble, but a concentrated solution tastes very sweet. It is insoluble in ether and alcohol. It stands between cane sugar and grape sugar in composition; for while cane sugar is $C_{12}H_{11}O_{11}$, and grape sugar $C_{12}H_{14}O_{14}$, lactine is $C_{24}H_{24}O_{24}=2(C_{12}H_{12}O_{12})$. By boiling with diluted acids it is converted into grape sugar. By the action of nitric acid it yields *mucic* or *saccholactic acid*. It combines with ammonia and with oxide of lead. Its presence prevents the precipitation of many metallic solutions. Sugar of milk is susceptible of the vinous fermentation, and it is well known that some nations prepare an intoxicating liquor from milk by fermentation. There is reason to think that previous to fermentation, it is like cane sugar converted into grape sugar; and at all events milk does not ferment until an acid has been formed in it, which acid converts lactine into grape sugar.

Sugar of milk forms two compounds with oxide of lead: first, neutral, $C_{24}H_{19}O_{19}$,5PbO: second basic, $C_{24}H_{19}O_{19}$,10PbO.

Mucic Acid, $C_{12}H_8O_{14}+2HO$, is formed when diluted nitric acid acts on sugar of milk, gum, or mannite. It is a white crystalline powder, of a feebly acid taste, soluble in 6 parts of boiling water, which deposits nearly the whole on cooling. Its solution when long heated and evaporated, yields the *modified mucic acid*. Mucic acid dissolves in oil of vitriol with a crimson colour. When heated it blackens, and yields among other products, *pyromucic acid*.

Mucic acid is bibasic, and forms two series of salts, one with 2 eq. fixed base,

the other with 1 eq. fixed base, and 1 eq. water. These salts have little interest. The *mucate of oxide of ethyle*, or *mucic ether*, crystallizes in four-sided prisms, soluble in hot water. When boiled with a base, it yields alcohol, and mucate of the base. Its formula is $C_{12}H_8O_{14}+2AeO$.

Modified mucic acid is more soluble in water, soluble in alcohol, from which solution it is deposited in square tables. Its aqueous solution, saturated at the boiling point, deposits on cooling ordinary mucic acid. Its salts are more soluble than the mucates, but the acid in them easily passes into the ordinary acid. It is probable that the modified acid contains 1 eq. of water more than the other.

Pyromucic acid, $C_{10}H_3O_5 + HO$, is formed by the dry distillation of mucic acid. 1 eq. of mucic acid, $C_{12}H_{10}O_{16}$, contains the elements of 1 eq. pyromucic acid, $C_{10}H_4O_6$, 6 eq. water, H_6O_6; and 2 eq. carbonic acid, C_2O_4. Pyromucic acid forms brilliant white scales, fusible at 266°, and volatilizes completely at a temperature somewhat higher. It is soluble in water and alcohol. Its salts are not important. *Pyromucate of oxide of ethyle*, $C_{10}H_3O_5$, AeO, is a solid crystallizable compound, fusible at 93°, volatile at 410°. Chlorine acts on this ether, forming a new compound, $C_{14}H_8Cl_4O_6$, the constitution of which is quite uncertain.

4. *Sugar of mushrooms.* Wiggers obtained from ergot of rye a saccharine compound, crystallizing in transparent rhombic prisms, soluble in water and alcohol, and susceptible of the vinous fermentation. An analysis of this sugar gave the formula $C_{12}H_{13}O_{13}$, that is, grape sugar, *minus* 1 eq. water. This may be a distinct kind of sugar; but the mushroom sugar of Braconnot is *mannite* or manna sugar.

We have seen that starch and woody fibre may be converted into grape sugar by boiling with dilute sulphuric acid: in like manner, salicine and phloridzine, boiled with the same acid, yield saliretine and phloretine, in each case along with grape sugar. But the action of the infusion of malt, is still more singular; we have seen that starch by contact with infusion of malt is rapidly converted into grape sugar. This action is ascribed to the presence of *diastase*, a nitrogenized body which exists in malt, and which, while it causes the conversion of starch into sugar, itself disappears. The action is not fully understood, but there is no doubt that when seeds germinate, the starch they contain is in this manner rendered soluble, and conveyed, as sugar, to all parts of the plant, there to be converted into woody fibre by a process the inverse of that by which woody fibre is converted into sugar. This latter is seen in the ripening of fleshy fruits, where a quantity of cellular matter (lignine) disappears, and the proportion of sugar very much increases.

VINOUS OR ALCOHOLIC FERMENTATION.

This name is given to that change by which sugar is resolved into alcohol and carbonic acid, by contact with a ferment. The sugar must be dissolved in water, and the solution must be exposed to a temperature or from 40° to 86°. If a ferment, such as yeast, be added, the sugar soon disappears, carbonic acid is given off in large quantity, and the liquid is found to contain alcohol, which may be separated by distillation. Now, grape sugar, $C_{12}H_{14}O_{14}$, contains the elements of 2 eq. alcohol, 4 eq. carbonic acid, and 2 eq. water, $2(C_4H_6O_2) + 4CO_2 + 2HO$; and, by very exact experiments it has been proved that 100 parts of grape sugar yield only 47·12 of alcohol, 44·84 of carbonic acid, together 91·96 parts,

the loss, 9·04 parts being the 2 eq. of water separated. On the other hand, cane sugar, $C_{12}H_{11}O_{11}$, requires the addition of 1 eq. of water to yield 2 eq. alcohol, and 4 eq. carbonic acid, $= 2\ (C_4H_6O_2) + 4CO_2$; and here also experiment has demonstrated, that 100 parts of cane sugar yields 53·727 parts of alcohol and 51·298 of carbonic acid, together 105·025; the increase, or 5·025 parts being due to the 1 eq. of water taken up to form dry grape sugar, $C_{12}H_{12}O_{12}$, into which cane sugar is converted before it undergoes fermentation. These facts prove that the ferment takes no direct part in the reaction, but only acts by inducing a state of change.

A considerable number of substances, if in a state of decomposition, act as ferments on a solution of sugar: among these are, besides yeast, vegetable gluten, albumen, caseine or fibrine, and the corresponding animal substances; also animal matter generally, if in a state of putrefaction.

The only explanation we can give is that the particles of these bodies, being in a state of decomposition, are in motion, and by communicating, mechanically, an impulse or motion to the particles of the sugar, destroy the balance of affinities to which the existence of sugar is owing; and thus give rise to a new balance or equilibrium, more stable under the given circumstances. The elementary particles of the sugar being disturbed in their previous arrangement, group themselves according to their individual affinities, and while the carbon forms, on one side, a compound containing all the hydrogen (alcohol), it yields on the other, a compound containing the greater part of the oxygen (carbonic acid).

When a natural juice, as that of the grape, ferments, some of the various substances it contains undergo a decomposition, probably of an analogous kind, giving rise to other new products, which are important in regard to the flavour of the liquid (wine, beer, or spirits), produced in the fermentation. Thus all wine contains œnanthic ether; potato spirit contains the oil of potato spirit (*fusel oel.* German): grain spirit contain a similar oil. It is not improbable, that besides the vinous fermentation which takes place in the greater part of the sugar, a peculiar reaction occurs, between a portion of the sugar and the ferment (or some other nitrogenized compound present), the result of which is the production of these peculiar oily liquids. The *bouquet*, or so much prized flavour of the finer wines, is doubtless owing to some etherial compound produced in a similar way, but the origin, properties, and composition of which are as yet altogether unknown. It may be mentioned here, however, that œnanthic ether, which is the cause of that peculiar smell which belongs to all wine, and is so marked that we can at once tell, after many weeks or months, that an empty bottle has formerly contained wine, is a compound of oxide of ethyle with a fatty acid; and the oil of potato spirit is a compound analogous to alcohol; the hydrated oxide of a radical *amyle*, $C_{10}H_{11}$.

VISCOUS FERMENTATION.

When certain saccharine juices, such as those of beet-root, carrots, onions, &c. are exposed to a temperature of from 86° to 104°, a peculiar fermentation takes place. The sugar disappears, but instead of alcohol and carbonic acid, there are obtained *mannite lactic acid*, and a mucilaginous substance, having the composition of gum; this latter renders the liquid ropy, and viscid, hence the name given to the process.

The composition of mannite is	$C_6 H_7 O_6$
That of lactic acid is	$C_6 H_5 O_5$
Together	$C_{12}H_{12}O_{11}$

It is evident, therefore, that 1 eq. of dry grape sugar, $C_{12}H_{12}O_{12}$, losing 1 eq. oxygen, might give rise to mannite and lactic acid. The gum has the same composition as sugar, so that we are led to believe that the nitrogenized constituents of the juice are acted on by the sugar, from which they obtain oxygen; and that these compounds are themselves decomposed by the oxygen, mannite, and lactic acid, which are very permanent, being produced from the sugar.

This peculiar fermentation is produced when cheese is added to a solution of sugar, and the whole kept at a proper temperature.

Mannite $C_6H_7O_6$ occurs as the chief ingredient of manna. It is also found in certain juices, in mushrooms, in roots, such as that of celery, and is formed artificially as above described. It is easily purified by solution in alcohol and crystallization. It forms, when crystallized in water, large prisms, of a weak sweet taste. It is not susceptible of the vinous fermentation. Nitric acid and permaganate of potassa act on it as on sugar. Concentrated arsenic acid gives it a brick red colour.

Lactic Acid, $C_6H_5O_5 + HO$, so called because it occurs in sour milk, is also formed abundantly, as above described, in a peculiar fermentation of certain saccharine juices at a high temperature. In milk it is derived from the sugar of milk; and by neutralizing sour milk with carbonate of soda, adding sugar of milk, allowing it again to become acid, again neutralizing, and so on in succession, as long as the caseine causes the peculiar change to take place, it may be obtained in large quantity. A still easier process is to dissolve 14 parts of cane sugar in 60 of water, and to add 4 of moist cheese and a sufficient quantity of prepared chalk. The mixture being kept some time at from 77° to 86° F. will at last become quite thick with crystals of lactate of lime. If the action of the caseous ferment be pushed further, and at a higher temperature, the lactate of lime is not obtained, but in its place *butyrate of lime* in large quantity. See *Butyric acid*. The above quantities will yield about 13 parts of lactate after it has been purified by crystallization; besides from $1\frac{1}{2}$ to 2 parts of mannite. The acid of sour crout is lactic acid, and by boiling the juice of sour crout with chalk or carbonate of zinc, lactate of zinc or of lime may be obtained.

From the lactate of lime, lactic acid may be obtained by the action of oxalic acid, which removes the lime as oxalate. The filtered solution is lactic acid, which is concentrated by evaporation, and purified by solution in ether. From the lactate of soda, lactate of zinc may be obtained by adding chloride of zinc to the hot saturated solution; on cooling, lactate of zinc, being sparingly soluble in cold water, crystallizes. This salt, acted on by barytic water, yields lactate of baryta, from which sulphuric acid removes the baryta, and the filtered liquid is pure diluted lactic acid.

In its most concentrated form, hydrated lactic acid is a syrupy liquid of a very strong but pleasant acid taste. Its sp. gr. is 1·215. Its formula $C_6H_5O_5 + HO = C_6H_6O_6$. It is therefore polymeric with dry grape sugar and with gum; both of which are $C_{12}H_{12}O_{12}$. At 482° the hydrate is decomposed, and yields a solid crystalline sublimate, $C_6H_4O_4$, which has been called anhydrous lactic acid, or sublimed lactic acid. This compound dissolves readily in hot water, and the solution if evaporated yields the original hydrate $C_6H_6O_6 = C_6H_4O_4 + 2HO$.

But when the acid is neutralized by bases, only one of the 2 eq. of water taken up by the sublimed acid is replaced by a base; and consequently we cannot look on the sublimed acid as the true anhydrous acid. The anhydrous acid, as it exists in the lactates, is $C_6H_5O_5$; and the sublimed acid is not lactic acid, but is converted into lactic acid when boiled with water.

The general formula for the lactates is $C_6H_5O_5$,MO. The lactates of the alkalies are very soluble and deliquescent: that of lime is less soluble in cold water and crystallizes readily. The lactate of zinc is sparingly soluble in cold water, and is hence well adapted for the extraction and purification of the acid.

XIX. Methyle. $C_2H_3 = Mt$.

This is the hypothetical radical of a numerous series of compounds, entirely analogous to those of ethyle. There is the *oxide of methyle*, MtO, analogous to oxide of ethyle; and the *hydrated oxide of methyle* MtO,HO, analogous to alcohol. This last is the compound from which all the others are obtained. The extraordinary analogy between ethyle and methyle will enable us to describe the compounds of the latter very briefly.

TABLE OF COMPOUNDS.

Hydrated Oxide of Methyle	C_2H_3O,HO
Oxide of Methyle	$(C_2H_3)O$
Chloride of Methyle	C_2H_3,Cl
Iodide of Methyle	C_2H_3,I
Sulphuret of Methyle	C_2H_3,S

1. Hydrated Oxide of Methyle. MtO,HO.

Syn. *Pyroxilic Spirit.* This compound is one of the chief products of the destructive distillation of wood, and is found in the watery portion, along with acetic acid, acetone, acetate of oxide of methyle, and several other etherial liquids, besides portions of the oily matter of the tar dissolved in them.

By rectification with chloride of calcium, the pyroxilic spirit, which combines with that salt, is separated from several other liquids which distil over in the heat of the vapour bath. The residue, if mixed with its own bulk of water, and again heated in the vapour bath, now gives off the pyroxilic spirit, which is still mixed with water. It is purified by rectification with quicklime, which also destroys any acetate of methyle that may be present.

Pure hydrated oxide of methyle is a liquid very similar to alcohol, having the same density, and the same degree of inflammability. Its odour is peculiar and etherial. It boils at about 140° or 150°.

When heated with peroxide of manganese, water, and sulphuric acid, it yields various products, among which the chief are, *formic acid* and *formomethylal*. It is decomposed by nitric acid, yielding oxalic acid, and by chlorine, yielding new products. It dissolves resins, and is used in making varnishes. It forms, with baryta a crystalline compound BaO + MtO,HO; and with chloride of calcium, another crystalline body in large hexagonal tables, CaCl + 2(MtO,HO).

By the action of platinum powder, pyroxilic spirit is oxidized into formic acid, which bears the same relation to it that acetic acid does to alcohol.

2. Oxide of Methyle. $MtO = (C_2H_3)O$.

This compound is obtained, like ether (oxide of ethyle), when the preceding

compound is distilled with its own volume of oil of vitriol; it escapes as an inflammable gas. Like oxide of ethyle, it is a base and neutralizes acids. It even forms a neutral sulphate, which oxide of ethyle cannot do. It is worthy of notice, that oxide of methyle is polymeric with alcohol; for $C_4H_6O_2 = 2(C_2H_3O)$: so that these two bodies have the same composition, in 100 parts; that is, the same relative proportions of the same element, but a very different absolute amount: the equivalent of alcohol being twice as heavy as that of oxide of methyle. The constitution of these compounds, moreover, is different, for one is a hydrate, $C_4H_4O + HO$: while the other is an anhydrous oxide, C_2H_3O.

3. *Chloride of methyle*, $C_2H_3,Cl = MtCl$, is a gas, of an ethereal smell, inflammable, of sp. gr. 1·1737. It is formed by the action of sulphuric acid and chloride of sodium on pyroxilic spirit. By the action of chlorine, aided by the sun's rays, it yields several new compounds containing chlorine.

4. *Iodide of methyle*, $C_2H_3,I = MtI$, is obtained by distilling 12 parts of pyroxilic spirit, 8 of iodine, and 1 of phosphorus. It is a liquid, boiling between 102° and 122°. The *fluoride* and *cyanide* of methyle are analogous liquids.

5. *Sulphuret of methyle*, $C_2H_3,S = MtS$, is best formed by the action of a current of chloride of methyle on sulphuret of potassium dissolved in alcohol. $MtCl + KS = MtS + KCl$. It is a mobile liquid, of a very offensive alliaceous odour, boiling at 104°. Its sp. gr. in the liquid form is 0·845; in the form of vapour, it is 2·115. With chlorine, it gives rise to several new compounds. The *hydrosulphuret* of *sulphuret of methyle* (corresponding to mercaptan) I obtained by distilling the double sulphate of methyle and potassa with the hydrosulphuret of potassium. $(KO,MtO,2SO_3) + HS,KS = 2(KO,SO_3) + HS,MtS$. Its formula is $HS,MtS = C_2H_3,S + HS$. It is a colourless liquid, lighter than water, which boils at 70°, and acts on the oxides of mercury and lead exactly as mercaptan does. Its odour is most offensive, resembling that of leeks highly concentrated.

SALTS OF OXIDE OF METHYLE.

1. *Neutral Sulphate.* MtO,SO_3, is obtained when pyroxilic spirit is distilled with a large excess of sulphuric acid. It forms an oily liquid, of a slightly alliaceous smell. It boils at 370°. Boiling water decomposes it into acid sulphate and hydrate of oxide of methyle. When heated with chlorides, cyanides, &c., it yields the compound of methyle with chlorine, cyanogen, &c.; with a salt of benzoic, succinic, or other organic acid, it yields benzoate, &c. of oxide of methyle. Ammonia converts it into *sulphamethylane*.

TABLE OF SALTS OF OXIDE OF METHYLE.

Bisulphate of Oxide of Methyle	$MtO,HO,2SO_3$
Nitrate	MtO,NO_5
Oxalate	MtO,C_2O_3
Benzoate	MtO,BzO
Acetate	MtO,AcO_3

2. *Bisulphate of Oxide of Methyle.* Syn. *Sulphomethylic Acid.* $HO,MtO,2SO_3$, is perfectly analogous to sulphovinic acid, and forms double salts, such as that of potassa, $KO,MtO,2SO_3$, which are often called sulphomethylates, and correspond exactly to the sulphovinates. The acid sulphate itself may be ob-

tained in crystals, which are very soluble and very acid. It is best obtained by the action of hot water on the neutral sulphates. The double salts, or sulphomethylates, are of no particular importance. They crystallize readily.

3. *Nitrate of Oxide of Methyle.* MtO,NO_5, is obtained when pyroxilic spirit is distilled with nitrate of potassa and sulphuric acid. It is an oily liquid, the vapour of which, if heated beyond 248°, explodes violently.

The neutral carbonate of methyle is not known; but double carbonates, analogous to those of ethyle with alkalies, may be prepared in the same way as those compounds.

4. *Oxalate of Oxide of Methyle*, $MtO,C_2O_3 = C_4H_3O_4$, is obtained in a manner analogous to that in which oxalic ether is prepared. It forms a crystalline solid, soluble in alcohol and pyroxilic spirit, which deposit it in large crystals. By the action of dry ammonia, it is converted into *oxamethylane* (analogous to oxamethane), which is the *oxamate of oxide of methyle*, $C_6H_5NO_6 = C_2H_3O + C_4H_2NO_5$. Liquid ammonia converts it into oxamide, as is the case with oxalic ether, only here pyroxilic spirit and not alcohol is formed at the same time. $C_2H_3O,C_2O_3 + NH_3 = C_2H_3O,HO + C_2O_2,NH_2$. This is perhaps the easiest way of obtaining oxamide in large quantity.

Bisulphuret of carbon and hydrated cyanic acid act on pyroxilic spirit exactly as on alcohol, producing analogous compounds.

5. *Benzoate of Oxide of Methyle*, MtO,BzO, is best obtained by distilling dry benzoate of lime or soda with neutral sulphate of methyle. It is an oily liquid, of a balsamic odour, analogous in other respects to benzoic ether.

6. *Acetate of Oxide of Methyle*, MtO,AcO_3, is obtained in the same way as acetic ether, which it resembles. It occurs in considerable quantity in raw pyroxilic spirit, and even in that which has only been purified by rectification. When quicklime is used in the rectification, it is destroyed, yielding an additional quantity of the pure hydrate of oxide of methyle. It is very volatile and inflammable, and for most purposes its presence in the wood spirit is not at all injurious. It is isomeric with formiate of oxide of ethyle: for $C_2H_3O + C_4H_3O_3 = C_4H_5O + C_2HO_3$.

The mucate of oxide of methyle is a crystalline solid, analogous in its preparation and properties to the corresponding salt of ethyle.

The action of chlorocarbonic acid on pyroxilic spirit is exactly analogous to its action on alcohol, producing an oily liquid, $C_4H_3Cl.O_4 = C_2\left\{\begin{matrix}O_3\\Cl.\end{matrix}\right. + C_2H_3O$. By the action of ammonia this liquid produces a compound, *urethylane*, (corresponding to *urethane*) $C_4H_5NO_4$ or $C_8H_{10}N_2O_8 = C_2H_4N_2O_2 + 2(C_2H_3O,CO_2)$; that is, a compound, possibly, of 1 eq. urea, with 2 eq. neutral carbonate of methyle.

When a current of ammonia is made to act on the neutral sulphate of methyle, there is produced a crystalline compound, $C_2H_5NS_2O_6$, which has been called *sulphamethylane*, and may be viewed as oxamethylane, in which sulphamide, SO_2,NH_2, has been substituted for oxamide, C_2O_2,NH_2; or SO_2 for C_2O_2. It may also be considered, if oxamethylane be the oxamate of oxide of methyle, $C_2H_3O + C_4H_2NO_5$, as composed of oxide of methyle and a peculiar acid, formed of hyposulphuric acid and amide; $C_2H_3O + (S_2O_5,NH_2)$.

When hydrated oxide of methyle is oxidized by means of plantinum powder, it is finally converted into pure formic acid. There is evidently, therefore, the

same relation between methyle and formic acid, as between ethyle and acetic acid; and on comparing the formulæ of pyroxilic spirit and of formic acid, C_2H_3O,HO and C_2HO_3,HO, we perceive that the former, to be converted into the latter, must have lost 2 eq. of hydrogen, and taken up 2 eq. of oxygen. This is exactly what takes place with alcohol, and there can be no doubt, that the pyroxilic spirit yields an intermediate compound, exactly analogous to aldehyde, although this has not yet been isolated. Such a compound would be the hydrated protoxide of a derived radical, *formyle*, analogous to acetyle, of which formic acid is the hydrated peroxide; and its formula would be $(C_2H)O + HO$. We shall, therefore, assume the existence of this radical, and proceed to describe its compounds, which are quite analogous to those of acetyle.

7. *Salicylate of Oxide of Methyle*, $MtO,SaO = C_{16}H_8O_6$, is found, nearly pure, in the oil obtained by distilling with water the flowers of *Gaultheria procumbens*, a plant found abundantly in New Jersey. This oil is most remarkable as containing two compounds, salicylic acid and oxide of methyle, neither of which was previously known except as a product of decomposition of organic substances by artificial means.

The oil is very fragrant. When acted on by nitric acid, the salicylic acid is first converted into nitrosalicylic or anilic (indigotic) acid, and the anilate of oxide of methyle is obtained in crystals. The further action of nitric acid produces nitropicric acid.

When the oil of gaultheria is added to an excess of solution of potassa, scaly crystals are formed, which are a compound of the oil with potassa, and from which acids separate the oil unchanged. But if heated with the potassa, hydrated oxide of methyle is given off, and salicylate of potassa is left, from which acids separate pure salicylic acid.

Salicylamide. When the oil is left for a few days in contact with six times its bulk of strong aqua ammoniæ, it is entirely, although slowly, dissolved, and the solution leaves, on evaporation, a mass of brown crystals of a peculiar aromatic odour. By distillation, this mass yields colourless prismatic crystals of a new compound, which is found to be *salicylamide* $(C_{14}H_5O_5,NH_3) - HO = C_{14}H_7NO_4$. This compound is isomeric (or polymeric) with protonitrobenzoene, and with anthranilic acid; but when distilled with lime or baryta, it does not yield aniline, as both these compounds do, but is resolved into carbolic acid, ammonia, and a carbo-hydrogen.

When the oil of gaultheria is made to drop on red-hot baryta, it is resolved into carbonic acid and anisole, $C_{16}H_8O_6 + 2BaO = 2(BaO,CO_2) + C_{14}H_8O_2$. It would appear that the formula of anisole, (which see farther on,) contains 1 eq. of hydrogen too little, and that the formula now given, namely, $C_{14}H_8O_2$, is the correct one, according to the most recent experiments.

XX. Formyle. C_2H=Fo.

This radical is unknown in a separate form, as are its protoxide and deutoxide, corresponding to aldehyde and aldehydic acid. But when hydrated oxide of methyle is distilled with sulphuric acid, water, and peroxide of manganese, a volatile liquid is obtained, which is a mixture of formiate of oxide of methyle and another liquid called methylal. When purified, this latter has the formula $C_6H_8O_4$, which indicates that it is composed of C_2HO,HO, or hydrated oxide of formyle, and 2 eq. of oxide of methyle, $2(C_2H_3O)$. This compound, briefly,

FoO,HO + 2MtO, corresponds to acetal in the series of ethyle; acetal being AcO,HO+AeO.

TABLE OF COMPOUNDS.

Formic acid (anhydrous)	FoO_3
Formic acid (hydrated)	FoO_3,HO
" "	FoO_3,2HO
Chlorides of Formyle	Fo + (Cl,Cl_2, Cl_3)
Perbromide "	$FoBr_3$
Periodide "	FoI_3

Formic Acid. C_2HO_3,HO=FoO_3,HO.

This remarkable acid occurs in the red ant, *formica rufa*, and may be obtained, in a diluted and impure state, by infusing these insects in water. Its production from pyroxylic spirit has been described above. It may also be prepared by distilling a mixture of starch or sugar with peroxide of manganese, water, and sulphuric acid: and it is formed under a great variety of circumstances from many organic compounds.

To prepare the hydrated acid pure and concentrated, the dry formiate of lead, PbO,FoO_3, is decomposed by sulphuretted hydrogen gas, and the vapour of the formic acid condensed in a well cooled receiver. It is boiled for a few moments to expel any sulphuretted hydrogen. It is a clear liquid of sp. gr. 1·235, fuming slightly, and has a very pungent acid smell. Below 32° it crystallizes in brilliant scales. It boils at 212°, and its vapour is inflammable, burning with a blue flame. This is probably owing to the formation of carbonic oxide, for the acid C_2HO_3,HO, contains the elements of 2 eq. carbonic oxide, C_2O_2, and 2 eq. water, H_2O_2.

With 1 eq. of water it forms the second hydrate FoO_3+2HO, which much resembles the first in properties. Its boiling point is 221°, and its sp. gr. is 1·110.

Both these hydrates are highly corrosive; a drop of either on any delicate portion of the skin causes a severe burn, which blisters, suppurates and is very painful and difficult to heal. In this respect, the formic acid can only be compared to hydrofluoric and hydrated cyanic acids.

A weaker acid is obtained by distilling formiate of soda, lime, or lead, with sulphuric acid, previously diluted with half its weight of water. Ten parts of formiate of lime, 8 of oil of vitriol, and 4 of water, yield 9 of formic acid, of sp. gr. 1·075.

The salts of the acid are best prepared from the weak and impure acid obtained by distilling a mixture of 10 parts of starch, 37 of peroxide of manganese, 30 of oil of vitriol and 30 of water. These materials yield 3·35 parts of formic acid, such that 100 parts neutralize 15 of dry carbonate of soda. From this acid, the formiate of lead may be easily prepared and purified; and from it, by the addition of carbonate of soda, formiate of soda may be obtained.

Formic acid is easily recognized by the action of sulphuric acid, which decomposes, without blackening, both it and its salts, causing the disengagement of pure carbonic oxide. It also reduces the oxides of all the noble metals, and is itself oxidized into carbonic acid. Formic acid not only reduces the oxides, but also, in most cases, the soluble salts, of the noble metals. 1 eq. formic acid can reduce 2 eq. of a protoxide, such as that of silver, $2AgO+C_2HO_3=Ag_2+HO+2CO_2$; or 1 eq. of a deutoxide, such as that of mercury; $HgO_2+C_2HO_3=Hg+HO+2CO_2$.

Formic acid is a very powerful acid, and forms salts with bases, all of which are soluble. They are generally similar to the acetates; but yet quite distinct. Many metallic formiates, when heated in close vessels, give off carbonic acid and carbonic oxide, leaving the metal reduced: others give off carbonic oxide, leaving the oxide.

Formiate of ammonia, NH_4O,C_2HO_3, contains the elements of hydrocyanic acid and water, $C_2NH+4HO$; and is converted into these compounds when its vapour is passed through a red-hot tube. *Formiate of oxide of ethyle*, prepared like the acetate, is a volatile ethereal liquid, with a peculiar aromatic smell. The corresponding salt of oxide of methyle is quite analogous. *Formiate of potassa* is very deliquescent. *Formiate of soda* is also very soluble, but may be obtained in crystals. It is a very powerful reducing agent, both in the moist and dry way. In the former, it reduces the noble metals, in the latter, at a red heat, by virtue of the carbonic oxide it gives off, it reduces most of the reducible metals, such as lead, copper, antimony, arsenic, cobalt, nickel, &c. *Formiate of lead* is sparingly soluble in cold water, and is therefore easily purified, and serves to prepare formic acid and formiate of soda. *Formiate of deutoxide of mercury* and *formiate of protoxide of mercury* both exist. When red oxide of mercury is dissolved in cold formic acid, the former salt is produced: but the slightest heat causes an effervescence, while formiate of the protoxide is deposited in silvery scales like the acetate. These, when warmed, are decomposed with effervescence and deposition of metallic mercury. *Formiate of silver* resembles the acetate; but is very easily decomposed by heat, the metal being reduced.

COMPOUNDS OF FORMYLE WITH CHLORINE, ETC.

When chlorine or hypochlorites act on oxide of methyle, hydrated oxide of methyle, and chloride of ethyle, a great variety of new compounds are produced, corresponding in most cases to the compounds obtained by the action of chlorine, &c., on alcohol, ether, and chloride of ethyle. Our space forbids us to give the details of these decompositions; but we may mention that two of the compounds formed by the action of chlorine on the compounds of ethyle and acetyle, may be viewed as *protochloride* and *bichloride of formyle*. These are $C_4H_2Cl_2=2(C_2H,Cl)$; and $C_4H_2Cl_4=3(C_2H,Cl_2)$. The *perchloride of formyle*, $FoCl_3=C_2H,Cl_3$, is also produced from a compound of the ethyle series, namely from chloral, by the action of alkalies. It is an oily liquid of a sweet taste and ethereal smell. When acted on by alkalies, it yields chlorides and formiates; thus, with potassa, $C_2HCl_3+4KO=3KCl+KO,C_2HO_3$.

When acted on by chlorine, perchloride of formyle yields perchloride of carbon $C_2Cl_4=C_2Cl,Cl_3$, just as perchloride of acetyle, C_4H_3,Cl_3 yields sesquichloride of carbon $C_4Cl_6=C_4Cl_3,Cl_3$.

Perbromide of formyle is obtained from bromal. Periodide of formyle, obtained by the action of alcohol on iodine and potassa, is a yellow crystalline, volatile, soljd, having an odour analogous to that of saffron.

When chlorine acts on an oxide of methyle, C_2H_3O, it produces, by substitution of chlorine for hydrogen, the compounds $C_2\left\{\begin{matrix}H\\Cl\end{matrix}\right.^2O$; $C_2\left\{\begin{matrix}H\\Cl_2\end{matrix}\right.O$; and finally, C_2Cl_3,O. The second may be considered as formic acid, C_2HO_3, in which two-thirds of the oxygen are replaced by chlorine, $C_2H\left\{\begin{matrix}O\\Cl_2\end{matrix}\right.$. It will then be an oxych

When chlorine acts on chloride of methyle, C_2H_3Cl, three compounds are formed by substitution. These are, 1st, $C_2H_2Cl_2=C_2\left\{\begin{matrix}H_2\\Cl\end{matrix}\right.$, Cl; 2d, perchloride of formyle, $C_2HCl_3=C_2\left\{\begin{matrix}H\\Cl_2\end{matrix}\right.$,Cl; and 3d, as before explained, perchloride of carbon, $C_2Cl_4=C_2Cl_3$,Cl.

The action of chlorine on sulphuret of methyle, C_2H_3,S, appears to yield, $C_2\left\{\begin{matrix}H_2\\Cl\end{matrix}\right.$S; $C_2\left\{\begin{matrix}H\\Cl_2\end{matrix}\right.$S; and C_2Cl_3S.

The action of chlorine on oxalate, benzoate, and acetate of oxide of methyle is quite analogous to its action on the corresponding compounds of ethyle, producing the oxalate, benzoate, and acetate of oxychloride of formyle, $C_2O_3+C_2H\left\{\begin{matrix}O\\Cl_2\end{matrix}\right.$; $C_{14}H_5O_3$, + $C_2H\left\{\begin{matrix}O\\Cl_2\end{matrix}\right.$; and $C_4H_3O_3+C_2H\left\{\begin{matrix}O\\Cl_2\end{matrix}\right.$. These curious results, like those which precede them, are here merely indicated, as we have explained the principle of their formation under the heads of ethyle and acetyle.

In some specimens of raw pyroxilic spirit there occurs a large proportion of a peculiar volatile liquid, which has been called *lignone* or *xylite*. As its constitution is quite uncertain, although it is believed to contain some compound of oxide of methyle, we shall state what is known of it when treating of the products of the dry distillation of wood.

XXI. Cetyle. $C_{32}H_{33}$=Ct.

This is the hypothetical radical of a series of compounds, derived from spermaceti. The principal one is *ethal*, the hydrated oxide of cetyle, analogous to alcohol.

Hydrated Oxide of Cetyle. $C_{32}H_{33}O,HO$=CtO,HO.

Syn. *Ethal.* This compound exists in spermaceti, in combination with margaric and oleic acids. When spermaceti is digested with strong caustic potassa, a soap is produced; and this being decomposed by sulphuric acid, yields a fatty mixture, composed of margaric and oleic acids and ethal. The whole is acted on by baryta, with which the acids unite; and the ethal is dissolved from the mixture by cold alcohol. It is afterwards purified by means of ether.

Ethal forms a white crystalline solid, like wax, fusible about 118°, volatile at a higher temperature, soluble in alcohol. As above mentioned, it is analogous to alcohol; and although the oxide of cetyle has not yet been obtained in a separate form, yet there have been formed the *chloride of cetyle*, and the *double sulphate of oxide of cetyle and potassa*, analogous to the corresponding compounds of ethyle.

When ethal is repeatedly distilled with anhydrous phosphoric acid, it loses the elements of 2 eq. of water, yielding a new compound, cetene=$C_{32}H_{32}$, analogous to olefiant gas or etherine. It is an oily inflammable liquid.

XXII. Amyle. $C_{10}H_{11}$=Ayl.

This is the hypothetical radical of a series of compounds, derived from oil of potato spirit, which is itself, when pure, the hydrated oxide of amyle, analogous to alcohol. Both the radical and its anhydrous oxide are unknown in the separate state: but a sufficient number of compounds has been obtained to render its existence highly probable.

Hydrated Oxide of Amyle. $C_{10}H_{11}O,HO$=AylO,HO.

TABLE OF COMPOUNDS.

Hydrated Oxide of Amyle	AylO,HO.
Chloride of Amyle	AylCl?
Bromide do.	AylBr.
Iodide do.	AylI.
Sulphamylic Acid	$AylO,HO,2SO_3$.
Acetate of Oxide of Amyle	$AylO,AcO_3$.
Hydrosulphuret of Sulphuret of Amyle	AylS,HS.
Valerianic Acid	$C_{10}H_9O_3,HO$.
Amilene	$C_{10}H_{10}$.

Syn. *Oil of potato spirit*; in German, *Fuseloel*. This compound distils over towards the end of the first distillation of spirits made from potatoes, rendering these last portions of the spirit milky and very offensive. It separates on standing as an oily liquid, which is washed with water to remove alcohol, dried by chloride of calcium, and rectified till its boiling point becomes steady at 269° or 270°. It is then pure.

It is a colourless oily liquid, very mobile, of a strong and nauseous odour, which produces stupefying effects. Its vapour, when inhaled, causes cough and spasmodic dyspnœa, resembling asthma, often followed by vomiting. Its taste is very acrid and nauseous. Its sp. gr. is 0·812. At —4° it crystallizes in shining scales. When heated with dry hydrate of potassa it is oxidized, hydrogen being given off, and the potassa is found combined with valerianic acid, $C_{10}H_9O_3$. When distilled with anhydrous phosphoric acid, it yields a new carbohydrogen, *amilene*, $= C_{10}H_{10}$.

The *chloride of amyle* has not yet been obtained; but the *bromide* and *iodide* are formed when the hydrated oxide is distilled along with phosphorus and bromine or iodine. They are both heavy oily liquids, and their formulæ are AylBr. and AylI.

The *bisulphate of oxide of amyle or sulphamilic acid*, $AylO,HO,2SO_3$, is analogous to sulphovinic acid. With bases, it forms double salts, the formula of which is $MO,AylO,2SO_3$, which are soluble in water and crystallizable. The solutions, when boiled, yield hydrated oxide of amyle, free sulphuric acid, and a neutral sulphate.

The *acetate of oxide of amyle* is an ethereal liquid, analogous to acetic ether. Its formula is $C_{14}H_{14}O_4=C_{10}H_{11}O,C_4H_3O_3=AylO,AcO_3$.

The *hydrosulphuret of sulphuret of amyle*, AylS,HS, is prepared in the same way as mercaptan, to which it is quite analogous. It is an oily liquid, boiling at 243°, of sp. gr. 0·835. It has, like the corresponding compounds of ethyle and methyle, a most penetrating odour of onions; and like them, it acts on red oxide of mercury, forming a white crystalline compound AylS,HgS.

The *sulphocarbonate of oxide of amyle*, very analogous to the bisulphocarbonate of oxide of ethyle, is formed when bisulphuret of carbon acts on a solution of potassa in oil of potato spirit.

OXIDATION OF HYDRATED OXIDE OF AMYLE.

Valerianic Acid. $C_{10}H_9O_3,HO$.

It has already been mentioned, that when oil of potato spirit is heated with dry hydrate of potassa, hydrogen is given off, and valerianate of potassa is formed.

Here the oil, $C_{10}H_{11}O,HO$, loses 2 eq. hydrogen, and gains 2 eq. oxygen; so that valerianic acid stands to amyle in the same relation as acetic acid to ethyle, and formic acid to methyle. The acid is easily separated by distilling the salt of potassa with diluted sulphuric acid. In composition and in all its properties, it agrees with the native valerianic acid, obtained by distilling the root of *valeriana officinalis* with water.

Valerianic acid is a limpid, oily fluid, of a disagreeable and peculiar smell. Its sp. gr. is 0·944, and it boils at 270°. With bases it forms soluble salts, which have a sweet taste.

The action of chlorine on hydrated oxide of amyle gives rise to the formation of a compound, *chloramilal*, supposed to be analogous to chloral, but the composition and nature of which are not fully known.

Amilene, the carbo-hydrogen obtained by distilling hydrated oxide of amyle with dry phosphoric acid, has the formula $C_{10}H_{10}$, and is, like cetene, isomeric with olefiant gas.

XXIII. Glyceryle. C_6H_7=Gl.

This is the hypothetical radical of glycerine, a basic compound which exists in all neutral fat oils combined with oily acids.

Hydrated Oxide of Glyceryle. $C_6H_7O_5+HO=GlO_5HO$.

Syn. *Glycerine*. To obtain it, olive oil is converted into plaster by long boiling with litharge and water. When the plaster is completely formed, the glycerine is found dissolved in the water. It is purified from lead by sulphuretted hydrogen, and is then concentrated in the vapour bath and finally in vacuo. When pure, it forms a viscid syrup, colourless or slightly yellow. It has a decided sweet taste, and its sp. gr. is 1·252. By the action of heat it is decomposed, yielding a peculiar volatile compound, *acroleine*, which attacks the eyes most powerfully. This substance has lately been studied by Redtenbacher: we shall give his results when treating of the action of heat on fat oils.

With sulphuric acid, glycerine forms an acid sulphate, $C_6H_7O_5,HO,2SO_3$; which forms double salts, analogous to the sulphovinates, the formula of which is, $MO,GlO_5,2SO_3$.

Having now briefly described the known or admitted organic radicals and their derivatives, we proceed to consider the organic acids whose composition is known, although we cannot speak with certainty of their constitution, their radicals being yet unknown.

ORGANIC ACIDS.

1. Citric Acid. $C_{12}H_5O_{11},3HO=\overline{Ci},3HO$.

This acid is found in many vegetable juices, especially those of sour fruits, as the lemon, lime, orange, red currant, &c. It is extracted by adding chalk to the acid juice, by which means an insoluble citrate of lime is formed. This is decomposed by diluted sulphuric acid with the aid of heat, and the solution, filtered from the sulphate of lime, gives on evaporation and cooling crystals of citric acid, consisting of $\overline{Ci}$, $2HO+aq$. A slight excess of sulphuric acid promotes the crystallization.

It forms large transparent crystals, very soluble in water, of a very strong and

agreeable acid taste. A diluted solution is soon decomposed, becoming mouldy. By spontaneous evaporation of a saturated solution, crystals may be obtained, which are $\overline{Ci}$,3HO+2 aq. At 212°, these lose the 2 eq. of water of crystallization. The other crystals, above mentioned, do not lose water at 212°, but melt at 256°; and when heated beyond 300°, both kinds are decomposed. Heated with oil of vitriol in excess, citric acid is decomposed, yielding

From 1 eq. citric acid . . .	$C_{12}H_8O_{14}$
2 eq. carbonic acid . . .	$C_2 \quad O_4$
2 eq. carbonic oxide . .	$C_2 \quad O_2$
2 eq. acetic acid . . .	$C_8 H_6 O_6$
2 eq. water . . .	H_2O_2
	$C_{12}H_8O_{14}$

In like manner, when fused with caustic potassa, citric acid is resolved into 2 eq. of acetic acid, 2 eq. oxalic acid, and 2 eq. water.

When citric acid is added to lime water, the liquid remains clear, but when heated becomes turbid, and deposits citrate of lime. This character serves to distinguish citric acid from most other vegetable acids.

SALTS OF CITRIC ACID.

Citric acid is tribasic, and forms three series of neutral salts, that is, of salts with 3 eq. of base, whether fixed base or basic water. It also forms basic salts, of the formula $\overline{Ci}$,3MO+MO or $\overline{Ci}$,3MO + MO+aq. These basic salts correspond in constitution to the two forms of crystallized acid.

When a dry citrate, with 3 eq. of fixed base, is decomposed by an alcoholic solution of hydrochloric acid, so that no more water is presented to the citric acid than the 3 eq. of basic water derived from the hydrogen of the hydrochloric acid and the oxygen of the base, there are formed, from 3 eq. dry citric acid, 2 eq. of the acid with 2 eq. of water of crystallization, and 3 eq. of the hydrated aconitic acid. $3(C_{12}H_5O_{11},3HO)=2(C_{12}H_5O_{11},3HO+aq.)+3(C_4HO_3,HO)$. This is the same change which takes place in citric acid when heated to a certain point, water being given off.

Citrate of Oxide of Ethyle, $\overline{Ci}$,3AeO, is an oily liquid of sp. gr. 1·142. By alkalies it is converted into citrates and alcohol.

Citrate of Potassa occurs in three forms. $\overline{Ci}$,3KO; $\overline{Ci}$, $\left\{\begin{matrix}2KO\\HO\end{matrix}\right.$ and $\overline{Ci}$ $\left\{\begin{matrix}KO.\\2HO\end{matrix}\right.$

All are very soluble and crystallize with difficulty.

Citrate of Soda also forms three salts. 1. $\overline{Ci}$,3NaO+11 aq. This salt forms large regular crystals. 2. $\overline{Ci}$,2NaO,HO; formed by adding to a solution of the preceding salt half as much citric as it already contains. It forms, by evaporation, needles of a very pleasant subacid taste. 3. $\overline{Ci}$,NaO,2HO. Formed by adding to a solution of No. 1, as much citric acid as it already contains. This salt does not crystallize in water, but forms a gummy mass. A saturated alcoholic solution, however, deposits crystalline grains. *Citrate of baryta* forms two varieties. 1. $\overline{Ci}$,3BaO+7 aq. which falls when citrate of soda is added to chloride of barium. 2. $2\overline{Ci}$ $\left\{\begin{matrix}5BaO\\HO\end{matrix}\right.$ +7 aq.=$\overline{Ci}$ $\left\{\begin{matrix}2BaO\\HO\end{matrix}\right.$ + $\overline{Ci}$,3BaO+7 aq. This is deposited on cooling, when a boiling solution of citrate of soda is added to a

boiling solution of chloride of barium and free citric acid. *Citrate of lime* also yields two salts. 1, neutral, $\overline{Ci}$,3CaO+4 aq. formed by mixing chloride of calcium and citrate of soda. It is insoluble. 2, basic: $\overline{Ci}$,3CaO + CaO + aq. formed when citric acid is heated with excess of lime water. The citrate of lime formed from lemon, or currant juice, by chalk, is an impure mixture of the basic and neutral salts. *Citrates of lead*, 1, $\overline{Ci}$,3PbO+aq. 2, $\overline{Ci}$,2PbO,HO+2 aq.: 3, basic: Ci,3PbO+3PbO: 4, also basic. $\overline{Ci}$,3PbO + PbO+aq. These are all sparingly soluble or insoluble, and are decomposed by washing. *Citrate of copper* is basic, $\overline{Ci}$,3CuO + CuO. *Citrate of silver* is a brilliant white, insoluble powder. $\overline{Ci}$,3AgO+aq. It loses its water under 80°. *Citrate of antimony and potassa* is a double salt, $\overline{Ci}$,Sb_2O_3 + $\overline{Ci}$,3KO+5 aq. It forms hard, brilliant, white prisms, which lose their water at 212°.

ACTION OF HEAT ON CITRIC ACID.

The first effect of heat on crystallized citric acid is to melt it, and the next, to expel the water of crystallization. The acid, if now dissolved, crystallizes unchanged. But if the heat be continued, there is given off gas and inflammable vapours, and the residue is no longer citric acid but hydrated aconitic acid.

	1 eq. crystallized citric acid	$C_{12}H_5 + O_{11}3HO + 2$ aq.
Yields, first,—	5 eq. of water . . .	$3HO + 2$ aq.
then—	1 eq. aconitic acid (hydrated)	$C_4 H_2O_4$
	4 eq. carbonic oxide . .	$C_4 O_4$
	1 eq. acetone . . .	$C_3 H_3 O$
	1 eq. carbonic acid . .	$C O_2$
		$C_{12}H_5O_{11} + 3HO + 2$ aq.

When the heat is increased, other products appear, particularly two new acids: but these are derived from aconitic acid. They are *itaconic* and *citraconic acids.*

Aconitic Acid. $C_4HO_3,HO = \overline{At}$

Syn. *Equisetic Acid.*—This acid occurs native in *aconitum napellus* and in *equisetum fluviatile.* It is formed by the action of heat on citric acid, as above. To obtain it, citric acid is heated till it ceases to give off inflammable vapours, and the residue, dissolved in alcohol, is treated with hydrochloric acid gas, which causes the formation of aconitic ether. The addition of water causes this to separate, and by caustic potassa it is converted into aconitate of potassa. From this aconitate of lead is prepared, and this salt, decomposed by sulphuretted hydrogen, yields the acid.

It forms indistinct crystals; and although the acid thus prepared has the same composition as that from aconite, and that from equisetum, yet each of the three varieties has some peculiarities. They may not, therefore, be identical, especially as two acids derived from malic acid, the maleic and paramaleic, or fumaric acids, have the same composition. The aconitic acid from citric acid, when heated, yields itaconic and citraconic acids: it is doubtful, at present, whether the other two varieties do so.

Aconitic acid, according to the present state of our knowledge, is monobasic, and the general formula of its salts is $\overline{At}$,MO. The aconitates are not important.

When aconitic acid (from citric acid) is heated to from 356° to 392°, it boils and yields a mixture of two acids; itaconic acid, which condenses in crystals, and citraconic acid, which appears as an oily liquid. When the distillation is very rapid, itaconic acid predominates; when it is slow, there is more citraconic acid. These two acids have both the formula $C_5H_2O_3,HO$.

Itaconic acid is readily purified by solution in hot water, as it crystallizes with great facility. It is soluble in water, alcohol, and ether. When heated it is resolved into water and anhydrous citraconic acid. It is a monobasic acid, and its formula is $C_5H_2O_3,HO = \overline{It},HO$. The formula of its salts is $\overline{It},MO$. It also forms acid salts, the formula of which is $2\ \overline{It},MO,HO$. The itaconates are not of special interest.

Citraconic acid is formed when the preceding acid is distilled, and then appears, in the anhydrous state, as a limpid oily liquid. It distils unaltered at 410°, and volatilizes slowly at much lower temperatures. It attracts moisture from the air, forming a crystalline hydrate, which, when heated, is again resolved into water and anhydrous acid. The formula of the anhydrous acid is $C_5H_2O_3 = \overline{Ct}$; that of the hydrate $\overline{Ct},HO$. It forms, like the preceding, both neutral and acid salts; and produces, with oxide of silver, a neutral salt with water of crystallization; an apparently anomalous case. The formation of these two acids takes place as follows:—3 eq. of aconitic acid, 3 ($C_4H_2O_4$) yield 2 eq. itaconic acid, 2 ($C_5H_2O_3,HO$), and 2 eq. carbonic acid, $2CO_2$. The itaconic acid, when formed, is partially resolved into water and anhydrous citraconic acid.

The three acids just described, aconitic, itaconic, and citraconic acids, require further investigation. It is probable that it will be found that they are not all monobasic. The existence of water of crystallization in the neutral citraconate of silver is a most unusual circumstance, and would seem to indicate that we do not yet know the constitution of the acid in that salt.

2. Tartaric Acid. $C_8H_4O_{10},2HO = \overline{T},2HO$.

This acid occurs in the juice of the grape as acid tartrate of potassa; also in many other plants. It is prepared from tartrate of lime, exactly as citric acid is from citrate of lime. Tartrate of lime is obtained by the action of chalk on acid tartrate of potash, or cream of tartar.

Tartaric acid crystallizes in large rhombic prisms, transparent and colourless. They are very soluble in water, and have a pleasant acid taste. When boiled with alcohol, tartaric acid forms acid tartrate of oxide of ethyle. A high temperature decomposes tartaric acid, giving rise to several new products.

An excess of potassa aided by heat, transforms it into acetate and oxalate of potassa. $C_8H_4O_{10},2HO = C_4H_3O_3,HO + 2\ (C_2O_3,HO)$. By peroxide of manganese and sulphuric acid it is converted into formic acid, carbonic acid, and other products. There is some relation between tartaric and formic acids: for if formic acid be FoO_3 ($Fo = C_2H$), tartaric acid is $2\ (Fo_2O_5)$.

Tartaric acid precipitates lime-water white, but an excess dissolves the precipitate. In solution of potassa, if the acid be added in excess, it causes a crystalline deposit of cream of tartar, which, where the potassa is in very minute proportion, is rendered more visible by the addition of alcohol.

It is a bibasic acid, and forms two series of salts: 1. Neutral $\overline{T},2MO$; 2. acid, $\overline{T},MO,HO$. It forms also two kinds of double salts: in one the 2 eq. of

fixed base are different protoxides, $\overline{T}, \left\{\begin{matrix} MO \\ mO \end{matrix}\right.$; in the other, one of the equivalents of fixed base is replaced by 1 eq. of a sesquioxide; $\overline{T}, \left\{\begin{matrix} MO \\ m_2O_3 \end{matrix}\right.$. This latter kind may be considered basic, since the sesquioxide, m_2O_3, usually neutralizes as much acid as 3 eq. of protoxide. Tartaric acid is remarkable for its tendency to form double salts.

Among the neutral tartrates are, *tartrate of ammonia* $\overline{T},2NH_4O + 2$ aq.; *tartrate of potassa*, or soluble tartar, $\overline{T},2KO$; *tartrate of soda*, $\overline{T},2NaO + 4$ aq.; *tartrate of lime*, $\overline{T},2CaO + 8$ aq., &c. &c.

Among the acid salts are, *acid tartrate of ethyle*, or tartrovinic acid $\overline{T},AeO,HO$—a crystallizable compound: acid tartrate of potassa, or tartar, $\overline{T},KO,HO$. This is the principal compound of tartaric acid. It exists in the juice of the grape, dissolved by the acid of the sugar present, and when that sugar is converted into alcohol, in which the tartar is insoluble, it is deposited on the sides of the fermenting casks. When purified it is quite white, and is called cream of tartar. It is much used in medicine as a safe and mild laxative. When calcined in a covered crucible it leaves a mixture of carbonate of potassa and charcoal, called black flux. Hence carbonate of potassa is called salt of tartar. Like all the tartrates, cream of tartar, when heated, gives off a very peculiar smell of burnt vegetable matter, peculiar to tartaric and racemic acids and their salts.

Among the very numerous double tartrates may be mentioned the *tartrate of potassa and ammonia*, $\overline{T},KO,NH_4O$: the *tartrate of potassa and oxide of ethyle*, $\overline{T}$, AeO,KO; *tartrate of potassa and boracic acid*, $\overline{T},KO,BO_3$; this is the soluble cream of tartar used as a laxative on the continent:—*tartrate of potassa and soda*, $\overline{T},KO,NaO + 10$ aq. This is the salt of Seignette or Rochelle salt. It crystallizes in very large transparent prisms, and is used as a mild laxative:—*tartrate of potassa and peroxide of iron*; $\overline{T},KO,Fe_2O_3$; this is the tartarized iron of the pharmacopœias:—*tartrate of potassa and antimony*, $\overline{T},KO,Sb_2O_3$. This is *tartar emetic*, one of the most valuable remedies. It must be considered as a basic salt; for Sb_2O_3, here substituted for HO or KO, in short for a protoxide, requires for its neutralization an additional equivalent of tartaric acid. It then yields the compound $2\,\overline{T} + \left\{\begin{matrix} KO \\ Sb_2O_3 \end{matrix}\right.$, which is neutral, since the bases contain 4 eq. of oxygen for 2 eq. of acid.

Tartar emetic is formed when 3 parts of oxide of antimony and 4 of cream of tartar are ground together, and made into a thin cream with water, which is heated to 158°, till a portion, tried separately, dissolves in 15 parts of cold water. When this is the case, 6 or 8 parts of water are added, and the whole boiled for half an hour. The liquid, filtered while hot, deposits, on cooling, crystals of tartar emetic. It forms white brilliant crystals which soon become opaque. It is soluble in 14 or 15 parts of cold water, and 2 parts of boiling water. The crystals are $\overline{T}$, KO, Sb_2O_3, + 2 aq.

When heated, the crystals first lose the 2 eq. of water of crystallization; and when the heat rises to 390°, 2 or more eq. of water are given off, without the acid being destroyed. The salt is then $C_8H_2O_{10} + \left\{\begin{matrix} HO \\ SbO \end{matrix}\right.$. That is to say, 2 eq. of oxygen, from the oxide of antimony, have been expelled along with 2 of hydrogen from the acid. It has been already shown that tartar emetic $C_{12}H_4O_{10}$

$+ \begin{cases} KO \\ Sb_2O_3 \end{cases}$ contains 2 eq. of oxygen in the bases, more than is required for a neutral salt, and it is apparently these 2 eq. of oxygen which are thus expelled as water. If we bear in mind that Sb_2O_3 is the equivalent of 3KO; or in other words, that Sb_3^2 is equivalent to K or to H, we can then see that tartar emetic heated to 390° is analogous in composition to neutral tartrate of potash.

Tartrate of potassa is	$C_8\ H_4\ O_{12} + K_2$
Tartar emetic, heated to 390° is, . .	$C_8 \begin{cases} H_2 \\ Sb_3^4 \end{cases} O_{12} + \begin{matrix} K \\ Sb_3^2 \end{matrix}$

In this point of view the 2Sb are divided, $\frac{4}{3}$Sb replacing hydrogen in the radical, and $\frac{2}{3}$Sb replacing potassium in the base.

The *neutral tartrate of potassa and antimony*, $2\overline{T}, \begin{cases} KO \\ Sb_2O_3 \end{cases} + 7$ aq. is always formed in the mother liquors of tartar emetic. It is also formed when tartar emetic is dissolved in tartaric acid.

Tartar emetic forms a double salt with cream of tartar, $\overline{T},KO,Sb_2O_3 + 3(\overline{T}, KO,HO)$. It crystallizes in scales.

ACTION OF HEAT ON TARTARIC ACID.

When crystallized tartaric acid is heated it melts, then loses $\frac{1}{4}$ of its water, leaving a new acid, tartralic acid; next it loses $\frac{1}{2}$ its water, and is converted into tartrelic acid; and finally it loses all its water and is converted into anhydrous tartaric acid. We may represent these changes as follows, doubling the formula of tartaric acid.

$C_{16}H_8O_{20} + 4HO =$ crystallized tartaric acid.
$C_{16}H_8O_{20} + 3HO =$ tartralic acid.
$C_{16}H_8O_{20} + 2HO =$ tartrelic acid.
$C_{16}H_8O_{20} =$ anhydrous tartaric acid.

In tartralic and tartrelic acids, the neutralizing power is diminished, in so far that tartralic acid neutralizes $\frac{1}{4}$th less base, and tartrelic acid $\frac{1}{2}$ less base than tartaric acid. Both of these acids, as well as the anhydrous acid, are, by long boiling with water, reconverted into tartaric acid. It would appear as if in the tartralic and tartrelic acids, an additional quantity of anhydrous acid has been added to the radical without affecting the neutralizing power, just as in phosphoric, pyrophosphoric, and metaphosphoric acids. If we represent the anhydrous acid by $C_4H_2O_5$, then we have

$2(C_4H_2O_5) + 2HO =$ crystallized acid.
$3(C_4H_2O_5) + 2HO =$ tartralic acid.
$4(C_4H_2O_5) + 2HO =$ tartrelic acid.

When tartaric acid, or rather anhydrous tartaric acid, is more strongly heated, it yields two pyrogenous acids, one liquid, the other crystallized. The former, $C_6H_3O_5,HO$, the latter, $C_5H_3O_3,HO$. In fact, 2 eq. of anhydrous tartaric acid contain the elements of 1 eq. of each of these new acids, 5 eq. of carbonic acid, and 2 eq. of water. The liquid acid is called pyroracemic acid, being obtained also from racemic acid: the solid acid may be called pyrotartaric acid.

Tartralic acid, $C_{12}H_6O_5,2HO$, is obtained by cautiously heating tartaric acid,

taking care not to cause it to become brown. It is combined with baryta, and the baryta separated from the soluble tartralate by diluted sulphuric acid. Tartralic acid forms a transparent mass, not crystalline, deliquescent and soluble in alcohol. It is converted into tartaric acid, slowly by cold water, rapidly by hot water. It appears to be bibasic, and most of its salts are soluble. By long contact with water, they are converted into tartrates and free tartaric acid.

Tartrelic acid, $C_{16}H_8O_{20},2HO$, is obtained by keeping the preceding acid long melted without raising the temperature. It is coloured brown, is deliquescent, and dissolves both in water and alcohol. Water rapidly changes it into tartralic and tartaric acids. Its salts are soluble, and undergo the same change as those of tartralic acid.

Anhydrous tartaric acid, $C_4H_2O_5$, is prepared by rapidly heating $\frac{1}{2}$ oz. of tartaric acid in a porcelain capsule. It swells up very much, gives off water, and is at last converted into a porous white mass. This is now heated for some time, in an oil-bath, to a temperature of 302°, then powdered and well-washed with cold water, and dried. It forms a white powder insoluble in water, alcohol, and ether. By the action of water and bases it is converted successively into tartrelic and tartaric acids.—*Pyroracemic acid; or liquid pyrotartaric acid*, $C_6H_3O_5$, $HO = \overline{pR},HO$, is one of the products of the distillation of tartaric and racemic acids. It is separated from the crystals which accompany it, combined with oxide of lead, and the well-washed pyrotartrate of lead decomposed by sulphuretted hydrogen. It is concentrated in vacuo, and forms a thick syrup nearly colourless, which cannot be distilled without partial decomposition. Its salts are not easily obtained in crystals, and when their solutions are heated, they lose the power of crystallizing. The general formula of the pyroracemates is $C_6H_3O_5$, MO. They are coloured dark-red by salts of protoxide of iron, and a crystal of sulphate of copper introduced into the solution of a pyroracemate causes a white precipitate. *Pyroracemate of oxide of ethyle* is a colourless liquid, of an aromatic smell, resembling that of *acorus*.

Pyrotartaric acid, $C_5H_3O_3,HO = \overline{pT},HO$, is formed along with the preceding acid in small quantity by the distillation of tartaric acid; it is obtained far more abundantly by the distillation of cream of tartar. The product of the distillation, which is liquid, is evaporated till it crystallizes, and the mother liquid, acted on by nitric acid to destroy the oily impurities, and again evaporated, yields an additional quantity. The crystals melt at 230° and volatilizes at from 284° to 300°. The salts of this acid are soluble, that of lead appears to be rather sparingly so. But the results of different experimenters on this subject are so discordant that we must wait for further researches.

3. Racemic Acid. $C_4H_2O_5,HO = \overline{R},HO$.

Syn. *Paratartaric acid*.—This remarkable acid, which has the same composition in 100 parts as tartaric acid, and very similar properties, is found along with tartaric acid in the grapes of certain districts. When both acids are present, the liquid obtained by boiling the tartrate and racemate of lime with diluted sulphuric acid deposits, on evaporation, racemic acid in hard crystalline crusts, before tartaric acid, which is more soluble, begins to crystallize. It may be distinguished from tartaric acid by not forming a double salt of potassa and soda.

The crystals of the racemic acid have a very sour taste, and are composed of $\overline{R},HO + aq$. At 212° they lose the 1 eq. of water of crystallization, and when

more strongly heated, yield the same products as tartaric acid. The solution of racemic acid forms a precipitate of racemate of lime when mixed with chloride of calcium, which serves to distinguish it from tartaric acid; but like tartaric acid, it causes a crystalline precipitate in the salts of potassa.

Racemic acid is monobasic, and for this reason does not, like tartaric acid, form double salts with two strong bases. It forms neutral salts, $\bar{R}$,MO, and acid salts, $\bar{R}$,MO + $\bar{R}$,HO. Thus the neutral racemate of potassa is $\bar{R}$,KO + 2 aq., and the acid racemate of potassa, analogous to cream of tartar, is $\bar{R}$,KO + $\bar{R}$, HO. These two salts, therefore, have precisely the same composition as the corresponding tartrates. The acid racemate of potassa, with oxide of antimony, yields a double salt analogous to tartar emetic, but of a different crystalline form. The relations of racemic acid to the oxides of ethyle and methyle are similar to those of tartaric acid. On the whole, racemic acid is interesting, from its presenting one of the best marked cases of isomerism, namely, with tartaric acid. In this case, not only is the composition the same, but the general properties, and most of the special ones, are identical. In fact, were it not that we must admit tartaric acid to be bibasic, we should find it difficult to account for the differences which exist between the two acids. We have here a very near approach to the occurrence of different properties with the same composition, and even the same arrangement. The two acid salts of potassa, for example, are $C_8H_4O_{10}\left\{\begin{matrix}KO\\HO\end{matrix}\right.$ for the bitartrate: and $C_4H_2O_5$,KO + $C_4H_2O_5$,HO for the bicarcemate. If we represent the latter as follows:

$$\begin{matrix}C_4H_2O_5\left\{\begin{matrix}KO\\HO\end{matrix}\right.\\C_4H_2O_5\end{matrix}$$

, we see how very nearly alike they are, even on the view we have adopted of the one acid being bibasic, and the other monobasic; and we must bear in mind that these two salts are strikingly similar in properties. The same remarks apply to the crystallized acids and to the double salts with antimony, although in the case of the two acids, we have evidence of one point of difference in the arrangement. Tartaric acid is $C_8H_4O_{10}$,2HO, while racemic acid is $C_4H_2O_5$,HO + aq., and loses the water of crystallization at 212°.

4. Malic Acid. $C_8H_4O_8$,2HO = $\bar{M}$,2HO.

This acid is of very frequent occurrence in acid fruits, as in the apple, and especially in the unripe berries of *Sorbus aucuparia*, or mountain ash. The best method of extracting it is to express the berries when they begin to turn red, and to add to the strained liquid a thin milk of lime so as not entirely to neutralize the acid. On heating, neutral malate of lime is deposited and removed by a skimmer. To the mother liquid more milk of lime is added cautiously, so as to produce an additional quantity of salt. The malate of lime is washed with cold water, and dissolved with the aid of heat in a mixture of 1 part nitric acid, and 10 of water. On cooling, acid malate of lime is deposited in regular crystals, which are almost always colourless. They are rendered quite pure by a solution in hot water and crystallization. From this salt, by the addition of acetate of lead, malate of lead is precipitated as a curdy white solid, which, if left in the liquid, changes into shining silky crystals. These, which are pure malate of lead, being decomposed by sulphuretted hydrogen, yield the acid, which when evaporated to a syrup forms a granular crystalline mass, deliquescent in the air, of a strong but agreeable acid taste. When the crystallized acid is kept for

some time at a heat of 280° it melts, and the melted acid is gradually filled with crystals. Cold water removes the unchanged malic acid, which if again heated undergoes the same change, till at length all the malic acid is converted into these crystals, which are *paramaleic* or *fumaric acid.*

If malic acid be distilled by a sharp heat, a great part passes over in the form of a volatile crystallizable acid, the *maleic acid.* At a certain period of the distillation, if the retort be removed from the fire, the boiling residue having become turbid and thick, it suddenly becomes quite solid, and is found to consist of fumaric acid.

Malic acid is bibasic; in proof of which, it forms acid salts with lime, magnesia, and oxide of zinc, which monobasic acids never do. There are two series of malates: 1. neutral, $\overline{M}$,2MO; 2. acid $\overline{M}$,MO,HO. Most of the malates are soluble in water, but not in alcohol. Lime water neutralized by malic acid, continues clear whether cold or hot, which serves to distinguish it from tartaric, citric, racemic and oxalic acids.

Acid malate of ammonia, $\overline{M}$,NH_4HO, is best formed by neutralizing with ammonia one of two equal portions of malic acid (as prepared from the crude malate of lead by diluted sulphuric acid), and then adding the other portion and evaporating to a syrup. On cooling, large and very regular crystals of the acid salt are deposited, which are easily decolorized by animal charcoal. This is an excellent method of purifying malic acid, when it is much contaminated with other substances. *Acid malate of lime* $\overline{M}$,CaO,HO + 6 aq., is prepared as above described. It forms very regular and pure crystals, soluble in their own weight of boiling water, but requiring 20 parts of cold water. When malic acid is saturated with chalk, an acid liquid is obtained, which, when boiled, deposits the *neutral* malate of lime, $\overline{M}$,2CaO. The *malate of lead* $\overline{M}$,2PbO + 6 aq. is remarkable for changing when left in the liquid in which it has been formed, from a curdy white precipitate to a mass of fine silky needles. In hot water this salt melts into a mass like pitch in consistence. *Acid malate of copper*, $\overline{M}$, CuO,HO + 2 aq. forms splendid large crystals of a fine cobalt blue colour. There appears to be a *basic malate of copper*, $\overline{M}$,2CuO + CuO + 6 aq., which forms green crystals. *Malate of silver*, $\overline{M}$,2AgO is a white powder, soluble in boiling water. The other malates are analogous to these, and possess little interest.

Maleic Acid, $C_8H_2O_6$,2HO = $\overline{Ma}$,2HO, is prepared as above mentioned, by distilling malic acid. This acid is bibasic, but has the same composition, in 100 parts, as aconitic, or equisetic acid. It forms crystals, which are very soluble in water, alcohol, and ether. When heated sharply, it yields water, and a white volatile solid, melting at 134°, and boiling at 350°, which appears to be anhydrous maleic acid. When the hydrated acid is kept melted for some time, it is changed, exactly as malic acid is, into fumaric acid. Hydrated maleic acid has precisely the same composition as anhydrous malic acid, which at once explains its formation.

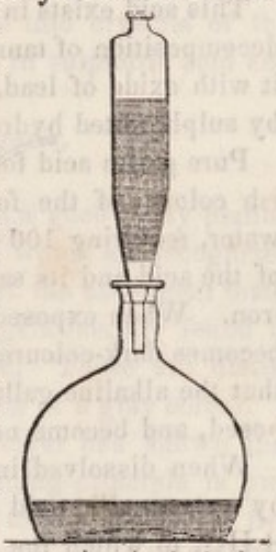
The general formula of its salts is $\overline{Ma}$,2MO for the neutral, and $\overline{Ma}$,MO,HO for the acid maleates. It forms an *acid maleate of silver*, $\overline{Ma}$,AgO,HO.

Fumaric or Paramaleic Acid, C_4HO_3,HO = $\overline{Fu}$,HO, is formed as above stated, by heating either malic or maleic acids to their melting-point, and keeping them melted for a long time. It occurs in *fumaria officinalis*, and in Iceland moss. It forms micaceous scales requiring 200 parts of cold water for solution. It is soluble in alcohol.

It is a monobasic acid, but has the same composition in 100 parts as maleic acid, which at once explains its formation from malic, or from maleic acid. Its salts are sparingly soluble. The *fumarate of oxide of ethyle* is a heavy oily liquid of an aromatic smell of fruits. When this ether, $\overline{Fu}$,AeO, is acted on by aqua ammoniæ, it forms a white insoluble powder, which is *fumaramide* $C_4HO_2 + NH_2$. This body has all the characters of a compound amide.

5. Tannic Acid. $C_{18}H_5O_9,3HO = \overline{Qt},3HO$.

Syn. *Quercitannic Acid. Tannine.* This acid occurs chiefly in oak-bark and in nut-galls, an excrescence on oak-leaves caused by the attacks of an insect which apparently pierces the leaf in order to deposit its eggs,



To obtain it, coarsely-powdered nut-galls are acted on, in an apparatus of displacement by ether, free from alcohol, but saturated with water. When the ether, after being left some time in contact with the powder, is allowed to drop into the lower vessel, it separates into two strata of liquid, the lower of which is a pure solution of tannic acid in water, which is drawn off and dried up after being washed with ether. The dry mass is redissolved in water, and again dried up in vacuo.

Tannic acid thus obtained is nearly white, and not at all crystalline. It is very soluble in water, and has a most astringent taste without bitterness. It is soluble in weak alcohol, but hardly soluble in ether. The aqueous solution, if exposed to the air, absorbs oxygen, produces an equal volume of carbonic acid, and is converted into *gallic* and *ellagic acids.* The addition of the mineral acids to a solution of tannic acid, causes a precipitate, which is composed of tannic acid and the acid employed (sulphuric, &c.), and which is very soluble in pure water. The precipitate formed by sulphuric acid, in a hot solution, dissolves in hot diluted sulphuric acid, and when this solution has been boiled a short time, it contains no tannic acid, the whole being converted into gallic acid.

Tannic acid combines with animal gelatine, forming an insoluble curdy precipitate. A piece of prepared skin, introduced into a solution of tannic acid, absorbs the acid, and is converted into leather. When heated, tannic acid is converted into metagallic and pyrogallic acids.

Tannic acid and its salts strike a deep blue, nearly black colour with persalts of iron; and it likewise causes a precipitate in the solutions of most of the vegetable bases.

It is a tribasic acid, and the general formula for the neutral tannates is $\overline{Qt}$, 3MO in the case of protoxides, and 3 $\overline{Qt}$, M_2O_3, in the case of sesquioxides. These salts, however, have been but little studied.

The conversion of tannic acid into gallic acid is not fully understood. In some circumstances, it appears to depend on the absorption of oxygen; and in fact, 1 eq. tannic acid, *plus* 8 eq. oxygen, contains the elements of 2 eq. gallic acid, 4 eq. carbonic acid, and 2 eq. water. But when the conversion is produced by sulphuric acid, no other substance is formed with the gallic acid, except a colouring matter, which appears not to be essential. There is some probability that gallic acid exists ready formed in tannic acid, and if we subtract

2 eq. anhydrous gallic acid, $2(C_7H_2O_4)$ from 1 eq. of hydrated tannic acid, $C_{18}H_8O_{12}$, there is left $C_4H_4O_4$, which is the composition of hydrated acetic acid; or, tripled, that of dry grape sugar. As tannic acid, or at least the powder of nut-galls, if moistened, is said to be susceptible of the vinous fermentation, it is not impossible that tannic acid may contain gallic acid, *plus* sugar, if not gallic acid, *plus* acetic acid. Tannic acid is converted into gallic acid as rapidly by the action of an excess of alkali as by that of acid; but the whole subject requires investigation.

6. Gallic Acid. $C_7HO_3,2HO=\bar{G},2HO$.

This acid exists in the seeds of mango, and is formed as above described by the decomposition of tannic acid. It is purified from colouring matter by combining it with oxide of lead, and decomposing the gallate of lead, suspended in water, by sulphuretted hydrogen; the sulphuret of lead acts as a decolorizing agent.

Pure gallic acid forms beautiful prisms of a silky lustre, and a slight yellowish colour, of the formula $C_7HO_3,2HO+aq$. It is sparingly soluble in cold water, requiring 100 parts, but dissolves in 3 parts of boiling water. Solutions of the acid and its salts, strike a black colour with persalts and proto-persalts of iron. When exposed to the air, the solution of gallic acid absorbs oxygen, and becomes dark-coloured; this change is very rapid in the presence of alkalies, so that the alkaline gallates, especially if the alkali be in excess, are rapidly decomposed, and become nearly black.

When dissolved in hot oil of vitriol, and precipitated from the cold solution by water, gallic acid is obtained in a peculiar form, as $C_7H_2O_4$, perhaps C_7HO_3+HO, in which the crystals have lost 2 eq. of water, 1 basic or hydratic, the other, water of crystallization. This peculiar gallic acid is a reddish-brown crystalline powder, which might be used in dyeing, as it yields colours on cloth like those from madder. When heated it forms fine red prisms, which call to mind alizarine, the crystalline matter found in madder.

By the action of heat, crystallized gallic acid yields, like tannic acid, pyrogallic and metagallic acids.

The gallates are little known. They are very easily decomposed by the action of the air. The *acid gallate of ammonia* is $\bar{G},NH_4O+\bar{G},2HO$. Acid gallate of lead has a similar composition. There is a bibasic gallate of lead, $\bar{G},2PbO$.

When tannic, or gallic acid, is heated by a sharp fire, carbonic acid, water, and *pyrogallic acid* distil over, while a dark solid remains in the retort, which is *metagallic acid.*

Pyrogallic Acid, C_2HO? $C_6H_3O_3$? or $C_8H_4O_4$? forms shining scales of a bitter and astringent taste; fusible at 240°, volatile at 410°. It is converted by a stronger heat into metagallic acid. It is formed from gallic acid, $C_7H_3O_5$, by the loss of 1 eq. carbonic acid. If acid at all, it is a very feeble acid, and nothing is known of its salts.

Metagallic Acid, $C_{12}H_3O_3$? $C_6H_2O_2$? is produced as above mentioned from tannic, gallic, and pyrogallic acids. It is a black powder, insoluble in water, soluble in alkalies. Of its salts little is known. It differs from gallic acid only by the elements of carbonic acid; $2(C_7H_2O_4)=2CO_2+C_{12}H_4O_4$. From pyrogallic acid it only differs by the elements of water.

Tannic acid contains the elements of gallic and pyrogallic acids. $3(C_{18}H_8O_{12})=6(C_7H_3O_5)+2(C_6H_3O_3)$; and since either gallic or pyrogallic acid may

produce metagallic acid, it is obvious that there is a close connection among these four compounds. The precise nature of this connection future experiments must ascertain.

When an infusion of nut-galls has been so long exposed to the air, that all the tannic acid has disappeared, the gallic acid is found mixed with an insoluble, or sparingly soluble powder, which is a new acid, *ellagic acid*. Its composition is $C_7H_3O_5$, and when dried at 240° $C_7H_2O_4$; so that it is isomeric with gallic acid, and with the modified acid produced by the action of oil of vitriol. It has not been much studied, and we do not know its actual atomic weight. When heated, it yields greenish-yellow vapours, which condense into crystals of the same colour, insoluble in water, alcohol, or ether; soluble in sulphuric acid and in alkalies.

This acid is said to occur in the root of *Tormentilla vulgaris*.

Tannic acid, and the substances derived from it, occur in a good many plants, besides those of the genus *quercus*; the infusions of all of which are recognized by their striking a bluish-black with persalts of iron. But the astringent taste, and the property of tanning, or combining with animal gelatine, are found in many plants, such as cinchona, kino, catechu, pinus, &c. These are distinguished by giving, with persalts of iron, either a dark green or a gray colour. It has not been proved that they contain tannic acid, but Geiger has shown that these different colours may occur even when the same tanning principle is present, and that the green is owing, at all events frequently, to the presence of free acid, while the addition of chalk, in some cases, changes the green to the characteristic bluish-black due to tannic acid. There are, however, some reasons for admitting more than one tanning or astringent principle. The whole subject requires investigation.

Catechu. Mimotannic Acid.

When catechu, the dried extract of *mimosa catechu*, is acted on by cold water, it yields a soluble matter very similar to tannic acid, if not identical with it when pure. It is, however, contaminated by some compound which causes it to redden when exposed to air. It does not appear to yield the same products when heated, as tannic acid does; but this is uncertain, and may be caused by the presence of impurities. Berzelius proposes to call this tannic acid *mimotannic acid*, from *mimosa*, to distinguish it from the tannic acid of galls, which he calls *quercitannic acid* from *quercus*.

The portion of catechu insoluble in cold water contains a peculiar compound, called *catechine* or tannigenic acid. It is soluble in hot water, and when pure forms a white silky crystalline powder, which is said to be composed of $C_{15}H_6O_6$. When heated it is said to be transformed into (mimo?) tannic acid. By the action of caustic potassa it yields a black acid, *japonic acid*, $C_{12}H_4O_4$,HO? Carbonate of potassa converts it into a red acid, *rubinic acid*, $C_{18}H_6O_9$(?) in the anhydrous state. The hydrated acid is said to have the same composition as japonic acid, possibly therefore $C_{18}H_6O_6$? But as the japonic acid, on the same authority, Svanberg, in combining with silver forms a salt $C_{24}H_8O_8$,AgO, in which 2 eq. of the acid have lost 2 eq. of water and gained only 1 eq. oxide of silver, it is evident that our knowledge of these compounds is very imperfect.

7. Meconic Acid. $C_{14}HO_{11},3HO=\overline{Me},3HO$.

A tribasic acid, found only in opium, the dried juice of *papaver somniferum*. To prepare it, the crude meconate of lime, obtained in the manufacture of muriate of morphia is mixed with 30 parts of boiling water, and 3 parts of strong hydrochloric acid added to the mixture, which must be removed from the fire, and not boiled after the acid has been added. On cooling, acid meconate of lime is deposited in shining crystals, which are collected on a cloth filter, squeezed, and treated a second time with the same quantities of acid and hot water. The strained acid liquid contains a large but variable proportion of sulphate of lime, always present, sometimes even to the extent of $\frac{1}{2}$ or $\frac{3}{4}$ in the crude meconate of lime. Hence the advantage of using so much hydrochloric acid, which also renders the meconic acid less soluble. This time the crystals are meconic acid, still much coloured. They are collected and squeezed as before, and to make sure that all lime is removed, a third time dissolved in 20 parts of hot water and 2 of hydrochloric acid. The addition of the acid not only removes the last traces of lime, but causes the meconic acid to crystallize almost entirely out of the liquid, it being nearly insoluble in diluted acid. The crystals, washed with a little cold water, and dried at the ordinary temperature, are now pure from everything but colouring matter, and when heated to redness leave no residue.

To get rid of the colour, the crystals are now mixed with warm water, and caustic potassa gradually added, so as nearly but not quite to neutralize the acid. As soon as the point of neutralization is reached, the reddish colour changes to green, and so much potassa must be added that any further quantity would produce the green colour. The whole is then heated in the water bath, till all is dissolved, hot water being added, if necessary. (Were the potassa now in excess, the whole acid would be decomposed into oxalic and carbonic acids.) On cooling, the meconate of potassa, $\overline{Me}\left\{\begin{matrix}2KO\\HO\end{matrix}\right.$ crystallizes, forming a semisolid mass, which is to be squeezed out. The colour is carried off for the most part in the mother liquor, which is very dark, and the squeezed salt, after a second, or if necessary a third, solution in hot water, crystallization, and squeezing, is snow white. This purified meconate of potassa is then acted on by pure hydrochloric acid, exactly as recommended for the meconate of lime, and after the third operation yields perfectly pure and white meconic acid in beautiful silvery scales, which, to remove any traces of the acid mother liquid adhering to them, may be once more dissolved in the smallest possible quantity of hot water, avoiding a heat of 212°, which decomposes the acid; the pure acid is deposited on cooling, as $\overline{Me},3HO+6$ aq.

Meconic acid, when gently heated, loses 6 eq. of water of crystallization. It is soluble in water and in alcohol. When boiled, its solution becomes coloured, producing comenic acid, carbonic acid, and a dark brown colouring matter. If boiled with hydrochloric acid, it is resolved into comenic acid and carbonic acid, without the production of colouring matter. When the dry acid is heated to 250°, the same change takes place. When heated with excess of aqua potassæ, meconic acid is entirely decomposed into oxalic acid, carbonic acid, and a dark colouring matter. Its distinguishing character is that of causiug, in persalts of iron, a deep blood-red colour, but no precipitate.

It forms three series of salts, like other tribasic acids. Thus there are three meco-

nates of potassa: 1, acid, $\overline{Me}$, $\left\{\begin{matrix}KO\\2HO\end{matrix}\right.$; 2. neutral, above mentioned, $\overline{Me}$ $\left\{\begin{matrix}2KO\\HO\end{matrix}\right.$ aq. Both of these crystallize. 3. tribasic, $\overline{Me}3KO$. This is yellow, and does not crystallize. There are also three meconates of soda; two of lime, acid and neutral or bibasic, and two of silver, bibasic $\overline{Me},2AgO,HO$, and tribasic $\overline{Me}$ 3 AgO. The meconate of peroxide of iron is very soluble, of an intense blood-red colour, but as it cannot be obtained pure or crystallized, its composition is still unknown.

8. Comenic Acid. $C_{12}H_2O_8,2HO=\overline{Co}2HO$.

This acid is formed as above described, from meconic acid by the action of heat, or of heat and an acid combined. 1 eq. dried meconic acid, $K_{14}HO_{11}+3HO = C_{14}H_4O_{14}$, yields 1 eq. comenic acid, $C_{12}H_2O_8,2HO$, and 2 eq. carbonic acid, $2CO_2$. The acid is readily obtained by boiling meconate of lime with an excess of diluted hydrochloric acid. It is deposited on cooling in coloured crystals, which may be decolorized by recrystallization with the aid of animal charcoal. The pure acid has a slight yellow tinge, and is very sparingly soluble in cold water. When heated, it is resolved into carbonic acid, *pyromeconic acid*, and a small quantity of a third substance, *paramcomenic acid*, which, in some few points, differs from comenic acid, but has the same composition, and in many points is so similar that it may possibly turn out to be essentially the same.

Comenic acid forms two series of salts, with 1 and 2 eq. of fixed base respectively. With persalts of iron it forms a deep red solution which deposits black crystals, of unknown composition.

Pyromeconic acid, $C_{10}H_3O_5,HO$, is obtained as a crystalline sublimate by heating meconic or comenic acids. In fact 1 eq. comenic acid, $C_{12}H_4O_{10}$, contains the elements of 1 eq. pyromeconic acid, $C_{10}H_4O_6$, and 2 eq. carbonic acid, $2CO_2$. It forms very soluble four-sided prisms, rather styptic to the taste; the solution of which forms with persalts of iron a crystalline salt of a fine red colour, the powder of which is like vermilion. This salt is $Fe_2O_3+3C_{10}H_3O_5$. Pyromeconic acid is so feeble an acid, that we can hardly class it with acids. It has more analogy with such bodies as acetone, derived from acetic acid, as pyromeconic acid is from meconic or comenic acid. It has the same composition as pyromucic acid.

9. Kinic Acid. $C_7H_4O_4,2HO$? or $C_{14}H_{11},O_{11},HO$?

This very remarkable acid occurs in cinchona bark. It is obtained in the manufacture of sulphate of quinine, in the form of kinate of lime, from which the lime is easily separated by means of oxalic acid. The liquid filtered from the oxalate of lime yields, on evaporation, the kinic acid in crystals. The lime may also be removed by sulphuric acid, and any adhering sulphate of lime separated by alcohol.

The salts of kinic acid are somewhat anomalous. Thus there is a salt of lead, $C_7H_4O_4 2PbO$, and a salt of copper, $C_7H_4O_4,CuO,HO$, while the crystals of kinic acid are $C_7H_6O_6$. All this would lead to the conclusion that the acid was a bibasic one, $C_7H_4O_4,2HO$. But the kinate of lime, and the kinate of silver, both quite neutral salts, are $C_{14}H_{11}O_{11},CaO$, and $C_{14}H_{11}O_{11},AgO$, as if the acid were monobasic, $C_{14}H_{11}O_{11},HO = C_{14}H_{12}O_{12}$. If we assume the acid to be quadribasic, we can then bring all the above salts into one series.

Thus,=Kinic acid would be . .	$C_{14}H_8O_8,4HO$
Kinate of lead . . .	$C_{14}H_8O_8,4PbO$
Kinate of copper . .	$C_{14}H_8O_8, \begin{cases} 2CuO \\ 2HO \end{cases}$
Kinate of lime . . .	$C_{14}H_8O_8, \begin{cases} CaO \\ 3HO \end{cases} + 10$ aq.
Kinate of silver . . .	$C_{14}H_8O_8, \begin{cases} HgO \\ 3HO \end{cases}$

But the objection to this view is that, if this be the true constitution of the acid, the salts of lime and silver ought to be very acid instead of being quite neutral.

PRODUCTS OF THE DECOMPOSITION OF KINIC ACID.

When kinic acid or kinate of lime is distilled with diluted sulphuric acid and peroxide of manganese, there is obtained a new compound called *kinone*, as a sublimate of fine golden yellow crystals, soluble in water, and very volatile, having a pungent smell in the state of vapour. Their composition is $C_{25}H_8O_8$. When acted on by reducing agents, it takes up 2 and 4 eq. of hydrogen, forming two new compounds, green and white hydrokinone. The *green hydrokinone*, $C_{25}H_{10}O_8$, is one of the most beautiful compounds known to chemists, forming long prisms of the most brilliant gold-green metallic lustre, surpassing those of murexide in beauty. It is best formed by adding a few drops of sulphurous acid to a solution of kinone. When an excess of sulphurous acid is used, the *white hydrokinone*, $C_{25}H_{12}O_8$, is formed, which crystallizes in six-sided prisms. When acted on by oxidizing agents, the solution of white hydrokinone becomes dark-red, nearly black, and almost immediately deposits the splendid crystals of the green compound. The latter is also formed by simply mixing solutions of kinone and white hydrokinone, being intermediate in composition between those bodies. Wöhler, to whom we are indebted for most of our knowledge in regard to these very curious compounds, has described a series of bodies obtained from the above by the action of hydrochloric acid, chlorine, and sulphuretted hydrogen. The following tabular view contains the names and composition of these substances, as far as we yet know them.

Kinone	C_{25}	H_8	O_8
Green hydrokinone . . .	C_{25}	H_{10}	O_8
White hydrokinone . .	C_{25}	H_{12}	O_8
Chlorohydrokinone . . .	C_{25}	$\begin{cases} H_{10} \\ Cl_2 \end{cases}$	O_8
Chlorokinone . . .	C_{25}	$\begin{cases} Cl_2 \\ H_6 \end{cases}$	O_8
Brown sulphohydrokinone . .	C_{25}	H_{11}	O_7S_4
Yellow ditto . . .	C_{25}	H_{12}	O_7S_5
Brown chlorosulphokinone . .	C_{25}	H_8	ClO_8S_4?
Orange ditto . . .	C_{25}	H_6	ClO_8S_4?

It will be observed, that in all these formulæ the carbon remains unaltered, and that several are instances of pure substitution, as $C_{25}H_8O_8$ compared with $C_{25}\begin{cases} H_6 \\ Cl_2 \end{cases}O_8$ and $C_{25}H_{12}O_8$, compared with $C_{25}\begin{cases} H_{10} \\ Cl_2 \end{cases}O_8$. We can also see the

relation of the sulphohydrokinones to kinone if we express them as follows—

$C_{25}H_8\left\{\begin{matrix}O\\S\end{matrix}\right.^7+3HS$; and $C_{25}H_8\left\{\begin{matrix}O\\S\end{matrix}\right.^7+4HS$.

We now come to a class of acids of very distinct and peculiar characters; those, namely, which occur as the chief constituents of fat oils and fats, vegetable or animal. Of these oily acids there are two kinds: 1. those which are volatile, and usually somewhat soluble in water; 2. those which have more the character of the oils and fats from which they are derived, and can seldom be distilled without decomposition. We shall begin with the volatile oily acids.

10. Butyric Acid. $C_8H_7O_3,HO$.

This acid exists in small proportion in butter, in the form of a neutral *butyrate of glycerine* or *butyrine*, to which the butter owes its peculiar and agreeable flavour. When butter is saponified by potassa, and the solution of the soap is decomposed by tartaric acid, the oleic and margaric acids are separated as an oily stratum, while three or four volatile acids are dissolved in the water. These are butyric, caproic, capric and caprylic acids. The butyric acid may be extracted from the mixture; but it is far better obtained by the fermentation of sugar. When sugar, either cane, grape or milk sugar, is mixed with cheese, water, and chalk, and kept in a warm place, lactic acid is at first formed, which combines with the lime. But if the fermentation be continued at a pretty high temperature, 90° to 100° for example, the lactate of lime disappears, and is at last replaced by butyrate of lime. This salt is now distilled with diluted hydrochloric acid, and the distilled liquid treated with chloride of calcium, when it divides into two strata. The lighter is butyric acid, still containing water. It is rectified until the boiling point rises to 318°. The previous portions contain water; what now passes is pure.

It is a clear, colourless, mobile liquid, of an odour resembling that of acetic acid and that of butter. An intense cold solidifies it. It is very acid and corrosive. Its sp. gr. is 0·963. It dissolves fats and fat oils.

Chlorine decomposes butyric acid, producing by substitution two acids, $C_8\left\{\begin{matrix}H_5\\Cl_2\end{matrix}\right.O_3,HO$; and $C_8\left\{\begin{matrix}H_3\\Cl_4\end{matrix}\right.O_3,HO$. The latter crystallizes; and both form volatile fragrant compounds with oxide of ethyle.

Butyrate of lime is remarkable as being very soluble in cold water, but separating from the liquid in transparent prisms when it is boiled. *Butyrate of baryta*, when placed on the surface of water, exhibits the same motions as camphor. *Butyrate of oxide of ethyle* or butyric ether, $AeO,C_8H_7O_3$, is formed with singular facility if a mixture of alcohol and butyric acid is distilled with the addition of a little sulphuric acid. It is a very mobile liquid of an odour somewhat similar to that of pineapples. It is very soluble in alcohol. This ether is employed to flavour spirits: and there is reason to believe that the peculiar flavour of rum depends on the presence of a little butyric ether. *Butyrate of oxide of methyle* is quite analogous. *Butyrate of oxide of glyceryle* or *Butyrine* exists in butter, and is supposed to be capable of being formed artificially, by warming a mixture of butyric acid, glycerine and sulphuric acid. If the oil thus formed is really butyrine, it will be the first example of a compound of glycerine formed or reproduced artificially.

Butyramide, $C_8H_7O_2+NH_2$ is formed when liquid ammonia acts on butyric

ether. $AeO,C_8H_7O_3 + NH_3 = AeO,HO + C_8H_7O_2,NH_2$. It crystallizes in pearly scales.

Butyrone, C_7H_7O, analogous to acetone, is formed along with carbonate of lime, when butyrate of lime is distilled. $C_8H_7O_3,CaO = C_7H_7O + CaO,CO_2$. By the action of nitric acid, butyrone is converted into two new compounds; one, an ethereal fragrant liquid, lighter than water, the composition of which is not yet known: the other, an oily liquid, heavier than water, of an aromatic smell and a sweet taste, which is an acid, *nitrobutyric or butyronitric acid.* It is formed by substitution of NO_4 for H; $C_7 \left\{ \begin{matrix} H_6 \\ NO_4 \end{matrix} \right. O,2HO$ from C_7H_7O. It forms crystallizable salts, and is bibasic, yielding two salts with oxide of silver, with 1 and 2 eq. of that oxide respectively.

By distillation with perchloride of phosphorus, butyrone is converted into an ethereal liquid, chlorobutyrene, the composition of which is $C_{14}H_{13}Cl$.

The caproic, capric and caprylic acids found in butter, are very analogous to butyric acid, but are not yet so well known. *Caproic acid* is $C_{12}H_{11}O_3,HO$. Its odour is like that of sweat. *Caproate of oxide of ethyle* has an odour somewhat analogous to that of butter. *Capric acid* is $C_{20}H_{19}O_3,HO$. It is very analogous to the preceding, but its odour is more like that of the goat. *Caprylic acid* is $C_{16}H_{15}O_3,HO$, and it is very analogous to the others.

It occasionally happens that butter, instead of yielding a mixture of volatile oily acids, of which butyric and caproic acid constitute the principal part, gives a mixture devoid of these acids, but containing in their place another acid, vaccinic acid, which is easily transformed into the other two. There can be no doubt that it contains the elements of butyric and caproic acids, $C_8H_7O_3,HO + C_{12}H_{11}O_3,HO = C_{20}H_{20}O_8$ or possibly $C_{20}H_{19}O_7 = C_{20}H_{18}O_6,HO$. In the latter case, it would require 1 eq. of water to yield the other acids. As, however, the solution remains neutral when vaccinic acid passes into caproic and butyric acids, it is most probably bibasic, $C_{20}H_{18}O_6,2HO$, and is, in fact, the sum of the other two. The cause of its occurrence is unknown.

Hircic Acid, the composition of which is unknown, is obtained from the fat of the goat, just as the preceding acids are from butter. It has an acid smell of goats, but is otherwise little known.

Phocenic Acid, $C_{10}H_7O_3,HO$, is a volatile acid occurring in the blubber of the dolphin, and in the berries of *viburnum opulus*. It is extracted like the acids of butter, and is a liquid of a strong smell like that of rancid butter. It forms crystallizable salts with bases. It may possibly be the same as valerianic acid.

Cevadic Acid is a crystalline volatile acid, obtained from the seeds of *veratrum sabadilla*: composition unknown.

Veratric Acid is contained in the same seeds. It is solid, crystallizable, and volatile. Its formula is $C_{18}H_9O_7,HO$. It forms a crystalline ether with oxide of ethyle; $AeO,C_{18}H_9O_7$.

Crotonic Acid is another solid volatile acid, found in the seeds of *croton tiglium*. It has a pungent, acrid taste, and a nauseous smell. It forms crystallizable salts.

11. Camphoric Acid. $C_{10}H_7O_3,HO = \overline{Ca},Ho$.

This acid is formed by the action of nitric acid on camphor. It forms crystalline scales, sparingly soluble in cold water, very soluble in alcohol and ether, fusible at 158°. These are the hydrated acid, which, if distilled, is resolved

into water and anhydrous camphoric acid. The camphorates are not peculiarly interesting. With oxide of ethyle, camphoric acid forms two compounds:—1. neutral, or *camphoric ether*, $\overline{Ca}$,AeO, an oily liquid, of a bitter taste and nauseous smell. 2. acid, $2\overline{Ca}$,AeO,Ho, also called camphovinic acid, as it forms double salts, 2 $\overline{Ca}$,AeO,MO. When chlorine acts on camphoric ether, $\overline{Ca}$,C_4H_5O, it gives rise to the compound $\overline{Ca}$,$C_4\left\{\begin{matrix}H_3\\Cl_2\end{matrix}\right.O$.

Anhydrous Camphoric Acid, $C_{10}H_7O_3$, forms, with bases, salts different from those formed by the hydrated acid. It is probable that it still retains some water replaceable by bases, being perhaps $C_{10}H_6O_2$,HO; or it may differ from ordinary camphoric acid as metaphosphoric acid does from common phosphoric acid. It is solid, crystalline, and volatile, and with dry ammonia forms a compound from which potassa disengages no ammonia: with liquid ammonia it yields a salt different from camphorate of ammonia. Its action on oxide of ethyle has not been studied; but the subject deserves investigation.

It is worthy of notice that camphoric acid is isomeric with phocenic acid, and has apparently the same atomic weight. Qu.! Is one or the other bibasic?

By the action of sulphuric acid on anhydrous camphoric acid, there is formed, with disengagement of carbonic oxide, a new acid, *sulphocamphoric acid*, ($C_9H_7O_3$,SO_2) HO + 2 aq. This acid is crystallizable, and forms crystallizable salts of the formula ($C_9H_7O_3$,SO_2) MO = $C_9H_7SO_5$,MO.

CAMPHOR.

There are two kinds of camphor; that of Japan, or common camphor, $C_{10}H_8O$; and that of Borneo, $C_{10}H_9O$, or $C_{20}H_{18}O_2$. The properties of common camphor, and its peculiar smell, are well known. Its sp. gr. is 0·985 to 0·996; it is very volatile, evaporating at ordinary temperatures. Small fragments of camphor, on the surface of water, evaporate more rapidly, with rotatory movements. It dissolves in alcohol, and is precipitated by water. When distilled with anhydrous phosphoric acid, it yields a carbo-hydrogen, called camphogen $C_{20}H_{14}$.

When camphor is passed in vapour over a heated mixture of hydrates of potassa and lime, it yields a new acid, *campholic acid*, $C_{20}H_{17}O_3$,HO. Nitric acid, with the aid of heat, converts camphor into camphoric acid. The *essence or oil of camphor* of commerce is $C_{20}H_{16}O$ = 2 eq. camphor *minus* 1 eq. oxygen.

Borneo camphor occurs in small crystalline fragments. Its odour is different from that of common camphor. I find that, if wrapped in paper, a distinctly alliaceous odour traverses the paper, and may thus be detected. Heated with phosphoric acid, it yields a carbo-hydrogen, $C_{20}H_{16}$; and this is also the composition of the essence which accompanies Borneo camphor. This essence is, therefore, Borneo camphor, $C_{20}H_{18}O_2$, minus 2 eq. water.

Common camphor is produced by the *Laurus camphora*; Borneo camphor is the produce of *Dryobalanops camphora*, and is, for some unknown reason, so highly prized by the Japanese, that it is not found in the markets of Europe.

Camphogen, $C_{20}H_{14}$, is the name given to the carbo-hydrogen obtained when common camphor is distilled with dry phosphoric acid. It occurs naturally in the oil of cumin. When acted on by sulphuric acid, it forms a new acid, *sulphocamphic* or *hyposulphocamphic acid*, $C_{20}H_{13}S_2O_5$,HO.

When camphor is passed over red-hot lime, another new compound is formed, namely, *camphrone*, $C_{30}H_{21}O = 3(C_{10}H_8O) - H_3 + O_2$. At a white heat, cam-

phor yields naphthaline, carburetted hydrogen, and carbonic oxide. 4 eq. camphor contain the elements ($C_{40}H_{32}O_4$) of 1 eq. naphthaline, $C_{20}H_8$; olefiant gas, $2C_4H_4$; marsh gas, $8CH_2$; and carbonic oxide, 4CO.

12. Valerianic Acid. $C_{10}H_9O_3,HO = \overline{Va},HO$.

This acid has already been mentioned as produced from hydrated oxide of amyle. It also occurs in the root of Valerian. It forms two hydrates, $\overline{Va},HO$, and $\overline{Va},HO + 2$ aq.

The general formula of the valerates is $\overline{Va},MO$. *Valerate of oxide of ethyle*, $\overline{Va},AeO$, is an oily liquid, of a smell like that of fruits and that of valerian at the same time.

By the action of chlorine, valerianic acid yields two new acids: 1. *Chlorovalerisic acid*, $C_{10}\left\{\begin{matrix}H_6\\Cl_3\end{matrix}\right.O_3,HO$. 2. *Chlorovalerosic acid*, $C_{10}\left\{\begin{matrix}H_5\\Cl_4\end{matrix}\right.O_3,HO$. Both these compounds are formed by substitution without change of type.

When valerate of lime is distilled, it is said by Löwig to yield a volatile oily compound, valerone, $C_9H_9O = C_{10}H_9O_3 - CO_2$.

13. Anisic Acid. $C_{16}H_6O_5,HO$.

This acid is obtained when the concrete essence of anise-seed is acted on by nitric acid. It is crystallizable and volatile, and forms salts which crystallize readily. When heated with an excess of baryta, it yields an oily liquid, called *anisole*.

The prolonged action of nitric acid on the concrete essence of anise produces another acid, *nitro-anisic acid*, in small yellow crystals. Its formula is $C_{16}H_5NO_9,HO = C_{16}\left\{\begin{matrix}H_5\\NO_4\end{matrix}\right.O_5,HO$. It is now found to be identical with nitrodracinic acid.

Anisole, the product formed when anisic acid is heated with baryta, is composed of $C_{14}H_7O_2 = C_{16}H_8O_5,HO - 2CO_2$. It is formed, also, when the salicylate of oxide of methyle is heated with baryta. By the action of bromine, anisole gives rise to two new products, in which 1 and 2 eq. of hydrogen are respectively replaced by bromine; $C_{14}\left\{\begin{matrix}H_7\\Br\end{matrix}\right.O_2$ and $C_{14}\left\{\begin{matrix}H_6\\Br_2\end{matrix}\right.O_2$. The latter is crystalline. Nitric acid acts violently on anisole, forming a crystalline mass, which dissolves in alcohol, with a rich green colour, but is deposited in colourless needles, corresponding to one of the bromine compounds. Fuming sulphuric acid dissolves anisole, producing two compounds; one, insoluble in water, analogous to sulphobenzine: the other, soluble, an acid analogous to sulphovinic acid. $2SO_3 + C_{14}H_7O_2,HO$.

Anisole, $C_{14}H_8O_2$, contains 2 eq. of hydrogen more than hyduret of benzoyle, $C_{14}H_5O_2,H$.

14. Œnanthic Acid. $C_{14}H_{13}O_2,HO$.

This acid, in combination with oxide of ethyle, forming œnanthic ether, is found in wine, in the oil of grain spirit, and in some other fermented liquors. It is, as œnanthic ether, the cause of that peculiar odour of wine which adheres so remarkably to vessels in which wine has been kept, and enables us at once to

say that an empty bottle or cask has contained wine. To obtain the acid, the ether is decomposed by caustic potash, and the œnanthate of potash distilled with dilute sulphuric acid. The hydrated acid is semisolid like butter, and is, in fact, a fat oil, insoluble in water, soluble in alcohol and ether.

Of its salts, the *œnanthate of oxide of ethyle*, œnanthic ether, is best known. It is a colourless liquid, of a peculiar vinous smell, which, when strong, has a stupefying effect. When hydrated œnanthic acid is distilled, it yields water, and anhydrous acid, more solid than the hydrate.

15. Roccellic Acid. $C_{17}H_{15}O_3,HO$?

This acid occurs in *Rocella tinctoria*. It is crystallizable, insoluble in water, soluble in alcohol and ether. It has most of the properties of a fat acid, and its salts with the alkalies resemble soaps.

16. Cuminic Acid. $C_{20}H_{11}O_3,HO$.

This acid is formed from the essential oil of cumin by oxidation with hydrated alkalies. It forms tabular crystals of singular beauty. It is fusible and volatile, insoluble in cold water, soluble in alcohol and ether. When heated with caustic baryta, it yields a carbo-hydrogen, analogous to benzole, which is called *cumene*.

It forms well-defined salts with bases. Cuminate of oxide of ethyle, formed by passing hydrochloric acid gas through a solution of cuminic acid in alcohol, is an ethereal liquid, of a fragrant smell like that of apples.

Cumene, obtained by heating cuminic acid with baryta, is a colourless liquid of a sweet smell. It is formed from cuminic acid, $C_{20}H_{12}O_4$, by the loss of 2 eq. carbonic acid, exactly as benzole is formed from benzoic acid; and its formula is consequently $C_{18}H_{12}$. Both nitric and sulphuric acid act on it and form new compounds, not yet fully examined. That formed by sulphuric acid is an acid, sulphocuminic acid, $C_{18}H_{11},S_2O_5 + HO$.

Essence of cumin (*cuminum cyminum*) contains two oils: 1. Cuminole, $C_{20}H_{12}O_2$, which is the true oil of cumin, analogous to hyduret of benzoyle; 2. Cymene, $C_{20}H_{14}$, isomeric with camphogen. It is an oil of an agreeable odour of lemons. The oil is acted on by nitric and sulphuric acids, which produce two new acids. That formed with sulphuric acid is $C_{20}H_{13},S_2O_5,HO$.

The *cuminole*, $C_{20}H_{12}O_2$, may be viewed as analogous to hyduret of benzoyle, in which case it becomes $C_{20}H_{11}O_2 + H$, the hyduret of a new radical, *cumyle*. Cuminic acid then becomes $C_{20}H_{11}O_2,O + HO$, analogous to benzoic acid. Chlorine acts on hyduret of cumyle, producing a compound, $C_{20}H_{11}O_2,Cl$, which is chloride of cumyle. Adopting the symbol $Cm = C_{20}H_{11}O_2$, we have CmH, CmO + HO, and CmCl, analogous to BzH, BzO + HO, and BzCl.

17. Eugenic Acid. $C_{20}H_{12}O_4$? or $C_{20}H_{13}O_5$?

This acid is found in cloves, along with a neutral oil, $C_{10}H_8$, or $C_{20}H_{16}$. The latter is separated by potassa, and the eugenic acid obtained by distilling the salt of potassa with dilute sulphuric acid. It is an oily liquid, of sp. gr. 1·079, having the strongest odour of cloves. It forms crystallizable salts with bases, and among them an acid salt of potassa, $2C_{10}H_{12}O_4 + KO + HO$?

Cloves, likewise, contain two crystallizable compounds: 1. *Caryophylline*, which forms yellow prisms; of the formula $C_{20}H_{15}O_2$, an oxide, therefore, of the

neutral oil of cloves. 2. *Eugenine*, which forms yellow pearly scales, the composition of which is the same as that of eugenic acid.

18. Cocinic Acid. $C_{27}H_{26}O_3$,HO.

This acid, the first of the proper fat acids which we have come to, is found in the butter of the cocoa-nut combined with glycerine. The butter is saponified by potassa, and the soap produced is decomposed by a mineral acid, when the fatty acid rises to the surface. It is purified by being again saponified, and finally by crystallization in alcohol. It forms snow-white crystalline scales, fusible at 95°, and volatile. The salts of this acid with the alkalies are soaps like those of all fatty acids. *Cocinate of oxide of ethyle* is a colourless ether, with a very fragrant smell of apples.

19. Myristic Acid. $C_{28}H_{27}O_3$,HO.

This acid is found combined with glycerine, as a fat or butter in the berries of *myristica moschata* or nutmeg. There are two fats in the seeds, one red and unctuous, the other, myristine, white, and crystalline. It is easily purified by dissolving it in hot alcohol, in which it is, like the cocinate of glycerine, very soluble. On cooling, the pure myristine or myristate of glycerine is deposited as silky needles, which being saponified by potassa, and the soap decomposed by an acid, yield myristic acid. The acid is purified by means of alcohol. It melts at 118°, and is decomposed by distillation.

The salts of this acid with the alkalies are soaps: very soluble in alcohol; and their aqueous solutions do not become viscid or ropy when concentrated. *Myristate of oxide of ethyle* is a colourless oil. Myristate of oxide of glycerine or *myristine* is purified as above described. It is a beautifully crystalline fat, melting at 88°. It is saponified with difficulty, and only by fusion with solid potassa. It does not appear to contain ordinary glycerine: at least its formula would indicate a glycerine composed of C_3H_2O. This point is at present very obscure.

The formula of hydrated œnanthic acid, doubled, or $C_{28}H_{28}O_6$, contains 2 eq. of oxygen more than 1 eq. of hydrated myristic acid, $C_{28}H_{28}O_4$; or the formula of dry œnanthic acid doubled, $C_{28}H_{26}O_4$, contains 1 eq. of hydrogen less and 1 eq. of oxygen more than dry myristic acid. $C_{28}H_{27}O_3$.

20. Palmitic Acid. $C_{32}H_{31}O_3$,HO.

This is the principal fat acid of palm oil. It is extracted by the usual process for fatty acids, and purified from oleic acid by crystallization in alcohol. It forms brilliant scales, similar to margaric acid, and melting at the same point, 140°, as that acid. It may be distilled in great part unchanged. Chlorine decomposes it, giving rise to new compounds.

The salts of this acid with the alkalies are soaps, and palm oil is much used in soap-making. Palmitate of glycerine, or palmitine, is the fat or butter of the palm oil, purified from the oleine or liquid part, by pressure, and then by crystallization in ether. It melts at 118°, and on cooling assumes the aspect of wax. Like myristine, it appears to contain the modified glycerine C_3H_2O, which is $\frac{C_6H_7O_5 - 3HO}{2}$; that is, glycerine, minus 3 eq. of water, and divided by 2. Pure palmitine (as also pure myristine), when distilled, yields *acroleine*,

derived from the glycerine; but no sebacic acid. The crude palm oil, or impure palmitine, however, yields abundance of sebacic acid, a compound derived from oleic acid, and proving, therefore, the presence of oleic acid or rather oleine.

21. Cetylic Acid. $C_{32}H_{31}O_3,HO$.

Syn. *Ethalic Acid.* This acid, which is isomeric with the preceding, is formed when ethal (hydrated oxide of cetyle) is heated with hydrates of lime and potassa. It is separated as usual in the case of fatty acids. It is a solid, fusible between 130° and 140°, and at 131°, solidifying in radiated groups of needles. It may be distilled unaltered. Its salts are like those of the preceding acids.

22. Margaric Acid. $C_{34}H_{33}O_3,HO$; or, $C_{68}H_{66}O_6,2HO$.

This is one of the most abundant and important of the fatty acids. Combined with glycerine, as margarine, it occurs in human fat and some other animal fats, and in many vegetable fats, such as olive oil. The acid may be extracted from soap made of these fats, but as it is mixed with much oleic acid, it is better to prepare it by oxidizing stearic acid (see below) by nitric acid, or by distilling either tallow or crude stearic acid. In the latter case, the product is well squeezed and purified by solution in alcohol, and crystallization. If prepared from pure stearic acid by nitric acid, it is pure from the first.

Margaric acid is a white solid fat, of distinct acid properties, fusible at 140°, very soluble in hot alcohol and in ether. It instantly combines with bases, decomposing the carbonates and forming perfect soaps with potassa and soda. The neutral margarates of potassa and soda are decomposed by the addition of much water, depositing the acid margarates in pearly scales. *Margarate of glycerine*, or *margarine*, is found pure in the solid part of human fat or of olive oil. It dissolves in hot alcohol, and crystallizes on cooling. *Margarate of oxide of ethyle* is a white fusible solid.

The general formula of the neutral margarates is $C_{34}H_{33}O_3,MO$, or $C_{68}H_{66}O_6$, $2MO$. We cannot say with certainty whether margaric acid is unibasic, as the first of these formulæ would indicate, or bibasic, according to the second. We shall return to this point after describing stearic acid, and we shall also then describe the action of heat on both acids.

23. Stearic Acid. $C_{68}H_{66}O_5,2HO = \overline{St},2HO$.

This is, perhaps, the most important and most abundant of the fatty acids. It exists, in combination with glycerine, as *stearine*, in beef and mutton fat, and in several vegetable fats, such as the butter of cacao. To obtain it, mutton suet is saponified by boiling with potassa, and the purified soap decomposed by an acid, when a mixture of stearic and oleic acids, the latter in small proportion, rises to the surface. It is strongly pressed between warm plates, so as to get rid of the oleic acid in great part, and it is finally purified by solution in hot alcohol, and crystallization, repeated till its melting point is constant at 167°. Or the stearic acid of commerce, which is nearly pure, may be purified by means of alcohol. Or again, tallow may be mixed with half its weight of oil of vitriol, and the mass melted in hot water, which removes a compound of sulphuric acid with glycerine, while the stearic acid rises to the surface and is to be purified as above. Finally, pure stearine, if saponified, and the soap acted on by an acid, yields at once pure stearic acid.

Stearic acid is a white solid, fusible at 167°, and on cooling forming brilliant white needles. It may be reduced to powder, and is, like all fat acids, insoluble in water, soluble in alcohol and ether. It burns like wax, and is used in the formation of improved candles.

By the action of nitric acid and other oxidizing agents, stearic acid is at once converted into margaric acid, and it will be seen that the addition of 1 eq. oxygen is sufficient to effect this change. $C_{68}H_{66}O_5,2HO + O = C_{68}H_{66}O_6,2HO$.

Stearic acid is bibasic, and forms two series of salts; $\overline{St},2MO$, and $\overline{St},MO,HO$. The neutral stearates of the alkalies are perfect soaps. They dissolve in from 10 to 20 parts of hot water, and the addition of a large quantity of water decomposes them into acid stearates which are deposited, and basic stearates which remain dissolved. For the same reason a hot solution of a neutral stearate becomes gelatinous on cooling, from the separation of the acid salt. *Acid stearate of oxide of ethyle*, $\overline{St},AeOHO$, and *neutral stearate* of the same base, $\overline{St},2AeO$, are both white crystalline fusible solids; as is likewise the *stearate of oxide of methyle*, $\overline{St},2MtO$.

Stearine, the chief ingredient of suet and tallow, appears to be the *acid stearate of oxide of glyceryle*, but its precise formula cannot be determined as long as we are doubtful about that of glycerine. If glycerine be C_3H_2O, then stearine will be $C_{68}H_{66}O_5 + C_3H_2O + 2HO = \overline{St},GlyO,2HO$; but if stearine be $C_6H_7O_5$, the formula will be $2(C_{70}H_{67}O_5) + GlyO + 2HO$; (using the older formula for stearic acid). Neither of these formulæ is satisfactory, as both exhibit 3 eq. of base and basic water, instead of two or four. When boiled with alkalies, stearine, like all other fats, is saponified: that is, the stearic acid combines with the alkali, forming soap, and glycerine is separated. Pure stearine is obtained by pressing tallow between hot plates, and afterwards dissolving in hot ether, which on cooling deposits the stearine. It is like wax in appearance when it has been melted, and it may be powdered.

Stearate of lead is an insoluble fusible soap, or, as it is called, a plaster. The same is true of margarate of lead, and in general of the compounds of lead with fat acids.

The composition of stearic acid stands in a very simple relation to that of margaric acid. If we call the compound $C_{34}H_{33}$, *margaryle*, and view it as a compound radical, representing it by the symbol Ml, then Ml_2O_5 = stearic acid and $Ml_2O_6 = 2MlO_3$ = margaric acid. These acids, therefore, bear to each other the same relation as that which subsists between sulphuric and hyposulphuric acids, SO_3 and S_2O_5. The only difference is that, while SO_3 neutralizes as much base as S_2O_5,MlO_3 only neutralizes half the quantity of base neutralized by Ml_2O_5, or in other words Ml_2O_6 neutralizes as much base as Ml_2O_5.

When stearic acid is distilled alone, or with lime, it yields much margaric acid, and a neutral fusible crystalline fat, margarone, besides a solid carbohydrogen $C_{34}H_{34}$, carbonic acid, and water. Margarone is either $C_{33}H_{33}O$, or $C_{34}H_{33}O$. In the former case it is formed from margaric acid by the loss of 1 eq. carbonic acid; in the latter, it is the oxide of the supposed radical magaryle, MlO. The production of these compounds is easily understood, for 2 eq. stearic acid are equal to 3 eq. margaric acid and 1 eq. oxide of margaryle; $2Ml_2O_5 = 3MlO_3 = MlO$. Again, 4 eq. of hydrated stearic acid contains the elements of 6 eq. hydrated margaric acid, 1 eq. margarone, $(C_{33}H_{33}O)$, 1 eq. water, 1 eq. carbonic acid, and 1 eq. of the carbo-hydrogen $C_{34}H_{34}$. It would appear that according to circumstances the margarone has a different composition, its pro-

perties varying little, so that different chemists have obtained different margarones: namely $C_{33}H_{33}O$; $C_{34}H_{33}O$; and even $C_{68}H_{66}O = Ml_2O$. When margaric acid is heated, part distils unchanged, and part is converted into the above products.

When margarine or stearine are distilled, they yield the very acrid vapours of acroleine, a product derived from the glycerine contained in these fats; but pure stearic and margaric acids yield not a trace of acroleine. Neither do they yield any sebacic acid among the products of their distillation, this acid being derived exclusively from oleic acid.

ACTION OF NITRIC ACID ON MARGARIC ACID.

By the action of nitric acid stearic acid is converted into margaric acid, with disengagement of nitrous acid vapours. But if the action of the nitric acid be prolonged, the margaric acid is gradually oxidized and dissolved, being converted into *suberic acid*, *succinic acid*, and an oil soluble in nitric acid.

24. Suberic Acid. $C_8H_6O_3,HO = \overline{Su},HO$.

This acid is formed when cork is oxidized by nitric acid, but especially when nitric acid acts on stearic acid, margaric acid, oleic acid, and other fatty bodies. The acid solution, obtained by boiling stearic or margaric acid with nitric acid till it is entirely dissolved, is evaporated to one half, and on cooling deposits a large quantity of suberic acid, which is easily purified by crystallization.

It forms small granular crystals, fusible, when moist, at 130°, when dried, at 248°, volatile at a higher temperature, and subliming in the form of long needles. It is sparingly soluble in cold water, very soluble in hot water, in alcohol, and in ether.

The general formula of the suberates is $\overline{Su},MO$, The *suberate of oxide of ethyle* is prepared like the ethers of all the fatty acids, by passing hydrochloric acid gas through the alcoholic solution of the acid. When suberate of lime is distilled, it yields, among other oily products, a liquid boiling at 366°, the formula of which is C_8H_7O. It may be either the oxide of C_8H_7, or the hyduret of C_8H_6O. It is converted into suberic acid by the action of the air and of nitric acid. In fact, the addition of 3 eq. of oxygen gives the composition of hydrated suberic acid, $C_8H_7O_4$. It is probable that there exists a radical *suberyle* $= C_8H_6O = Su$; and that we have $\overline{Su}H$, and $\overline{Su}O_2,HO$ for the oil and suberic acid, analogous to the hyduret of benzoyle and benzoic acid.

25. Succinic Acid. $C_4H_3O_4,HO = \overline{S},HO$.

This acid exists ready formed in amber, and may be obtained by distilling that body. But the mother liquor of the suberic acid, formed from margaric acid, &c., by nitric acid, contains a large quantity of succinic acid, along with a little suberic acid. The mixture, being dried up, is acted on by ether, which dissolves the suberic acid, leaving the succinic acid; it is finally purified by sublimation.

It forms regular crystals, which may be easily sublimed. The formula of the sublimed crystals is $2\,(C_4H_4O_3) + HO$; but by repeated sublimation it may be obtained anhydrous. The first hydrate $\overline{S},HO$, melts at 356°, and boils at 455°,

subliming, however, slowly at 284°. The sublimed hydrate, 2 Su + HO, melts at 320°, and boils at 468°; and the anhydrous acid melts at 257°, and boils at 482°.

By the action of anhydrous sulphuric acid, it yields a new acid, apparently $C_8H_2S_2O_{10}$,4HO, hyposulphosuccinic acid.

The constitution of the succinates is still doubtful; but the most recent researches of Fehling, who has twice examined these salts with care, lead to the general formulæ of $C_4H_2O_3$,MO for the neutral, and 2 $(C_4H_2O_3)$ + MO,HO, for the acid salts. The *succinates of lead* present some anomalies. By the action of ammonia, NH_3, on succinic ether, $C_4H_2O_3$,C_4H_5O, there is formed succinamide, $C_4H_2O_2$,NH_2, while alcohol, C_4H_5O,HO is given off. When acid succinate of ammonia is heated there is sublimed a new body, bisuccinamide, $C_8H_3O_4$,NH_2. It is formed from 2 eq. succinic acid and 1 eq. ammonia, by the separation of 2 eq. water. In their mode of formation these two bodies resemble oxamide and oxamic acid, only bisuccinamide has no acid properties.

The origin of *amber* is very uncertain: but it is most probably derived from some resin, formerly liquid or soft. It may possibly have arisen from the slow oxidation of a fatty matter, as we see succinic acid formed from fats by oxidation. Amber is a clear brittle yellow solid, becoming electric by friction. It is for the most part insoluble in all menstrua. When heated it yields succinic acid and a volatile oil, and there is left a large proportion of a matter which may be called bituminous, and forms the principal part of the amber.

26. Oleic Acid. $C_{44}H_{39}O_4$, HO? = $\overline{Ol}$, HO.

This acid, in combination with glycerine, constitutes, as oleine, the liquid or most fusible portion of fats and fat oils. It exists in small proportion in tallow or suet; more abundantly in human fat and hog's lard; and it predominates in olive oil and especially in almond oil. To obtain it, almond oil is saponified, and the mixed fat acid obtained from the soap is digested with half its weight of oxide of lead, by which means margarate and acid oleate of lead are formed. Ether dissolves the latter only, and the ethereal solution of oleate of lead is acted on by hydrochloric acid, when the ether rises to the surface, holding the oleic acid in solution. The ether being distilled off, the oleic acid is left somewhat coloured. When pure it is a nearly colourless oily fluid, freezing in cold weather.

It forms salts with bases, and the oleates of the alkalies are soaps. Naples soap is chiefly oleate of potash: oleate of soda is harder.

Nitric acid converts oleic acid into suberic acid and other products. By hyponitric (nitrous) acid or nitrate of mercury it is converted into *elaidic acid*.

When distilled, oleic acid gives rise to sebacic acid, and this is an infallible test of the presence of oleic acid or oleine in any fat. This character applies to all the varieties of oleic acid, although we have reason to think that the oleic acids of fat oils and of drying oils are very different. Indeed, according to recent researches, the oleic acid of linseed oil is $C_{46}H_{38}O_5$,HO.

Of the oleates, the most important are those of potash and soda, which exist in most soaps, and constitute the chief part of those made with olive or almond oil, or whale oil, and that of lead, which is a valuable ingredient of most plasters. *Oleate of oxide of glycerile*, as already mentioned, is *oleine*, the liquid part of fats and fat oils, which is hardly known in a perfectly pure state. Oleate of oxide of ethyle is an oily liquid.

27. Sebaic Acid. $C_{10}H_8O_3,HO = \overline{Se},HO$.

When any oil or fat, containing oleine or oleic acid, is distilled, and the product boiled with water, the hot filtered liquid deposits, on cooling, *sebacic acid* in small crystals resembling benzoic acid. It is soluble in alcohol and ether, and sublimes without alteration. The salts of sebacic acid are not remarkable, with the exception of the *sebate of oxide of ethyle*, which has a fragrant smell of melons. When we wish to ascertain the presence of oleine in a fat, a portion is distilled, the product is boiled with water, and the liquid, even if it deposit nothing, is tried by acetate of lead, with which it forms a white precipitate if sebacic acid be present.

28. Elaidic Acid. $C_{72}H_{66}O_5$.

This acid is formed by the action of nitrous acid on oleic acid. If a current of nitrous acid be passed through well-cooled oleic acid, the latter soon solidifies in large scales, which are *elaidic acid*. It is purified by solution in alcohol. It forms silvery scales, melting at 112°, very soluble in alcohol, and volatile without decomposition, except to a very small extent. The salts of this acid are soaps, and resemble those of the other fat acids.

Oleine is converted into *elaidine* (elaidate of glycerine), and oleic ether into elaidic ether, by the action of nitrous acid; but we cannot yet account for the production of elaidic acid in these cases or in that of its fermentation from oleic acid; since the reaction is accompanied by the production of other substances, not yet examined.

ACTION OF NITRIC ACID ON OLEIC ACID.

When oleic acid is acted on by nitric acid, it yields several acids, only one of which, suberic acid, occurs in the action of nitric acid on other fat acids. The remaining acids are, *azelaic acid? pimelic acid*, *adipic acid*, *lipic acid*, and *azoelic acid*.

The action of nitric acid on oleic acid is violent. When completed, the liquid is evaporated to one-half, and on cooling deposits suberic acid, which according to Laurent, is accompanied by azelaic acid, very similar to it, the composition of which he describes as the same as that of suberic acid, or only differing by 1 eq. of water, while he gives the formula $C_{10}H_8O_4,HO$, that of suberic acid being $C_8H_6O_3,HO$. There is probably here an error of the press. But the existence of azelaic acid is very doubtful.

Pimelic acid crystallizes on evaporation after the suberic acid has been removed, in hard granular crystals, fusible and volatile. Its formula is $C_7H_5O_3,HO$. In the mother liquid are found:—*Adipic acid* in round radiated masses, fusible and volatile. Formula $C_6H_4O_3,HO$ (Laurent), $C_{14}H_9O_7,2HO$ (Bromeis), probably different acids. The *Lipic acid* forms long tables, very fine when formed in alcohol. Formula $C_5H_3O_4,HO$. *Azoleic acid*, according to Laurent, occurs in the form of an oily liquid, and œnanthic acid is also found. According to Bromeis, azoleic acid is doubtful, and the acid taken for it and for œnanthic acid is impure butyric acid, the formation of which is not improbable, since butyric acid contains exactly 1 eq. hydrogen more than suberic acid.

When oleic acid and elaidic acids are heated with potassa there are produced acetic acid and a new fatty acid, $C_{32}H_{30}O_3,HO$. The difference between the

formula of this acid and that of oleic acid is equal to 3 eq. acetic acid, which accounts for its production. Again, elaidic acid, $C_{72}H_{66}O_5$, *plus* 7 eq. oxygen, yields 2 eq. of the new acid, and 2 eq. acetic acid. This acid only differs from palmitic (ethalic) acid by 1 eq. hydrogen.

ACIDS OF CASTOR OIL.

Castor oil is a very peculiar oil. When saponified, it yields two fat acids, one crystallizable, *margaritic acid*; the other liquid, *ricinic acid*. The latter is little known. The former is said to be $C_{35}H_{31},O_6$. Castor oil is a mixture of the compounds of glycerine with these two acids. It is soluble, when pure, in its own bulk of alcohol. Nitrous acid converts it into a solid crystallizable fat, palmine, analogous to elaidine, but differing from it.

When castor oil is acted on by nitric acid, it yields a new volatile oily acid, of an agreeable aromatic odour, which is called *œnanthilic acid*, as its formula is that of œnanthic acid, *plus* 1 eq. oxygen; $C_{14}H_{13}O_3,HO$. It forms an ether of a very agreeable aromatic smell. In the residue is found suberic acid.

Palmine, the fat formed by the action of nitrous acid on castor oil, is a white crystalline fat, which when saponified, yields glycerine and a fatty acid, *palmic acid*, not yet fully investigated. A current of sulphurous acid passed through castor oil is said to produce palmine, or at all events a fat which yields palmic acid. This, if true, is a very singular fact, since nitrous acid, an oxidizing agent, and sulphurous acid, a deoxidizing one, would thus produce the same result.

NATURAL FATS AND FIXED OILS.

These are all compounds of glycerine with fatty acids. When heated with alkalies they yield soaps; with oxide of lead, plasters; while in both cases glycerine is set free. The most common of all these compounds are *stearine*, *margarine*, and *oleine*, of which always too, and often all three, are present, stearine predominating in the hard, margarine in the soft, and oleine in the liquid fats. It is only the compounds of glycerine with volatile acids, such as butyric acid, that have a strong smell.

There are two kinds of fat oils: the fat oils proper, and the drying oils. The latter contain much oleine, the oleic acid of which is different from the usual oleic acid, and they absorb oxygen from the air, drying into a kind of varnish. When oils become rancid, they are partly decomposed: and, generally, some of the acid, as well as of the glycerine, is set free, while oxygen is absorbed. Pure stearine, margarine, and oleine do not become rancid, and that change depends on a process of decay or slow oxidation going on in the impurities of the oil, and from them passing to the oil itself.

ACTION OF HEAT ON OILS AND FATS. ACROLEINE.

When oils are distilled they produce a variety of compounds, such as margaric acid, sebacic acid, margarone, carbohydrogens, &c. &c., and one most remarkable compound, *acroleine*, derived from glycerine.

Acroleine, $C_6H_4O_2$, is best obtained by distilling glycerine with phosphoric acid. The whole operations must be carried on in vessels full of carbonic acid

gas, as the acroleine is very rapidly oxidized by the air. Its vapour attacks the eyes and nose in a most painful, indeed intolerable, degree. It may be considered as the hydrated oxide of a radical C_6H_3, (*acryle*, analogous to acetyle) $C_6H_3,O + HO$, analogous to aldehyde. It rapidly absorbs oxygen and forms *acrylic acid*, $C_6H_3O_3,HO$, analogous to acetic acid. In certain circumstances, the solution of acroleine exposed to the air, deposits a white solid, $C_{10}H_7O_4$.

The presence of acroleine among the products of the distillation of an oil or fat is a convincing proof of the presence of glycerine in that oil. It is worthy of remark that glycerine, $C_6H_7O_5$, is hydrated oxide of acryle, plus 3 eq. water, so that oils and fats may be called compounds of acroleine as well as of glycerine. It is even conceivable that acroleine may be C_3H_2O, which we have seen to be a probable form of glycerine in some fats; or that the glycerine in these fats may be acroleine, as above given, $C_6H_4O_2$, and that when this glycerine is separated by an alkali, it takes up 3 eq. of water.

Castor oil, so peculiar in other respects, exhibits a peculiar decomposition by heat. It yields acroleine, and a volatile oil, composed of two oils insoluble in alkalies; besides some saponifiable acids. When about one-fifth has been distilled, the residue suddenly consolidates into a spongy, yellow, elastic mass, insoluble in all menstrua, except caustic alkalies, with which it forms peculiar soaps. These, when decomposed by an acid, yield a tough viscid substance having the characters of an acid. The product of the distillation again distilled with water, yields several oily compounds, one of which is crystalline, and not yet fully studied. The less volatile residue being again distilled yields a peculiar crystalline fatty acid, and another oily acid. Neither of these has been properly investigated.

When oils or fats are decomposed at a red heat, they yield much combustible gas (oil gas), formed of olefiant gas and marsh gas, and several liquid carbohydrogens: in particular benzole, $C_{12}H_6$, Faraday's quadricarburetted hydrogen, C_4H_4, or C_8H_8, and another isomeric compound, which is only liquid at very low temperatures.

ACTION OF SULPHURIC ACID ON FAT OILS.

Sulphuric acid, if added in small quantity to oils, combines with their glycerine; but if used in excess gives rise to a number of new products. In the first instance they are formed, when a mixture of oleine and margarine is acted on, two new acids *sulpholeic acid* and *sulphomargaric* acid. These acids have not been isolated, but when their solution in water is heated, the sulphuric acid separates, and the oleic and margaric acids are transformed into four new acids, *metamargaric* and *hydromargaritic* acids, and *metoleic* and *hydroleic acids*. The two former are solid, crystallizable, and partly volatile. A compound of the two exists, which acts like a single acid and has been called *hydromargaric acid*; it is also a fusible solid. The two latter are oily, and all five appear to be bibasic. Their composition cannot be considered as ascertained, but the three first are nearly allied to margaric acid. It would lead to confusion here to mention the different formulæ proposed by Frémy, Berzelius, and Liebig, for these acids, more especially when it is considered that we have no sufficient evidence of the perfect freedom from foreign admixture of the acids analyzed, and that the recent observations of Miller show an amount of variation in the melting points which leads to the suspicion of impurity. The subject is interesting, but difficult, and requires a very minute investigation.

Metoleic and hydroleic acids, when distilled, yield water, carbonic acid, and two carbo-hydrogens, *oleéne* and *elaéne*, both of which contain carbon and hydrogen in an equal number of equivalents; oleéne is supposed to be $C_{40}H_{40}$, and elaéne, $O_{45}H_{45}$; but this is not established.

ACTION OF NITROUS ACID ON FAT OILS.

Nitrous acid, or solution of nitrate of mercury, as already mentioned, causes fat oils to become solid, converting oleine into elaidine. This curious change takes place in olive oil, almond oil, rape-seed oil, hazel-nut oil, castor oil and others: but the drying oils, such as oils of linseed, hemp-seed, walnut, poppy-seed, &c., are not at all affected by nitrous acid. In all the oils which are changed into elaidine, except in castor oil, the product is the same. It is the formation of this solid fat which causes the mercurial ointments, made with nitrate, to become hard when kept. The elaidine, when purified by pressure and crystallization in alcohol and ether, yields neither margaric nor oleic acid when saponified, but only *elaidic acid*. Hence, the elements of both the original acids have taken a share in the transformation. The conversion of oleic acid into elaidic acid by means of nitrous acid is accompanied by the formation of a red substance. The probable formula of elaidic acid is $C_{70},H_{68}O_6$. As elaidine contains 2 per cent. more carbon than elaidic acid, it is plain that elaidine cannot be a compound of elaidic acid with a glycerine containing 5 eq. of oxygen to 6 eq. carbon. ($C_6H_7O_5$). It is therefore probable that elaidine is one of those fats in which the base is not ordinary glycerine but acroleine $C_6H_4O_2$, or C_3H_2O.

Castor oil, as has been already mentioned, yields, with nitrous acid, a new fat *palmine*, which contains a new acid, *palmic* acid. These resemble elaidine and elaidic acid, but are quite distinct.

ACTION OF BASES ON FAT OILS. SOAPS AND PLASTERS.

When fat oils are boiled with solution of caustic alkalies, they are gradually dissolved in the water, if there be not too great an excess of alkali present, forming ropy or gelatinous solutions, which gelatinize on cooling. These are solutions of soaps, that is, potassa and soda salts of the fatty acids, along with the glycerine set free. In order to have the soaps in a solid form, the solutions are boiled down, and when the alkali reaches a certain concentration, the soap becomes insoluble, and rises to the surface in a soft, half melted state. This is drawn off into moulds, and the mass formed on cooling is soap. Another method of causing the soap to separate from the water in which it is dissolved, consists in adding sea-salt, which at once coagulates the soap, converting it into a soap of soda, if it is a soap of potassa. Of course, the glycerine, in both cases is carried off in the mother liquor. Such is the theory of soap-making, which is very simple, depending on the affinity between the alkalies and the fat acids; on the solubility in water of the alkaline stearates, margarates, oleates, palmitates, &c.; and finally on the power of a certain amount of free alkali or of sea-salt to coagulate the soap and render it insoluble in the liquid in which it swims, and which in fact, runs off its surface as water does off the surface of fat, while yet the soap retains perfectly its solubility in pure water.

The soaps of lime, baryta, &c., are insoluble in water, and have no detergent power: hence the waste occasioned by using hard, that is, calcareous, water for washing. All the salts of lime in such water must first be entirely precipitated

in the form of curdy flocculi before any soap can be dissolved so as to act as a detergent.

The soaps of potassa are soft, compared with those of soda, which are called hard soaps. White soap is stearate with some oleate, of soda. Naples soap is oleate and margarate of potassa. Common soft soap is chiefly oleate of potassa, but as it is made from whale oil or seal oil, it contains also phocenate of potassa, which gives it a disagreeable smell.

Castile soap is oleate and margarate of soda, coloured by metallic oxides, chiefly oxides of iron, in such a way as to give the desired mottled appearance. Much and excellent soap is now made of palm oil, and is, therefore, palmitate of soda.

Soaps are soluble in alcohol, forming tincture of soap, which is an admirable liniment for bruises, and is much used along with laudanum, as tincture of soap and opium; also with camphorated spirit, forming opodeldoc.

Plasters are soaps of certain metallic oxides, chiefly oxide of lead, which are insoluble in water, but fusible, and possess useful properties. Litharge plaster is made by boiling finely 5 parts of powdered oxide of lead with 9 parts of olive oil and some water, till the combination is complete. It is plastic at ordinary temperatures, and melts when heated. When solution of acetate of lead is added to solution of soap, plaster, that is oleate and margarate of lead, is precipitated. When prepared in this way it becomes hard. White lead plaster, made with carbonate of lead, is very plastic and fusible, and is much used. Iron plaster and mercurial plaster are of small importance.

The chief liquid fat oils and drying oils of the vegetable kingdom have already been mentioned. In the animal kingdom, there are fish oils, characterized by containing phocenine; also cod liver oil, &c. &c.

The solid oils or fats of the vegetable kingdom, are butter of cacao (*theobroma cacao*); of nutmeg (*myristica moschata*); of cocoa-nut (*cocos nucifera*); of laurel (*laurus nobilis*); palm-oil (*Avoira elais: elais Guianensis*); galam butter (*Bassia butyracea*); and some others. Those of the animal kingdom are tallow, or suet, butter, hog's lard, human fat, &c.

Spermaceti is a peculiar fat found in the head of *physeter macrocephalus*. When purified from a small quantity of a liquid oil, it constitutes *cetine*, which is a compound of ethal (hydrated oxide of cetyle) with oleic and margaric acids. Cetine crystallizes beautifully when melted or when dissolved in hot alcohol.

Cholesterine is a fat found in bile, and also, in small proportion, in the blood, and in much larger quantity as an ingredient of cerebral matter. It forms the chief ingredient of biliary calculi. It dissolves in hot alcohol, crystallizes on cooling, in silvery scales, but cannot be saponified by boiling with potassa. Its formula is either $C_{34}H_{33}O$, or $C_{36}H_{32}O$. When acted on by nitric acid, it yields a new acid, *cholesteric acid*, which contains nitrogen, probably as nitrous acid.

Ambreine, a fat analogous to cholesterine, is found in ambergris. It yields, with nitric acid, *ambreic acid*. Castorine is a similar fat found in castoreum.

Wax is another peculiar fatty body, the origin of which is derived from flowers, whence it is collected by the bee. It melts at about 150°. It is a mixture of two fats, *cerine* and *myricine*, the former soluble, the latter insoluble, in hot alcohol. Cerine is partly saponified, by boiling with potassa, yielding apparently magaric and oleic acids (?) along with a neutral fat, *ceraine* having the same composition as myricine. There are several kinds of vegetable wax, but they are all much more easily saponified than bees' wax. When bees' wax is

distilled, it yields neither acroleine nor sebacic acid, and would therefore appear to contain neither oleic acid nor glycerine.

Cerosine is the name given to a waxy substance occasionally found on the surface of the sugar-cane. It is not saponifiable, and appears to contain $C_{48}H_{50}O_2$.

Athamantine, from the root of *athamanta creoselinum*, is a crystalline fat-like body, containing valerianic acid, united to a body, *oreoselone*, which supplies the place of glycerine in the neutral athamantine. Oreoselone is $C_{14}H_5O_3$, that is, isomeric with dry benzoic acid. Athamantine is $C_{24}H_{15}O_7 = C_{14}H_5O_3$ (1 eq. oreoselone) + $C_{10}H_{10}O_4$ (2 eq. valerianic acid). Athamantine combines with hydrochloric acid, and the compound, when boiled with water, deposits crystals, which are ereoselone *plus* water = $C_{14}H_6O_4$, and isomeric with crystallized benzoic acid.

Having now briefly described the best known organic acids, it is necessary to mention a number of acids, found in the analyses of different vegetables, but not yet sufficiently studied to decide whether they exist independently or may not rather be, in many cases, identical with some of the acids above described. Such are chelidonic acid, caincic, crameric, caffeic, boletic, fungic, tanacetic, lactucic, atropic, cocognidic, solanic, coneic, aceric, moroxylic, kinovic, and menispermic acids, besides others.

VOLATILE OR ESSENTIAL OILS.

These oils are so called because they are obtained by distillation of vegetables, generally along with water, and because, having, in most cases, the concentrated odour of the plant, they are usually called essences. Most of them exist ready-formed in the plant, which owes its smell to them: but some, as oil of bitter almonds and oil of spiræa, are formed by a kind of fermentation, excited in the case of the former, as already stated, by the contact of amygdaline, emulsine and water.

Many plants, when cut, yield balsams, which are mixtures of essential oils and resins. In many essential oils a crystalline matter is deposited, called a camphor or stearoptene. They are all soluble in alcohol. Many absorb oxygen from the air and become acid, as oil of cinnamon. They are violently acted on by nitric acid and iodine, chlorine, bromine, &c.

They may be divided into three kinds: 1st, those containing only carbon and hydrogen, as oil of turpentine. 2nd, those containing also oxygen, as oil of cloves. 3rd, those containing sulphur, as oil of garlic.

1. Non-Oxygenated Essential Oils.

Almost every one of these (which constitute a very numerous class of oils), as yet accurately analyzed, has been found to contain carbon and hydrogen in the proportion $C_{10}H_8$, or what is the same thing, C_5H_4, or $C_{20}H_{16}$. The following are the most important.

Oil of turpentine, $C_{10}H_8$, or $C_{20}H_{16}$, is obtained by distilling, with water, turpentine, the juice exuding from many species of *pinus*. Rosin, resin, or colophonium, remains in the retort. The oil has a peculiar smell, and burns with a smoky flame. Its sp. gr. is 0·86. It boils at 312°. Strong nitric acid sets fire to it, and it is also decomposed with flame by chlorine. It dissolves sulphur,

phosphorus, and fat oils. When exposed to hydrochloric acid gas, it combines with it, forming a white crystalline solid like camphor, and a liquid compound. The solid is $C_{20}H_{17}Cl=C_{20}H_{16},HCl$. When heated with lime, it yields a pure oil, *dadyle* $C_{20}H_{16}$. The liquid hydrochlorate, heated with lime, yields another pure oil, *peucyle*, rather more volatile than dadyle, but having the same composition. Oil of turpentine would seem to be composed of peucyle and dadyle, both $C_{20}H_{16}$; the former giving a liquid, the latter a solid compound, with hydrochloric acid.

Nitric acid, by long boiling, converts oil of turpentine into an acid, turpentinic acid. $C_{14}H_9O_7,HO$?

Oil of turpentine is used in medicine, internally, as a vermifuge, especially in cases of the larger worms, such as *tænia*; externally, as an excellent rubefacient and counter-irritant. In the arts it is much prized as a solvent for resins in making varnishes.

Oil of juniper has the same composition as oil of turpentine, but possesses its own peculiar odour, which it communicates to alcohol in *gin*. This oil is diuretic.

Oil of savine has the same composition. It is also diuretic. *Oil of elemi* has the same composition, and a pleasant odour. *Oil of storax*, or *styrole*, appears to have the composition of C_2H, or some multiple of it. Nitric acid acts on it, producing hydrocyanic acid, benzoic acid, and a fragrant crystalline body, nitrostyrole. Styrole itself is a very remarkable substance, differing as it does from all the other non-oxygenated oils. Dr. Blyth has been for some time engaged in its investigation, and has obtained very interesting results, not yet ready for publication.

[The formula recently assigned to styrol by Drs. Blyth and Hoffman is $C_{16}H_8$. When heated in a closed tube to the temperature of about 425°, it curiously changes from a limpid fluid to that of a vitreous solid, having precisely the same composition, as the fluid styrol, to which they gave the name of *metastyrol*.]

Oil of lemons has the probable composition, C_5H_4. Like oil of turpentine it is composed of two isomeric oils, *citrene* and *citrylene*, which combine with hydrochloric acid, forming a liquid and a solid compound, decomposed by heating with lime. The solid camphor seems to be, $C_{10}H_9Cl=C_{10}H_8,HCl$. The oils of *cedro*, *cedrat*, *oranges*, and *limes*, are all essentially identical with oil of lemons. *Oil of neroli*, or of *orange-flower*, is quite distinct, having the odour of the flower, while the others have that of the rind of the fruit. Its composition is not accurately known.

Oil of copaiva is another isomeric form of oil of turpentine, which it very much resembles, forming a camphor with hydrochloric acid. It is diuretic, and much used in affections of the bladder and urethra. *Oils of pepper* and *of cubebs* are still of the same composition in 100 parts, although the latter is supposed to be $C_{15}H_{12}$.

2. Oxygenated Essential Oils.

The principal oils of this class have been already considered, their radicals being known. These are *oil of bitter almonds*, or hyduret of benzoyle; *oil of spiræa*, or hyduret of salicyle; *oil of cinnamon*, or hyduret of cinnamyle; *oil of cloves* (eugenic acid) *oil of cumine*, or hyduret of cumyle; *oil of aniseed*, the solid part of which is $C_{20}H_{12}O_2$, and with nitric acid yields anisic acid, and other

compounds already described at p. 666; *oil of valerian*, chiefly valerianic acid, &c. The essence of valerian, according to Gerhardt, generally contains several compounds, especially if old. When fresh, it contains no valerianic acid, but an oil, *valerole*, which is crystallizable, and soon passes into valerianic acid in the air. This oil is $C_{12}H_{10}O_2$, and is isomeric with metacetone, also with Kane's oxide of mesityle, and with oxide of allyle (see oil of garlic, p. 683). Besides valerole, the essence contains a carbo-hydrogen, *borneéne*, $C_{10}H_8$, identical with the oil obtained from borneo camphor; and finally, a camphor, which is identical with borneo camphor.

Oil of cinnamon, according to Mulder, is, when quite fresh, $C_{20}H_{11}O_2$. It rapidly attracts oxygen, and $3(C_{20}H_{11}O_2)+O_8=1$ eq. cinnamic acid, 1 eq. resin alpha, $C_{12}H_5O$, 1 eq. resin beta, $C_{30}H_{15}O_4$, and 6 eq. water H_6O_6. With hydrochloric acid it yields two different resins, $C_{20}H_8O$, and $C_{14}H_7O$, besides other products. With oil of vitriol it yields two more resins, $C_{30}H_{15}O_2$, and $C_{30}H_{15}O$, which together are equal to 3 eq. of the oil *minus* 3 eq. water. With nitric acid the fresh oil forms a crystalline compound, $C_{18}H_9NO_7=C_{18}H_8O_3+NO_3+HO$. With water this body yields hyduret of cinnamile, $C_{18}H_8O_2$. If dissolved in sulphuric acid and mixed with water it gives cinnamic acid, $C_{18}H_7O_3$. Along with the crystals, nitric acid yields a red oil, which, with water, gives another oil, $C_{15}H_7O_2$.

Oil of anise, $C_{20}H_{12}O_2$, yields with bromine a compound in fine crystals, $C_{20}\left\{\begin{matrix}H_9\\Cl_3\end{matrix}\right.O_2$. When acted on by strong acids, or by the chlorides of tin or antimony, oil of anise is converted into an isomeric body, anisoine, analogous to benzoine.

Of the remaining oils of this class may be mentioned the oils of *dill*, of *fennel*, of *parsley*, of *carraway*, of *coriander*, of *pimpernel*, of *peppermint* ($C_{10}H_{10}O$, or $C_{20}H_{20}O_2$; this oil yields several new compounds with chlorine), of *marjoram*, of *lavender*, *rosemary*, *basil*, *thyme*, *rue* ($C_{28}H_{28}O_3$), *cascarilla*, *chamomile*, *wormwood*, *tea*, *cardamom*, *nutmeg*, *cajeput*, *rhodium*, *rose* (otto or attar of roses), *bergamot*, *saffron*, *sassafras*, and *sweet bay* ($C_{20}H_{16}O$). Of these, little certain is known, and almost all require a careful study. The oil of sassafras, $C_{10}H_5O_2$, when cooled, deposits very large and beautiful crystals, measuring $1\frac{1}{2}$ inch on the side. With bromine, the solid essence yields crystals, composed of $C_{10}H\,Br_4O_2$.

The oil or essence of *semen contra* is said to be $C_{18}H_{15}O_2$. That of *artemisia dracunculus*, or essence of estragon, yields, when treated with sulphuric acid, *anisoine*, identical with that of oil of anise, and in fact contains the same oxygenated oil (stearoptene of anise), along with a different carbo-hydrogen. Laurent has obtained from essence of estragon a series of new compounds. He represents the essence by $C_{32}H_{20}O_3$. With nitric acid it yields draconic acid, $C_{32}H_{13}O_{10},2HO$; this, with chlorine and bromine, gives chlorodraconesic and bromodraconesic acids, $C_{32}H_{11}Cl_3O_{10},2HO$, and $C_{32}H_{11}Br_2O_{10},2HO$. Nitric acid yields further; $C_{32}\left\{\begin{matrix}H_{12}\\NO_4\end{matrix}\right.O_{10},2HO$, which is called nitrodraconasic acid: and $C_{32}\left\{\begin{matrix}H_{11}\\2NO_4\end{matrix}\right.O_{10},2HO$, which is nitrodraconesic acid. The former of these two acids, with chlorine and bromine, yields nitrochlorodraconesic acid, $C_{22}\left\{\begin{matrix}H_{11}\\Cl\\NO_4\end{matrix}\right.O_{10}$

2HO; and nitrobromodraconesic acid, $C_{32}\left\{\begin{matrix}H_{11}\\Br\\NO_4\end{matrix}\right.O_{10},2HO$. With chlorine, the essence, $C_{22}H_{20}O_3$, gives chloride of draconyle, $C_{32}H_{15}Cl_7O_3$ (?), which, when acted on by potassa, yields chloride of potassium and chlorodraconyle, $C_{32}H_{14}Cl_6O_3$. If formed by direct substitution, like the preceding compounds, the chloride of draconyle ought to be $C_{32}\left\{\begin{matrix}H_{15}\\Cl_5\end{matrix}\right.O_3$, the sum of the chlorine and hydrogen being 20 eq. as in the chlorodraconyle, in which, however, Laurent admits $\frac{1}{2}$ eq. of hydrogen more. These researches of Laurent are very interesting; and it has very recently been established by Gerhardt and Laurent that draconic acid is identical with anisic acid, and that dracole, an oil obtained by heating draconic acid with baryta, is identical with anisole. I presume that the true formulæ are those of draconic acid and its derivatives, so that the formula of anisic acid will have to be doubled.

The concrete essence of the tonka bean is called *coumarine*. It is very fragrant, and its formula is said to be $C_{18}H_7O_4$. Potassa changes it into salicylic acid, and hot nitric acid converts into nitropicric acid. Cold nitric acid produces a white volatile crystalline solid, $C_{18}\left\{\begin{matrix}H_6\\NO_4\end{matrix}\right.O_4$. Coumarine also combines with chloride of antimony, forming yellow crystals.

3. Sulphuretted Essential Oils.

This class of oils is distinguished by a pungent peculiar smell, and acrid burning taste, as in oil of mustard, or an intense alliaceous odour, as in oil of garlic or of onions. The more important of them have been lately investigated, and have yielded very striking results.

Essence of mustard is prepared from mustard-seed in the same way as oil of bitter almonds from that seed. The seed is macerated with water and afterwards distilled, when it yields an oil of a most remarkable nature, containing not only sulphur, but also nitrogen. The pure oil is colourless, of sp. gr. 1·010, and boils at 298° or 300°. Its formula is $C_8H_5NS_2$, so that it contains no oxygen. With ammonia it forms a crystalline compound, which is, in fact, an organic base or alkali, *Thiosinnamine* $= C_8H_8N_2S_2$. This is a bitter compound, which forms, like nearly all organic bases, crystalline compounds with chloride of platinum and chloride of mercury.

Thiosinnamine, acted on by dry oxide of lead or of mercury, loses all its sulphur, forming a new base, *sinnamine* $= C_8H_6N_2 = C_8H_8N_2S_2 - 2HS$. It is, therefore, Thiosinnamine, minus 2 eq. sulphuretted hydrogen, which have acted on the oxide of lead, forming water and sulphuret of lead. Sinnamine forms definite compounds with chlorides of mercury and platinum. It is a powerful base, and very bitter to the taste.

When oil of mustard is acted on by moist hydrated oxide of lead, it loses both sulphur and carbon, in the proportion CS_2, forming sulphuret of lead and carbonate of lead, along with a new base, *sinapoline*, which dissolves in hot water, in alcohol and in ether. Its formula is $C_{14}H_{12}N_2O_2$; and it is formed from 2 eq. oil of mustard, with 6 eq. oxide of lead and 2 eq. water, as follows: $2(C_8H_5NS_2)+6PbO+2HO=C_{14}H_{12}N_2O_2+4PbS+2(PbO,CO_2)$.

When oil of mustard is acted on by an alcoholic solution of potash, there is separated neutral carbonate of potassa, and the addition of water causes the separation of an oily liquid, which is in its relations analogous to oil of mustard. It

appears to be $C_{28}H_{25}N_3S_4O_4$. By the action of baryta upon it, sulphuret of barium is formed, and a basic compound not further examined. The liquid from which this oil has separated contains the potassium salt of a very remarkable acid, which forms with a salt of lead the compound $C_8NH_6S_4,Pb,=C_8H_5NS_2$, $HS+PbS$. These compounds are produced as follows: 6 eq. oil of mustard, 10 of water, and 2 eq. of potassa, $6(C_8H_5NS_2)+10HO+2KO$, yield 1 eq. of the new oil $C_{28}H_{25}N_3S_4O_4$, 1 eq. ammonia NH_3, 4 eq. carbonic acid, C_4O_8, and 2 of the new salt of potassium $2(C_8H_6NS_4,K)$. It is probable, however, that the first change is more simple, and that 3 eq. oil of mustard, 5 of water and 1 of potassa, yield 1 eq. of an oil $C_{14}H_{14}N_2S_2O_2$, 2 eq. carbonic acid, C_2O_4, and 1 of the potassium salt $C_8H_6NS_4,K$. Two eq. of the oil $C_{14}H_{14}N_2S_2O_2$ lose 1 eq. ammonia, and give rise to the oil $C_{28}H_{25}N_3S_4O_4$.

These very interesting facts, important in a high degree from their bearing on the theory of organic bases, are taken from a paper by Dr. Will lately published, to which I refer the reader. Dr. Will points out some curious relations. Thus sinapoline, $C_{14}H_{12}N_2O_2$, may be derived from 2 eq. oil of mustard and 6 eq. water, which yield 1 eq. sinapoline, 2 eq. carbonic acid, and 4 eq. sulphuretted hydrogen. If we now suppose 2 of the 4 eq. of HS to combine with 1 eq. sinapoline, they will produce the oil, $C_{14}H_{14}N_2O_2S_2$, which is supposed to be first formed and afterwards to lose ammonia: while, if the 2 other eqs. of HS combine with 1 eq. of unchanged oil of mustard they will form the acid of the new potassium salt: $C_8H_5NS_2+2HS=C_8H_7NS_4$.

Again, sinapoline may be viewed as hyduret of benzoyle, *plus* 2 eq. ammonia, $C_{14}H_6O_2,2NH_3$; and the hypothetical oil is then $C_{14}H_6O_2,N_2H_8S_2$, or hyduret of benzoyle, *plus* 2 eq. sulphuret of ammonium.

The separation of the elements of bisulphuret of carbon from oil of mustard, and the simultaneous formation of a series of basic compounds, would indicate that oil of mustard might be a compound of sulphocyanogen; since sulphocyanide of ammonium (see p. 576), when heated, gives off bisulphuret of carbon, and gives rise to a series of basic compounds, melamine, ammeline, &c. Now it is very remarkable that oil of mustard admits of being considered as $C_6H_5+C_2NS_2$, that is, the sulphocyanide of a new radical *allyle*, C_6H_5; of which, as we shall presently see, oil of garlic is the sulphuret. Finally, oil of mustard may be a compound of hydrocyanic acid with the hydrosulphuret of sulphuret of acryle: $C_6H_3S,HS+C_2NH$. Its very pungent smell and powerful action on the eyes certainly rank it beside acroleine, C_6H_3O,HO. But all these views and relations are mentioned here as an example of the way in which such relations may be discovered, rather than as being in any way demonstrated.

Oil of mustard contains an indifferent nitrogenized body, *myrosine*, which, analogous to emulsine, yields the essential oil after maceration of the seed with water, and fermentation. The fermentation of myrosine is prevented in the same way as that of emulsine, namely, by coagulation. The seeds also contain a crystalline body, *sinapisine*, resembling a fat. The substance, which, along with myrosine, yields the oil, appears to be *myronic acid*, or rather *myronate of potash*, a body not yet fully studied. The seeds of sinapis alba contain the myrosine, as sweet almonds contain emulsine; but, being destitute of myronic acid or myronate of potassa, as sweet almonds are of amygdaline, they yield none of the oil.

It has very recently been shown, by Hubatka and Wertheim, that the essential oils of cochlearia armoracia (horse-radish), cochlearia officinalis, and alliaria officinalis, consist almost entirely of oil of mustard, although the latter oil has

also a very strong smell of oil of garlic, an oil which has not been discovered in it.

The essential oil of garlic, from the bulbs of *allium sativum*, is a peculiar sulphurized compound. Wertheim has lately studied it, and shown that it is the sulphuret of a new radical Allyle=C_6H_5=All, and its formula is C_6H_5,S=AllS. The crude oil contains a little of a higher sulphuret, possibly $AllS_2$, and also some of the oxide of allyle, C_6H_5O=AllO, which is an oily liquid of an offensive smell. The radical allyle appears to enter into numerous combinations, and, among others, Wertheim analyzed the following: the sulphuret, or pure oil of garlic, AllS; the compounds of that sulphuret with the sulphurets of platinum, palladium and silver, $5AllS+6PtS_2$; $2AllS+3PtS_2$; 2AllS+3PdS; and xAllS+AgS?; double compounds with the sulphurets and chlorides of mercury and platinum; $3(AllS+PtS_2)+(AllCl+PtCl_2)$; and $(AllS+2HgS)+(AllCl+2HgCl)$; and lastly nitrate of the oxides of silver and allyle, $(AllO+AgO)+NO_5$. Our space does not permit us to do more than point out the existence of these curious compounds.

The essential oil of *assafetida* appears to consist of at least two oils, one of which, if not both, contains sulphur. It has a very offensive odour. It does not combine with ammonia like the oil of mustard. Dr. Douglas Maclagan finds, as might be expected from the odour, that one of the oils it contains is sulphuret of allyle.

The essential oils of *hops*, of *water pepper*, and of *arum maculatum*, are believed to contain sulphur.

CONCRETE VOLATILE PRINCIPLES, ALLIED TO THE ESSENTIAL OILS.

There are several substances which may be classed under this head; such as *Hellenine* from *inula helenium*, which is a volatile crystalline solid, $C_{15}H_{10}O_2$. With nitric acid it yields *nitrohellenine* $C_{15}\left\{\begin{matrix}H_9\\NO_4\end{matrix}\right.O_2$. When distilled with anhydrous phosphoric acid, hellenine loses 2 eq. water, yielding *helleníne*, a carbo-hydrogen, $C_{15}H_8$. With chlorine it yields the compound $C_{15}\left\{\begin{matrix}H_9\\Cl\end{matrix}\right.O_2+HCl$.

Asarone from *asarum europæum* is a volatile solid, having a remarkable tendency to crystallize in beautifully defined forms, and also to pass into the amorphous condition, from which it may be again brought into the crystalline state. Schmidt has very recently studied its crystallization, under the microscope, and has obtained results which are most interesting in reference to the formation of crystals in general. I must refer to his elaborate paper in the "Annalen der Chemie and Pharmacie," for February, 1845. Its composition is, $C_{20}H_{13}O_5$.

Anemonine, from various species of *anemone*, is a volatile, crystallizable solid, the formula of which is $C_5H_2O_2$. It forms with oxide of lead a compound, $3(C_5H_2O_2)+PbO$. With bases it yields *anemonic acid*, the composition of which is unknown.

Cantharidine, the active principle of Spanish flies, is a volatile acrid solid, the composition of which is $C_{10}H_6O_4$.

The following plants, *epidendron vanilla*, *quassia amara*, *tanghinia madagascariensis*, *primula auricula*, and *primula veris*, contain concrete volatile essences, not yet analyzed.

CAOUTCHOUC, OR GUM ELASTIC.

Caoutchouc is a substance *sui generis*, which in composition approaches more nearly to the essential oils than to any other class of compounds. It is the coagulated or inspissated juice of many tropical trees, the chief of which is *siphonia elastica* (*iatropha elastica*, *hevea guianensis*). The juice, as it flows from the tree is made to dry on moulds of clay, which are afterwards broken out, leaving a bottle of caoutchouc. It is generally blackened by smoke, but when pure it is white and transparent, it is highly elastic, and the freshly cut surfaces adhere strongly if pressed together. It is insoluble in water, alcohol, and acids; but it dissolves in ether, naphtha, coal-tar naphtha, bisulphuret of carbon and essential oils. Its solutions in ether and coal-tar naphtha, when dried up, leave the caoutchouc in an elastic state. On this principle waterproof cloth is made. Caoutchouc is much used in chemical operations to form flexible connecting tubes.

When exposed to heat, caoutchouc first melts, and then distils, yielding a mixture of several oily liquids, all of which, as well as pure caoutchouc itself, are carbo-hydrogens. Some of these oils boil at 90°, others at 680°, and at intermediate points. I found that one highly rectified oil which boiled at 96°, and had the composition of olefiant gas, when acted on by sulphuric acid, yielded an oil which boiled at 428°, and had the same composition. But most of these oils have the composition of oil of turpentine, C_5H_4 or $C_{10}H_8$. One of these, called *caoutchine*, gives with chlorine an oil, $C_{10}H_8+HCl$.

RESINS.

Resins are generally found along with essential oils, and many of these oils, by the action of the air, are converted into resins. In this change, the essential oils lose a part of their hydrogen, which is converted into water, and take up some oxygen besides. In fact, the resins, as a class, are acid bodies, they are insoluble in water, but become soft in boiling water. They dissolve in alcohol, and often crystallize from that solvent.

The acid resins combine with bases; their salts with the alkalies are called resinous soaps. The resins are not volatile, although very inflammable. They are purified from essential oils by distilling off the latter along with water; but, as thus obtained, they are generally mixtures of several resins.

Turpentine and *Colophony, or Common Resin.* Turpentine is the semifluid juice which exudes from many species of *pinus*. When distilled with water, it yields oil of turpentine, $C_{10}H_8$ or $C_{40}H_{32}$, while colophony or resin remains behind, which is $C_{10}H_7O$ or $C_{40}H_{28}O_4$, or, more accurately, $C_{40}H_{30}O_4$. Here the oil, $C_{40}H_{32}$, has lost 2 eq. hydrogen, replaced by 2 eq. oxygen, $C_{40}H_{30}O_2$, and this compound, like aldehyde, has taken up 2 eq. of oxygen to form the acid resin, $C_{40}H_{30}O_4$.

Colophony contains two different resins: resin *alpha*, or *pinic acid*, and resin *beta*, or *sylvic acid*. The latter is said to be $C_{20}H_{15}O_2$, the former $C_{40}H_{30}O_4$; and their properties are isomeric with it, very similar, being those of colophony which is formed of them. The sylvic acid is crystallizable.

When distilled with lime, colophony yields two oily liquids, *resineone*, $C_{26}H_{23}O$, and *resinone*, $C_{10}H_9O$.

The *resin of copaiva* is $C_{40}H_{30}O_4$, according to Rose; but there is some reason to believe that it is isomeric with the preceding. A variety of it has occurred,

containing $C_{40}H_{30}O_8$, and when combined with oxide of lead, $C_{40}H_{28}O_6$. This resin crystallizes.

The *resin of elemi* contains two resins, one crystallizable. Both are said to be $C_{20}H_{16}O_2$. *Anime* also contains two resins. *Euphorbium* yields a resin having the same composition as elemi. *Benzoin* contains, besides benzoic acid and a volatile oil, three resins, *alpha*, $C_{70}H_{42}O_{14}$; *beta*, $C_{40}H_{22}O_9$; and *gamma*, $C_{30}H_{20}O_5$. The resin alpha contains the sum of the other two, and by long boiling with carbonate of soda, which dissolves the resin gamma alone, is resolved into them.

Balsam of Tolu contains, besides essential oil, benzoic and cinnamic acids, and a carbo-hydrogen, $C_{24}H_{18}$, a resin, $C_{18}H_{10}O_5$. It contains the elements of benzoic ether, *plus* 1 eq. oxygen. When the balsam is distilled, *per se*, it actually yields benzoic ether, along with a new carbo-hydrogen, called benzoéne, $C_{14}H_8$. This last compound yields with sulphuric acid a new acid, $C_{14}H_7S_2O_5 + 3HO$; and, with nitric acid, two new nitrogenized compound, $C_{14}\left\{\begin{matrix}H_7\\NO_4\end{matrix}\right.$, called *protonitrobenzoéne*, and another, binitrobenzoéne. The former is isomeric salicylamide. With chlorine, benzoéne also yields several new products.

Styracine, the resin of styrax, is $C_{24}H_{11}O_2$. When acted on by nitric acid, it yields the products of decomposition of cinnamic acid.

The resin of guaiacum is remarkable to its tendency to become blue by the contact of may different substances. It contains two resins, but their composition is not ascertained. *Lac* contains four resins, besides colouring matter. *Dammara*, *mastic*, *dragon's blood*, and *sandarach*, are resins much used in making varnishes.

Jalap contains two resins; one, a soft resin, soluble in ether, $C_{42}H_{34}O_{18}$; and an acid resin insoluble in ether, which, from striking a fine red colour with sulphuric acid, is called *rhodeoretine*, $C_{42}H_{35}O_{20}$. When combined with bases, it takes up 1 eq. water, forming *hydrorhodioretine*, very similar to rhodeoretine, but soluble in water, $C_{42}H_{36}O_{21}$. When rhodeoretine is acted on by hydrochloric acid, it is resolved into grape sugar, $C_{12}H_{12}O_{12}$, and an oily liquid *rhodeoretinole*, $C_{30}H_{23}O_8$. This reaction places rhodeoretine near to salicine and phloridzine. On the other hand, if we compare 7 eq. of starch, 7 $(C_{12}H_{10}O_{10})$= $C_{84}H_{70}O_{70}$ with 2 eq. rhodeoretine, 2 $(C_{42}H_{35}O_{20})$=$C_{84}H_{70}O_{40}$, we can see how this resin may be formed from starch, &c. by deoxidation. It is also worthy of notice that rhodeoretine agrees with salicine and phloridzine in the number of eqs. of carbon. Salicine is $C_{42}H_{29}O_{22}$ and phloridzine $C_{42}H_{29}O_{24}$. *Rhubarb* contains 3 resins, *aporetine*, *phæoretine*, and *erythroretine*. The two first are both $C_{16}H_8O_7$; the third is $C_{19}H_9O_7$. They are accompanied by an intensely yellow crystallizable acid, chrysophanic acid $C_{10}H_4O_3$ or $C_{40}H_{16}O_{12}$. This latter substance is also found in lichens, such as *parmelia parietina*, *squamaria elegans*, &c. *Copal*, which of all the resins is the most insoluble, is said to contain five. Copal varnish is made by adding hot oil of turpentine to copal fused at a gentle heat.

Turf or peat contains several resinous bodies, examined by Mulder. In the turf of Friesland he found four resins: *alpha*, $C_{30}H_{40}O_9$; *beta*, $C_{77}H_{67}O_9$; *gamma*, $C_{104}H_{94}O_9$; and *delta*, $C_{131}H_{121}O_9$. A lighter kind of turf from another locality yielded two resins: *alpha*, $C_{35}H_{28}O_5$; and *gamma*, $C_{90}H_{84}O_6$.

Resinous varnishes are made by dissolving resins in oil of turpentine and other essential oils; or in drying oils. Spirit varnishes are made by dissolving resins in very strong alcohol.

ACTION OF HEAT ON RESINS.

When resins are distilled in close vessels, they yield a great deal of gas of a high illuminating power, and many volatile liquid compounds of carbon and hydrogen.

Pinic acid yields, when heated, *colopholic acid*. Colophony yields *resineine*, an oil, $C_{20}H_{15}O$; also *retinaphtha*, $C_{14}H_8$, which with chlorine forms a compound $C_{14}H_6Cl_2$; *retinyléne*, $C_{18}H_{12}$, which with sulphuric acid yields an acid, isomeric with sulphocumenic acid, $C_{18}H_{11}S_2O_5,HO$; *retinole*, $C_{32}H_{15}$; and finally a solid product, *retisteréne*, fusible at 152°, having the same composition as naphthaline, $C_{20}H_8$.

COLOURING MATTERS CONTAINING NO NITROGEN.

1. Yellow colouring matters.

The following are the most important of the yellow vegetable colouring matters, many of which are used in dyeing.

Curcumine, from the root of *curcuma longa*, is resinous, and is dissolved by alkalies, which change it to brown. Hence it is used as a test for alkalies, under the name of *turmeric*. *Gamboge yellow* is extracted from gamboge, the dried juice of *Garcinia gambogia*. It is resinous and powerfully purgative. *Annotto* or *Anatto* is obtained from the seeds of *Bixa orellana* and *Metella tinctoria*. *Carotine* is the colouring matter of the carrot, *Daucus carota*. *Rhabarberine* is a name formerly given to the yellow acid of rhubarb, now called *chrysophanic acid*, which is found also in lichens as above stated. It has great colouring power, and yields a fine violet with alkalies. It is fusible and volatile. Formula, $C_{10}H_4O_3$. From occurring in *parmelia parietina*, it has been called *parietine* and *parietinic acid*. *Luteoline*, the colouring principle of *Reseda luteola* or *Woad*, is volatile and crystallizable. *Quercitrine*, from the bark of *quercus tinctoria*, is crystalline, and its composition is $C_{16}H_8O_9,HO$. Other yellow colouring matters are *Morine*, from *Morus tinctoria*; *Safflower yellow*, from *Carthamus tinctorius*; *Polychroite* from *Saffron*, and others of less interest.

2. Red colouring matters.

Draconine, or Dragon's blood, is a red gum resin, from *Dracæna draco*. It is much used to colour varnishes. *Santaline*, the colouring matter of *pterocarpus santalinus*, is also resinous, and has an intense red colour. *Anchusine*, from *Anchusa tinctoria*, is the source of the colour of alkanet; it is resinous and yields violet vapours when heated. *Carthamine* is the red colouring matter of safflower, *carthamus tinctorius*. It is a very fine and intense red, much used for dyeing rose colour, for pink saucers and for rouge, at least the *rouge végétale*.

Madder, the root of *rubia tinctorum*, contains three different red colouring matters, *madder purple*, *red*, and *orange*. All three are volatile, and the sublimed crystals of madder red, which are of a fine orange red colour, are called *alizarine*. This is the substance which yields the turkey red dye. With alkalies it yields purple or violet colour, with acids yellow. When dissolved in hot water or alcohol, alizarine yields rose-coloured solutions. The composition of pure madder red is unknown.

Hæmatoxyline is the red of *logwood*, *hamatoxylum campechianum*. It is soluble in water and alcohol, and yields orange crystals, which give to water a red colour, brightened by acids and turned to a violet or blue by alkalies. With

alum, logwood yields various shades of violet; with an iron mordant, grey and black. Black cloth and hats are dyed with it, which is the reason they are reddened by acids. According to Erdmann, pure hæmatoxyline is pale yellow, and is coloured red by the atmosphere. Its formula he found to be $C_{40}H_{17}O_{15}$. When acted on by ammonia it yields *hemateine*, which is dark red, and forms with excess of ammonia a splendid purple matter. Hæmateine is $C_{40}H_{15}O_{16}$; and the purple compound with ammonia is $C_{40}H_{15}O_{16} + 2NH_3 + aq.$ *Brazil-wood* and *Camwood* yield colouring matters very similar to hæmatoxyline, if not identical with it.

Many flowers contain a red colouring matter, which is turned green by alkalies, and is very fugitive. It is soluble in water and alcohol.

3. Blue colouring matters.

These are chiefly found in flowers and fruits. They are very closely allied to the red of flowers and fruits, which are no doubt often derived from them by the action of acids. They are all turned green by alkalies and red by acids. Such blue colouring matters as are more permanent contain nitrogen, and will be considered hereafter.

4. Green colouring matter. Chlorophylle.

This is the green of leaves. It is of a nature allied to that of wax, soluble in ether and alcohol, insoluble in water. It is very neutral or indifferent in its relations to other substances.

Polychrome is the name given to a peculiar crystalline principle found in some vegetables, such as quassia. It gives to water the quality of exhibiting a curious play of colours, among which blue predominates, like that of the opal, when the solution is viewed by reflected light, 1 part will give this property to 1,500,000 of water. Its formula is said to be $C_{16}H_8O_9$,HO, which is the same as that of *quercitrine*, and contains 2 eq. of oxygen more than the *aporetine* of rhubarb.

NON-AZOTIZED VEGETABLE COMPOUNDS, THE NATURE OF WHICH IS NOT YET ASCERTAINED.

In this subdivision may be included a number of compounds, most of which crystallize and have a bitter taste, but are neutral and cannot yet be referred to any particular series of compounds. Salicine, phloridzine, and rhodeoretine, which would formerly have been here described, are now treated of along with substances allied to them. The substances now to be briefly mentioned have usually been termed the bitter and extractive principles of plants.

Gentianine, from *Gentiana lutea*, forms yellow needles, very bitter. *Menyanthine*, from *Menyanthes trifoliata*, is bitter, but does not crystallize. *Absinthine*, from *Artemisia absintheum* or wormwood, is a semi-crystalline mass, very bitter, soluble in alcohol. *Tanacetine*, from *tanacetum vulgare*, is very similar to it. *Santonine* is a beautifully crystallizable compound, obtained from *Artemisia contra*. It is soluble in alcohol, bitter to the taste, volatile, and coloured yellow by the action of light. *Populine*, from the bark and leaves of *populus tremula*, forms white crystals, of a sweetish and acrid taste, coloured red by sulphuric acid. It may possibly be connected with salicine. *Liriodendrine* is a crystalline bitter substance, from the bark of *liriodendron tulipifera*. *Picrolichenine* is an intensely bitter crystalline compound, found in the lichen *variolara amara*. It is princi-

pally febrifuge. In contact with ammonia and without the excess of air, it is changed into a reddish yellow-matter, which finally deposits yellow crystals, not bitter. With access of air, it yields with ammonia a deep-red very soluble matter. *Cetrarine* is another bitter principle, from the lichen, *cetraria islandica*, or Iceland moss. It is coloured deep blue by hydrochloric acid. It is said also to be febrifuge. *Ilicine*, from *ilex aquifolium*, forms brownish-yellow crystals very bitter and febrifuge. *Syringine* is the bitter principle of the lilac, *syringa vulgaris*. It is crystalline and soluble in alcohol. *Daphnine* is a bitter crystalline substance, obtained from *Daphne Mezereon*. *Hesperidine* is a crystalline body found in the spongy envelope of oranges and lemons. *Elaterine* is the active principle of *Momordica Elaterium*, is crystalline, bitter, and very purgative. Its formula is $C_{20}H_{14}O_5$. *Colocynthine*, the active principle of colocynth, is amorphous, intensely bitter and purgative. *Bryonine*, from *Bryonia alba* and *dioica*, is similar in its properties. *Mudarine* is the emetic principle of *calotropis mudarii*. It is a brown amorphous matter, the solution of which in water gelatinizes at 95° and becomes again liquid on cooling. *Scillitine* is the bitter of *scilla maritima*. It is amorphous, bitter, purgative and emetic. *Cathartine* is the bitter purgative principle of senna. *Antiarine*, $C_{14}H_{15}O_5$, is the active principle of the poison called *upas antiar*. It is, when introduced into a wound, especially along with soluble matters such as sugar, a most powerful poison, and hitherto no means are known by which its fatal action can be arrested.

Zanthopicrine is a bitter crystalline substance from the bark of *Zanthoxylum Clava Herculis*. It has been little studied. *Picrotoxine*, the bitter principle of *menispermum cocculus* (cocculus indicus), forms white prisms. The composition of these is not certain, and recent researches seem to show that picrotoxine is a vegetable base, and contains nitrogen, like all that class of compounds. *Columbine* is a crystalline bitter substance, obtained from *columbo*, the root of *menispermum palmatum*, and somewhat analogous to picrotoxine. *Quassine* is a yellow, crystalline, and very bitter substance from the wood of *quassia amara*. Its formula is said to be $C_{20}H_{12}O_6$. *Lupuline*, the bitter principle of hops, is not crystallizable. *Lactucine* is a crystalline resinoid bitter substance, from the juice of *lactuca virosa* (lactucarium). It has anodyne properties. *Ergotine* is an uncrystallized brown powder, extracted from ergot of rye by hot alcohol, after the fatty matters have been removed by ether. It appears to be poisonous, and is probably the active matter of the ergot. *Porphyroxine* is a crystallizable substance found in Bengal opium. Its solution in diluted acids becomes red when boiled. It requires further investigation. *Saponine* is a peculiar principle, found in the root of *saponaria officinalis*. It is white, amorphous, and has a taste first sweet, then styptic, and finally acrid. It is a powerful sternutatory. It is soluble in water, and its solution, even when much diluted, froths when agitated, like a solution of soap. The root is used as a tetergent. When acted on by alkalies, it is converted into an acid, saponic acid, $C_{26}H_{23}O_{12}$. *Asparagine*, $C_8H_8N_2O_6,2HO$, is a crystallizable substance found in asparagus, in althæa officinalis, and in other plants, especially those grown in the dark. When boiled with alkalies it loses ammonia, NH_3, and forms *aspartic acid* $C_8H_5NO_6,2HO$, which is a bibasic acid. The crystals of asparagine are very large, colourless, and transparent, also hard and brittle. Not only alkalies, but acids, and ferments transform it into aspartic acid and ammonia. *Smilacine* is a crystalline substance, found in *smilax sarsaparilla*. Its composition is $C_{15}H_{13}O_5$. In *China nova* there is found a substance very analogous to smilacine, the composition of which

is $C_{15}H_{12}O_4$: that is, smilacine, *minus* 1 eq. water. *Seneguine* is an acrid and astringent substance found in *Polygala senega*. It excites sneezing powerfully. Formula, $C_{22}H_{18}O_{11}$. *Gaiacine* appears to be the active principle of guaiacum. It is acrid and bitter. *Plumbagine*, extracted from the root of *plumbago europæa*, forms yellow prisms, the taste of which is first sweet and styptic, then acrid and hot. The yellow colour of its aqueous solution is turned cherry-red by alkalies. *Cyclamine* is a crystalline matter from the root of *cylamen europæum*. It is very acrid, purgative, and emetic. *Peucedanine* is a very acrid crystalline principle derived from the root of *peucedanum officinale*. Formula, C_4H_2O. *Imperatorine*, $C_{24}H_{12}O_5$, is a crystallizable compound, obtained from the root of *imperatoria ostruthium*. It is very acrid and styptic. *Phillyrine*, from the bark of various species of *phillyrea*, crystallizes in silvery scales, which are bitter. *Fraxinine*, from the bark of *fraxinus excelsior*, is a crystallizable bitter principle. *Tanguine* is a similar substance from *tanghinia madagascariensis*. It is poisonous. *Melampyrine* is a tasteless, neutral, crystalline substance, from *melampyrum nemorosum*. *Meconine* is a neutral, crystalline compound contained in opium. It is soluble in water, alcohol, and ether. It is acrid to the taste, fusible, and volatile. Formula $C_{10}H_5O_4$. With nitric acid it yields *nitromeconine* or *nitromeconic* acid, $C_{20}H_9NO_{12}$. As meconine may be $C_{20}H_{10}O_8$, nitromeconine is $C_{20}\left\{\begin{matrix}H_9\\NO_4\end{matrix}\right.O_8$; in which 1 eq. hydrogen is replaced by 1 eq. nitrous acid. Chlorine transforms meconine into crystals, containing chlorine, which, however, by the action of alkalies, yield an acid free from chlorine, mechloic acid, $C_{14}H_7O_{10}$?

Cubebine, $C_{34}H_{17}O_{10}$, is a crystalline compound contained in cubebs. *Olivile*, $C_{12}H_9H_4$, is a crystallizable acrid substance, found in the gum of the olive-tree. *Olivine* is another crystalline matter found on the leaves of the same plant. It is bitter. *Cnicine* is a crystalline matter, found in *centaurea benedicta*, and in the numerous family of the *cynarocephalæ*. It is neutral and bitter, and very similar to columbine. Its formula is $C_{28}H_{18}O_{10}$, or $C_{42}H_{27}O_{15}$, and in some respects it approaches to salicine and phloridzine, which may render the second formula more probable, as these bodies contain 42 eq. carbon. *Limonine*, or *Limone*, a bitter crystalline matter found in the seeds of oranges, lemons, &c., is $C_{42}H_{28}O_{13}$, when reduced to 42 eq. carbon. This would be Cnicine, *minus* 2 eq. water. *Angelicine* is a crystallized compound found in angelica root.

Besides the above, which have merely been briefly catalogued for want of space, at least an equal number of substances, chiefly crystallizable, and either bitter, acrid, or in a few cases tasteless, have been extracted by various chemists, from many different genera and species of plants, but have been so little examined hitherto that we cannot safely describe them as distinct and peculiar.

NITROGENIZED COLOURING MATTERS, AND ALLIED SUBSTANCES.

There are several fine and valuable colours, which contain nitrogen as an essential element, and probably in the form of ammonia or amide. Such colours are *archil*, *litmus*, *cudbear*, derived from certain species of lichens; and *indigo*, derived from the juice of various plants, especially different species of *indigofera*. All these colours are derived from colourless compounds, by the combined action of air and ammonia. Of these colourless substances, the most important are, *Lecanorine*, *Orcine* and *Erythrine*.

1. *Lecanorine* occurs in *lecanora tartarea*, *variolaria lactea*, and other lichens.

It is extracted by ether, and forms minute white crystals, insoluble in water, soluble in alcohol and ether. Its formula is $C_{18}H_8O_8$. When heated with alkalies, such as baryta, a carbonate is deposited, and a sweet substance remains dissolved, which crystallizes on evaporation. This is *orcine*, $C_{16}H_8O_4$, that is, lecanorine, *minus* 2 eq. carbonic acid, C_2O_4. The same change takes place when lecanorine is boiled with water, or even with ordinary alcohol, and for this reason orcine alone is obtained when the lichens are extracted by these solvents.

2. *Orcine* forms large transparent crystals, is very soluble in water, and has a sweet taste. When anhydrous, it may be distilled unchanged. When mixed with ammonia, and exposed to the air, it gradually acquires a deep blood-red colour, forming a nitrogenized colouring matter, *orceine*, soluble in ammonia with a deep red, in fixed alkalies with a rich violet colour. Crystallized orcine, $C_{16}H_{11}O_7$ ($C_{16}H_8O_4+3HO$) with the addition of 5 eq. of oxygen and 1 eq. of ammonia, NH_3, yields 1 eq. orcéine=$C_{16}H_9NO_7$, and 5 eq. water, H_5O_5.

3. *Erythrine* is another colourless substance, found in *Parmelia rocella*, when that lichen has been boiled with alcohol. It is probably a product of decomposition (just as orcine is) of some substance analogous to lecanorine. When exposed to the air along with ammonia, it slowly becomes red, and finally yields a brown bitter compound, which dissolves in fixed alkalies with a purple colour.

4. *Pseudo-erythrine* is a similar substance, occasionally obtained, and occasionally altogether wanting, in the alcoholic solutions of the lichens. It is evidently subject to decomposition, when its solutions are boiled. Schunck has rendered it highly probable that it is a compound of lecanorine with oxide of ethyle.

5. *Variolarine* is a substance quite analogous to the above-mentioned, and found in *variolaria dealbata*. The whole subject of the substances actually existing in these lichens is still very obscure. With the exception, perhaps, of lecanorine, all the above substances are products of decomposition. Even lecanorine may be a product of the decomposition of another substance, not yet isolated.

According to Kane, the following is the composition of

Erythrine (Erythriline, Kane)	$C_{22}H_{16}O_6$
Pseudo-erythrine (Erythrine, Kane) . . .	$C_{22}H_{13}O_9$
Amarythrine (the bitter product)	$C_{22}H_{12}O_{14}$
Telerythrine (a further product of oxidation) . . .	$C_{22}H_{10}O_{19}$

6. Archil contains, according to the same chemist, two blue compounds, which he calls *alpha-orcéine* and *beta-orcéine*, $C_{18}H_{10}NO_5$, and $C_{18}H_{10}NO_8$; besides a third of an acid nature, *erythroleic acid*, $C_{26}H_{22}O_8$.

7. Litmus contains (according to Kane) a red fluid, *erythroleine*, $C_{26}H_{22}O_4$; and three solids, of a purple colour, *erythrolitmine*, $C_{26}H_{23}O_{18}$; *azolitmine*, which contains nitrogen, and is the principal constituent of litmus; and *spaniolitmine*, $C_{18}H_7O_{16}$. According to Gélis, litmus contains three colouring matters, one soluble in ether, which is orange red; one soluble in alcohol, blood-red, and one soluble in water. The second is the chief ingredient of the dye. All give blue compounds with alkalies.

8. *Phloridzéine* is the deep blue compound formed from phloridzine by the action of air and ammonia. Its formula is $C_{42}H_{29}N_2O_{26}$.

9. Indigo.

This valuable dye has been long known; but it is only since 1827 that its chemical relations have been accurately studied. No substance, in the whole range of chemistry, has yielded a greater variety of most interesting products; and the study of the metomorphoses of indigo has already thrown much light on the laws of the decomposition of organic substances. For what is known on this subject, we are indebted, first, in point of time, to Chevreuil, Runge, Walter, Crum, Liebig, Berzelius, and Dumas; more lately, and in an especial manner, to the comprehensive researches of Erdmann, Fritzche, and Laurent; the last of whom has made known several interesting series of new compounds derived from indigo, and has both confirmed and extended, as well as corrected, in some cases, the previous results obtained by Erdmann.

Indigo is obtained from various plants, chiefly of the genus *indigofera*, as *I. tinctoria*, *anil*, *argentea*, &c., but also of other genera, as *Nerium*, *Isatis*, *Pergularia*, *Gymnema*, *Polygonum*, *Terphrosia*, *Amorpha*, and others. In the juice of these plants, it exists in the form of a colourless soluble compound, probably a compound of white indigo with an alkali. When exposed to the air, it is converted into the blue compound, and becomes at the same time insoluble, just as in an artificial solution of white or reduced indigo in an alkali. The manufacture of indigo is not thoroughly understood, but it would appear that ammonia, as well as air contributes to the formation of the colour, probably by converting into white indigo some compound present in the fresh juice, the nature of which, however is still uncertain. In the Antilles and in the East Indies, the leaves are made to ferment in water, during which much ammonia is formed, and the indigo is found in the soluble state, ready to become blue and insoluble by absorbing oxygen. But in North America, the dried leaves are infused in warm water, or boiled with water, till the liquid becomes green, when, on exposure to the air, it deposits blue insoluble indigo. Here the same change must, in great part at least, have taken place during the drying, as during the fermentation of the other process.

The indigo of commerce is a deep blue powder, often cohering in cakes, and exhibiting, when polished by rubbing with the nail or any hard substance, a coppery colour and lustre. It is tasteless and inodorous, insoluble in water, and nearly so in alcohol and ether. It may be purified by treating it successively with boiling diluted sulphuric acid and with water, which remove a glutinous matter; with aqua potassa, at a gentle heat, which dissolves a brown colouring matter; and with boiling alcohol, which takes up a red colouring matter. When fresh alcohol becomes no longer red, but blue, the indigo is as pure as it can be made by such means.

To purify it still further, it is digested with water, lime, and grape or starch sugar, which deoxidizes or reduces the indigo, while the lime combines with the reduced indigo, forming a soluble compound, of a wine yellow tint. This being filtered into dilute hydrochloric acid, which removes the lime, deposits pure indigo as a blue powder. Cloth steeped in the above solution of indigo, and exposed to the air, is quickly dyed blue, as the indigo, at the moment of being rendered insoluble, combines with the fibre of the cloth, to which it adheres very firmly, so that it cannot be washed away. If indigo, grape sugar, soda, and alcohol, be digested together in proper proportions, a yellow solution is obtained, which, when exposed to air, deposits pure indigo in crystals. (Fritzche.)

Pure indigo, when rapidly heated on a slip of platinum, volatilizes, yielding purple vapours, which condense in purple crystals on a cold surface. These crystals are called Indigotine: but they are nothing else than sublimed indigo, and have all the chemical characters of pure indigo. When distilled, indigo yields, among other products common to all nitrogenized organic matters, a very curious oily liquid, of powerfully basic properties, and forming salts with acids which crystallize with singular facility. This base is *aniline* (*crystalline*, *kyanol*), and is found in the oil of coal tar, as well as in the products of distillation of many nitrogenized bodies.

Oil of vitriol dissolves indigo with a deep blue colour, forming two blue acids. This solution is much used in dyeing. Nitric acid, chloric acid, chromic acid, chlorine and bromine, all dissolve indigo, giving rise to oxygenized and chlorinized or brominized products, all of which are yellow and orange-coloured. When boiled with strong aqua potassa, indigo is also oxidized and dissolved in the form of new acids.

When placed in contact with deoxidizing or reducing agents, such as protosalts of iron, tin, and manganese, or honey and grape sugar, along with an alkali such as soda or lime, indigo is decolorized and dissolved in combination with the alkali. The addition of diluted hydrochloric acid, air being carefully excluded, precipitates *reduced* or *white indigo*.

White or reduced indigo, $C_{16}H_6NO_2$, obtained as above described, is a crystalline powder of a dirty white, which, if washed with water previously boiled to expel air, and cooled in closed vessels, and dried in vacuo, is bluish externally, but grey within. The blue parts being removed, the remainder is reduced indigo. When moist, it very rapidly passes into blue indigo, oxygen being absorbed: when dry, the change is more slowly effected. It is insoluble in water and acids, very soluble in alkaline solutions; its solutions, if exposed to the air, deposit pure indigo blue as a powder.

The first accurate analysis of indigo blue was made by Walter Crum; and his results have been confirmed by all succeeding experimenters. The formula now adopted for indigo, as agreeing best with its numerous metamorphoses, is one first proposed by Dumas; namely, $C_{16}H_5NO_2$. This formula is the same with that of cyanide of benzoyle, or of benzile, $C_{14}H_5O_2 + C_2N = C_{16}H_5NO_2$.

The relation of white indigo to blue indigo is, according to one view, the same as that of hyduret of benzoyle to benzoyle, or of alloxantine to alloxan. Thus we have

Benzoyle	$C_{14}H_5\ O_2$	Hyduret of Benzoyle	$C_{14}H_5\ O_2 + H$
Alloxan	$C_8\ H_4N_2O_{10}$	Alloxantine	$C_8\ H_4N_2O_{10} + H$
Indigo blue	$C_{16}H_5N\ O_2$	Indigo white	$C_{16}H_5\ NO_2 + H$

According to another hypothesis, white indigo is the hydrate of an inferior degree of oxidation of the same radical of which blue indigo is the higher oxide. Blue indigo, on this view, is $C_{16}H_5N + O_2$, and white indigo is a hydrate $C_{16}H_5N + O + HO$. This latter view is the more probable, not only in regard to indigo, but also in regard to alloxan, for, assuming *uryle* to be $C_8N_2O_4 = Ul$, alloxan will be $Ul + O_2 + 4HO$, and alloxantine will be $Ul + O + 5HO$.

The action of grape sugar, in reducing indigo, tells in favour of the latter hypothesis. For if white indigo is blue indigo *plus* hydrogen, this hydrogen is derived from water, the oxygen of which must have combined with the hydrogen of the sugar (to convert the sugar into formic acid, which is produced in

this operation). Here, then, we should have oxygen leaving hydrogen to combine with hydrogen, or, in other words, water produced and decomposed at the same time, which is in the highest degree improbable. To demonstrate this, let the radical of indigo be assumed to be Anyle $= C_{16}H_5N =$ An: let blue indigo be An O_2, and white indigo An O_2, H or An O, HO. Then 12 eq. of blue indigo, 12 of water, and 1 of grape sugar act on each other, and, according to the view which makes white indigo the hyduret of blue indigo, the reaction is as follows: $12\ An\ O_2 + 12HO + C_{12}H_{12}O_{12} = 12\ (An\ O_2,H) + 6\ (C_2HO_3) + 6HO$. In this explanation it is evident that 6 eq. of oxygen have quitted hydrogen to combine with hydrogen. On the other view, the reaction is as follows, free from any such absurdity: $12AnO_2 + 12HO + C_{12}H_{12}O_{12} = 12AnO,HO + 6(C_2HO_3) + 6HO$. Here the 12 eq. of deutoxide of anyle (blue indigo) lose 12 eq. oxygen, which are replaced by 12 eq. water; and the 12 eq. oxygen acting on the sugar, 6 eq. take 6 eq. hydrogen, forming water, and 6 eq. convert the residue into formic acid. The student will bear in mind that C_2HO_3 is the formula of formic acid, and $C_{12}H_{12}O_{12}$ that of dry grape sugar.

We shall therefore consider white indigo as the hydrated protoxide of anyle ($C_{16}H_5N,O + HO$), and blue indigo as the anhydrous deutoxide ($C_{16}H_5N,O_2$). White indigo forms compounds with bases, in which, no doubt, its hydratic water is replaced by an equivalent of metallic oxide, as in the general formula, $C_{16}H_5N,\ O + MO$.

ACTION OF SULPHURIC ACID ON INDIGO.

When powdered pure indigo is added to 15 parts of oil of vitriol, and gently warmed, a deep blue solution is formed, which mixes perfectly with water. But if only 8 or 10 parts of acid are used, the addition of water causes the deposition of a purple powder, while a blue solution is obtained. The purple powder, which, although insoluble in dilute acid is soluble in pure water, is sulphopurpuric acid; the blue solution contains two acids, sulphoindigotic and hyposulphoindigotic acids. When neutralized with potassa, these acids form salts, which separate from the liquid when it is saturated with any alkaline salt, such as acetate or carbonate or potassa. The two blue salts may be separated from each other by alcohol, but the composition of the hyposulphoindigotate of potassa is not known. The sulphoindigotate appears to be strictly a hyposulphoindigotate, and its formula is in all probability $C_{16}H_4NO_2,S_2O_5 + KO$. Here the indigo has lost 1 eq. of hydrogen, and the 2 eq. sulphuric acid 1 eq. oxygen. Dumas's view, according to which the salt is a double sulphate, analogous to sulphovinate of potassa, $C_{16}H_4NO,SO_3 + KO,SO_3$, is not supported by the chemical relations of these substances. Dumas conjectured that indigo blue was analogous to alcohol, and that its formula was $C_{16}H_4N,O + HO$, the body $C_{16}H_4N,O$ being analogous to oxide of ethyle. But, as already stated, this view is far-fetched, and does not agree with the chemical relations of indigo. It would make, for example, white indigo $C_{16}H_4N,O + H + HO$ or $C_{16}NH_4 + 2HO$, both most improbable formulæ.

The blue solution of indigo in oil of vitriol, if diluted and digested with flannel or woollen cloth, is entirely deprived of blue colour, while the cloth is so effectually dyed that the colour cannot be washed out. It can, however, be dissolved from the cloth by carbonate of ammonia, and by this means the sulphoin-

digotates of ammonia, and from these, the other salts of the blue acids, are prepared.

The sulphopurpuric acid, according to Dumas, contains the elements of 2 eq. sulphuric acid and 2 eq. indigo, and neutralizes only 1 eq. of base. But the indigo in it has probably lost hydrogen (while the acid has lost oxygen), or hydrogen and oxygen.

PRODUCTS OF THE OXIDATION OF INDIGO.

Isatine, $C_{16}H_5NO_4$. This interesting compound, which is blue indigo, *plus* 2 eq. oxygen, is formed by digesting indigo along with water, sulphuric acid, and bichromate of potassa, or by heating indigo with weak nitric acid. It dissolves, and the solution on evaporation deposits aurora red crystals of isatine, sparingly soluble in cold water, more soluble in hot water and in alcohol. By the action of chlorine, it yields two compounds in which hydrogen is partially replaced by chlorine. It may be volatilized if heated on a plate of metal. When acted on by a strong solution of potassa, isatine is dissolved with an intense violet colour, which an addition of water and evaporation changes to yellow, and the liquid deposits pale yellow crystals, which contain potassa, united to a new acid, isatinic acid, formed from isatine by the addition of 1 eq. water. When separated from its salts by stronger acids, isatinic acid is at once resolved into isatine and water; but if isatinate of lead be decomposed by sulphuretted hydrogen, and the filtered solution evaporated spontaneously in vacuo, the acid is obtained as a white flocculent powder, which when dissolved in boiling water, instantly becomes red, and the solution on cooling deposits crystals of isatine. Isatinic acid is $C_{16}H_6NO_5HO$. Its salts have the formula $C_{16}H_6NO_5,MO$. The violet-coloured compound first formed when isatine acts on potassa is a compound of isatine and potassa, which, when heated with water, soon passes into isatinate of potassa.

With sulphurous acid, or rather sulphites, isatine forms salts of the formula $C_{16}H_5NO_4,2SO_2+MO$; which may be formed also by the action of sulphurous acid on isatinates.

By the action of chlorine, isatine is converted into two compounds, chlorisatine and bichlorisatine. When chlorine is passed through isatine or indigo suspended in water, both these compounds are formed, and they are separated by crystallization, chlorisatine being the least soluble of the two.

Chlorisatine, $C_{16}\left\{\begin{matrix}H_4\\Cl\end{matrix}\right.NO_4$, forms transparent orange yellow 4-sided prisms, isomorphous with isatine, and very analogous to it in all respects. When acted on by potassa, there is first formed a deep red solution, which when heated soon becomes yellow, and on cooling deposits brilliant pale yellow crystals of *chlorisatinate of potassa*, $C_{16}\left\{\begin{matrix}H_5\\Cl\end{matrix}\right.NO_5,KO$, a salt perfectly analogous to isatinate of potassa, and containing an acid, chlorisatinic acid, which is chlorisatine, *plus* 1 eq. water, $C_{16}H_5ClNO_5$. Like isatinic acid, when separated from its salts it is speedily resolved into chlorisatine and water. *Chlorisatinate of silver*, $C_{16}\left\{\begin{matrix}H_5\\Cl\end{matrix}\right.NO_5,AgO$ forms yellow crystals, soluble in hot water. *Chlorisatinate of baryta*, $C_{16}\left\{\begin{matrix}H_5\\Cl\end{matrix}\right.NO_5,BaO,+3$ aq. forms golden yellow tables. *Chlorisatinate of lead*,

$C_{16}\left\{\begin{matrix}H_5\\Cl\end{matrix}\right. NO_5,PbO$, when first precipitated from the salt of potassa by nitrate of lead, forms a gelatinous yellow precipitate, which soon becomes flocculent, acquiring a splendid scarlet colour. The red salt is crystalline, the yellow amorphous. Chlorisatinate of copper forms at first a brownish yellow bulky precipitate, which soon changes to a heavy granular blood-red powder.

Like the isatinates, the chlorisatinates combine with the sulphurous acid, forming salts of the formula $C_{16}\left\{\begin{matrix}H_4\\Cl\end{matrix}\right. NO_4,2SO_2+MO$. In short, the analogy between isatine and chlorisatine, insatinates and chlorisatinates, &c., is such as to furnish a very beautiful example of the substitution of chlorine for hydrogen, while the type or chemical character of the compound is unaffected. In bichlorisatine, we shall see an aditional example of the same truth.

Bichlorisatine, $C_{16}\left\{\begin{matrix}H_3\\Cl_2\end{matrix}\right. NO_4$, is formed along with the preceding compound. It is more soluble than chlorisatine, but is otherwise remarkably similar to it. With aqua potassæ it first forms a deep red solution (here as in the case of isatine and chlorisatine a compound of it with potassa), which when heated changes to yellow, and on evaporation yields yellow scales of a salt compound of potassa and *bichlorisatinic acid*. The acid may be separated by stronger acids as a yellow powder, which when dissolved and warmed is resolved into bichlorisatine and water. Its formula is $C_{16}\left\{\begin{matrix}H_4\\Cl_2\end{matrix}\right. NO_5,HO$. The salt of *baryta*, $C_{16}\left\{\begin{matrix}H_4\\Cl_2\end{matrix}\right. NO_5$, BaO, forms golden yellow needles. The salt of *copper* is at first bulky and brown, but soon becomes greenish yellow and crystalline, and finally, a heavy granular powder of a fine carmine red colour.

Bichlorisatine with sulphites forms compounds analogous to those above mentioned of isatine and chlorisatine. In this case also, therefore, the type is perfectly retained, although 2 eq. of the hydrogen of isatine have been replaced by chlorine.

Bromine acts on isatine, and forms two compounds, *bromisatine* and *bibromisatine*, entirely analogous to chlorisatine and bichlorisatine, forming *bromisatinic* and *bibromisatinic* acids, and also compounds with sulphites analogous to those just mentioned. We have, therefore, from isatine, and isatinic acid, by substitution, the following compounds :—

Isatine	$C_{16}\ H_5\ NO_4$
Isatinic Acid	$C_{16}\ H_6\ NO_5+HO$
Chlorisatine	$C_{16}\left\{\begin{matrix}H_4\\Cl\end{matrix}\right. NO_4$
Chlorisatinic Acid	$C_{16}\left\{\begin{matrix}H_5\\Cl\end{matrix}\right. NO_5+HO$
Bichlorisatine	$C_{16}\left\{\begin{matrix}H_3\\Cl_2\end{matrix}\right. NO_4$
Bichlorisatinic Acid	$C_{16}\left\{\begin{matrix}H_4\\Cl_2\end{matrix}\right. NO_5+HO$
Bromisatine	$C_{16}\left\{\begin{matrix}H_4\\Br\end{matrix}\right. NO_4$
Bromisatinic Acid	$C_{16}\left\{\begin{matrix}H_5\\Br\end{matrix}\right. NO_5+HO$
Bibromisatine	$C_{16}\left\{\begin{matrix}H_3\\Br_2\end{matrix}\right. NO_4$
Bibromisatinic Acid	$C_{16}\left\{\begin{matrix}H_4\\Br_2\end{matrix}\right. NO_5+HO$
Isatinosulphites	$C_{16}\ H_5\ NO_4,2SO_2+MO$

Chlorisatinosulphites . .	$C_{16}\left\{\begin{matrix}H_4\\Cl\end{matrix}\right. NO_4,2SO_2+MO$
Bichlorisatinosulphites . .	$C_{16}\left\{\begin{matrix}H_3\\Cl_2\end{matrix}\right. NO_4,2SO_2+MO$
Bromisatinosulphites . .	$C_{16}\left\{\begin{matrix}H_4\\Br\end{matrix}\right. NO_4,2SO_2+MO$
Bibromisatinosulphites . .	$C_{16}\left\{\begin{matrix}H_3\\Br_2\end{matrix}\right. NO_4,2SO_2+MO$

Isatyde, $C_{16}H_6NO_4 = C_{16}H_5NO_4,H$, is formed when an alcoholic solution of isatine is acted on by sulphuret of ammonium. It is a grey crystalline powder, and may be considered to represent isatine *plus* 1 eq. hydrogen.

Sulphésatyde, $C_{16}H_6N\left\{\begin{matrix}O_2\\S_2\end{matrix}\right.$ is isatyde, in which 2 eq. oxygen are replaced by sulphur. It is formed by the action of sulphuretted hydrogen on isatine dissolved in alcohol, and is a greyish yellow amorphous powder. *Sulphisatine* is the name of a compound obtained in the same way by Erdmann, which he considers to be different from sulphésatyde.

Chlorisatyde, $C_{16}\left\{\begin{matrix}H_5\\Cl\end{matrix}\right. NO_4$, is a white powder somewhat crystalline, obtained by the action of sulphuret of ammonium on chlorisatine. It is perfectly analogous to isatyde. By the action of sulphuretted hydrogen on chlorisatine, a compound is formed which is $C_{16}\left\{\begin{matrix}H_5\\Cl\end{matrix}\right. NS_4$: that is chlorisatyde, in which all the oxygen is replaced by the sulphur.

Bichlorisatyde, $C_{16}\left\{\begin{matrix}H_4\\Cl_2\end{matrix}\right. NO_4$ and *bibromisatyde*, $C_{16}\left\{\begin{matrix}H_4\\Br_2\end{matrix}\right. NO_4$, are perfectly analogous, in formation and properties, to chlorisatyde.

Sulphasatyde, $C_{16}H_6N\left\{\begin{matrix}O_3\\S\end{matrix}\right.$ is formed by the action of potash on sulphésatyde, from which it differs in having only 1 eq. oxygen replaced by sulphur. It is a white crystalline powder.

Indine, $C_{16}H_6NO_2$ is a crystallized substance, of a beautiful rose colour, formed by the action of potash on sulphesatyde, along with the preceding; or by the action of potash on sulphasatyde or isatyde. In the last case, isatinate of potash is also formed, thus, $3(C_{16}H_6NO_4)+2KO=2(KO,C_{16}H_6NO_5)+C_{16}H_6NO_2$. It is sulphesatyde, *minus* 2 eq. sulphur, and is also isomeric with white indigo. It is decomposed by nitric acid, and by bromine, which give rise to new products.

When indine, moistened with alcohol, is covered with a lukewarm solution of potash, it forms a black solution which in a few moments becomes a semi-solid mass of black needles, which are a compound of potash with indine or rather with indinic acid, an acid formed from indine, like isatinic acid from isatine, by the assimilation of 1 eq. water, and which is very easily again resolved into indine and water.

Hydrindine is a yellow crystalline compound formed by heating indine, sulphasatyde, or isatyde with potash. Its composition is $C_{32}H_{13}N_2O_5$, that is 2 eq. indine *plus* 1 eq. water; and when strongly heated, it is resolved into indine and water. It is not composed of these substances, however, for it forms with potash white salt, hydrindinate of potash. The acid in this salt appears to be formed, like some of those already described, by the addition of water to hydrindine; its formula is probably $C_{16}H_{15}N_2O_7,2HO$.

Nitrindine, $C_{16}H_4N_2O_7$, is a beautiful violet-coloured powder formed by the action of nitric acid on indine and hydrindine. It is indine, in which 2 eq. hydrogen are replaced, one by oxygen, the other by nitrous acid; $C_{16}\left\{\begin{matrix}H_4\\NO_4\\O\end{matrix}\right\}NO_2$.

Chlorindine $C_{16}\left\{\begin{matrix}H_5\\Cl\end{matrix}\right\}NO_2 + 2HO$, is a powder of a dirty violet colour, formed by the action of heat on chlorisatyde. Analogous compounds are obtained from *bichlorisatyde* and *bibromisatyde*. Bichlorindine is like chlorindine. Bibromindine is very dark red, and dissolves in alcohol with a fine purple colour.

The action of potash on isatyde appears to be the type of its action on chlorisatyde, bromisatyde, bichlorisatyde, and bibromisatyde. When isatyde is acted on by potash, it yields isatine (or isatinate of potash); indine (or indinate of potash); and hydrindine (or hydrindinate of potash). 6 eq. isatyde, ($6C_{16}H_6NO_4$) are equal to 4 eq. isatine ($4C_{16}H_5NO_4$) + 2 eq. indine ($2C_{16}H_6NO_2$) + 4 eq. water: or they are equal to 4 eq. isatine ($4C_{16}H_5NO_4$) + 1 eq. hydrindine ($C_{32}H_{13}N_2O_5$) + 3 eq. water. Both changes probably occur, and the three compounds, isatine, indine, and hydrindine, alike take up the elements of water to form the acids, which, to avoid confusion, are not here expressed. Now there is good reason to believe that precisely analogous changes occur when potash acts on bichlorisatyde and on bibromisatyde, each yielding three corresponding compounds and the three acids derived from these. The reader, by strictly following the analogy of the formulæ given above for the action of potash on isatyde, will easily be able to construct the equations for the other analogous cases.

When sulphesatyde is acted on by bisulphite of ammonia, there is formed among other products not fully investigated, a salt formed of ammonia united to a new acid, *sulphisatanous acid*, quite different from the acid in the salts formed when isatine is acted on by sulphites. This new acid is $C_{16}H_6NO_3,2SO_2 + HO$, or perhaps rather $C_{16}H_6N\left\{\begin{matrix}O_2\\2SO_2\end{matrix}\right\} + HO$; that is sulphesatyde, in which the 2 eq. of sulphur have been replaced by 2 eq. sulphurous acid.

The action of bisulphate of ammonia on sulphesatide sometimes gives rise to the formation of different products; among others, to an insoluble white powder, *isatan*, $C_{16}H_6NO_3$, which when heated yields isatine and indine; $3(C_{16}H_6NO_3) = C_{16}H_5NO_4 + 2(C_{16}H_6NO_2) + HO$. Both indine and nitrindine, when acted on by bisulphite of ammonia, appear to produce compounds analogous to those derived from sulphesatyde.

Chlorindopten is the name given by Erdmann to a volatile crystalline substance, formed along with chlorisatine and bichlorisatine, when chlorine acts on indigo. When the chlorinised mass is distilled with water, this substance passes over in white crystals, which are acid, and evidently a mixture of two substances. When this chlorindopten is heated with potassa, a neutral substance passes over, in white crystals similar to the original ones; this is *chlorindatmit*; while the potassa retains an acid of a disagreeable odour, *chlorindoptenic acid*.

Chlorindoptenic acid, $C_{12}H_4Cl_3O,HO$, is separated from its potash salt by acids, as a white flocculent matter of a very disagreeable odour. Laurent has identified it with his chlorophenisic acid, an acid derived from coal tar by the

action of chlorine, and makes its formula $C_{12}\left\{\begin{matrix}H_2\\Cl_3\end{matrix}\right\}O,HO$. Chlorindatmit appears to be $C_{12}\left\{\begin{matrix}H_4\\Cl_3\end{matrix}\right\}N$ (Hoffmann).

By the further action of chlorine on chlorisatine or bichlorisatine, dissolved in alcohol, new compounds are formed, among which are, *chlorinized chlorindopten*, which, like chlorindopten, is a mixture apparently of chlorindatmit, with an acid, *chlorinized chlorindoptenic acid*, $C_{12}Cl_5O,HO$; which is the *chlorophenusic acid* of Laurent. This acid is accompanied by *chloranile*, $C_{12}Cl_4O_4$, a neutral body in volatile golden yellow scales, soluble in hot alcohol, which is also derived from the oil of coal tar, or rather from the hydrate of phenyle or carbolic acid of that oil, from which chlorophenisic and chlorophenusic acids are obtained.

Chloranile dissolves in weak potassa with a deep purple colour, and the solution deposits dark, purplish-red crystals, composed of potassa and a new acid, *chloranilic acid*. This acid forms scarlet or yellow crystals, according as it contains water of crystallization or not. Its formula is $C_{12}Cl_2O_6,2HO$, or C_6ClO_3,HO.

When chloranile is acted on by aqua ammoniæ, it is dissolved, forming a blood-red solution, which deposits chesnut-brown crystals of *chloranilammon* $C_6H_3NClO_3+4$ aq. $=C_6ClO_3+NH_3+4$ aq. It dissolves in water with a purple colour, and when a saturated solution is mixed with hydrochloric acid, it deposits very brilliant black needles of great length. These are a new compound, *chloranilam*, $C_{12}Cl_2H_3NO_6=C_{12}Cl_2O_6+NH_3$; that is 2 eq. of chloranilammon, $2(C_6ClO_3,NH_3)=C_{12}Cl_2O_6,N_2H_6$; minus 1 eq. ammonia NH_3. Both these compounds give precipitates with metallic solutions, which are the same from both, but distinct from those formed by chloranilic acid or its salts. Chloranilammon, according to Laurent, is the ammonia salt of an acid containing amide as an ingredient. Chloranilam is the acid itself.

By the action of ammonia on isatine there are produced several new compounds, varying with the strength of the ammonia, and the menstruum employed. In these compounds, oxygen is replaced by *amide*, NH_2, or *imide*, $\frac{1}{2}$ NH=Im.

Imasatine is formed when dry ammonia is passed through an alcoholic solution of isatine. It forms fine deep yellow crystals, the formula of which is $C_{16}H_6N_2O_2=C_{16}H_5N\left\{\begin{matrix}O_2\\2Im.\end{matrix}\right.$

Imasatine is formed when aqua ammoniæ acts on a solution of isatine in alcohol. It is a greyish yellow crystalline substance, the formula of which is $C_{16}H_5N\left\{\begin{matrix}O_3\\Im\end{matrix}\right.$?

Imasatinic acid is formed along with the preceding, and is dissolved along with ammonia. By the addition of an acid it is precipitated as a beautiful scarlet crystalline powder, soluble in hot alcohol, which deposits it in splendid tabular crystals similar to the sublimed periodide of mercury. It dissolves sparingly in acids with a violet colour, and these solutions deposit violet crystals. Its formula is $C_{16}H_5N\left\{\begin{matrix}O_3\\Im\end{matrix}\right\}+HO$.

Amasatine is formed along with the two preceding bodies. It has a fine yellow colour, and dissolves in acids with a violet colour, apparently passing into imasatinic acid. Its formula is $C_{16}H_5N\left\{\begin{matrix}O_3\\Ad\end{matrix}\right\}+HO$. (Ad=$NH_2$=amide.)

The analogy between chlorisatine, &c. and isatine, holds in regard to the action of ammonia on them. By the action of dry ammonia on an alcoholic solution of chlorisatine there is formed a yellow crystalline compound, analogous to imesatine. It is called *Imachlorisatinase*, and its formula is $C_{16}\left\{\begin{matrix}H_4\\Cl\end{matrix}\right\}N\left\{\begin{matrix}O_2\\2HN.\end{matrix}\right.$

Imachlorisatinase is analogous to imasatine. Its formula is $C_{16}\left\{\begin{matrix}H_4\\Cl\end{matrix}\right\}N\left\{\begin{matrix}O_3\\NH.\end{matrix}\right.$ It forms brownish yellow crystals.

Imabromisatinase, formed by the action of dry ammonia on bibromisatine in alcohol, is $C_{16}\left\{\begin{matrix}H_3\\Br_2\end{matrix}\right\}N\left\{\begin{matrix}O_3\\NH.\end{matrix}\right.$ It is a deep orange crystalline powder.

We have now briefly run over the catalogue of the very remarkable compounds derived from indigo by the action of sulphuric acid and bichromate of potassa, which produces isatine, and by the action of chlorine either on indigo or on isatine, of bromine on the same, and of potassa, ammonia, sulphuretted hydrogen and sulphuret of ammonium on the products of these actions. The nomenclature of these compounds is in a very imperfect state, and requires reformation, but this cannot be effected until the substances themselves have been more thoroughly studied. It is most important to observe, that by or through chloranile and the chlorindoptenic acids, the series to which indigo belongs connects itself with that of carbolic acid or hydrate of phenyle (to be afterwards described), and these again with the series of salicyle. We have now to mention one or two products of the action of nitric acid on indigo which are common to all these series, and like chloranile, seem likely to be very frequently met with as products of the decomposition of organic compounds.

Anilic acid, Syn. *Indigotic acid*, *Nitrosalicylic acid*, $C_{14}H_4NO_9$,HO. This acid is formed by the long-continued action of weak nitric acid on indigo. It is also formed in the preparation of isatine, if the action be pushed too far. It is identical with nitrosalicylic acid, obtained by the action of nitric acid on salicylic acid or on salicine. It forms fine yellowish-white prisms, which are light and bulky, and shrink much in drying. It is fusible and volatile. By the action of strong nitric acid it is converted into oxalic and picric acids. It requires 1000 parts of cold water for solution. Its salts crystallize well, and their general formula is $C_{14}H_4NO_9$,MO. The anilate of oxide of methyle is obtained as a crystalline compound by the moderated action of nitric acid on the salicylate of oxide of methyle (oil of gaultheria). The anilate of oxide of ethyle is exactly similar.

Picric acid, Syn. *Carbazotic acid*, *Nitropicric acid*, *Nitrophenisic acid*, $C_{12}\left\{\begin{matrix}H_2\\3NO_4\end{matrix}\right\}O$,HO. This acid is formed by the action of nitric acid on anilic acid, indigo, salicine, salicylic acid, hydrate of phenyle or carbolic acid, coumarine, silk, aloes (?) and other substances. It is most easily formed from carbolic acid, salicine or oil of gaultheria, by the action of an excess of fuming nitric acid assisted by heat. It is purified by solution in hot water and recrystallization. It forms pale yellow or even white scales of a silvery lustre. They dissolve in hot water with a strong yellow colour, and a very bitter taste. The acid is fusible and volatile. Its salts crystallize most readily, and all explode when

heated. When these salts are put in contact with lime and green vitriol, blood-red solutions are formed, containing the lime salt of a new acid. The picrate of potassa is so sparingly soluble, especially in alcohol, that an alcoholic solution of picric acid may be used as a test for potassa.

Picric acid is interesting as occurring among the products of the decomposition by nitric acid of so many different substances. It is easily derived from the series of phenyle, that is, from carbolic acid, $C_{12}H_5O$, HO. Derived from this, we have Chlorophenesic acid, $C_{12}\left\{\begin{matrix}H_3\\Cl_2\end{matrix}\right\}O$, HO, Chlorophenusic acid, C_2Cl_5O,HO, and Picric acid, $C_{12}\left\{\begin{matrix}H_2\\3NO_4\end{matrix}\right\}O$,HO. It is, therefore, carbolic acid in which 3 eq. of hydrogen are replaced by 3 eq. of nitrous acid.

When indigo is heated with concentrated potassa, there are formed two new acids: *chrysanilic acid*, the composition of which is uncertain, and *anthranilic acid*, $C_{14}H_7NO_4 = C_{14}H_6NO_3$,HO. The latter is purified in the form of anthranilate of potassa, and the acid separated by an excess of acetic acid. It forms transparent yellow scales, which, however, when quite pure, are colourless. It is derived from blue indigo, $C_{15}H_5NO_2$, by the loss of 2 eq. carbon and the addition of 2 eq. water.

When anthranilic acid is mixed with powdered glass, and rapidly heated, it is resolved into carbonic acid and an oily liquid, which is *aniline*, a very powerful base, devoid of oxygen, identical with the *crystalline* of Unverdorben, and the *kyanol* of Runge, $C_{12}H_7N$. This metamorphosis is very simple: $C_{14}H_7NO_4 = C_2O_4 + C_{12}H_7N$. Since aniline is obtained in many other cases of decomposition of organic matters by heat, it becomes a substance of great interest.

Aniline is recognized by its property of striking a deep violet blue colour with chloride of lime. It obtained the name *kyanol* from this property. Its other name, *crystalline*, indicates its great tendency to form crystallizable salts with acids.

The recent researches of A. W. Hofmann have greatly extended our knowledge of this remarkable compound. He has shown that it is not confined to the products of the decomposition of indigo, but that it is formed when other substances, isomeric with anthranilic acid, are exposed to heat along with bases, such as lime or baryta. Such substances are salicylamide and protonitrobenzoéne, both of which have the empirical formula $C_{14}H_7NO_4$. The former yields little, but the latter is entirely resolved into aniline and carbonic acid. He has also fully identified aniline with the *crystalline* of Unverdorben, a base occurring with others among the products of distillation of animal matter, and in coal tar. It is worthy of remark that a close connection may be traced between aniline and carbolic acid (hydrate of phenyle). The latter is $C_{12}H_5O$,HO. The carbolate of ammonia, $C_{12}H_5O,NH_4O$, minus 2 eq. water would yield an amide, *phenylamide*, which would be $C_{12}H_5,NH_2 = C_{12}H_7N$; and this is aniline. Now in Hofmann's experiment above mentioned, in which salicylamide was heated with lime, it did not yield much aniline, but, on the other hand, it furnished a large quantity of carbolic acid.

It is further to be noticed that carbolic acid (hydrate of phenyle) and aniline (phenylamide) occur together in coal tar; and that all the substances which yield either one or other of these are also converted into picric acid, $C_{12}\left\{\begin{matrix}H_2\\3NO_4\end{matrix}\right\}O$,HO, by the action of nitric acid. Thus carbolic acid, indigo, sa-

llcine, and salicylic acid, are all transformed into pricric acid by excess of nitric acid.

Another point in which all these substances agree is this, that when acted on by a mixture of hydrochloric acid and chlorate of potassa, they are all converted into chloranile, $C_{12}Cl_4O_4$. It is more than probable that all those bodies, such as indigo, salicine, carbolic acid, &c. which in this way yield chloranile, either belong to the series of phenyle or are nearly allied to that series, and readily pass into it. The fundamental or primitive compound of that series appears to be some compound of the formula $C_{12}\triangle_8$, where $\triangle$ stands for hydrogen, chlorine, bromine, iodine, oxygen, nitrous acid, &c., &c. Assuming this, and supposing $\triangle$ to be represented by H, then we have the following series, which will exhibit in a practical form the doctrine of substitutions.

$C_{12}H_8$ = Supposed origin or nucleus of the series.

$C_{12}\{H_6, O_2\}$ = $C_{12}H_5O,HO$ = hydrate of phenyle.

$C_{12}\{H_4, Cl_2, O_2\}$ = $C_{12}\{H_3, Cl_2\}O,HO$ = chlorophenesic acid

$C_{12}\{H_3, Cl_3, O_2\}$ = $C_{12}\{H_2, Cl_3\}O,HO$ = chlorophenisic acid.

$C_{12}\{H, Cl_5, O_2\}$ = $C_{12}Cl_5,O,HO$ = chlorophenusic acid.

$C_{12}\{Cl_4, O_4\}$ = chloranile

$C_{12}\{H_7, N\}$ = aniline.

$C_{12}\{H_4, 2NO_4, O_2\}$ = $C_{12}\{H_3, 2NO_4\}O,HO$ = nitrophenesic acid.

$C_{12}\{H_3, 3NO_4, O_2\}$ = $C_{12}\{H_2, 3NO_4\}O,HO$ = nitrophenisic (picric) acid

$C_{12}\{H_3, Br_3, O_2\}$ = $C_{12}\{H_2, Br_3\}O,HO$ = bromophenisic acid.

Hofmann has shown that isatine, when distilled with potassa, yields aniline; and that chlorisatine, so analogous in all respects to isatine, undergoes a similar decomposition, yielding a new base *chloraniline*; also that other compounds may be formed containing more chlorine, but still belong to the same series; finally, that bromisatine also yields a base, bromaniline. The following are the formulæ of these new compounds, which, it will be observed, are still referable to the original formula, $C_{12}\triangle_8$ or $C_{12}H_8$.

$C_{12}\{H_6, Cl, N\}$ = chloraniline, a powerful base.

$C_{12}\{H_5, Cl_2, N\}$ = dichloraniline, a weak base.

$C_{12}\{H_4, Cl_3, N\}$ = trichloraniline = chlorindatmit of Erdmann, a neutral body.

$C_{12}\{H_6, Br, N\}$ = bromaniline, a base.

$C_{12}\{H_5, Br_2, N\}$ = dibromaniline, a weak base.

$C_{12}\left\{\begin{matrix}H_4\\Br_3\\N\end{matrix}\right\}$ =tribromaniline=bromaniloid of Fritzsche, a neutral compound.

It may here be mentioned, that although, in order to include the water of the hydrated acids, I have adopted $C_{12}H_8$ as the nucleus of these compounds, we may also refer them to $C_{12}H_6$=phene or benzine. The oxide of phenyle and the different acids will then be represented as anhydrous, thus, $C_{12}\left\{\begin{matrix}H_5\\O\end{matrix}\right.$ oxide of phenyle, &c. Aniline will be $C_{12}\left\{\begin{matrix}H_5\\NH_2\end{matrix}\right.=C_{12}\left\{\begin{matrix}H_5\\Ad\end{matrix}\right.$ =phenylamide: and chloraniline will be $C_{12}\left\{\begin{matrix}H_4\\Cl\\Ad\end{matrix}\right.$; and so on. The only compound which does not adapt itself to this formula is chloranile, $C_{12}Cl_4O_4$; which might, however, be $C_{12}\left\{\begin{matrix}Cl_3\\O_2\\ClO_2\end{matrix}\right.$, or $C_{12}\left\{\begin{matrix}Cl_2\\O_2\\2ClO\end{matrix}\right.$.

Our space will not permit us to enter into any details concerning the preparation and properties of these interesting compounds; but it may be remarked that chloraniline by the action of hydrochloric acid and chlorate of potassa, yields chloranile; and that the same substance, when passed over lime (hydrated?) at a low red heat, yields aniline, thus affording additional proof that all these compounds belong to one series, and are different subtypes of one general type. Nor must it be forgotten, that in the case of aniline, chloraniline, and bromaniline, we have chlorine and bromine substituted for hydrogen in a basic compound, without affecting its basic characters. This is the first known example of a base formed by substitution from another base, although similar facts, in regard to acids and neutral bodies had long been known.

10. Carmine.

This name has been given to the colouring matter of cochineal which is nitrogenized, and may be obtained in dark red crystalline grains, very soluble in water and alcohol. It forms with alumina a beautiful red lake, well known as carmine. Its precise formula is not determined, but it approaches to $C_{32}H_{24}NO_{20}$.

ACTION OF NITRIC ACID ON ALOES.

This action so much resembles, in some points, the action of nitric acid on indigo, that it may be properly mentioned here. Aloes is the well-known inspissated juice of certain species of *aloe*, and is very bitter and purgative. The nature of its active principle is still unknown: but when heated with nitric acid it yields a yellow bitter substance, which is converted, by the further action of the acid, into two crystallizable acids, chrysammic and chrysolepic acid. The artificial bitter of aloes appears to be formed of two acids, aloetic and aloeretinic acids, which form red salts, but the composition of which is not exactly ascertained.

Chrysammic acid, $C_{15}HN_2O_{12},HO$, is obtained as a yellow precipitate, when water is added to the solution obtained by heating aloes with excess of nitric acid. It is purified by being combined with potassa, and this salt, after recrystallization, is dissolved in hot water and decomposed by diluted nitric acid. The

chrysammic acid is deposited as a powder formed of golden yellow shining scales. Its solution is of a fine purple. All its salts are crystallizable and of a deep red colour, frequently with green reflection, like muroxide. The chrysammate of ammonia forms dark green crystals, which, when dissolved and acted on by nitric acid, deposit brilliant black scales, which are not chrysammic acid, but are transformed into it when boiled with acids or bases. The solution of chrysammate of ammonia gives with metallic salts peculiar precipitates distinct from those formed with the same salts by chrysammate of potassa.

Chrysolepic acid, $C_{12}H_2N_3O_{13},HO$, has the formula and many of the properties of picric acid; but it is said by Schunck, who discovered it, to be different. It is darker in colour, and its salts with potassa, is much more soluble than picrate of potassa. It would, however, appear that the two acids are essentially the same; for their salts are in general very similar, and all explode when heated. Now that picric acid is recognized as so frequent a product of the action of nitric acid, we have no difficulty in understanding its occurrence here.

ALKALOIDS OR ORGANIC BASES.

These names are given to a class of nitrogenized organic compounds which, in their relations, are quite analogous to ammonia, or rather to oxide of ammonium. They are to be distinguished from such basic oxides as oxide of ethyle, oxide of methyle, &c., which contain no nitrogen, and, although they form neutral compounds with acids, yet exist in a peculiar state in these compounds, which cannot be decomposed, like ordinary salts, by double decomposition. Thus oxalate of oxide of ethyle, does not precipitate with nitrate of lime, and chloride of ethyle does not decompose nitrate of silver. But the case is quite different with the alkaloids; for their salts undergo the same decompositions as those of ammonia.

Most of the alkaloids are found in vegetable juices, seeds, or roots; these are called vegetable alkalies, and they are generally the active principles of the plants, for the most part poisonous, in which they are found. But of late organic bases quite analogous to those produced by nature, have been formed in a variety of processes; as, for example, the singular bases containing platinum, described at pp. 269-271; the bases containing arsenic, or arsenic and platinum, mentioned at pp. 382-384; the bases of coal-tar, of which aniline, formed in several different processes, is one; the bases, chloraniline, &c., derived from aniline; the bases derived from oil of mustard, (see p. 349); those derived from the decomposition of natural alkaloids, as *quinoleine* and *cotarnine*; and, finally, those formed by the action of sulphuret of ammonium on certain nitrogenized bodies, as aniline from nitrobenzide, naphthalidine from nitronaphthalese, &c. Most of these artificially formed bases are of very recent discovery, and it is evident that they must throw much light on the theory of the production of the natural alkaloids, and that the careful study of this part of the subject will, in all probability, eventually lead to the artificial formation of the natural organic bases.

The alkaloids possess, for the most part, very decided basic properties; when dissolved they act on vegetable colours like the inorganic alkalies; and they neutralize the strongest acids completely, generally forming crystallizable salts. Most of them, at the ordinary temperature, are expelled from their salts by ammonia, but many of them at the heat of boiling water expel ammonia from its salts, owing to the volatility of the latter alkali.

Their basic properties are not derived from the oxygen they contain, for no variation in the amount of that element affects their neutralizing power. On the other hand, there is every reason to believe that their basic character depends on the nitrogen they contain; for they all, without exception, contain nitrogen, although several are devoid of oxygen. Moreover, most, if not all of those which have been formed artificially, are prepared with the aid of ammonia, or some compound of ammonia, or amidogen. It is quite conceivable that they may be composed of ammonia or amidogen, *plus* some compound of carbon and hydrogen, or of carbon, hydrogen, and oxygen, the addition of which does not diminish the basic energy of the ammonia, or amidogen. Thus, the three bases containing platinum, formerly described, may be represented as PtO,NH_3, $PtO,2NH_3$, and $PtClO,2NH_3$; and these formulæ will at all events show their relation to ammonia.

The alkaloids occur in combination, generally with vegetable acids; and they are separated from these combinations by the same means which are employed in the case of inorganic bases, modified in each case, according as the alkaloid is soluble or insoluble in water and other solvents, fixed or volatile when heated. Thus quinine, morphia, and strychnia, are separated by adding to their soluble salts, lime, ammonia, or magnesia, which form soluble salts with the acids which are present, while the alkaloids, being insoluble, are precipitated; codeine, being soluble in ether as well as water, is first set free by potassa, and ether being added to the aqueous liquid, is agitated with it, and rises to the surface, carrying the codeine along with it, and the same process applies to other alkaloids. Lastly, conia, nicotine, and other volatile alkaloids, are obtained by distilling their salts with an excess of liquor potassæ.

The alkaloids, like ammonia, combine with hydrogen acids forming salts, without the addition of water or its elements being necessary; they also, like ammonia, refuse to combine with anhydrous oxygen acids, requiring 1 eq. of water to form dry salts. Their hydrochlorates, like sal ammoniac, form double salts with the bichlorides of platinum and of mercury.

The salts of most of the alkaloids are precipitated as tannates by infusion of galls.

The alkaloids are generally decomposed by chlorine, bromine, and iodine, forming coloured compounds not yet fully investigated. They are also decomposed by nitric acid, some of them with a deep red colour.

Some of them, such as quinine, strychnia, &c. when heated with strong caustic potassa, yield an oily compound, which is also a base, and is called quinoleine.

We shall now briefly describe the individual alkaloids, dividing them into groups, according to their characters.

1. Liquid Volatile Bases.

a. Aniline, $C_{12}H_7N$, has been already mentioned as formed by the action of potassa on isatine, and by the action of heat and bases on anthranilic acid and protonitrobenzoene, and on salicylamide, although the latter only yields a very small proportion. It also occurs as one of the most remarkable ingredients in the oil of coal-tar, where it is associated with two other bases, leukol and pyrrol; also in the oil obtained by distilling indigo, or animal matter. In coal-tar it is associated or combined with carbolic acid, and the relation between aniline

(phenylamide) and carbolic acid (hydrate of phenyle) has already been explained. It is obtained pure by rather a tedious process.

Aniline is an oily liquid, boiling at 358°, rather heavier than water (sp. gr. 1·028), of a very high dispersive and refractive power. It has a hot pungent taste, and an agreeable vinous odour. It forms crystalline salts with most acids, and strikes a deep violet-blue colour with solution of bleaching-powder. By the action of nitric acid it is converted into picric acid, and by that of a mixture of hydrochloric acid, and chlorate of potash, it is converted into chloranile. Chromic acid causes a deep bluish-black colour. With chlorine it yields chlorinized compounds, especially chlorophenisic (chlorindoptenic) acid, and tricloraniline (chlorindatmit). Bromine converts it into tribromaniline (bromaniloide). Aniline is very acrid and poisonous. The two bases, chloraniline, C_2H_6ClN, and bromaniline, $C_{12}H_6B_2N$, derived from aniline by substitution, have been already mentioned. They are very analogous to aniline.

b. Leukol, $C_{18}H_8N$. This base is found in the oil of coal-tar, along with aniline, from which it is separated by distillation, aniline being the more volatile of the two. Leukol is an oily liquid, of a still higher refractive and dispersive power than aniline; it has an unpleasant smell, and a burning taste. It boils at 463°. Its sp. gr. is 1·081. Neither bleaching-liquor nor chromic acid produce, with leukol, the blue colour which they give rise to with aniline. It combines with acids, but its salts do not crystallize so readily as those of aniline.

c. Nicotine, $C_{10}H_8N$. This base is found in tobacco, and is obtained by distilling the concentrated infusion of the leaves along with potassa. The distilled liquid, which contains nicotine, water, and ammonia, is neutralized by sulphuric acid and the neutral solution dried up. Alcohol then dissolves the sulphate of nicotine, leaving undissolved the sulphate of ammonia. The pure sulphate, distilled with potassa, yields pure nicotine, which appears as an oily, limpid, colourless liquid, having a weak smell of tobacco. Its sp. gr. is 1·048. It is decidedly alkaline, and mixes with water, alcohol, and ether. It is highly poisonous. With acids it forms salts which crystallize with difficulty. The hydrochlorate of nicotine combines with bichloride of platinum, forming a double salt, which yields large regular orange-red crystals, of the formula $O_{10}H_8N,HCl + PtCl_2$. It is probable that nicotine, besides being found in the fresh leaves of tobacco, is produced in larger quantity during the fermentation to which the leaves are subjected in the manufacture of tobacco; and there is also reason to believe that it is produced by the action of heat on tobacco, as in smoking, and that, from the comparative simplicity of its formula, it will be found among the products of the distillation of organic compounds, containing nitrogen. Its analogy, in composition and properties, to the two preceding bases, is very obvious.

d. Conine. Syn. *Conia.* $C_{16}H_{16}N$? This base occurs in the hemlock, *coinum maculatum*, and is extracted by a process quite analogous to that above described for nicotine. It is also an oily liquid, boiling at 338°, highly poisonous, and easily decomposed. Its taste and smell are both very acrid and disagreeable, and somewhat analogous to those of nicotine. Its salts are acrid and poisonous, crystallizing with difficulty. As it is the active principle of the conium, conine, either pure or as a salt, ought to be used instead of the extract or tincture, which are very variable.

e. Quinoline, $C_{19}H_8N$. This base is formed artificially, by distilling quinine, cinchonine, or strychnine, along with caustic potassa. It is an oily liquid, of sp. gr. 1·084, which is volatile at a high temperature. It forms two hydrates,

with 1 and 3 eq. of water respectively. It is very bitter, and strongly alkaline, and forms crystallizable salts with acids. Its production from quinine and cinchonine will be explained under these bases. Quinoleine is now believed to be identical with leukol.

2. Bases derived from Oil of Mustard.

Under the head of Oil of Mustard, these bases have been already described. They are *Thiosinnamine*, $C_8H_4NS_2$; *Sinnamine*, C_8H_3N; and *Sinapoline*, $C_{14}H_6NO_2$.

3. Bases of Cinchona Bark.

a. Quinine, $C_{20}H_{12}NO_2$. This important alkaloid is found along with cinchonine, in most species of cinchona bark. It predominates in yellow bark, *Cinchona flava*, *China regia*, or *C. calisaya*; and is obtained by boiling with an excess of milk of lime the decoction in diluted hydrochloric acid of the bark, and treating the precipitate with hot alcohol, which dissolves cinchonine and quinine. On evaporation, the cinchonine is deposited in crystals, and the quinine remains dissolved. Water is added, which causes the quinine to separate as a resinous mass. It may be obtained in crystals by the spontaneous evaporation of its solution in absolute alcohol. It is very sparingly soluble in water, but very soluble in alcohol and in acids. Its solutions are very bitter. When heated with hydrate of potassa, it yields carbonate of potassa, hydrogen gas, and quinoline. $C_{20}H_{12}NO_2+KO+KO,CO_2+C_{19}H_8N+H_4$.

Quinine is decidedly alkaline, and neutralizes the acids. Its salts, especially the sulphate, are very much used in medicine, especially as febrifuge and tonic remedies, in most cases very superior to the bark in substance. The sulphate of quinine used in medicine is a basic salt, $2(C_{20}H_{12}NO_2)+SO_3+8HO$. The neutral sulphate is much more soluble in water; hence, in draughts, sulphate of quinine is generally dissolved in diluted sulphuric acid. The hydrochlorate, phosphate, citrate, and ferrocyanate of quinine have also been employed in medicine.

b. Cinchonine, $C_{20}H_{12}NO$. This base predominates in the grey bark, *Cinchona condaminea*, or *C. rubiginosa*, and is also found in large quantity, as well as quinine in red bark, *C. oblongifolia*. Its preparation has been above described. It crystallizes very readily, and is not so bitter as quinine, although highly febrifuge. When heated, a considerable part is sublimed. When distilled with potassa, it yields quinoline. $C_{22}H_{12}NO+HO,KO=KO,CO_2+C_{19}H_8N+H_5$. It neutralizes the acids, forming crystallizable salts, which may be substituted for those of quinine.

It is very important to observe that cinchonine only differs from quinine by 1 eq. oxygen; and although hitherto no one has succeeded in converting one into the other, little doubt can be entertained that this will be accomplished in process of time. The fact that both yield quinoline is very interesting.

c. Quinoidine. This name has been given by Sertuerner to a third alkaloid, which he has found in the mother liquors of the preceding. It would appear to possess a very great neutralizing power, but it is not yet known in a state of purity. The subject requires investigation.

d. Aricine, $C_{20}H_{12}NO_3$. This base was found, in 1828, in a cinchona bark from Arica, in Peru, and has not since occurred. It is very similar to cincho-

nine, from which it differs in being soluble in ether. According to the analysis of Pelletier, it contains 1 eq. oxygen more than quinine, and 2 eq. more than cinchonine, so the three bases may be viewed as oxides of the same radical. Aricine forms salts which are crystallizable, bitter and febrifuge.

Besides the above four, other alkaloids are said to have been found in different species of cinchona; as *pitoyine*, in the *China pitoya*, *chinovine* in the *China nova*, another alkaloid in the *China of Carthagena*, *blanquinine* in the the *China blanca*, which is the bark of *cinchona ovifolia* and *C. macrocarpa*; and *cinchovatine* in *Cinchona ovata*. This last crystallizes well, and forms crystallizable salts. It has been analyzed, and the results lead to the formula $C_{46}H_{27}N_2O_8$.

4. Bases of the Papaveraceæ.

a. Morphine, $C_{35}H_{20}NO_6$. This alkaloid occurs in opium, which is the inspissated juice of *papaver somniferum*. Perhaps the easiest method of extracting it is the following. The soluble part of opium is extracted by water, and the concentrated infusion is mixed with solution of chloride of calcium, this salt being added in slight excess. On standing, especially if warmed, the mixture deposits a copious brownish grey precipitate of mixed meconate and sulphate of lime (the morphia being in the opium partly as meconate, partly as sulphate), while hydrochlorate of morphia remains in solution with a very large proportion of dark brown colouring matter. The brown solution is evaporated till, on cooling, the hydrochlorate crystallizes, forming a nearly solid mass, which is subjected to very strong pressure in flannel. A thick viscid, nearly black mother liquor is thus expressed, which contains all the narcotine and colouring matter. The squeezed mass or cake of hydrochlorate of morphia is of a fawn colour. It is redissolved in hot water, filtered if necessary, and recrystallized, so much water being used, that on cooling a semisolid mass is obtained. This is again squeezed out, and if the squeezed cake is not quite white, it is only necessary to repeat the operation. A little animal charcoal, in the second, or better still in the third, crystallization, assists in removing the last traces of colour. The second and third mother liquids, although coloured, are not to be thrown away, but should be added to the solution of a fresh portion of opium, so that the small quantity of hydrochlorate which is retained in solution shall not be lost. In crystallizing hydrochlorate of morphine, the liquid should always be acidulated with hydrochloric acid (after the animal charcoal is separated), because in this way very little indeed is retained in solution.

The purified hydrochlorate, which still contains about $\frac{1}{30}$ of codeine, is now dissolved in hot water, and supersaturated with ammonia; on cooling, the morphine is deposited as a snow-white crystalline powder, which may be crystallized by means of hot alcohol. The codeine remains in the mother liquor.

Morphine forms hard transparent brilliant crystals, almost insoluble in water, soluble in hot alcohol, insoluble in ether. It is decidedly alkaline, neutralizing acids, and forming crystallizable salts. All its solutions are bitter, and act as narcotic poisons. It is coloured red by nitric acid, and brownish-red by iodic acid; it also strikes a deep blue with perchloride of iron.

The salts of morphine are much used in medicine, especially the hydrochlorate, the acetate, and the sulphate. A solution of any of these salts, of five grains to the ounce, may be administered in the same dose as tincture of opium (laudanum). The hydrochlorate or muriate is prepared as above described, and is used in the state in which it is obtained by repeated crystallization, contain-

ing $\frac{1}{15}$ of its weight of a double hydrochlorate of morphia and codeine, which has much the same action. The acetate and sulphate are best made directly by dissolving in acetic and sulphuric acids the precipitated morphine till they are neutralized, and then evaporating. 1 lb. of good opium yields $1\frac{1}{2}$ oz. of hydrochlorate of morphine. These salts are most valuable anodynes, and do not derange the stomach nearly so much as an equivalent dose of laudanum; but they do not act so decidedly in producing sleep as in allaying pain and irritation; at least the sleep they induce does not come on so soon as in the case of laudanum. The patient, however, even when he does not sleep, feels refreshed, almost as if he had slept, and on the whole the preparations of morphine are preferred by the physician, and have, in this country at least, nearly banished the use of laudanum. The black drop contains impure citrate of morphine.

b. Codeine, $C_{35}H_{20}NO_5$. This alkaloid is obtained as above described from the mother liquor of the precipitated morphine, which, being evaporated, deposits the double hydrochlorate of morphine and codeine. This salt being purified, is acted on by potassa, which dissolves the morphine, while the codeine is left as a viscid mass, which soon becomes hard and crystalline. It is purified by solution in ether or in water, both of which solvents leave the morphine, which may be mixed with it, undissolved. The ethereal solution, by spontaneous evaporation, deposits it, especially if a little water be added, in fine anhydrous prisms; the aqueous solution gives large octahedral crystals, which are a hydrate, with 2 eq. of water.

Codeine is a powerful base, forming neutral salts with acids. Its solutions are bitter, and would seem to have an anodyne action on the system. But in certain circumstances they appear to excite intolerable itching of the whole skin. It is therefore possible, that the itching caused in some persons by opium, and by the commercial muriate of morphine, proceeds from codeine.

It is important to observe that, as cinchona bark contains three alkaloids differing only in the proportion of oxygen they contain, so the two principal bases of opium differ only by 1 eq. oxygen. Hitherto, however, it has been found impossible to convert codeine into morphine by oxidation, or morphine into codeine by deoxidation.

c. Thebaine. This base also occurs in opium. It is nearly insoluble in water, soluble in alcohol and ether. Its solutions are alkaline, and have an acrid metallic taste. It forms crystallizable salts with acids. According to Kane, its formula is $C_{25}H_{14}NO_3$.

d. Pseudomorphine, $C_{27}H_{18}NO_{14}$? This base is occasionally found in opium. It forms shining scales. It is sparingly soluble in water and weak alcohol, insoluble in absolute alcohol and in ether. It is readily dissolved by caustic potassa or soda. It is coloured blue by perchloride of iron. It forms salts with acids, which are as yet little known.

e. Narceine, $C_{28}H_{20}NO_{12}$? This, which is a feeble base, also occurs in opium. It is sparingly soluble in water, soluble in alcohol, insoluble in ether. It melts at 197°. It is coloured blue by hydrochloric acid, but not by perchloride of iron. Acids dissolve it, but hardly form definite salts with it. In short, it ought rather to be described as an indifferent substance, were it not that its composition so much resembles that of the alkaloids.

f. Narcotine, $C_{46}H_{25}NO_{14}$. This is another weak base, found in opium in larger proportion than any other, except morphine. It may be obtained, either from the mother liquor of muriate of morphia by adding ammonia, or by digesting

the insoluble part of opium in diluted acetic acid, and precipitating by ammonia. The impure narcotine is purified by solution in hot alcohol, with the aid of animal charcoal. On cooling, narcotine is deposited in crystals, which are insoluble in water and alkalies, soluble in alcohol, ether, and acids. Its salts are bitter, and crystallize with great difficulty.

The very recent researches of Liebig, Wöhler, and Blyth, have made known a series of products of decomposition derived from narcotine, when acted on by peroxide of manganese and sulphuric acid, and also by bichloride of platinum. These our space will only permit us briefly to mention.

1. *Opianic acid*, $C_{20}H_9O_{10}=C_{20}H_8O_9,HO$. This acid crystallizes in slender prisms, and forms soluble and crystallizable salts with baryta and the oxides of lead and silver, and with oxide of ethyle. When melted, opianic acid passes into an insoluble state, its composition remaining the same.

2. *Opiammon*, $C_{40}H_{17}NO_{15}$. This compound is derived from 2 eq. opianate of ammonia by the loss of 1 eq. ammonia and 4 eq. water. It is a pale yellow powder, which, by boiling with water, is converted into opianic acid and opianate of ammonia.

3. *Xanthopenic acid.* When opiammon is acted on by alkalies, it gives off ammonia and yields opianate and xanthopenate of potassa. An acid separates the xanthopenic acid as a yellow flocculent precipitate. It forms salts of a fine yellow colour, but has not been fully examined. It contains nitrogen.

4. *Opiano-sulphurous acid*, $C_{20}H_8O_{11}S_2,HO$, is formed by the action of sulphurous acid and opianic acid, and is produced by the substitution of 2 eq. sulphurous acid for 2 eq. water. It has a bitter taste, and forms crystallizable salts.

5. *Sulphopianic acid.* $C_{20}H_8\left\{\begin{matrix}O_7\\S_2\end{matrix}\right\},HO$. This acid is formed by the action of sulphuretted hydrogen on opianic acid, and is, in fact, opianic acid, in which 2 eq. oxygen are replaced by 2 eq. sulphur. It is an amorphous yellow powder, which crystallizes from alcohol. Its salts are soon decomposed, yielding sulphurets of the metals.

According to Wöhler, opianic acid is $(C_{20}H_6O_7,2HO)+HO$; and in the two preceding acids the 2 eq. of water represented within the brackets are replaced by 2 eq. sulphurous acid and 2 eq. sulphuretted hydrogen. Opiammon, on this view, is $(C_{20}H_6O_7,2HO)+(C_{20}H_6O_7,NH_3)$. He considers it probable that narcotine is a compound analogous to opiammon, and containing opianic acid.

6. *Himipinic acid.* $C_{10}H_4O_5,HO$. This is a product of oxidation of opianic acid. 1 eq. anhydrous opianic acid, $C_{20}H_8O_9$, *plus* 1 eq. oxygen, is $C_{20}H_8O_{10}=2(C_{10}H_4O_5)$. The hemipinic acid crystallizes in regular four-sided prisms. It forms insoluble salts with the oxides of lead and silver.

7. *Cotarnine.* $C_{25}H_{13}NO_6$. This is a base formed along with opianic acid. 1 eq. narcotine, $C_{46}H_{25}NO_{14}$, and 7 eq. oxygen yield 1 eq. cotarnine, $C_{25}H_{13}NO_6$+1 eq. opianic acid $C_{20}H_9O_{10}$+ 1 eq. carbonic acid CO_2+3 eq. water, 3HO.

Cotarnine forms a deep yellow radiated mass, soluble in alcohol and in water. It is bitter and alkaline, and forms crystallizable double salts with the bichlorides of mercury and platinum.

8. *Humopinic acid* is a dark brown humus-like acid formed by the action of heat on narcotine. Its composition is not established with certainty, but resembles that of other similar bodies. It contains no nitrogen.

9. *Apophyllic acid.* This seems to be a product of decomposition of cotarnine.

It forms crystals very like those of apophyllite and equally cleavable. When heated it yields an oily liquid, evidently quinoline. Its composition is not yet known, but it contains nitrogen.

10. *Narcogenine*, $C_{36}H_{19}NO_{10}$, is formed, along with opianic acid, when narcotine is not so far oxidized as to yield cotarnine. 2 eq. narcotine with 5 eq. oxygen yield 2 eq. narcogenine, 1 eq. opianic acid, and 3 eq. water. It forms a crystallizable double salt with bichloride of platinum, but when separated, it is resolved into narcotine and cotarnine. 2 eq. narcogenine, with 2 eq. oxygen, contain the elements of 1 eq. narcotine, 1 eq. cotarnine, and 1 eq. carbonic acid.

11. *Narcotinic acid* When narcotine is heated with potassa it forms a soluble compound which contains an acid, apparently isomeric with narcotine, or differing from it only by 1 or 2 eq. water. When this acid, which is called narcotinic acid, is separated from its salts, it rapidly passes into narcotine, so that it is unknown in a separate form. Its atomic weight seems to be half that of narcotine, so that 1 eq. narcotine probably forms 2 eq. of the acid.

Such is a very brief and imperfect account of the results of the recent researches of Wöhler and of Blyth on narcotine. They are of very great importance as indicating a method which may lead to the discovery of the true constitution of the alkaloids.

g. Chelidonine $C_{40}H_{20}N_3O_6$. This alkoloid occurs in *chelidonium majus*, along with *chelerythrine*. It is bitter, insoluble in water, and alkaline, forming crystallizable salts.

h. Chelerythrine is found in the same plant, forms a grey powder which excites violent sneezing. With acids it forms red salts, which are narcotic and poisonous.

i. Glaucine. This alkaloid occurs in the leaves and stem of *Glaucium luteum*. It may be obtained in pearly scales; its taste is bitter and acrid, and it forms salts with acids. Its composition is not yet ascertained.

k. Glaucopicrine is found in the root of the same plant. It is bitter and forms salts of a bitter and nauseous taste. Its composition is unknown.

5. Alkaloids of the Solanaceæ, the Strychneæ, and other Vegetable Families.

a. Hyoscyamine. This base is found in *Hyoscyamus niger* and other species of hyoscyamus. Its composition is not yet known. It is extracted from the seeds by a difficult and tedious process, and may also be obtained, although with much loss, by distillation with potassa, like conine. It is very prone to decomposition when in contact with mineral alkalies. It crystallizes, when pure, in radiated groups of needles, but sometimes forms a viscid amorphous mass. When moist it has a stupefying smell like that of tobacco. It is very poisonous, causing, like conine, tetanic spasms. It dilates the pupil powerfully. It is fusible and volatile, but is partly decomposed when distilled. It dissolves in water, alcohol, and ether. It neutralizes the acids, forming crystallizable salts which are very poisonous.

b. Daturine. This base is obtained from the seeds of *Datura stramonium*. It is, in preparation and properties, very analogous to hyoscyamine. It is, however, less soluble in water, and crystallizes in fine brilliant prisms, from its alcoholic solution. It is fusible, volatile, and very poisonous, dilating the pupil. Its salts are crystallizable and very poisonous. Its precise composition is unknown.

c. Stramonine. This is another crystalline compound found in *stramonium.* It is crystallizable, volatile, soluble in alcohol and ether, insoluble in water. Its nature is uncertain and its composition unknown.

d. Atropine. $C_{34}H_{23}NO_6$? This alkaloid is the active principle of *Atropa belladonna.* It is obtained like daturine, and being equally prone to decomposition, much is always lost. It is sparingly soluble in water and ether, more soluble in alcohol. It crystallizes in white silky prisms, and sometimes forms an amorphous mass like glass. It is very bitter, acrid, and poisonous, dilating the pupil like hyoscyamine and daturine. It is fusible and volatile, and neutralizes acids, forming salts which are bitter, acrid and poisonous, and which crystallize. These salts, from their very powerful action in permanently dilating the pupil, are very well adapted for medical use, being much more uniform than the extract.

e. Solanine, $C_{84}H_{78}NO_{28}$? This alkaloid occurs in many species of *Solanum,* as in *S. nigrum, S. dulcamara,* and in the potato, *S. tuberosum.* In the latter it is found especially in large quantity in the shoots, when the tubers have germinated in dark cellars. The shoots are extracted with dilute sulphuric acid, and the solution precipitated while hot by ammonia. The precipitate is purified by solution in alcohol. It forms a crystalline powder, very bitter and acrid, and highly poisonous, but not dilating the pupil. Its salts do not crystallize readily. There is some reason to suspect that the alkaloid of the shoots of potatoes may be distinct from that of the bittersweet, *Solanum dulcamara.*

f. Veratrine. $C_{34}H_{26}NO_6$? This alkaloid is found in *Veratrum sabadilla, V. album, &c.* It is extracted as atropine is, and is generally obtained as a crystalline powder, nearly white, very acrid and poisonous, exciting when introduced into the nostril violent and even dangerous sneezing. It is insoluble in water, but very soluble in alcohol, and may be obtained, by the spontaneous evaporation of its alcoholic solution, in prismatic crystals several lines in length. It is coloured red both by nitric and sulphuric acid.

Veratrine, in the form of tincture, and still more in that of ointment (1 drachm, or $\frac{1}{2}$ drachm to 1 oz. of lard), is now much used as an external application in neuralgia and obstinate rheumatic pains. Its effects in many cases are highly beneficial. In making the ointment, the veratrine should first be rubbed with a few drops of alcohol to an impalpable powder, and the lard then added. If this be not done, the gritty particles of veratrine in the ointment cause so much irritation when rubbed into the skin as to prevent its use for any length of time. We are indebted chiefly to Dr. Turnbull for our knowledge of the valuable properties of this alkaloid.

g. Sabadilline. This name has been given by Conerbe to a second crystalline body found by him along with veratrine. It is alkaline, soluble in hot water, insoluble in ether, and forms crystallizable salts with acids. Conerbe states its formula to be $C_{20}H_{13}NO_5$; but, according to Simon, it is a compound of veratrine with resin, containing also resinate of soda.

h. Colchicine. This alkaloid is similar to veratrine, for which it was formerly taken. It is found in *Colchicum autumnale.* It is crystallizable, bitter, and very poisonous. Nitric acid colours it blue or violet. It is soluble in water, alcohol, and ether. Its salts are crystallizable, bitter, acrid, and poisonous. They might probably be used in medicine advantageously, instead of the very uncertain preparations of colchicum which are at present employed. In a very

small dose, colchicine causes purging and vomiting. Its composition is unknown.

i. Aconitine. This alkaloid, the composition of which is unknown, is found in *Aconitum napellus*, and, probably, also in *A. ferox* and other species. It is obtained by the usual method, but, being very prone to suffer change, much is lost. It forms a crystalline powder, or occasionally a vitreous amorphous mass. It is in the highest degree bitter, acrid, and poisonous, and is said by Geiger to dilute the pupil. On the other hand, the plant contracts the pupil and causes numbness of the part to which it is applied, and Dr. Turnbull has obtained an aconitine possessing these properties in a very high degree. Either, therefore, there are two bases in the aconite, or, as is much more probable, the aconitine of Geiger having an action different from that of the plant, is a product of decomposition, while that of Turnbull is unchanged.

Turnbull's aconitine is an invaluable remedy in the same painful diseases in which veratrine is employed. It is unfortunately obtained in small proportion, and as yet is very expensive. A cheaper and more productive method of preparing it is a very great desideratum.

k. Delphine, $C_{27}H_{19}NO_2$? This alkaloid, analogous to veratrine, is found in *stavesacre, Delphinum staphysagria.* It has only been obtained hitherto as a yellowish white powder, not crystallyzed, very acrid, and poisonous. It forms neutral salts hitherto little examined. It may be used in the same affections and in the same manner as veratrine.

l. Staphisine. This is a substance found along with delphine, and said to be $C_{32}H_{23}NO_4$. It is acrid and poisonous, but is probably only a compound of delphine.

m. Emetine. $C_{37}H_{27}NO_{10}$? This is the active principle of ipecacuanha, the root of *Cephaelis ipecacuanha.* When pure, it is a white powder, alkaline, soluble in alcohol and in hot water, insoluble in ether. $\frac{1}{16}$ of a grain acts as an emetic. In a dose of from 2 to 4 grains it is poisonous. Its salts do not crystallize.

n. Chiococcine and *o. Violine* are two very similar alkaloids, found in *Chiococca ramosa* and *Viola odorata.* They are supposed by some to be emetine disguised by a little foreign matter.

p. Strychnine. $C_{44}H_{23}N_2O_8$, or $C_{44}H_{24}N_2O_8$. This alkaloid is found in nux vomica, the seeds of *Strychnos nux nomica*, in St. Ignatius's bean, the seed of *S. Ignatii*, in the wood of *S. colubrina*, and in the poison called *Upas tieuté*, derived from *S. tieuté*. It is extracted by decoction with dilute sulphuric acid, precipitating the decoction with milk of lime, and acting on the precipitate, after washing it with cold alcohol, by boiling alcohol, which on cooling deposits the strychnine in very regular transparent brilliant crystals. If brucine is present, it remains chiefly in the mother liquid, but the two bases may be separated by converting both into nitrates, and crystallizing; the nitrate of strychnine crystallizes readily, while the nitrate of brucine remains dissolved.

Strychnine is very insoluble, requiring 7000 parts of water. It is so bitter, that 1 part gives a very strong and persistent bitter taste to 40,000 parts of water. It dissolves in hot alcohol, although sparingly if the alcohol be pure, and is insoluble in ether. When pure, it is only coloured yellow by nitric acid; a trace of brucine causes it to be reddened by that acid. It forms crystallizable salts, which are intensely bitter. Their solutions are precipitated white by alkalies, by tincture of galls, and by iodide of potassium, in white

crystals by sulphocyanide of potassium, and as yellow powders by solutions of gold and platinum.

Strychnine and its salts, especially the latter, from their solubility, are most energetic poisons. They produce spasmodic motions, and are used in very small doses as remedies in paralysis; they seem to have a specific action on the lower part of the spinal column. The average dose is $\frac{1}{12}$ of a grain. In the event of an overdose the best antidote is infusion of galls or strong tea, which also contains tannine.

q. Brucine. $C_{44}H_{25}N_2O_7$. This alkaloid occurs along with strychnine in nux vomica, and also in the false angustura bark, the bark of *Brucia antidysenterica*. It is prepared as strychnine. Besides the methods above mentioned for separating the two bases, there is another, which is to boil the mixture with water as long as it dissolves brucine, or till the strychnine is no longer reddened by nitric acid. Brucine forms large transparent crystals, which I have found to become opaque in closely stopped phials. It is very bitter and poisonous, but much less so than strychnine. It may be used for the same purposes in a rather larger dose. It is reddened strongly by nitric acid, and the red solution becomes violet on the addition of solution of tin. It is thus distinguished from strychnine and morphine. Its salts, for the most part, crystallize with facility.

r. Jervine. $C_{60}H_{45}N_2O_3$. This alkaloid is found in white hellebore, *Veratrum album*, along with veratrine, from which it is separated easily, as it crystallizes first from the alcoholic solution; and its sulphate is also far less soluble than that of veratrine. It forms a crystalline powder, fusible, insoluble in water, soluble in alcohol, and forming with sulphuric, nitric, and hydrochloric acids, very sparingly soluble salts, so that the solution of the acetate is precipitated by these three acids.

s. Curarine. This alkaloid is obtained from the South American poison called *curari*, which is derived from some plant of the family Strychnea. It is a deadly poison when introduced into a wound, but may be swallowed with impunity. The curarine forms a yellowish amorphous bitter mass, which is more poisonous than the curari which yields it. Its salts are bitter, but do not crystallize.

t. Corydaline. $C_{34}H_{22}NO_{10}$? Found in the root of *Corydalis bulbosa* and *C. fabacea*. It forms a light grey powder, very soluble in alcohol, which deposits it in crystals. It is reddened by nitric acid, and forms crystallizable salts with acetic and sulphuric acids.

u. Carapine. Found in *Carapus guianensis*. It is a white pearly fusible powder, very bitter, soluble in water and alcohol, insoluble in ether, forming crystallizable salts with hydrochloric and acetic acids.

v. Cusparine. Found in the true angustura bark, that of *Bonplandia trifoliata* or *Cusparia febrifuga*. It forms fusible octahedral crystals, sparingly soluble in water, very soluble in alcohol.

w. Daphnine. Occurs in the bark of *Daphne gnidium* and *D. mezereon*. It is obtained by distilling the infusion with magnesia. It is alkaline and acrid, and forms crystallizable salts with nitric and sulphuric acids, according to Vauquelin. Baer and Gmelin could not obtain it.

x. Bebeerine is the active principle of the bark of the *bebeeru* tree of Guiana, which seems to be analogous to quinine. It has not been obtained crystallized or colourless, but as a brown mass, the composition of which is not yet ascertained. Bebeerine and its salts are bitter and highly febrifuge. Dr. Douglas

Maclagan and Mr. Tilley have found its composition to be the same as that of morphine, namely $C_{35}H_{20}NO_6$.

y. Sanguinarine is found in *Sanguinaria canadensis.* It forms a grey powder, which is alkaline and yields red salts. It excites sneezing, and is possibly identical with chelerythrine.

z. Azadirine, found in *Melea azadirachta*, is alkaline, forms a crystallizable salt with sulphuric acid, and is powerfully febrifuge.

aa. Capsicine is the active principle of the capsules of *Capsicum annuum* or cayenne pepper. It has a resinous aspect and a burning taste, but when quite pure may be crystallized. It forms crystallizable salts with acetic, nitric, and sulphuric acids. It is soluble in alcohol, insoluble (when pure) in ether and in water.

bb. Crotonine occurs in the seeds of *Croton tiglium*, and may be obtained from croton oil by boiling it with water and magnesia. It forms crystals, which are fusible, soluble in alcohol, insoluble in water. It forms crystallizable salts with sulphuric and phosphoric acids.

cc. Buxine. Occurs in Boxwood bark. It forms a bitter, brown, amorphous mass, soluble in alcohol, alkaline, and forming a crystalline sulphate. It excites sneezing.

dd. Apyrine. Found in *Cocos lapidea.* It is a white alkaline powder, forming crystalline salts with acids.

ee. Cynapine. From *Æthusa cynapium.* It is crystallizable, soluble in water and alcohol, and forms a crystalline sulphate.

ff. Cissampeline, or *Pelosine*, from Cissampelos Pareira, is a white powder, soluble in alcohol and ether; alkaline, forming soluble salts, of which the hydrochlorate crystallizes.

gg. Oxyacanthine and *Berberine* are two bitter substances found in the barberry, *Berberis vulgaris.* The former is decidedly alkaline, and forms crystallizable salts. The latter is bitter, yellow, and feebly, if at all, alkaline. It crystallizes, and is used in dyeing. Its formula is $C_{33}H_{18}NO_{12}$.

hh. Surinamine and *Jamaicine* are two alkaloids, found in *Geoffræa Surinamensis* and *G. inermis.* Both are crystallizable, and form crystallizable salts; those of the latter are precipitated by tannine and corrosive sublimate.

ii. Piperine, $C_{34}H_{19}NO_6$. This compound is found in pepper, *Piper nigrum*, and *P. longum.* It is crystallizable, soluble in alcohol, very pungent. It is a feeble base, but does form salts, especially double chlorides, containing hydrochlorate of piperine.

kk. Menispermine and *Paramenispermine* are found in *cocculus indicus*, the seed of *Menispermum cocculus.* Menispermine is white, fusible, crystallizable, and forms salts, of which the sulphate crystallizes. Its formula is $C_{18}H_{12}NO_2$.

Paramenispermine has the same composition. It is less fusible, but sublimes at a high temperature. It does not appear to form definite salts. Both are insoluble in water, and soluble in alcohol; and paramenispermine is insoluble in ether.

ll. Harmaline, $C_{24}H_{13}NO$. This alkaloid occurs united with phosphoric acid in the seeds of *Peganum Harmala.* It forms brownish-yellow prisms, bitter, astringent, and acrid, very soluble in alcohol, little soluble in water or ether. It is fusible, and partly volatile. It forms, with acids, yellow crystallizable salts. By oxidizing agents, harmaline is transformed into a red matter, which forms red salts with acids. The harmala red of commerce is the powder of the seeds already tranformed into the phosphate of the red harmaline. It is used in dye-

ing, especially in giving to silk every shade of red, rose-colour, and pink. It is produced abundantly in the steppes of southern Russia, and is little known out of that country.

mm. Theobromine, $C_9H_5N_3O_2$. This is a crystalline compound, found in cacao, the seed of *Theobroma cacao*. It can hardly be called an alkaloid. It is very analogous to the next substance, caffeine.

nn. Caffeine, $C_8H_5N_2O_2$. Syn. *Théine. Guaranine.* This remarkable compound is found in *coffee*, in *tea*, in *guarana officinalis*, or *paullinia sorbilis*, and in *ilex paraguayensis*. It is best obtained by adding to a decoction of tea a slight excess of acetate of lead, and evaporating to dryness the filtered liquid. The dry mass mixed with sand, is heated in the apparatus described for benzoic acid, when caffeine is obtained in crystals. Tea yields more than 1 per cent.

Caffeine forms fine white prisms, of a silky lustre, which are soluble in water, alcohol, and ether, bitter, fusible and volatile. It is a feeble base, but forms with hydrochloric acid and sulphuric acid, salts which yield very large crystals.

It is very remarkable, that caffeine should approach so nearly in composition to alloxan and alloxantine. Anhydrous alloxan, plus 1 eq. water, is $C_8N_2H_5O_{11}$, and alloxantine is $C_8N_2H_5O_{10}$, while caffeine is $C_8N_2H_5O_2$, differing from the one by 9, from the other by 8 eq. oxygen.

Further, caffeine, $C_8N_2H_5O_2$, added to 9 eq. water and 9 eq. oxygen (that is, to H_9O_{18}), is $C_8N_2H_{14}O_{20}$, which is equal to 2 eq. taurine, a nitrogenized principle derived from the bile. We shall hereafter see how close a connection can be traced between the bile and the urine; but in the meantime it is a most striking fact, that tea, coffee, Paraguay tea, and guarana, are all used by different and distant nations for the same purpose, namely, as a refreshing and gently stimulating drink, which notoriously promotes the vital functions, while all these plants contain the very same compound, and that one allied to the bile and the urine, the chief products of the vital metamorphosis. The quantity of caffeine in tea is indeed small, but not too small to have a perceptible influence on the system. Peligot has shown that gunpowder-tea contains 6 per cent. of théine (caffeine).

By the action of nitric acid, caffeine yields a crystalline nitrogenized compound, *nitrothéine.*

Besides caffeine, or théine, tea contains 14 or 15 per cent. of caseine, and the leaves are therefore nutritious, when eaten, as they are, by some oriental nations.

The following substances have been noticed as alkaloids, but are very little known: *Castine* in *Vitex agnus castus*; *Cicutine* in *Cicuta virosa*; *Chærophylline* in *Chærophyllum bulbosum*; *Esenbeckine* in *Esenbeckia febrifuga*; *Digitaline* in *Digitalis purpurea*; *Eupatorine* in *Eupatorium cannabinum*; *Euphorbine* in *Euphorbium*; *Convolvuline* in *Convolvolus scammonium*; and *Pereirine* in *Pereyra bark.*

We now come to a class of compounds, very widely distributed in the vegetable kingdom, but not exhibiting the same varieties as the classes hitherto described, and not characterized by the same marked properties. This is the class of neutral or indifferent non-azotized bodies, which are never poisonous, hardly even possessed of medicinal properties, and exhibit no striking chemical chaacters. It includes starch, gum, or mucilage, pectine or vegetable jelly, and woody fibre or lignine, with their derivatives. We can only describe them briefly.

INDIFFERENT NON-AZOTIZED COMPOUNDS.

1. Starch. $C_{12}H_{10}O_{10}$.

This very important compound is universally diffused in the vegetable king-

dom. It occurs in seeds, as in those of wheat and other cerealia, and also in the leguminosæ; in roots, as in the tubers of the potato; in the stem or pith of many plants, as in Sagus Rumphii; in some barks, as that of cinnamon; and in pulpy fruits, such as the apple. Finally, it is contained in the expressed juice of most vegetables, such as the carrot, in a state of suspension, being deposited on standing.

It is chiefly extracted from wheat flour (*common starch*); from potatoes (*potato starch*); from the root of *Jatropha manihot*, (*tapioca*); from that of *Maranta arundinacea* (*arrow root*); from the stem and pith of *Sagus farinifera Rumphii* (*sago*); the substances known by these different names being all essentially the same.

When flour is kneaded with water in a cloth, the water carries off the starch in suspension, and deposits it on standing, leaving behind the gluten. By a similar process starch is purified from the cellular substance and other matters mixed with it in potatoes, which are rasped, and then treated with water as above. Sago, being finally dried at a somewhat high temperature, acquires a horny and translucent appearance.

Pure starch is a snow-white powder, of a glistening aspect, which makes a crackling noise when pressed with the finger. It is composed of transparent rounded grains, the size of which varies in different plants. Those of the potato are the largest, those of the leguminosæ, as peas, are very small, and those of wheat and rice are the smallest. Starch is insoluble in cold water, alcohol, and ether; but when heated with water it first becomes viscid, and is then converted into a kind of solution, which, however, is not complete, but is rather formed by the swelling of the grains of starch into a mucilaginous mass. On cooling, the whole forms a stiff, semi-opaque jelly. If dried up, this yields a translucent mass, which softens and swells into a jelly with water, like tragacanth. The solution, or mixture of starch and water, has the remarkable property of striking a deep blue colour with free iodine. This appears to be owing not so much to a chemical or definite combination, as to the mechanical division of the iodine; there is even reason to think that the blue colour is that of iodine finely divided, adhering to the starch as a dye does to the fibres of cloth.

When starch is warmed with water, to which has been added either some infusion of malt or some diluted acid, the viscidity of the mixture disappears, and the fluid solution is no longer coloured blue by iodine. As soon as this is the case, the whole of the starch has disappeared, and has been converted into a soluble gum called *dextrine*, from its power of causing the plane of polarization to deviate to the right. According to the proportion of malt or of acid, and the temperature employed, the change is more or less rapid; and when the action is continued the dextrine is in its turn converted into *glucose*, or grape sugar, which from this circumstance is also called starch-sugar.

In contact with oil of vitriol, starch appears to form a compound or coupled acid, *sulphoamidic acid*. Strong nitric acid, rubbed up with potato starch, dissolves it, forming a viscid liquid, from which water precipitates a white compound, called *xyloidine*. This compound has some of the properties of gum-tragacanth, but it contains the elements of nitric acid, and has not yet been fully investigated. According to Pelouze, its formula is $C_6H_4O_4+NO_5$; according to Ballot, it is $C_{15}H_{12}NO_{16}$. When starch is distilled, with moderately-strong sulphuric acid, it yields carbonic acid, formic acid, and a pungent volatile oil, hitherto very little examined.

The blue compound of iodine and starch is best prepared by adding to the liquid

filtered from the viscid paste obtained by boiling starch with water, first iodide of potassium, and then solution of chlorine, as long as it causes a blue precipitate, which is to be washed till the water passes deep blue, and dried in vacuo. Its colour is so intense as to be nearly black. It does not appear to be a compound in definite proportions. The best method of using starch as a test for iodine in mineral waters, &c., is to add to the water some starch paste, and then a little nitric acid or chlorine. The latter is best added in the form of gas, its weight allowing it to be poured like water; while in this way we are less likely to add an excess which would destroy the blue colour. Or we may place in the bottom of a phial the liquid to be tested, adding a little oil of vitriol, and suspending from the stopper a slip of paper moistened with starch paste. After a time, if iodine be present, the paper will exhibit a tinge of blue. By these tests $\frac{1}{40000}$th part of iodine in a liquid may be detected.

With bromine, starch forms an orange yellow precipitate, which cannot be dried without decomposition.

Dextrine is best obtained by heating to about 120° a mixture of 20 parts of starch paste and 1 part of strong infusion of malt, until iodine no longer colours the mixture blue. The addition of strong alcohol now precipitates the dextrine as a thick syrup, while any sugar remains dissolved. When dried, dextrine much resembles gum, from which, however, it differs in the extreme facility with which it is converted into sugar when warmed with dilute sulphuric acid or infusion of malt, and by not yielding mucic acid when acted on by nitric acid. The composition of dextrine is the same as that of starch. In fact, dextrine is supposed by some to be the substance which is contained in the grains of starch, inclosed in an insoluble membrane, which is burst in the process of conversion of starch into dextrine, or solution of starch, by means of acids and infusion of malt. The substance present in the malt which has the property of effecting this change, is called *diastase*. It contains nitrogen.

According to other observers, the grains of starch are composed of concentric layers of one and the same substance (dextrine?), the outer layer being insoluble in water. As starch is found to contain a small proportion of a matter analogous to wax or to caoutchouc, we may suppose that the presence of this matter in the outer layer is the cause of its insolubility, or that the whole mass of the grains is, by its means, rendered insoluble, and endowed with the property of swelling up with water to a paste or jelly. Dextrine will then be the purified, and consequently soluble, matter of starch. If the outer coat be different from the contents of the grains, it has still the same composition; for analysis shows no difference between starch, dextrine, and the insoluble matter left on the filter when starch is boiled with diluted acids.

Leiocome. This name is given to a substance having the properties of gum, which is prepared by simply roasting or torrefying starch at about 300°. It is, in fact, capable of being used instead of gum in calico-printing, and is made on the large scale. It has a yellowish-brown colour. It is probably dextrine, more or less pure, generally containing some undecomposed starch. When well made it dissolves in cold water like gum.

Inuline. $C_{24}H_{18}O_{18}$? $C_{32}H_{24}O_{24}$? $C_{24}H_{21}O_{21}$? This is a substance analogous to starch in the roots and tubes of *inula helenium*, *dahlia variabilis*, *helianthus tuberosus*, and many other synantherous plants, which do not yield ordinary starch.

It is extracted from the roots by boiling water, and is deposited by the con

centrated decoction as a brittle white mass, formed of crystalline grains, or as a fine powder. It is tasteless, insoluble in cold, very soluble in hot water. Diluted sulphuric acid, with the aid of heat, rapidly converts it into grape sugar, from which, like starch, it differs only by a certain amount of the elements of water. This may be seen by the above formulæ, which represent inuline from different plants, as it exists in its compounds with oxide of lead. It would appear to differ in different vegetables, but always retaining the character of this class of bodies, namely, the presence of hydrogen and oxygen in the proportions to form water. Iodine colours it slightly brown.

Lichenine, $C_{12}H_{10}O_{10}$. This is a variety of starch found in *lichen islandicus*, or iceland moss. It forms, when pure, a nearly colourless, tasteless mass, which swell up into a transparent jelly with cold water, and dissolves entirely in hot water. When its solution is boiled, it forms pellicles, like milk, which adhere to the vessel. Its solution is not coloured by iodine, but the jelly is rendered blue by that test. By diluted and boiling sulphuric acid it is converted into sugar; by nitric acid into oxalic and saccharic acids. It has the composition of starch.

Saponine is the name given to a variety of starch obtained from the root of *saponaria officinalis*. Its properties are little known.

2. Gum.

This name was formerly given to almost all exudations from plants. It is now limited to certain rather abundant substances, which are solid, uncrystallizable, transparent, or translucent, colourless, or nearly so, tasteless, inodorous, soluble in water, or at least softening in it, and insoluble in alcohol, ether, fat and volatile oils. They yield mucic acid when acted on by nitric acid. They may be divided into gums, which dissolve in cold water (arabine, mucilage), and gums which only swell up to a jelly (tragacanth or bassorine, cerasine, pectine). Arabine and cerasine contain oxygen and hydrogen in the proportion to form water: the other gums are nearly analogous in composition.

Arabine, or gum arabic, is found as an exudation from several species of acacia. What is called gum senegal is essentially the same. It is nearly colourless, transparent, hard, and brittle, and has a mild taste. It is very soluble in cold water, and forms a viscid mucilage, from which alcohol precipitates the gum. The diluted solution is precipitated by silicate of potassa, subacetate of lead and protonitrate of mercury. When a mixture of gum, water, and sulphuric acid is kept for some time at a temperature near boiling, it is converted into grape sugar. The composition of gum is $C_{12}H_{11}O_{11}$, that is, the same as that of cane sugar, which accounts for the transformation. Arabine yields 2 or 3 per cent. of ashes, containing a good deal of lime.

Mucilage is the name given to a substance resembling gum, found in many vegetables, such as *linseed*, *althæa*, and others. It differs from arabine in being less hard when dry, and less transparent. It would appear, however, that the mucilage of althæa-root is essentially starch enclosed in cells formed of woody fibre or cellulose. The different mucilages are resolved into grape sugar by being heated with dilute sulphuric acid, and therefore may be considered as containing, like starch and arabine, water plus carbon. Since all these mucilages contain much mineral matter, the mucilage of linseed, for example, leaving 11 per cent. of ashes rich in lime, it is probable that their peculiar qualities depend

on the presence of phosphate of lime or other salts of lime, disguising either starch or arabine.

Bassorine is the name given to a substance which forms the chief part of *gum tragacanth* and of *gum bassora*, and also, according to some, of *salep*, a mucilaginous substance, obtained from the bulbs of *orchis mascula*. According to Schmidt, however, salep is really formed of swelled up grains of starch.

Pure bassorine resembles arabine in appearance, but is less transparent, and instead of dissolving in cold water, only swells up to a very great extent, forming a viscid mass. Its composition is analogous to that of arabine, and by digestion with diluted sulphuric acid, it is transformed, like salep, into grape sugar and cellulose. *Cerasine* is the name given to that part of the gum of the cherry, plum or almond trees, which is insoluble in cold water. It is probably identical with bassorine, or with salep.

During what is called the viscous fermentation, which takes place in certain sweet vegetable juices, as that of beet-root, there is formed, along with lactic acid and mannite, a mucilaginous compound, which causes the viscidity. When dried, it has nearly the characters and composition of arabine.

Pectine is the substance which causes the juice of some pulpy fruits, as apples and pears, to coagulate or gelatinize when mixed with alcohol, by which the pectine is precipitated. When dried, it resembles gum or isinglass, and forms a jelly with water. By the action of nitric acid it yields oxalic and mucic acids. It generally yields about 8 per cent. of ashes, containing much phosphate of lime. In contact with alkalies, it is transformed into pectic acid. *Pectic acid* is easily obtained from many vegetables, as, for example, rasped carrots, by washing them well with distilled water, and then boiling 50 parts of the squeezed residue with 300 of water and 1 of potassa. The pectate of potassa is deposited as a jelly in the filtered liquid on cooling. Either this salt or the pectate of lime may be decomposed by diluted hydrochloric acid, which leaves the pectic acid as a jelly, which dries up into transparent laminæ, insoluble in water but very soluble in alkalies. From these solutions acids precipitate it as a jelly. In this form it is slightly soluble in boiling water, but the solution gelatinizes on the addition of acids, salts, alcohol or sugar. It is supposed not to exist ready formed in the plants, but to be produced by the action of alkalies on pectine.

The alkaline pectates, when dry, form gummy solids, soluble in water. Alcohol causes the solution to gelatinize, and even an excess of potassa or soda has the same effect. The earthy and metallic pectates are gelatinous and insoluble. When dried, pectine, pectic acid, and all the pectates, assume a cellular structure, so to speak.

The jelly formed in current juice as well as other juices by the addition of sugar is pectine or pectic acid. The boiling of such juices probably promotes the formation of jelly; for it has been shown that when the insoluble part of unripe currants, after being washed, is boiled with water acidulated with a vegetable acid, a considerable quantity of pectine is formed, probably by a transformation of the cellular tissue.

The composition of pectic acid is not fully ascertained. According to Regnault it is $C_{12}H_8O_{11}$, or $C_{12}H_7O_{10},HO$. According to Mulder, it is $C_{12}H_8O_{10}$. But the researches of Chodnew have led him to adopt the formula $C_{28}H_{18}O_{24}$, $2HO=C_{28}H_{20}O_{26}$. In all the formulæ there is an excess of oxygen over hydrogen.

The whole subject of the mucilaginous compounds, including pectine and pectic acid, is still very obscure and requires renewed investigations.

Apiine is a substance analogous to pectine, found in parsley, *apium graveolens*. *Glycyrrhizine* is the name given to a substance resembling both sugar and gum, which is the chief ingredient in liquorice, the juice of the root of *glycyrrhiza glabra*. It is soluble in hot water, and gelatinizes on cooling. Its taste is sweet and also acrid, but it does not, like sugar, undergo the vinous fermentation. Its formula is said to be $C_{16}H_{12}O_6$.

Sarcocolline is a gummy matter found in the sococolla of commerce, which is the dried juice of *penæa mucronata*. It is soluble in alcohol and water, and has a taste both sweet and bitter. Formula $C_{22}H_{19}O_{10}$? or $C_{40}H_{32}O_{14}$!

§ 3. Woody Fibre.

The skeleton of plants, after everything soluble in water, alcohol, ether, diluted acids, and diluted alkalies has been removed, is called woody fibre. It varies in aspect and in composition as obtained from different plants. That of box or willow, when dried, is $C_{12}H_9O_9$; that of oak is $C_{36}H_{22}O_{22}$; and that of beech is intermediate between these two. All varieties, however, may be represented as composed of carbon plus water.

Recent researches have shown that wood is composed of two parts: 1. *cellulose*, which forms the parietes of the vegetable cells; and 2. *lignine*, which fills those cells, or forms an incrustation on their walls. The latter dissolves in strong nitric acid, the former is left undissolved. Again, oil of vitriol dissolves cellulose without blackening, and appears to convert it into dextrine, with which it agrees in composition; while lignine separated from cellulose is said to contain $C_{35}H_{24}O_{20}$.

By the continued action of acids or of hot alkalies, woody fibre yields a substance which is coloured blue by iodine. Linen, cotton, or paper, all of them different forms of woody fibre, when moistened with pretty strong sulphuric acid, are converted apparently first into dextrine, and afterwards into grape sugar. When heated with a more diluted acid, linen yields an amylaceous pulp hardly soluble in water, the composition of which is $C_{12}H_{10}O_{10}$.

When exposed to air and moisture, wood undergoes eremacausis, being slowly converted into a friable mass, which contains a larger proportion of carbon than the original wood. It would appear that the oxygen of the atmosphere combines with the hydrogen, and that carbon and oxygen are given off from the residue as carbonic acid, CO_2. As the residue is found still to consist of carbon and water, it is evident that for every equivalent of carbon removed, there are separated 2 eq. of oxygen and hydrogen, so that the proportion of carbon to water in the residue is constantly increasing. Woody fibre $C_{36}H_{22}O_{22}$ will thus yield first a residue of $C_{35}H_{20}O_{20}$; then $C_{34}H_{18}O_{18}$, $C_{33}H_{16}O_{16}$, and so on. When air is left in contact with moist wood, its oxygen is removed and replaced by an equal volume of carbonic acid. This is one chief source of the insalubrity of marshy districts; and the effect is seen still more strikingly in the case of houses which have been submerged in an inundation, which are very unwholesome as long as the wood is moist.

The tendency of wood to decay is checked or destroyed by acids and many salts, especially corrosive sublimate. Out of contact of air, moist wood putrefies, yielding a white friable residue, containing less carbon than the wood. One

specimen yielded $C_{33}H_{17}O_{20}$, while the corresponding product of eremacausis above mentioned is $C_{35}H_{20}O_{20}$, and the wood $C_{36}H_{22}O_{22}$.

The composition of brown coal is analogous to that of wood partially decayed, but subjected to changes of the nature of putrefaction, as well as to eremacausis. Two specimens of brown coal yielded $C_{33}H_{21}O_{15}$ and $C_{32}H_{15}O_{9}$.

All the above products of decomposition of wood may be derived from oak wood, $C_{36}H_{22}O_{22}$, by the fixation of oxygen, and the separation of water and carbonic acid.

When the substance called mould, which contains the debris of decayed vegetable matter, is boiled with alkalies, the filtered solution deposits, on the addition of acids, a brown precipitate, which has been called ulmine, humus, humine, geine, ulmic acid, humic acid, and geic acid. It is generally admitted that this precipitate is a product of the action of the alkali on the decayed vegetable matter, and the name of humus, humine, or geine is given to the substance which is believed to yield the humic acid. But this humus has not been isolated, and is not known.

Mulder examined the precipitates obtained from a variety of different sources, decayed wood, turf, peat, mould, &c. With one exception, he found all to contain nitrogen, varying from 2·5 to 7 per cent. It is evident that these substances are vegetable matter in different stages of decay. Mulder considers these precipitates as compounds of water, or water and ammonia, with three different acids: 1. acid of mould $C_{40}H_{12}O_{14}$: 2. humic acid, $C_{40}H_{12}O_{12}$: 3. ulmic acid, $C_{40}H_{14}O_{12}$.

When sugar is boiled with diluted acids, it yields brown substances analogous to, if not identical with, these acids of Mudler.

It is important to observe the general presence of ammonia in mould, &c. This ammonia has no doubt been absorbed from the air in great part; and this will explain the favourable influence which these substances exert on vegetation. They act also in furnishing, by their slow decay, a continual supply of carbonic acid.

Crenic Acid and *Apocrenic Acid* are two brown extractive matters, analogous to the preceding, and derived from decaying vegetable matter, which are found in certain mineral waters. They both appear to contain nitrogen.

PRODUCTS OF THE DISTILLATION OF WOOD.

When wood is heated in close vessels, it gives rise to an immense variety of products, according to the kind of wood and to the presence or absence of resinous or oily matters. In all cases there are formed gaseous, liquid, and solid products, with a residue of charcoal.

The gases are carbonic acid, carbonic oxide, olefiant gas and marsh gas. The liquids are partly soluble in water, partly insoluble. The latter constitute the tar, and are of a semifluid consistence.

The substances soluble in water are, besides water itself, acetic acid, acetone, pyroxylic spirit (hydrate of oxide of methyle), acetate of oxide of methyle, lignone, xylite and mesite.

The oily substances, insoluble in water, are very numerous, including creosote, picamar, eupion, capnomor, &c. Along with these are the compounds which at the ordinary temperature are solid, such as paraffine, naphthaline, cedriret, pittacall, pyréne, chryséne, and pyroxanthine. The last mentioned, being very volatile, chiefly accompanies the acetic or pyroligneous acid.

1. Volatile Products, soluble in water.

Acetic Acid. This is one of the chief products of the distillation of woods. Its mode of purification and its properties have been already described. As prepared from this source, it is often called pyroligneous acid. The crude or impure acid is highly antiseptic; not only because vinegar, like most acids, is so, but also because it contains much creosote dissolved. Hence it not only preserves meat, but gives to it a powerful and agreeable smoked flavour.

Pyroxylic Spirit. This name is given to the spirituous liquid, distilled from the crude pyroligneous acid before the latter is purified. It is a mixed fluid, the chief component being hydrated oxide of methyle, which is accompanied by acetate of oxide of methyle, unless it has been rectified with quicklime, which decomposes the latter. *Lignone* is the name given to a volatile liquid, somewhat resembling alcohol, observed in pyroxylic spirit by Gmelin and Liebig. Its formula is not ascertained, since it does not, as far as we know, form definite compounds, from which its equivalent might be deduced. *Xylite* is another similar volatile liquid, which, according to Schweitzer, is $C_{12}H_{12}O_5 = 2(C_2H_3O) + (C_8H_6,O_3) = 2MtO + Ac_2O_3$; that is a compound of 2 eq. oxide of methyle and 1 eq. of a sesquiacetylic acid. When acted on by potassa, it yields a crystalline salt, $C_{13}H_{15}O_7,KO$, while hydrated oxide of methyle separates. An excess of patassa causes the formation of three products: *xylitic naphtha*, $C_{12}H_{12}O_3$; *xylitic oil*, $C_{12}H_9O$; and *xylitic resin*, C_8H_6O. When distilled with sulphuric acid, xylite, if moist, yields a new compound, *mesitène*, a volatile liquid, $C_6H_6O_3$. If anhydrous, it yields, besides, another compound, *methol*, a less volatile liquid, which appears to be a carbo-hydrogen, C_4H_3; isomeric with acetyle, if it be not that radical. *Mesite* is another volatile ethereal liquid found in pyroxylic spirit, which, according to Schweitzer, is $C_6H_6O_2$; isomeric with acetone. He considers it as composed of oxide of methyle and oxide of acetyle, $C_2H_3O + C_4H_3O = MtO + AcO$. The liquid called mesite by Reichenbach would appear to be acetate of oxide of methyle, $MtO + AcO_3$, mixed with a more highly carbonized body, apparently composed of $C_{26}H_{25}O_{15}$. This latter is resolved by the action of lime into 3 eq. acetic acid ($C_{12}H_9O_9$), and a volatile liquid, $O_{14}H_{16}O_6$. Along with the above, another liquid appears to occur in the mesite of Reichenbach, the composition of which is $C_{21}H_{23}O_{10}$. In addition to all the liquids above mentioned, as occurring in pyroxylic spirit, acetone is frequently found.

The very great similarity in properties of so many substances, namely, hydrated oxide of methyle, acetate of oxide of methyle, lignone, xylite, mesite, and acetone, is worthy of notice. Most of these liquids have nearly the same density and boiling point; they are all inflammable, and their solubility in water is nearly equal. Hence they all occur mixed, and are with great difficulty separated, so as to obtain each in a state of purity; indeed, in most of them we cannot be sure that this has yet been accomplished. It is highly probable, that, like the two first, all the rest will be found to be compounds of methyle. Our knowledge on the subject is still very limited.

The purified pyroxylic spirit, or hydrated oxide of methyle, has been already fully described, along with its chief derivatives.

2. Volatile Oily Products, insoluble or sparingly soluble in Water.

a. Creosote (from κρεας, flesh, and σωζω, I preserve). This is one of the most

important products of the distillation of wood. It is found, partly dissolved, in the pyroligneous acid, partly along with other oils, in the tar. When the crude pyroligneous acid is saturated at 167° with dry carbonate of soda, an oil separates, which contains much creosote. In like manner, by the rectification of tar, an oil of tar is obtained, the heavier portions of which contain a good deal of creosote. These oils are neutralized with carbonate of potassa, and the fluid thus deprived of acid is distilled with water. The distilled oil is acted on by dilute phosphoric acid to remove ammonia and, probably, traces of oily bases, again distilled, and dissolved in aqua potassæ, sp. gr. 1·12, which dissolves the creosote, along with portions of other oils, but separates a good deal of eupion, &c. The alkaline solution is now supersaturated with dilute sulphuric acid, (after having been boiled in the air till it has become dark brown,) when the impure creosote separates. It is again rectified, and the treatment with potassa, boiling, addition of sulphuric acid, and rectification repeated till the rectified oil dissolves entirely in weak potassa, and this alkaline solution on being boiled acquires only a slight tinge of colour. It is then finally rectified, and is pure when it continues colourless on being kept. The tar of peat appears to be very rich in creosote, and it also occurs in coal tar. Good tar, from beech wood, is said to contain from 20 to 25 per cent.

Pure creosote is a colourless transparent liquid, of a high refractive and dispersive power, of a tolerably fluid but oily consistence. Its sp. gr. is 1·037, according to Reichenbach, its discoverer, and other chemists; but there is some discrepancy on this point, Dr. Christison having always found it as high as 1·060 and upwards. Its boiling point is 397°. It gradually becomes coloured brown when kept, unless absolutely pure. Creosote has a very strong, peculiar, persistent smell of smoke, analogous also to that of castoreum, not fetid, but unpleasant when concentrated. Its taste is burning, with a sweetish aftertaste. It disorganizes the skin, causing a white spot, where the cuticle soon peels off, without inflammation. When applied to the interior of the mouth and to the tongue it smarts strongly, whitening and disorganizing the cuticle.

Internally it is a powerful poison, but in a small dose may be employed advantageously in some cases of vomiting and disease of the mucous membrane. It is given much diluted with water. Externally, it may be employed, either in the form of aqueous solution, of ointment, or pure, as a styptic, and is a valuable application to indolent ulcers, and to many chronic cutaneous affections. Pure creosote, applied to the hollow of a decayed tooth, so as to touch the exposed nerve, instantly relieves, in many cases, the most violent toothache. It acts apparently by coagulating the secretions, and thus forming a covering for the nerve.

Creosote dissolves in about 80 or 100 parts of water, and is exceedingly soluble in alcohol and in acetic acid. These solutions have the smell, taste, and antiseptic power of the creosote.

Creosote possesses a singular antiseptic power. Flesh of all kinds, if steeped for a few hours in a weak solution of creosote, becomes unsusceptible of putrefaction; and the same effect is produced when the flesh is exposed to the vapour of creosote. This is the reason why the smoke of wood possesses antiseptic properties: smoked meat or fish is merely meat or fish which has absorbed the vapour of creosote from the smoke in which it has been suspended. The creosote appears to act on flesh, &c. in virtue of its remarkable power of coagulating albumen, which also accounts for its styptic action. Tongues and hams may

be smoked and effectually cured by immersing them for 24 hours in a mixture of 1 part of pure creosote and 100 of water or brine; and when thus prepared, they have the delicate smoked flavour observed in reindeer tongues, as usually cured by smoking.

Owing to the difficulty of obtaining creosote quite pure, its composition is hardly ascertained with certainty. According to Deville, whose researches are the most recent, it may be regarded as the alcohol, so to speak, of the series of benzoyle. His analyses lead to the formula $C_{14}H_8O_3$ or $C_{14}H_7O_2$, HO; but I cannot ascertain whether this is the formula he adopts.

It is particularly to be noticed, that there is a very great resemblance between creosote and carbolic acid (or hydrate of phenyle, $C_{12}H_5O$, HO), a substance obtained from coal tar, and which will soon be described. So great is this resemblance, that I am almost inclined to consider creosote as a somewhat pure carbolic acid. The taste, smell, density, (according to some), boiling point, solubility in water, &c., poisonous and antiseptic action, of these two bodies, are the same. Both combine with alkalies, forming crystallizable compounds, and, what is more important, their composition in 100 parts is almost identical. The chief differences seem to be, that carbolic acid may be obtained in crystals, which, however, on contact with the air instantly liquefy and retain the liquid form, without any appreciable change of composition, apparently from the effect of a trace of moisture. Also, the salts of carbolic acid with bases are more easily formed and more permanent than those of creosote. A splinter or shaving of fir wood, dipped into carbolic acid and then into nitric or muriatic acid, becomes first blue and then brown; which does not appear to be the case with creosote. But Laurent has recently shown, that creosote, when acted on by a mixture of hydrochloric acid and chlorate of potash, yields abundance of chloranile, a character in which it agrees with carbolic acid. Both substances also yield nitropicric acid when acted on by nitric acid, although in the case of creosote this acid is accompanied by others not yet examined. These results I have myself also obtained; and it would appear, that if creosote be not carbolic acid, contaminated with some foreign matter, these two bodies are at least closely connected, and belong apparently to the same series, which is either that of benzoyle or that of phenyle. It is not improbable that creosote may be a definite compound of carbolic acid with some substance of closely allied composition, but of basic properties.

Creosote dissolves many organic substances, such as indigo, camphor, fats, essential oils, and resins, and undergoes numerous changes by the action of acids, alkalies, and other reagents, such as chlorine, potassium and others. With oil of vitriol it is coloured purple, and appears to form a coupled acid. None of these reactions or products have been properly investigated, and we shall, therefore, not confuse the reader by a description of them, more especially as the composition of creosote itself is doubtful.

b. Picamar is the name given by Reichenbach to another oil discovered by him along with creosote in the heavy oil of tar. It is purified by a tedious process, with the aid of potassa, with which it forms a crystalline compound. When pure, it is a colourless oil, of sp. gr. 1·10, of a burning and very bitter taste (hence its name from *pix* and *amarus*), and a slight smell. It boils at about 510°. It combines with alkalies, forming crystallizable salts, and may therefore be viewed as an acid in some sense, although it is quite neutral to test paper. Its composition is unknown.

c. Capnomor (from καπνος, smoke, and μοῖρα, part), is another oil, discovered by Reichenbach, in the heavy oil of tar, along with creosote and picamar. When the creosote is purified by solution in weak potassa, the oil left undissolved contains a good deal of capnomor, which is purified by a tedious process. It is a limpid, colourless oil, of a high refracting power, with an aromatic odour of ginger, and a somewhat styptic after-taste. Its sp. gr. is 0·9775; it is quite neutral, and boils at 365°. With sulphuric acid it is coloured red, and yields a coupled acid. Nitric acid converts it into oxalic acid, nitropicric acid, and another crystalline substance not yet examined.

d. Eupion (from εὖ, fine, and πιὸν, oil or fat), is a fourth oily liquid, discovered by Reichenbach in oil of tar. Being more volatile than the rest, it is purified chiefly by rectification. When pure it is colourless, very fluid, not greasy to the feel, but less soft than water, tasteless, and of a somewhat agreeable odour, like that of some flowers, such as *narcissus*. Its sp. gr. is 0·740; and Reichenbach states that he has even obtained it so low as 0·633, being the lightest known liquid. It is volatile, boiling at 117° or lower. It is in the highest degree indifferent, resisting the action of the strongest acids and alkalies. In fact, as it is prepared from the oil of tar by rectification, and the action of potassa, sulphuric, and nitric acids alternately on the rectified oil, it is evident that it must resist these agents. There is good reason to believe that several, even many different liquids have been described under this name, and that most of these are not ready formed in the tar, but products of the action of acids, &c., on the oil of tar. Reichenbach, however, by simple rectifications of the oil obtained by distilling rape oil, obtained a liquid having the characters of eupion. So much is certain, that similar liquids are formed by the action of oil of vitriol on oil of tar. The whole of the liquids called eupion are carbo-hydrogens, and their formula is either CH, or some multiple of this, or else one nearly approaching to such a multiple, as C_5H_6, &c. It is very remarkable that some of them are very volatile, while others, apparently of the same composition, require a strong heat, from 400° to 500° for example, to boil them.

The purest varieties of eupion burn with the aid of a wick, and yield a very brilliant luminous white flame, free from smoke, and may hereafter be turned to account.

3. Solid Products of the Distillation of Wood.

a. Paraffine. This name is given (from *parum* and *affinis*, because its affinities are feeble) to a white solid volatile substance, very similar to wax, discovered by Reichenbach in tar. It occurs in the last portions of the rectification of the tar, which are semisolid. It is squeezed out, and purified by one or two crystallizations in ether, which dissolves it when boiling, and deposits it on cooling in beautiful silvery scales. These, when melted, assume, on cooling, the aspect of pure white wax.

Paraffine exists in large quantity in the Rangoon petroleum, and some other bituminous mineral products. It is formed in large quantity in the distillation of wax. It melts at 110°, and distils unchanged at a high temperature. Its sp. gr. is 0·870. It burns, in a wick, with a beautiful clear white light, free from smoke, fully equal to that of the finest wax, if not superior to it. Like eupion, it is highly indifferent, and it is, like eupion, a carbo-hydrogen, containing either CH, or some multiple of it, or a near approach to such a multiple. According

to Lewy, it is $C_{20}H_{21}$. It is acted on by chlorine with the aid of heat, but the reaction is not yet studied. The strongest acids and alkalies do not act on it, even with the aid of heat, if we except fuming sulphuric acid.

b. Cedriret. This is another compound discovered by Reichenbach in oil of tar. When impure creosote is dissolved in potassa, and acetic acid added, an oil separates, which contains the creosote and other oils; but a certain quantity of oily matter remains dissolved in the acetate of potassa. This is distilled, until what passes over causes a red precipitate in a solution of sulphate of iron. It is then collected separately, being pure cedriret. It is a volatile solid, which crystallizes in a solution of sulphate of iron, forming a net-work of orange-red crystals, which dissolve in oil of vitriol with a blue colour. Much of the colour of oil of tar is probably owing to this substance.

c. Pittacal. This is still another compound obtained by Reichenbach from the heavy oil of tar. When the heaviest portions are nearly neutralized by potassa, the addition of barytic water gives rise to a deep blue colour. This belongs to pittacal, but the mode of its purification is not published. When pure, it is a solid, like indigo, of a very fine deep-blue colour, exhibiting on the polished surface the aspect of gold. It admits of being fixed on cloth, and would make a valuable dye-stuff. Its composition is unknown; but it appears to contain nitrogen. Its name is derived from πιττα, pitch, and καλλος, beautiful. It is a compound of very great interest, although most probably a product of decomposition of the oil of tar, and not ready formed in it. It is very desirable that it should be further investigated.

d. Pyroxanthine. This is a volatile crystalline solid, first observed by Scanlan in the crude pyroligneous spirit. When this is rectified with lime, the lime becomes dark brown; and when this coloured mass is acted on by hydrochloric acid, there is left undissolved a dark-brown matter, which is a mixture of pyroxanthine and a resinous matter. The mass is boiled with hot alcohol, which, on cooling, deposits the pyroxanthine in crystals, which are purified by recrystallization. They are of an intense yellow colour, fusible, and volatile in a current of air, or with the vapour of other substances, but partly decomposed when heated alone in a dry tube. Pyroxanthine dissolves in sulphuric acid with a deep bluish-red, and in strong hydrochloric acid with a splendid purple colour, which soon passes to dark brown. I found its composition to be very nearly $C_{21}H_9O_4$; but as it forms no definite compounds, I could not control the analysis.

Such are the chief products of the distillation of wood, as far as they are yet known. Their importance is very great, and will be still greater when they shall have been better studied, as most of them will admit of useful applications. But no doubt can be entertained that the above numerous list is far from being complete, and that more compounds remain to be discovered in tar. Indeed, there is even now good reason to believe that several or most of the substances characterizing coal tar occur also, although in smaller quantity, in wood tar. Such substances are naphthaline, anthracene, and others. It is to be borne in mind that the composition of wood tar varies, according to the kind of wood, the presence or absence of oily or resinous substances, the comparative abundance of nitrogenized matter, and finally the temperature at which the distillation is carried on.

Wood coal, brown coal, or *lignite* yields, when distilled, an oil of the consistence of butter, in which creosote, paraffine, and probably eupion, are found, along with other products not yet examined.

PRODUCTS OF THE DISTILLATION OF COAL.

Coal differs from wood in several points, although it is unquestionably derived from the decay, under pressure, of woody fibre and the other substances which made up the mass of the early vegetation of which our coal-beds are the remains. Coal contains much less water, and a much larger per centage both of carbon and nitrogen, than wood. Hence it is decomposed at a higher temperature, and yields much ammonia, cyanogen, and other nitrogenized products. We shall not here dwell on ammonia and cyanogen, further than to mention that out of the aqueous products of the coal gas-works large quantities of ammonia are obtained; and that so much hydrocyanic acid is also present, that a patent was taken out some years since for the preparation of Prussian blue from the gas liquor. We proceed to describe the chief ingredients of coal tar.

a. Carbolic acid. Syn. *Hydrate of phenyle.* $C_{12}H_5O,HO$. This remarkable acid is found in that portion of the oil of coal of tar which boils between 300° and 400°. This is agitated with twice its volume of potassa ley, and the aqueous solution, on the addition of an acid, yields hydrated carbolic acid (impure) as a heavy oil. It is purified by rectification with a very little solid potassa.

When pure, carbolic acid generally appears as an oily liquid, colourless, and of a high refracting power, neutral to test paper, of sp. gr. 1·062 to 1·065. It has a burning taste, and the odour of creosote, to which it has a very great resemblance. In certain circumstances it forms long needle-shaped crystals, which very readily lose the solid form by exposure to the atmosphere, and which also liquefy in sealed tubes without any obvious cause. The crystals melt at 94°, and boil at 368°. The extraordinary resemblance between carbolic acid and creosote has been noticed above; and there can be little doubt that, if not essentially the same, they are closely connected and belong to the same series, or contain the same radical.

A splinter of pine-wood, if dipped, first in carbolic acid, and then in moderately strong nitric acid, becomes of a deep-blue, which soon passes into brown.

According to Laurent, carbolic acid is the hydrated oxide of phenyle, $C_{12}H_5$, and its formula is $(C_{12}H_5)O,HO$. This radical, phenyle, gives rise to a series of derived compounds which may be represented as follows:

Hydrate of Phenyle, or Carbolic Acid . .	C_{12}	H_5,O	$+HO$
Sulphocarbolic Acid (Sulphophenic Acid) . .	C_{12}	H_5	$O, HO+2SO_3$
Chlorophenesic Acid	C_{12}	$\left\{\begin{matrix}H_3\\Cl_2\end{matrix}\right\}$	O,HO
Chlorophenisic Acid, identical with the Chloridoptenic Acid of Erdmann	C_{12}	$\left\{\begin{matrix}H_2\\Cl_3\end{matrix}\right\}$	O,HO
Bromophenisic Acid	C_{12}	$\left\{\begin{matrix}H_2\\Br_3\end{matrix}\right\}$	O,HO
Nitrophenesic Acid	C_{12}	$\left\{\begin{matrix}H_3\\2NO_4\end{matrix}\right\}$	O,HO
Nitrophenisic Acid, identical with Nitropicic Acid	C_{12}	$\left\{\begin{matrix}H_2\\3NO_4\end{matrix}\right\}$	O,HO

Thus the carbolic acid is connected with the derivatives of indigo, of salicyle, and other bodies, which yield nitropicric acid. This connection is also shown in the formation of chloranile, from carbolic acid, by the action of chlorate of potassa and hydrochloric acid. (See under Indigo, the formation of chloranile from aniline). It is also shown, by the fact, that salicylic acid, $C_{14}H_6O_6$, when distilled alone, with lime, or with pounded glass, is resolved into carbonic acid,

$2CO_2$, and carbolic acid, $C_{12}H_6O_2$. The action of carbolic acid, on organic compounds, is the same as that of creosote. Thus it dissolves indigo, &c. and coagulates albumen, preventing the putrefaction of animal substances.

With bases, it forms salts, some of which crystallize, but which retain an alkaline reaction. With oil of vitriol, it yields a coupled acid, sulpho-carbolic, or sulphophenic acid, which forms a soluble salt with baryta.

The formulæ in the above table illustrate the formation, by substitution, of the chlorophenesic and chlorophenisic, of the nitrophenesic and nitrophenisic acids. It is not necessary here to do more than point out their relation to carbolic acid and phenyle. The chlorobenzide of Mitscherlich, $C_{12}H_6Cl_6$ is, according to Laurent, hydrochlorate of chlorophenise, $3HCl+C_{12}\left\{\begin{matrix}H_3\\Cl_3\end{matrix}\right.$. This last body, chlorophenise, which is obtained by the action of potassa on chlorobenzide, would appear to be derived by substitution, not from phenyle $C_{12}H_5$, but from benzole $C_{12}H_6$; although it may be derived also from oxide of phenyle $C_{12}\left\{\begin{matrix}H_5\\O\end{matrix}\right.$; as may benzole itself. Chlorophenise cannot be obtained directly from hydrate of phenyle, or its derivatives; but, on the other hand, the series of benzole has an obvious relation to that of phenyle. In fact, Laurent considers benzole as in some measure the fundamental compound, or nucleus, and calls it phene $=C_{12}H_6$.

It has already been stated that nitrophenisic acid is identical with nitropicric acid. Nitrophenesic acid is somewhat similar, and forms salts which crystallize with facility, and detonate when heated. The nitrophenesate of baryta is a beautiful salt, like bichromate of potassa.

b. Volatile Bases of Coal Tar.

Besides carbolic acid, Runge found in coal-tar two other acids, *rosolic* and *brunolic acids* (of which little is known), and three basic volatile oils, *kyanol*, *leukol*, and *pyrrol*. The last has been little examined; but the recent researches of Hoffmann have confirmed Runge's statements as to the first two, which have also been identified with bases produced from different quarters. They have, therefore, acquired a very high degree of interest.

1. *Kyanol*, $C_{12}H_7N$. Syn. *Aniline*, *Crystalline*, *Benzidam*. This very remarkable base has already been described as a product of the distillation of indigo with potassa, and of anthranilic acid *per se*, under the name now generally adopted, of aniline. It has also been shown to be identical with the crystalline of Unverdorben, an oily base, extracted from animal oil of tar; and with benzidam, an oil formed by the action of sulphuretted hydrogen, or sulphuret of ammonium on nitrobenzide. Hoffmann has traced the production of aniline in various cases, as when protonitrobenzoene, $C_{14}\left\{\begin{matrix}H_7\\NO_4\end{matrix}\right.$ is heated with lime. The reaction is as follows: $2\,CaO+C_{14}H_7NO_4=2(CaO,CO_2)+C_{14}H_7N$. In fact protonitrobenzoene being isomeric with anthranilic acid, it is not wonderful that both of them should be resolved into aniline and carbonic acid.

That there is a relation between aniline and carbolic acid appears from their formulæ; for aniline is the amidide of carbolic acid, or *phenamide*, being thus deduced from carbolate of ammonia. $C_{12}H_5O,NH_3=HO+C_{12}H_5,NO_2$. The relation may be better exhibited thus :—

Carbolic Acid (anhydrous), or Oxide of Phenyle . .	$=C_{12}H_5O$
Aniline, or phenylamide	$=C_{12}H_5Ad$

As another experimental proof of this relation may be mentioned that salicylamide, $C_{14}H_5O_4,NH_2=C_{14}H_7NO_4$, which has the same composition as protonitrobenzoene and anthranilic acid, both of which yield aniline, when heated with lime gives not aniline but carbolic acid, ammonia, and probably a carbo-hydrogen.

Aniline is recognized by striking a deep violet-blue colour with chloride of lime (bleaching liquor), hence the name *kyanol*. It combines with acids, forming salts which crystallize with the utmost facility, hence the name *crystalline*. It is easily extracted from coal-tar oil, by agitating with hydrochloric acid, mixing the acid solution with an excess of milk of lime, and rectifying the basic oil which separates, and which is a mixture of aniline and leukol. The former is the more volatile, and when the distilled liquid ceases to be coloured blue by chloride of lime, the leukol is coming over nearly pure, the aniline being found in the first distilled portions.

Aniline, when acted on by chlorine, yields trichloraniline (chlorindatmit of Erdmann) $C_{12}\left\{\begin{matrix}H_4\\Cl_3\end{matrix}\right\}N$ along with chlorophenusic acid $C_{12}\left\{\begin{matrix}H\\Cl_4\end{matrix}\right\}O,HO$. With chlorate of potassa, and hydrochloric acid, it yields chloranile, $C_{12}\left\{\begin{matrix}H_4\\Cl_4\end{matrix}\right.$. With bromine it yields tribromaniline $C_{12}\left\{\begin{matrix}H_4\\Br_3\end{matrix}\right\}N$ (bromaniloide of Fritzche). Strong nitric acid first colours aniline blue, and then yellow, with a violent reaction, the result of which is the conversion of aniline into nitropicric acid.

2. *Leukol*, or *Quinoleine?* $C_{18}H_8N$ (Hoffmann), or $C_{18}H_7N$ (Laurent, Gerhardt), is prepared as above. Its properties have been formerly mentioned, although under a different name; for the most recent researches tend to the conclusion, that it is identical with quinoleine, the oily base obtained by the action of heat, aided by potassa, on cinchonine, quinine, strychnine, and probably other bases. This identification is very curious, like that of aniline and kyanol, and the occurrence of quinoleine in coal-tar is a very remarkable fact. The formula here given for quinoleine differs from that given under that head, which is $C_{10}H_8N$. As, however, there may still be some doubt as to the identity of leukol and quinoleine, I shall not alter the formula first given for quinoleine, until further experiments have decided the exact composition of that base, and have also fixed that of leukol.

Of *pyrrol*, and of *rosolic and brunolic acids*, so little is known that we need not dwell on them.

c. Volatile Carbo-hydrogens in Coal Tar.

a. Naphthaline, $C_{10}H_4$, or $C_{20}H_8$. This remarkable compound occurs in all kinds of tar, but most abundantly in coal-tar, as being formed at a very high temperature. It is formed in additional quantity when any of the elements of oil of tar, such as creosote, carbolic acid, &c., or even alcohol and ether, are passed through tubes heated to a strong red heat. It is easily obtained by re-distilling coal-tar, when the latter portions are so full of naphthaline as to be semisolid. It is well squeezed out, and purified by sublimation and crystallization in hot alcohol. Or the oil of coal-tar is saturated with chlorine gas, which, by destroying some of the oils, allows the naphthaline to crystallize.

Pure naphthaline is colourless and volatile, and forms large tabular transparent crystals, of a very peculiar smell, and an acrid aromatic taste. It boils at 414°, but distils easily with the vapours of water, and is dissipated, like camphor, if left exposed at the ordinary temperature.

It is acted on by chlorine and bromine, which combine with it in the first instance, and also give rise to a large number of compounds formed by substitution; and by sulphuric and nitric acids, each of which produces a number of new compounds with it. These changes have been studied with singular perseverance and remarkable sagacity, by Laurent, more especially the action of chlorine, bromine, and nitric acid. His researches have been attended with unusual success, and he may be said to have originated and established, by these researches, the now received doctrine of substitutions. I cannot hope to give even an accurate outline of all that Laurent has done in this department, because I have nowhere seen a complete account of these curious results as they now stand; but until the author himself publish a complete account of his researches on naphthaline, I shall place before the reader such a general account of them as shall show the great importance of the subject, and some of the interesting facts already ascertained.

1. Action of Chlorine and Bromine on Naphthaline.

(It is necessary here to explain the principle of nomenclature, provisionally adopted by Laurent, especially for cases like this of substitutions, where the ordinary nomenclature is entirely inapplicable. The nomenclature of Laurent may be thought, by some, uncouth: but it is simple, systematic, and consistent with itself. Beginning with naphthaline, he gives to the compounds formed by the successive substitution of chlorine for hydrogen, names beginning with *chlo*, and ending with a syllable in which the vowels a, e, i, o, and u, are employed to designate the replacement of 1, 2, 3, 4, and 5 eq. of hydrogen. Thus, if, in naphthaline, $C_{20}H_8$, 1 eq. of hydrogen is replaced by chlorine, we have the compound $C_{20}\left\{\begin{matrix}H_7\\Cl\end{matrix}\right.$. This is called chlonaph*tase*. The compound $C_{20}\left\{\begin{matrix}H_6\\Cl_2\end{matrix}\right.$ is chlonaph*tese*; $C_{20}\left\{\begin{matrix}H_5\\Cl_3\end{matrix}\right.$ is chlonaph*tise*, &c. The corresponding compounds of bromine are bronaph*tase*, bronaph*tese*, and bronaph*tise*. When we get as far as chlonaph*tuse* $C_{20}\left\{\begin{matrix}H_3\\Cl_5\end{matrix}\right.$ as there are no more vowels, we begin again with *a*, adding a syllable to the word. Thus, $C_{20}\left\{\begin{matrix}H_2\\Cl_6\end{matrix}\right.$ is chlonaph*talase*, $C_{20}\left\{\begin{matrix}H\\Cl_7\end{matrix}\right.$ is chlonaph*talese*, and $C_{20}Cl_8$ is chlonaph*talise*, and so on with bromine. When hydrogen is replaced, partly by chlorine, partly by bromine, then the name is so constructed that the final syllable indicates the sum of the equivalents of chlorine and bromine, while both chlorine and bromine are prefixed. Thus, chlonaphtose is $C_{20}\left\{\begin{matrix}H_4\\Cl_4\end{matrix}\right.$; and the compound $C_{20}\left\{\begin{matrix}H_4\\Cl_3\\Br\end{matrix}\right.$ is chlor*i*bronaph*tose*; $C_{20}\left\{\begin{matrix}H_4\\Cl\\Br_3\end{matrix}\right.$ is chlor*a*bronaph*tose*. The former of these two may also be brom*a*chlonaph*tose*, and the latter brom*i*chlonaph*tose*. We shall see, hereafter, that it may

be necessary to use both forms to distinguish different compounds which are isomeric. Again, where hydrogen is replaced by NO_4, we have, (NO_4=X), $C_{20}\left\{\begin{matrix}H_7\\X\end{matrix}\right.$ nitronaphtalase, and so forth. It is evident that this nomenclature, although it gives rise to words of a singular aspect, is yet easily understood, and may even, in many cases, serve as well as a formula to remind us of the composition. Laurent has applied it to many other series, as we have seen in the series of phenyle, where we have chlorophenesic, chlorophenisic, and chlorophenusic acids, &c.)

When chlorine is brought in contact with naphthaline, the latter melts, and there are are formed at once two compounds of chlorine and naphthaline; the chloride of naphthaline, $C_{20}H_8+Cl_4$; and the subchloride of naphthaline $C_{20}H_8+Cl_2$. At the same time hydrochloric acid is disengaged, arising from the action of chlorine on one of these chlorides. The former is a solid, which is best purified by solution in hot oil of petroleum, which deposits it on cooling in crystals. It may also be purified by means of boiling ether, which dissolves it to a certain extent, and deposits it on cooling. Chloride of N. is decomposed by heat, yielding no less than four different isomeric forms of chlonaphtese. An alcoholic solution of potassa converts it into two more forms of chlonaphtese. It is also acted on by chlorine, bromine, nitric acid, and sulphuret of ammonium, yielding many new compounds.

Subchloride of N. is an oily liquid, which by the action of heat is partially changed into hydrochloric acid, and one form of chlonaphtase. An alcoholic solution of potassa also converts it into chlonaphtase and chloride of potassium. Chlorine converts it into two chlorides of chlonaphtase, isomeric but distinct; if the heat is too strong there is formed one kind of chlonaphtise.

When bromine is made to act on naphthaline, no bromide of N. is formed, but hydrobromic acid is separated and bronaphtase is produced.

Chlonaphtase, $C_{20}(H_7Cl)$ is obtained by acting on subchloride of N. by alcoholic solution of potassa. On the addition of water, an oily liquid separates, which is purified by rectification, and is then chlonaphtase. No isomeric modification of it is yet known, but the existence of such is extremely probable. Bromine acts on it, converting it into bromide of chlorabronaphtese, $Br_4+C_{20}H_6ClBr$.

Bronaphtase, $C_{20}(H_7Br)$ is formed by the direct action of bromine on naphthaline, care being taken to avoid excess of bromine, which would form bronaphtese, and excess of naphthaline which would remain unchanged. Bronaphtase is a colourless oil, decomposed by chlorine and bromine, the latter converting it into bronaphtese and the products of the further action of bromine on bronaphtese. As yet only one form of bronaphtase is known.

Chlonaphtese, $C_{20}(H_6Cl_2)$, occurs in no less than 7 different isomeric forms. These are distinguished by Laurent as modifications *a*, *c*, *ad*, *e*, *f*, *x*, and *y*, but I am not aware of the principle on which these letters are selected. *a*, *c*, *f*, and *x*, are obtained by the action of heat on the chloride of N.; *ad* and *e* by boiling chloride of N. with tincture of potassa; and *y* by the action of chlorine on nitronaphtese. *a* and *x* are liquid, all the rest crystallize easily. The solid forms have each a different point of fusion, and the whole 7 give different results when acted on by chlorine and bromine. Since, therefore, the composition of all 7 is the same, we are compelled to adopt the conclusion that it is not the same

2 eq. of hydrogen which are replaced by chlorine, and that it is not indifferent which equivalents of hydrogen are thus replaced, but that, on the contrary, the properties of these compounds depend on the particular equivalents or molecules of hydrogen replaced by chlorine, and that consequently the arrangement, or relative as well as absolute position of these molecules in the compound molecule, is a matter of far greater importance, in reference to chemical characters, than the properties of the elements, or their place in the electro-chemical arrangement.

Referring to what I have said on the subject of types, at pp. 530, 531, I would here point out that napthaline is a type, the molecule of which is made up of 20 equivalents (not single atoms, but molecules) of carbon, and 8 equivalent molecules of hydrogen; and that chlonaphtese is a sub-type, in which the 20 molecules of carbon are associated, as in the fundamental type, with 8 other molecules, not all, as before, of hydrogen, but 6 of hydrogen and 2 of chlorine, a body usually considered as entirely opposed to hydrogen, chlorine being strongly negative, and hydrogen strongly positive. Yet the type remains unchanged, and we cannot help seeing that the 2 molecules of chlorine, *in virtue of their position in reference to the* 20 *of carbon*, are playing the part of 2 molecules of hydrogen.

Further, if we conceive the 8 molecules of hydrogen in the fundamental type to occupy each a fixed position, in relation to the 20 of carbon, we see from the wonderful phenomena just indicated, from the existence of 7 distinct forms of chlonaphtese, that, in each of these, a different pair of molecules of hydrogen has been replaced by chlorine. If the 8 molecules of hydrogen be supposed to be numbered, according to the fixed position of each in the compound molecule of the type, then we can see that in chlonaphtese *a*, the molecules 1 and 2 may be those replaced, while in *c* the molecules 6 and 7 may be those replaced by chlorine, and so on. It is easy to calculate that in this way at least 28 different isomeric forms of chlonaphtese may exist, and of these 7 are already known.

Our space will not admit of details on the different forms of chlonaphtese, but I have thought it indispensable to explain the view now taken of these singular compounds, in a general way. It is evident that we may expect much light to be thrown on the obscure subject of the molecular arrangement of compounds by continued researches in the same direction. The recent progress of those departments of physics which are most closely allied to chemistry, has established the existence of certain relations between the atomic weight and constitution of compounds and their physical properties, such as volume or density, volatility, state in regard to cohesion, solidity, fluidity, &c., and crystalline form. We now see a prospect of tracing the connection between the molecular arrangement of compound bodies and their chemical properties; and we may even hope hereafter to be enabled, simply by accurate observation of the external properties of a body, physical and chemical, to ascertain its composition and constitution; and also to predict with accuracy the properties of compounds yet unformed, the formation of which will probably become a problem, solvable by a few rules of universal application.

For the present, we have only the distant prospect of these results; but we have only assiduously to pursue the study of nature on true inductive principles, in order to be hereafter enabled to bring into order the chaos, so to speak, of interesting and important observations, the number of which is hourly increasing,

while a large proportion of them have not yet found a use or an application. We must now return to the derivatives of napththaline, which we have only space briefly to name.

Bronaphtese, $C_{20}(H_6Br_2)$, is easily formed by the action of bromine on napthaline or on bronaphtase. It is a crystallizable solid, and probably corresponds to chlonaphtese, *c*. Only one bronaphtase is yet known. It forms several compounds with bromine.

Chlonaphtise, $(C_{20}H_5Cl_3)$ occurs in 6 different forms (out of 55 which are possible), *a*, *ac*, *c*, *g*, *d*, and *ad*, all of which are crystallizable solids. They are obtained in different ways: *a* by boiling with tincture of potassa the oily modification of chloride of chlonaphtase; *ac* by the action of chlorine on chlonaphtese *ad*, melted; *c* and *g*, along with some of *a*, by boiling with tincture of potassa the crystallized chloride of chlonaphtase; *d* by distilling the crystallized chloride of chlonaphtase; and *ad* by boiling with tincture of potassa the double chloride of naphthaline and of chlonaphtase; *a* is converted by chlorine into chlonaphtose *a*; and bromine converts it into chloribronaphtose *a*.

Bronaphtise $C_{20}(H_5Cl_3)$ is obtained by heating the bromide of bronaphtise, when bromine is given off. It is crystallizable. Only one form is yet known.

Chlonaphtose $C_{20}(H_4Cl_4)$ occurs in four isomeric forms, *a*, *b*, *e*, and *k*, out of a very large number which are possible. They are all crystallizable. It is unnecessary to mention the methods employed to obtain them, which are analogous to those already described for chlonaphtise or chlonaphtese.

Bronaphtose, $C_{20}(H_4Br_4)$ appears to exist in two forms, *a* and *b*, both crystallizable.

Chlonaphtuse, $C_{20}(H_3Cl_5)$ and *Bronaphtuse*, $C_{20}(H_3Br_5)$, are not yet known.

Chlonaphtalase, $C_{20}(H_2Cl_6)$ is obtained by the action of chlorine on chlonaphtise *a*. It forms soft flexible prisms.

Chlonaphtalese, $C_{20}(HCl_7)$ is not yet known.

Chlonaphtalise, $C_{20}Cl_8$, the compound in which all the hydrogen of naphthaline is replaced by chlorine, is obtained by continuing the action of chlorine on chlonaphtise *a*. It is also crystallizable. Laurent, apparently from its crystalline form, considers it to correspond with the modifications *c* of chlonaphtese and chlonaphtise; and for the same reason he considers the only chlonaphtalase known, as chlonaphtalase *a*. In the case of chlonaphtalise, if different modifications can occur, they must depend on a different principle from that which regulates the modifications of those compounds in which both chlorine and hydrogen are concerned. But until Laurent shall publish a complete account of his views, it is not easy to ascertain exactly what those views are. I suspect some error in the only account of these researches to which I could refer.

Besides the above, there are a number of compounds derived from naphthaline, in which the hydrogen is replaced by bromine and chlorine at once.

Chlorebronaphtise a, $C_{20}(H_5Cl_2Br)$ is a crystalline solid very similar to chlonaphtise *a*.

Chlorebronaphtose b, $C_{20}(H_4Cl_2Br_2)$ is obtained by the action of bromine on chlonaphtese *f*.

Chloribronaphtose a, *Bromachlonaphtose a*, and *Bromachlonaphtose b*, are three isomeric compounds. The first is obtained by the action of bromine on chlonaphtise *a*, and the bromine is, therefore, placed second in the name. The two others are both formed when chlorine acts on bronaphtese. They furnish a very

beautiful proof of the truth that the position of the replaced or replacing molecule is all-important. They are all crystallizable.

Bromechlonaphtose b, $C_{20}(H_3Cl_3Br_2)$ is a crystalline solid, obtained by boiling chloride of bromechlonaphtise with tincture of potassa.

Chloribronaphtuse, $C_{20}(H_3Cl_3Br_2)$ is a crystalline solid, formed by the action of bromine on chloride of naphthaline.

There remain to be described some compounds, analogous to the chlorides of naphthaline, and containing consequently chlorine or bromine, in addition to the type or subtype.

Chloride of chlonaphtase $Cl_4+C_{20}(H_7Cl)$, is obtained by the action of chlorine on the subchloride of naphthaline. It is the most remarkable of the whole series from the great size and beauty of its crystals. It occurs in an isomeric form as an oily liquid. When distilled, these compounds yield different forms of chlonaphtise mixed together.

Chloride of chlonaphtese, $Cl_4+C_{20}(H_6Cl_2)$ occurs in three isomeric forms. *a* and *x* are oily liquids, derived respectively from chlonaphtese *a* and *x* by the action of chlorine. *c* is derived from chlonaphtese *c* in the same way, and is crystalline. They all yield chlonaphtose when heated, but in different forms.

Bromide of chlonaptese, $Br_4+C_{20}(H_5Cl_2)$ is obtained by the action of bromine on chlonaphtese *c*. It is crystalline. An excess of bromine produces at least five different compounds.

Bromide of chlorabronaphtese, $Br_4+C_{20}(H_6BrCl)$, is formed when bromine acts on chlonaphtase. It is crystalline.

Bromide of bronaphtese, $Br_4+C_{20}(H_6Br_2)$ is formed by the action of bromine on bronaphtese. It is crystalline, and when distilled yields hydrobromic acid and bronaphtose.

Subbromide of bronaphtise, $Br_2+C_{20}(H_5Br_3)$ is formed along with the preceding. It is also crystalline.

Bromide of bronaphtise, $Br_4+C_{20}(H_5Br_3)$ is also a highly crystalline solid.

Subchloride of bronaphtase, $Cl_2+C_{20}(H_7Br)$, formed by the action of chlorine on bronaphtase, crystallizes in regular rhomboidal plates.

Chloride of bronaphtese, $Cl_4+C_{20}(H_6Br_2)$ crystallizes in long prisms. *Perchloride of bronaphtise*, $Cl_5+C_{20}(H_5Br_2)$ crystallizes in right prisms with rhombic base.

Chloride of bromechlonaphtise, $Cl_4+C_{20}(H_5Br_2Cl)$ crystallizes in oblique rhombic prisms. When boiled with tincture of potassa it yields *bromechlonaphtuse*, $C_{20}(H_3Br_2Cl_3)$.

All the preceding compounds have been discovered, studied, analyzed, and described by Laurent, besides a large additional number of derivatives of naphthaline, under the agency of chlorine and bromine, which he has not so fully examined. Those here named are sufficient to illustrate the endless variety of compounds attainable. Every subtype of the original type of naphthaline admits of numerous permutations, and where both chlorine and bromine are present, the number of possible permutations is enormously increased. In short, these remarkable researches have only made us acquainted with a very small selection of the possible products of the action of chlorine and bromine on naphthaline, *the type remaining unchanged.*

Thus the subtype chlonaphtose $C_{20}(H_4Cl_4)$, admits of 65 isomeric modifications, all different, as does of course brohaphtose also. But these subtypes,

may yield the modified subtypes, chlorabronaphtose, chlorebronaphtose, chloribronaphtose, bromachlonaphtose, bromechlonaphtose, and bromichlonaphtose, and others, difficult to name, depending on the relative proportions and positions, in the molecule of the subtype, of the 4 eq. chlorine and bromine. It is easy to imagine 14 such modified subtypes, and there appears no reason why each of them, with the two subtypes, should not admit of at least 65 isomeric forms. This would give 1040 isomeric forms, all included under the two subtypes chlonaphtose and bronaphtose, or under one subtype which may be called *naphtose*, $C_{20}(H_4X_4)$. X is here put for chlorine or bromine.

2. Action of Sulphuric Acid on Naphthaline.

When naphthaline is dissolved in warm oil of vitriol to saturation, the solution, if left exposed to the air, becomes a semisolid mass of a dirty purplish colour. This, dried on a porous brick, leaves a quantity of scales, very soluble in water and alcohol, which are a mixture of two acids.

a. Hyposulphonaphthalic acid, $C_{20}H_8,S_2O_5+HO$? The above mixture, being dissolved in water, is saturated with carbonate of lead, which forms insoluble sulphate of lead, and two soluble salts, one of which is soluble in alcohol and contains this acid, and yields it when decomposed by sulphuretted hydrogen. The acid forms a hard crystalline fusible mass of an acid and bitter taste. Its salts are soluble and crystallizable. Their formula is $C_{20}H_{16}S_2O_5,MO$.

b. Hyposulphonaphtic acid, $C_{11}H_5S_2O_6=C_{11}H_4S_2O_5,HO$? The lead salt insoluble in alcohol contains this acid, the salts of which are soluble, bitter, and hardly crystallizable. It is probable that a third acid accompanies these two: for Faraday obtained a third salt of baryta and Berzelius found a third salt of lead in the mother liquid of the other two. Faraday's salt, which remains with the sulphate of baryta formed in the process by the free sulphuric acid, and may be extracted by boiling water, yields about 42 per cent. of sulphate of baryta when calcined.

The vapours of anhydrous sulphuric acid, passed over fused naphthaline, form with it a red liquid. If the acid be in excess, there is formed a new acid, the *hyposulphoglutinic acid*, besides small quantities of the preceding acids; if there be excess of naphthaline there are formed two neutral bodies, *sulphonaphthaline* and *sulphonaphthalide*.

Hyposulphoglutinic acid, when pure and dry, is a hard glassy mass. When precipitated from its salts by stronger acids, it forms a viscid hydrate like turpentine. Its salts are generally soluble and do not crystallize. Its composition is unknown.

Sulphonaphthaline, $C_{20}H_8SO_2$? is a crystalline fusible solid.

Sulphonaphthalide, $C_{24}H_{10}SO_2$? is a crystalline powder not fusible at 212°.

3. Action of Nitric Acid on Naphthaline, and its Derivatives.

Nitric acid acts on naphthaline, and gives rise to a whole series of compounds in which NO_4 is substituted for hydrogen. The same principles apply here as in the action of chlorine and bromine on naphthaline. It is to Laurent that we are indebted for our knowledge of these compounds, which our space will only allow us to name.

Nitronaphtalase, $C_{20}H_7X$, (X is here put for NO_4), is best formed by causing nitrous acid to pass through melted naphthaline. It is purified by means of alcohol, and forms long prisms of a sulphur-yellow colour, fusible at 110°. Chlo-

rine decomposes it, producing chlonaphtose. Nitric acid converts it into *nitronaphtalese*.

Nitronaphtalese, $C_{20}(H_6X_2)$, forms a crystalline powder fusible at 365°, insoluble in water, very sparingly soluble in alcohol.

Naphtalase, $C_{20}(H_7O)$ is a yellow crystalline solid formed by gently heating nitronaphtalase with 10 parts of lime slightly moistened. It communicates to oil of vitriol a magnificent blue colour. It is insoluble in alcohol as well as in water, otherwise it would recal pyroxanthine, which is yellow and volatile and colours sulphuric acid purple.

Nitronaphtaleise, $C_{20}(H_{5\frac{1}{2}}X_{2\frac{1}{2}})$? is a crystalline compound formed when naphthaline is added in small quantities to a large mass of hot nitric acid. Nitronaphtalese is produced along with it. It is pale-yellow and very fusible, becoming liquid even in boiling alcohol. This great fusibility prevents us, notwithstanding its strange formula, from considering it as a mixture of nitronaphtalese and nitronaphtalise, the former of which melts at 365°, the latter at 410°, and which are very insoluble in ether, in which liquid nitronaphtaleise readily dissolves.

Nitronaphtalise, $C_{20}(H_5X_3)$ is formed along with the preceding, and crystallizes in rhomboidal plates of a pale-yellow colour, fusible at 410°.

Nitronaphtale, $C_{19}H_5N_3O_{11}$, is a crystalline substance, formed by the long-continued action of nitric acid on the mother liquor of all the preceding. It melts at 420°, and sometimes solidifies in an amorphous state; a slight heat, or touching the melted substance with a point, causes it to crystallize.

Nitronaphtalesic acid, $C_{16}H_{4\frac{1}{4}}N_{1\frac{1}{4}}O_4$? $C_{32}H_9N_3O_8$? This acid is formed when nitronaphtalese is boiled with tincture of potassa, and is separated from the potassa by nitric acid. When dry it is brownish-black, and forms brown salts, which are soluble and uncrystallizable. *Nitronaphtaléisic acid*, $C_{12}H_4O_6N_{1\frac{1}{2}}$, or $C_{24}H_8O_{12}N_3$, is a similar acid, formed from nitronaphtaléise. *Nitronaphtalisic acid* is another brown acid, formed in the same way from nitronaphtalise.

Oxide of chloroxénaphtose, $O_2+C_{20}(H_4Cl_2O_2)$, is formed when nitric acid acts on crystallized chloride of chlonaphtose. It appears as as a yellow crystalline solid. It is accompanied by chloranaphtisic acid, into which it is also converted by boiling with tincture of potassa.

Chloranaphtisic acid, $C_{20}H_5ClO_6$, is formed from the preceding compound, as follows: $C_{20}H_4Cl_2O_4+HO+2KO=KCl+(C_{20}H_5ClO_6+KO)$. It is separated from the potassa by adding an acid, and forms yellow crystals, fusible at 392°. Its salts are for the most part insoluble, and exhibit the most beautiful colours, including yellow, orange, red, and carmine.

Oxide of chloroxenaphtalise, $O_2+C_{20}Cl_6O_2$, is obtained along with chlophtalisic acid and other compounds, when nitric acid is boiled with *chlonaphtalase*, $C_{20}H_2Cl_6$. It forms golden scales.

Chloroxénaphtalesic acid, $C_{20}HCl_5O_6$, is formed when the preceding compound is acted on by potassa, which at once changes it into a fine carmine-red substance, from which acids separate the new acid as a yellow crystalline powder. It forms beautiful red salts with potassa and ammonia. It is formed as follows: $C_{20}Cl_6O_4+HO+2KO=(C_{20}HCl_5O_6+KO)+KCl$.

Phtalic or naphtalic acid, $C_{16}H_4O_6$, $2HO=C_{16}H_6O_8$, is formed by the action of nitric acid on chloride of naphthaline. It forms rounded groups of lamellar crystals, and yields crystallizable salts. When distilled with lime, it yields

benzole (phéne), and carbonic acid, $C_{16}H_6O_8=4CO_2+C_{12}H_6$. When the hydrated acid is distilled, it yields the anhydrous acid in fine elastic needles.

The acid phtalate of ammonia, $C_{16}H_4O_6,NH_4O,HO$, when heated yields water, 4HO, and *phtalimide*, $C_{16}H_5NO_4$.

Phtalamide, $C_{16}H_6NO_5$, is obtained by acting on anhydrous phtalic acid by ammonia. It appears that phtalimide is acid phtalate of ammonia, minus 4 eq. water, while phtalamide is anhydrous phtalate of ammonia, $C_{16}H_4O_6+NH_3$, minus 1 eq. water. Both are crystalline solids, and both appear to form definite compounds with oxide of silver.

Nitrophtalic acid, $C_{16}H_3NO_{10},2HO$, is derived from phtalic acid by the substitution of 1 eq. NO_4 for 1 eq. hydrogen. $C_{16}H_4O_6-H+NO_4=C_{16}H_3NO_{10}$. It forms beautiful pale-yellow crystals; and when gently heated, it yields the anhydrous acid in fine white needles.

Chlophtalisic acid, $C_{16}HCl_3O_6$, is formed along with the oxide of chloroxenaphtose when chlonaphtalase is boiled with nitric acid. It is crystallizable, and represents anhydrous phtalic acid, in which 3 eq. hydrogen have been replaced by 3 eq. chlorine.

4. Action of Sulphuretted Hydrogen on the Nitrogenized Compounds derived from Naphthaline.

Naphtalidam, $C_{20}H_9N$. This is a very interesting base, formed by the action of sulphuretted hydrogen, aided by ammonia, on an alcoholic solution of nitronaphtalase. It may be obtained, although more slowly, without the use of ammonia. The mixture becomes of a dirty green, and the addition of sulphuric acid causes the solution to become thick from the separation of sulphate of naphtalidam. This salt is purified, and decomposed by ammonia, when the liquid is soon filled with fine white needles of pure naphtalidam. It is a very powerful base, melting at 86°, and boiling at 582°. When distilled, it is apt to continue liquid till cooled to 32°. The liquid base, if exposed to the air, absorbs oxygen, and becomes of a dirty violet colour. It forms white crystallizable salts with all the acids, and its hydrochlorate forms double salts with the bichlorides of platinum and mercury.

The discovery of this base, and of the ingenious method by which it is formed, is due to Zinin, who has also found that the other nitrogenized derivatives of naphthaline, treated in the same way, form similar bases. That from nitronaphtalese is crystallizable, and forms a hydrochlorate in scales.

The formation of these bases throws great light on the true nature of the vegetable alkalies. Zinin obtained from nitrobenzide, by the same method, a base, an oil which he called benzidam; but Hoffmann has shown its identity with aniline.

To judge from the action of chlorine unaided by heat, and of nitric acid, on naphthaline, that body, $C_{20}H_8$, is composed of two carbo-hydrogens, $C_{16}H_4$ and C_4H_4, the latter of which is more easily altered. The former, plus 6 eq. oxygen, yields phtalic acid, $C_{16}H_4+O_6$; and the substitution in phtalic acid of NO_4 (=X), for H yields nitrophtalic acid, $C_{16}\begin{Bmatrix}H\\X\end{Bmatrix}^3+O_6$.

β. *Anthracene*, $C_{30}H_{12}$. This compound, which is isomeric with naphthaline, is also found in coal-tar, and is sometimes called paranaphthaline. It melts at 356°, and distils at 392°, yielding foliated plates. When acted on by nitric

acid, it gives rise to a series of compounds, in which oxygen is substituted for hydrogen, while the compounds thus formed combine with hyponitrous acid. Thus, we have

Anthracene	$C_{30}H_{12}$
Hyponitrite of Anthracenase	$C_{30}H_{11}O + NO_3$
Bi-hyponitrite of Anthracenese . . .	$C_{30}H_{10}O_2 + 2NO_3$
Ter-hyponitrite of Anthracenise . . .	$C_{30}H_9O_3 + 3NO_3 + 3HO.$
Hyponitrite of Anthracenose . . .	$C_{30}H_8O_4 + NO_3$
Hyponitrite of Anthracenuse . . .	$C_{30}H_7O_5 + NO_3 + HO$
Anthracenuse	$C_{30}H_7O_5$
Chloranthracenese	$C_{30}H_{10}Cl_2$

The second compound of the above list is not known; but its existence is probable. In all the works to which I have access, there appear to be errors, probably of the press, in the table, which I have ventured to correct, so as to bring the formulæ into correspondence with the systematic names devised by Laurent, who discovered all these substances, on the same principle as in the case of naphthaline.

γ. *Chrysene*, C_3H or $C_{12}H_4$, is found among the last portions of the rectification of coal-tar. It is a yellow crystalline solid, insoluble in most liquids. It melts at 455°.

δ. *Pyrene*, $C_{10}H_2$ or $C_{15}H_3$, is found accompanying the preceding. It is a good deal more fusible. When acted on by nitric acid, both of the above compounds yield modifications, called, by Laurent, the hyponitrites of chrysenase and of pyrenase, $C_{12}H_3O + NO_3$ and $C_{15}H_2O + NO_3$. The former, by the continued action of nitric acid, is converted into $C_{24}H_5O_3 + 2NO_3$, which Laurent calls *nitrite of chrysenese* (properly, of *chrysenaese?*)

When bituminous shale is distilled, it yields a thick empyreumatic oil, composed of several products. Among these is an oil apparently identical with eupion, and another very peculiar oil, called *ampeline*. This oil has neither taste nor smell, but is in some points more analogous to creosote than to any other substance. It dissolves in water, but a few drops of acid cause it to separate. Its composition is still unknown. It may possibly be a product of the action of oil of vitriol, which is used in its preparation, on some other substance.

Ampelic Acid is formed by the action of nitric acid on that part of the oil of schist which distils at 300°. It is oily, soluble in hot water, and forms very soluble salts. Its composition is not known with certainty. A similar oil, obtained from coal-tar, was found to contain $C_{14}H_6O_6$. This would be isomeric with hydrated salicylic acid.

FOSSIL RESINS, WAX, OIL, NAPHTHA, &c.

Retinite or *Retinasphalt*, is a fossil resin found in lignite or wood-coal. It is fusible and combustible, and almost entirely soluble in alcohol. *Retinic acid*, $C_{21}H_9O_3$, was found by Johnston in the retinasphalt of Bovey.

Hatchetine is another fossil resin found in the lignites of Wales. It is colourless, or slightly yellow, fusible and volatile.

Scheererite is a colourless, translucent substance, of a pearly lustre, found in

the Swiss lignites. Both Hatchetine and Scheererite appear to be carbo-hydrogens, and much resemble paraffine, not quite pure.

Middletonite is a fossil resin, found, near Leeds, in coal.

Idrialine is a remarkable solid carbo-hydrogen, found in the quicksilver-mines of Idria. Its composition is C_3H, or perhaps $C_{21}H_7$; it colours oil of vitriol intensely blue, forming a coupled acid. *Succisterene*, a solid body obtained by Pelletier and Walter in the distillation of amber, has the same composition, and colours sulphuric acid blue. It is, therefore, in all probability, identical with idrialine.

Ozokerite or *Fossil Wax* is found in large masses in the bituminous schist of Slamick in Moldavia. When distilled, it yields a substance like wax, and also a good deal of paraffine. Ozokerite is very fusible, and burns with a bright flame.

Fichtelite is a fusible, volatile, crystallizable solid, found in branches of pine-trees, in the peat of the turbaries in the Fichtelgebirge. It appears to have the formula $C_{20}H_{15}$, and is probably derived from essence of turpentine, $C_{20}H_{16}$.

Tekoretine, *Phylloretine*, *Xyloretine*, and *Boloretine*, are the names of four resinous compounds, found in the peat of Denmark, on the remains of pine-trees. Tekoretine and Phylloretine are both fusible, volatile, and crystallizable. The former appears to be $C_{10}H_9$, the latter C_5H_3. Xyloretine is less fusible, and is decomposed by heat. It crystallizes, and its formula is said to be $C_{40}H_{33}O_4$, which only differs from that of sylvic acid by 1 eq. hydrogen. Boloretine is fusible, but does not crystallize. Its formula is $C_{40}H_{32} + 3HO$, but it occurs also with 5 or 6 eq. of water.

Asphaltum, *Mineral Pitch*, *Pitch of Judea*. These are the names of certain substances of similar characters, found in different parts of the world, as in Trinidad, in Hanover, and at the Dead Sea in Palestine. They all resemble pitch in aspect, and are composed of a dark-brown resin, mixed with more or less of a brilliant black matter, *asphaltene*, $C_{20}H_{15}O_3$, or of a liquid volatile oil, *petrolene*, $C_{20}H_{16}$. The former of these is probably an oxide of the latter. The different kinds of asphaltum are much used for waterproof cements, and for pavements, or roofs. *Naphteine* is a somewhat analagous substance, found in the limestones of the Maine et Loire.

Petroleum and *Naphtha*. In certain spots, in the neighbourhood of the Caspian, in Ava, at the Tegernsee in Bavaria, at Amiano in Italy, and near Neufchatel, as well as in other places, pits dug in the earth become filled with water, on which floats, more or less abundantly, an oily matter, formerly called rock-oil. The purer kinds are little coloured and very fluid, and when distilled with water leave hardly any residue. These are called naphtha. Other kinds, as the petroleum of Rangoon in Ava, are dark-coloured and semisolid, but become liquid at 80° or 90°. These yield by distillation, first, much naphtha, nearly colourless, and then much paraffine, which is easily purified. Naphtha, when pure, has the sp. gr. 0·755, and its formula is C_6H_5. Rectified naphtha is used for the purpose of preserving potassium and sodium, which have no action on it if water be not present. In many places the native naphtha is used to give light.

Reichenbach found that coal, distilled with water, yielded a little of an oil very similar to petroleum.

All the above substances are formed by the decay or destruction of organic matter, chiefly wood. It is not altogether improbable that those kinds which, like the Rangoon petroleum, contain paraffine ready formed, may have been

formed by the action of heat on beds of vegetable remains, situated pretty deep in the crust of the earth.

Soot and *Lamp Black* are produced by the imperfect combustion of organic matters. They contain much carbon, mixed, in soot, with an acid resinous matter, and with a substance analogous to humus, but containing nitrogen, and called asboline. Lamp-black, besides a little resin and oily matter, often contains naphthaline, which may be extracted by alcohol.

SULPHURIZED AND NUTRITIOUS ANIMAL AND VEGETABLE PRINCIPLES.

We have already seen that some essential oils contain a large proportion of sulphur, and it is probable that these oils are derived from the decomposition of compounds existing in the plants which contain much sulphur, but the true nature of which is not yet known. But while such compounds only occur in a few plants, there is another class of sulphurized compounds which occur in all plants without exception. These compounds contain nitrogen and oxygen, both in considerable proportion to the carbon and hydrogen, and a small proportion of sulphur. They are all solid, and when heated yield products containing ammonia and sulphur. They have neither a medicinal nor a poisonous action on the animal system, but are nutritious in the strict sense of the word.

Such are vegetable albumen, vegetable fibrine, and vegetable caseine, as well as animal albumen, animal fibrine, and animal caseine. The latter, when compared with the former respectively, are found to differ from them only in form, agreeing with them in all essential chemical characters. Every one of the six dissolves in strong hydrochloric acid, gently warmed, with a purple colour; and all of them likewise dissolve in caustic potassa, forming a solution which (after all the sulphur has been converted into sulphuret of potassium by boiling) gives, on the addition of acetic acid, sulphuretted hydrogen gas, and a gelatinous precipitate, which in every case is the same substance, called *Proteine*, by Mulder, its discoverer. Hence the above substances are called *proteine compounds*,—not that we can prove them to contain proteine ready formed, but because they all yield proteine in the same circumstances.

1. *Vegetable Albumen* has only been studied as yet in the coagulated or insoluble state. It occurs, however, dissolved, or in the soluble form, in vegetables, and especially in the oily seeds, along with caseine. It is always combined with alkali, to which it owes its solubility. Its distinguishing character is that of coagulating or becoming insoluble when heated to from 140° to 160°. Once coagulated it no longer dissolves, even in the liquid in which it was formerly quite dissolved. When a fresh vegetable juice is filtered and boiled, it yields a coagulum, which is nearly pure albumen. Its solutions are also coagulated by acids, by infusion of galls, by creosotes, and by corrosive sublimate. When dried, it is translucent. In all these characters it agrees with animal albumen.

2. *Vegetable Fibrine* is the essential part of what is called the *gluten* of wheat. It is chiefly found in the seeds of the cerealia. When wheat, softened in water, is kneaded under water in linen bags to obtain the starch, and the residuary masses are beat up with rods, the pure fibrine adheres in elastic, transparent filaments to the rods. These, after being treated by ether, to remove fat oil, are pure fibrine. When dried, it becomes greyish and translucent, like horn. When heated, it yields the usual products of animal matters; and when left to itself in the moist state, it putrefies, disengaging fetid gases. It is quite insoluble in water. Diluted phosphoric and acetic acids dissolve it easily: these solutions

are precipitated by ferrocyanide of potassium, and by infusion of galls. Diluted potassa also dissolves it; and this solution, when neutralized by phosphoric or acetic acid, yields a precipitate which dissolves in an excess of either of these acids.

3. *Vegetable Caseine.* Syn. *Legumine*, is an essential part of the seeds of the leguminosæ, and also of the oily seeds. It is only known in combination with acids and with alkalies. To obtain it, kidney-beans, lentils, or pease, are softened in water, then brayed in a mortar, the pulp mixed with much cold water, and strained through a fine sieve, which retains the husks, and allows the caseine and starch to pass, the former dissolved, the latter suspended. On standing, the starch settles to the bottom, leaving a solution of caseine, which may be decanted. It is sometimes milky if much oil be present, sometimes clear. When exposed to the air, it quickly becomes acid, lactic acid being formed, and coagulates exactly as skimmed milk does when it becomes sour. The solution of caseine does not coagulate by heat, but, like milk, forms a pellicle which is renewed as fast as it is removed. It is coagulated by the addition of an acid, and the coagulum dissolves in an excess of all vegetable acids, except acetic acid, which with mineral acids produces a permanent precipitate. This precipitate is well washed with cold water, alcohol, and ether, dissolved in hot water with a little ammonia, and this solution is precipitated by alcohol. It still contains ammonia, but is otherwise nearly pure.

In this state it is like paste of starch, and when dried it is nearly transparent, and liquefies when heated. In water it softens, and this paste is coagulated by acids, corrosive sublimate, infusion of galls, and creosote. Caseine is very soluble in tartaric and oxalic acids, also in caustic and carbonated alkalies if diluted. The coagula, or precipitates formed by mineral acids in solutions of caseine, are compounds of caseine with the acid: they are soluble in strong acids.

4. *Emulsine*, or *Synaptase*, is the name given to a peculiar compound of this class, found in certain oily seeds, as in almonds, &c. An emulsion of these seeds is very like milk. On standing, the oil rises, like cream, to the top, and the watery liquid is *now* coagulated by acetic acid, as milk would be. It coagulates also by boiling; and in this case, the whey, separated from the coagulum, again coagulates on standing twenty-four hours, and is found to contain lactic acid. The emulsine agrees with albumen, in being coagulated by heat, and with caseine in being coagulated by acetic acid. It exerts a peculiar decomposing agency on amygdaline, in which it is also itself decomposed.

Fungine is the substance of which mushrooms are chiefly composed. Its true nature is uncertain, but it contains nitrogen.

Gliadine is the name given to the viscid ingredient of gluten. It contains sulphur, and approaches in composition to vegetable albumen. It is probably a mixture.

When a vegetable juice, containing one or more of these compounds along with sugar, is exposed to the air, oxygen is absorbed, and a change is commenced in the albumen, fibrine, caseine, gluten, &c., which is soon communicated to the sugar, causing it to undergo the vinous fermentation. The temperature rises, and occasionally the viscous fermentation takes place, producing lactic acid, gum, and mannite. During fermentation, a grey deposit is formed; this is yeast or ferment. When the whole of the azotized principles have not been decomposed or rendered insoluble, the liquid, if excluded from air, remains

without further change: but if air be admitted, the alcohol is converted into acetic acid, oxygen being absorbed by the azotized matters, the contact of which causes the alcohol also to absorb oxygen. When the sugar is in excess, only part of it is converted into alcohol, and part of the azotized matter takes the form of insoluble yeast, the rest being decomposed. The saccarine and spirituous liquid undergoes no further alteration. All the above statements apply to the juice of the grape and to the formation of wines and vinegar.

When the juice, as that of the grape, contains tartaric acid, ethers are formed, which give the liquid a peculiar smell and flavour, such as œnanthic ether, which is characteristic of all wines. When a juice contains sugar and caseine, it is most apt to undergo the viscous fermentation, or, at least, the caseine favours the production of lactic acid from the sugar. But at a high temperature, such as 100°, butyric acid is formed, instead of lactic acid.

Vegetable fibrine, as it is found in wheat flour, is subject to continual alteration by contact with water; and in this state it has the singular property of converting starch into dextrine, a soluble gum, and then into sugar. This remarkable power is best seen in germinating grain, as in malt, of which a small part mixed with a large quantity of starch in a thick paste, and warmed to 150° or 160°, very soon renders the whole quite fluid and dissolved, and finally converts it into grape sugar. That part of the fibrine which acts on the starch has become soluble in water. It is called *diastase*.

Diastase is made by rubbing up malt with a little water, expressing the mixture, adding just enough alcohol to separate the albumen, and to allow the liquid to filter. The filtered liquid, mixed with more alcohol, deposits the diastase. It is purified by being repeatedly dissolved in water and precipitated by alcohol. It is finally dried at a temperature of 100° or 110°. Thus prepared, diastase cannot be a pure compound, but it possesses in a high degree the power of promoting a solution of starch, that is, its conversion into dextrine and sugar. One part of diastase can convert into dextrine, with a little sugar, no less than 2000 parts of starch. Diastase is evidently fibrine altered, and still more prone to change. Its solution cannot be kept, it becomes acid, and loses its action on starch.

Malt is made by softening barley in water, and then exposing it to the air in moderately thick layers, at a moderate temperature, turning it frequently. In about four days the seeds germinate, if they have not been allowed to become too hot, and if the air has had free access. As soon as the germ has acquired the length of the seed, the operation is checked by drying the seeds in a current of warm air. They now constitute malt. In this operation, much carbonic acid is given off, oxygen being no doubt absorbed; the azotized matter in the seeds has undergone a change, and has acquired the properties of diastase; and the starch has in part disappeared, its place being supplied by grape sugar and dextrine.

When the malt is infused in warm water, the metamorphosis of the starch is completed, and the whole dextrine passes into sugar, which dissolves, along with extractive matter and salts. The solution is called *must*. When sufficiently concentrated hops and yeast are added, and fermentation being carried on, the result is *beer* or *ale*, according to the strength of the must. When the malt has been in part roasted, the beer becomes very dark-coloured, as in the case of *porter*.

To obtain grain spirit, the meal, either of barley, oats, or rye, or a mixture, is

digested in warm water along with 1 part of malt for 4 of meal, till the mass, at first thick, becomes fluid, a proof that all the starch has been metamorphosed. Yeast is then added, and, after fermentation, the must or *wort* as it is called, is distilled and rectified. Potato spirit is obtained in the same way, only using potato starch, instead of barley meal or rye flour.

Many other vegetable matters, and many fruits, may be made to yield spirit, malt or diastase being used in all cases where starch is to be converted into sugar.

Potato spirit is accompanied by the hydrated oxide of amyle, or oil of potato spirit; grain spirit by an oily matter, consisting chiefly of margaric and œnanthic acids, probably in part as margaic and œnanthic ether, and of a volatile oil, called by Mulder *oleum siticum*, that is, oil of grain. Wine spirit, that is, *brandy*, contains œnanthic ether, and the spirit of molasses, or *rum*, owes its flavour to butyric ether. The oils which contaminate potato and grain spirit are offensive and even injurious to health; they are included by the Germans under the general term *faseleol.*

Panification. Bread may be made from any flour containing, as all good flour does, vegetable fibrine, sugar, and starch. The flour being made into a paste with warm water, and yeast being added, it is set aside in a warm place. After a time, more flour is kneaded into the mass, which has begun to rise, and the whole is now heated in the oven, or baked. The yeast induces the vinous fermentation in the sugar of the flour, and the alcohol and carbonic acid escaping, raise the bread and render it porous. The starch in general is little changed, but the sugar disappears, as well as a part of the gluten or fibrine. To avoid this loss, bread is now raised by means of carbonate of soda or ammonia and a diluted acid, which are added to the dough, and the effect is perfectly satisfactory. Equally good or better bread is obtained, and the quantity of flour which will yield 1500 loaves by fermentation, furnishes 1600 by the new method, the sugar and fibrine being saved. The addition of a little alum to the dough is useful in arresting that decomposition in the flour which is apt to occur if it have been kept in a moist place. Too much alum cannot be introduced, as it would prevent the fermentation.

The nutritive properties (using the word in its strict sense) of different kinds of flour or meal is directly proportional to the fibrine or albumen they contain; because it is these substances alone which can be converted into blood or flesh. Hence a working man requires more oat bread than wheat bread to restore the daily waste of the body, oatmeal containing much less fibrine &c. than wheat flour. The starch is consumed in the body, up to a certain point, but beyond this it is discharged in the excrements. We shall see hereafter what its function probably is. Even the best wheat flour contains more starch than is consumed; and the excess is greater in other grains.

In germination, the azotized principles of the seeds become soluble and prone to further change. When now dissolved, they are in the same state as those of the grape juice which at once cause fermentation when air is admitted. Diastase is merely gluten, that is, fibrine, in this soluble form or period of change.

When left in water, gluten swells, putrefies and disengages carbonic acid, hydrogen, and sulphuretted hydrogen gases: it then becomes fluid and ropy, the water becomes very acid, and contains a peculiar compound called caseous oxide, with acetate, phosphate, and caseate of ammonia. When vegetable caseine pu-

trefies, it gives out the odour of putrid cheese, and yields sulphuretted hydrogen gas.

Ferment, Yeast, Lees of Wine. These are names given to the deposit formed in fermenting liquids, which possess the property of exciting fermentation in must, wort, grape juice, infusion of malt, or solution of sugar. When solution of sugar is employed in excess, the ferment gradually diminishes, till about 15 per cent. are left, of a substance containing no nitrogen, and insoluble. This is *cellulose*, or *hordeine*. On the other hand, in grape juice, or infusion of malt, the ferment is reproduced from the azotized principles present.

Mulder and Schlossberger have shown that ferment is composed of regular cells, formed of cellulose, and containing an azotized matter, very easily decomposed, which is a proteine compound. This body rapidly decomposes the deutoxide and persulphuret of hydrogen, but loses this property after it has been heated to 212°. Mulder thinks that, after boiling, it is a superoxide of proteine.

The power of yeast or ferment to act on sugar is destroyed by boiling water, by absolute alcohol, by pyroligneous acid, salts of mercury, essential oils, sulphurous acid, &c.

Caseous Oxide, Caseic Acid, or *Aposepidine*, are names given to the crystalline compound formed during the putrefaction of gluten under water. It contains nitrogen, but its formula is unknown. It is soluble in water, insoluble in alcohol.

We now proceed to the consideration of the parallel compounds, *animal albumen, fibrine*, and *caseine*.

5. *Animal Albumen* is hardly known in a state of purity. The purest appears to be that prepared by exactly neutralizing serum of blood or white of egg with acetic acid, and adding a large quantity of water. The albumen separates in translucent flocculent masses, which, when washed with water, assume the aspect of paste. (Denis.) Albumen is best known in the form of the serum of the blood and that of white of egg.

Serum of blood, dried in a very gentle heat, leaves a translucent mass, which dissolves completely by digestion with water. Both in this form, and in the preceding, it dissolves far more easily in the most diluted alkaline solutions.

White of egg consists of very delicate cells, filled with a ropy liquid. By beating with water, the cells are broken, and are afterwards deposited, being insoluble. Dried at a gentle heat white of egg is yellow, translucent, and brittle. In water it again softens into its original state. When calcined, it leaves 6 or 7 per cent. of salts, common salt, carbonate, phosphate, and sulphate of soda, and phosphate of lime.

The action of heat on albumen is remarkable. When heated alone, or after dilution with water, to between 145° and 165°, it coagulates into the well-known white elastic mass, which, when dried, becomes yellow, horny, and brittle. It is now quite insoluble in water; but if, after being coagulated and dried, it is placed in water, it swells up into the original elastic mass of coagulated albumen.

The albumen prepared by the process of Denis dissolves readily not only in acids and alkalies, but also in neutral salts, such as nitrate or sulphate of potassa or soda. It is owing to the presence of such salts in serum or white of egg that

their albumen is soluble in water. When the pure albumen of Denis is dissolved in solution of nitre, it is coagulated by boiling exactly like serum.

Solutions of albumen are coagulated by acids; the addition of free alkalies prevents even the action of heat. Serum and white of egg, when mixed with water, being both alkaline, may be neutralized carefully by acids, without coagulation. Acid solutions of albumen are precipitated by corrosive sublimate and ferrocyanide of potassium, by infusion of galls, by creosote, and by alcohol. The real difference between soluble and insoluble or coagulated albumen is not yet known.

When albumen putrefies, it yields sulphuret of ammonium, sulphuretted hydrogen, and other products. When heated, it burns with the odour of burnt horn or animal matter.

6. *Animal Fibrine* is found in blood, chyle, and lymph dissolved, and forms the chief part of the muscles. It may be obtained by whipping up blood with rods, when it adheres to the rods, and is finally purified by kneading with water to remove colouring matter, and by digestion with alcohol and ether, which dissolve fatty substances. When dry it is somewhat similar to albumen, and when heated burns with the same smell, leaving from 0·77 to 2·55 per cent. of ashes, phosphates of lime and magnesia. Recent fibrine loses, in vacuo, about 80 per cent. of water, the greater part of which it again takes up when placed in water. When long boiled with water, it slowly dissolves; and when left long, that is, for some months, under water, it gradually disappears.

The fibrine of venous blood dissolves, at a gentle heat, in solutions of acetate of soda, sal-ammoniac, and nitre. These solutions are coagulated by heat, and exhibit the properties of dissolved albumen. Muscular fibrine may also be thus dissolved; but neither arterial fibrine, nor the fibrine of the buffy coat, can undergo this change. Venous fibrine loses this property by exposure to the air, when it absorbs oxygen and gives off carbonic acid. Fresh fibrine rapidly decomposes deutoxide of hydrogen: but boiling water or alcohol deprive it of this property.

The most striking character of fibrine is its spontaneous coagulation, as in the blood; which is also seen in vegetable fibrine in some juices. In regard to acids and alkalies, fibrine acts like albumen.

7. *Animal Caseine* is chiefly found in *milk*. It is not known in a state of purity, but only combined with bases or acids, for both of which it has a powerful attraction. Uncombined caseine is insoluble: in milk it is dissolved by virtue of the potassa which renders that fluid alkaline. If carefully neutralized by an acid, milk is not coagulated, but it is then coagulated by boiling. The coagulum or curd formed by excess of acids is very soluble in oxalic and tartaric acids, sparingly so in the mineral acids. This coagulum contains, along with caseine, a good deal of the acid employed.

The coagulum caused in milk by alcohol yields, when burned, 10 per cent. of ashes, chiefly phosphate of lime. What is called soluble caseine is a compound containing much potassa. With lime, baryta, &c., caseine forms insoluble compounds.

Milk, ar any other solution of caseine, when evaporated in the air, forms a pellicle, which is renewed as fast as it is removed. This is insoluble, and yields ashes containing lime and phosphate of lime.

Milk may be analyzed by drying it up in vacuo, dissolving the butter by a mixture of ether and alcohol, and the sugar of milk and salts by cold water. The caseine remains in this way undissolved, the salts having been first removed.

When exposed to the air, milk undergoes a peculiar change. The caseine enters into decomposition, and this decomposition passes to the sugar of milk, which yields a little lactic acid, and this causes the caseine not yet decomposed to coagulate. But the decomposition continues: the sugar of milk is at last entirely converted into lactic acid, mannite and gum; and if the acid be neutralized, and fresh sugar added, it will undergo the same change as long as any caseine remains. This is the method followed for obtaining lactic and lactates. The coagulum, separated from the whey when first formed, and pressed out, forms cheese. In making the better kinds of cheese, the milk, instead of being allowed to coagulate spontaneously, is coagulated by contact with water in which part of the lining membrane of a stomach has been infused. This infusion is called rennet, and it acts by virtue of containing albumen or gelatine in a state of decomposition, which is at once communicated to the sugar.

When milk, spontaneously coagulated, is exposed to a heat of from 75° to 85°, without any addition, the sugar of milk passes into grape sugar, and vinous fermentation ensues. The fermented milk, distilled, yields a spirit containing traces of butyric ether.

If sugar is made to ferment with caseine at about 100°, carbonic acid and hydrogen gases are disengaged, and butyric acid is formed in large quantity.

The chief mineral substances in milk are potassa and phosphate of lime, which are found in its ashes. The ashes also contain sulphates, although milk does not. The sulphuric acid in the ashes is derived from the oxidation of the sulphur of the caseine.

The proportions of water, caseine, sugar of milk, butter, and salts, are very variable in milk. It generally contains about 86 per cent. of water, 4 to 7 of caseine, 3·5 to 5·5 of butter, and 3 to 5·5 of sugar of milk and salts. For the best method of analyzing milk, proposed by Haidlen, I must refer to the "Annalen per Chemie und Pharmacie, xlv., 274." By this method Haidlen obtained as follows:—

	From Cow's Milk.	Human Milk.	Do.
Butter	3	3·4	1·3
Sugar of milk, and salts soluble in alcohol	4·6	4·3	3·2
Caseine and insoluble salts	5·1	3·1	2·7
Water	87·3	89·2	92·8
	100·0	100·0	100·0

The colostrum, or milk given immediately after parturition, differs from normal milk in containing 15 to 25 per cent. of albumen, with less caseine, butter, and sugar of milk.

The milk of bitches, according to Simon, contains from 14·6 to 17·4 of caseine, 16·2 to 13·3 of butter, and no sugar.

Cheese is caseine in a state of incipient or progressive decomposition or putrefaction. In the finer kinds of cheese, there is a large proportion of butter, and to the volatile acids of the butter may be ascribed the flavour of cheese. Some kinds of cheese are full of what are called eyes, that is, hollows, caused by the formation of bubbles of gas; and in these hollows a liquid is sometimes found, containing free ammonia, a product of decomposition, which greatly heightens the flavour. When the blue mould appears in cheese, it is in a state of rapid

decay or eremacausis, and much ammonia is given off. Little is yet known of the chemical differences in the making of different kinds of cheese. The richest are made almost entirely from cream, as Stilton and Parmesan. Others, as Gruyère, Gloucester, Cheshire, and Dutch cheese, are made with fresh uncreamed milk, or mixtures of this with cream; and more or less salt is used, as well as different methods of coagulating, in different places,

Animal Mucus is somewhat analogous to albumen, when dry. In water, it softens and swells, like tragacanth. It is precipitated by picric acid. It contains sulphur.

8. *Horny Matter.* This name may be given to the substance of which the epidermis, hair, wool, silk, feathers, nails, claws, hoofs, horns, shell, and probably also sponge, are composed. All these substances dissolve in potash-ley when heated with it, giving off ammonia, and forming a solution from which, by neutralization with acetic acid, a white gelatinous matter is precipitated. (See *Proteine.*) They all contain sulphur. Sponge leaves 3½ per cent. of ashes, among which is found iodide of potassium. All the above substances, when heated or burned, give out the same peculiar and well-known smell, known as that of burnt feathers.

COMPOSITION OF THE PRECEDING SUBSTANCES.

According to the researches of Mulder, Liebig, Dumas, and many other chemists, vegetable albumen, fibrine, and caseine, have all the same, or very nearly the same, composition, as far as concerns the carbon, hydrogen, nitrogen, and oxygen, including under oxygen the sulphur and phosphorus, which occur in small proportion. Thus we have, in vegetable

	Albumen.	Caseine.	Fibrine.
Carbon	54·74	54·14	54·095
Hydrogen	7·77	7·16	7·308
Nitrogen	15·85	15·67	15·659
Oxygen and sulphur, &c. . . .	21·64	22·03	22·938
	100·00	100·00	100·000

The above are analyses, taken at random from a number by different observers. Gluten, as being formed chiefly of fibrine and a modified albumen, has the same composition.

We find, further, that animal albumen, fibrine and caseine, agree in composition. Thus we find, in animal

	Albumen.	Caseine.	Fibrine.
Carbon	54·803	54·668	54·443
Hydrogen	7·021	7·302	6·997
Nitrogen	15·677	15·683	15·824
Oxygen and sulphur, &c. . . .	22·499	22·347	22·726
	100·000	100·000	100·000

The composition of horny matter, of mucus, of the inner coat of arteries, &c., is analogous to the above, but not identical with it.

PROTEINE.

The remarkable similarity in composition of all the truly nutritive substances, whatever their origin, is not confined to the proportions of the elements in 100 parts, but appears also to belong to their intimate constitution. Thus, when their solution in potassa, boiled until the whole sulphur is removed, is neutralized with acetic acid, there is formed from every one of the preceding, a gelatinous precipitate, which contains neither sulphur, phosphorus, nor salts, and which Mulder calls *Proteine*, as being, in his opinion, the first or leading compound, from which all the others are derived.

Proteine is very soluble in acetic and phosphoric acids of any degree of concentration; it dissolves in hot and strong hydrochloric acid with a deep blue or purple colour, which changes to black on boiling. The composition of proteine is as follows:

Carbon	54·848
Hydrogen	6·959
Nitrogen	15·847
Oxygen	22·346
	100·000

That is to say, exactly the same as the organic part of albumen, &c. It is evident, therefore, that we may consider albumen, fibrine, and caseine, both animal and vegetable, as formed of proteine, along with alkaline and earthy salts, different in each case, and also along with a little sulphur and phosphorus, or, as in caseine, sulphur without phosphorus. We are not entitled to say that these bodies are actually compounds of proteine with salts, sulphur, &c., for, in truth, proteine is rather a product of decomposition than a compound pre-existing. But there is an advantage to the memory in taking the above view; and, besides, it is certain that albumen, &c., all agree so closely in constitution, as to yield the same product of decomposition.

When boiled with potassa, proteine gives rise to three new products; *erythroprotide*, *leucine*, and *protide*.

Mulder deduces from the analysis of proteine the formula $C_{40}H_{31}N_5O_{12}$; Liebig prefers that of $C_{48}H_{36}N_6O_{14}$, which agrees as well with the results of analysis, and throws more light on certain transformations which occur in the body. Both formulæ are to be considered as tentative only.

Mulder obtained by long boiling of fibrine with water, a substance which appeared to be a binozide of proteine, $=C_{40}H_{31}N_5O_{14}$. The same substance was found by him in the buffy coat of blood in inflammatory diseases; and was also obtained along with proteine by Van Laer among the products of the action of boiling diluted potassa on hair.

When fibrine and albumen are long boiled with water they yield, according to Mulder, a *teroxide of proteine*, $C_{40}H_{31}N_5O_{15}$.

By the action of chlorine on solutions of the proteine compounds there is formed a substance in white flocculent particles, nearly insoluble. This is *chloroproteic acid*; and its formula is $C_{40}H_{31}N_5O_{12}+CO_3$. (Mulder.)

Leucine crystallizes in brilliant white scales, very soluble in hot water and alcohol, also in ether. With nitric acid it forms *nitroleucic acid*. This acid crystallizes in needles. The composition of these products is not fully ascertained.

According to Mulder, *erythroprotide* is, $C_{13}H_8NO_5$, and protide, $C_{13}H_9NO_4$.

ACTION OF ACIDS ON PROTEINE COMPOUNDS.

When moist fibrine is placed in water acidulated with $\frac{1}{2000}$ of hydrochloric acid, it swells up to a jelly which finally dissolves, all except a few flocculi, to which Bouchardat gives the name of *Epidermose*. Albumen and vegetable fibrine undergo a similar change. Bouchardat gives to the dissolved matter the name of *albuminose*; but it is either proteine, or binoxide of proteine. (Mulder.)

When the buffy coat of inflammatory blood is boiled with water, the filtered liquid on cooling forms a jelly. This, according to Mulder, is tritoxide of proteine, and not gelatine as supposed by Bouchardat.

When compounds of proteine are dissolved with the aid of heat in strong hydrochloric acid, they yield a purple solution, which becomes black on exposure to the air. It then contains sal ammoniac and humate of ammonia. We have, on the one hand,

Proteine	.	$C_{48}N_6H_{36}O_{14}$		yielding, on the other	Humic Acid	C_{48}	$H_{24}O_{24}$
Water	.	H_6O_6					
Oxygen	.	O_4			Ammonia	.	NH_3
Hydrochloric Acid		H_5	Cl_5		Sal Ammoniac 5 eq.		N_5H_{20} Cl_5
		$C_{48}N_6H_{47}O_{24}$	Cl_5				$C_{48}N_6H_{47}O_{24}Cl_5$

This reaction enables us to see how proteine might be formed from the elements of sugar and ammonia, water and oxygen being eliminated. For, abstracting from the hydrochloric acid, and bearing in mind that humine or humic acid, $C_{48}H_{24}O_{24}$, is merely sugar minus water, grape sugar (dry) being $C_{12}H_{12}O_{12}$, and 4 eq. of it being equal to $C_{48}H_{48}O_{48}$; let us then suppose 4 eq. of grape sugar to lose half the water they contain, leaving this variety of humic acid, and to take up 6 eq. of ammonia. Let us further pursue the process, which is opposite to that above explained, and subtract 4 eq. oxygen and 6 eq. water, and proteine will remain. The reader will observe that we can actually, with the aid of hydrochloric acid, cause proteine to take up oxygen and water, and to produce or be resolved into ammonia and humic acid, and that this humic acid only differs from sugar by the elements of water. So that we may expect hereafter to reverse the process and to cause sugar or humic acid, taking up ammonia and giving off water and oxygen, to give rise to proteine. At all events it is evident that proteine might thus be derived from sugar and ammonia, which meet in plants; and although in general we are unable artificially to produce the more complex substances, and can only decompose or resolve them into less complex forms, yet there are, even now, some cases in which more complex molecules may be artificially formed by the coalescence of more simple ones; and it is probably, in these very circumstances, that the vital force interferes and modifies the results. We may represent as follows the conceivable change, (the converse of that actually observed,) by which we may conceive proteine to originate from sugar and ammonia.

Sugar	. . .	C_{48} $H_{43}O_{48}$	=	Proteine	.	$C_{48}N_6H_{36}O_{14}$
Ammonia	. .	N_6H_{18}		Oxygen	.	O_4
				Water	.	$H_{30}O_{30}$
		$C_{48}N_6H_{66}O_{48}$	=			$C_{48}N_6H_{66}O_{48}$

The action of nitric acid on proteine compounds gives rise to xantho-proteic acid, an orange-yellow insoluble mass, not crystalline. Its formula is, $C_{34}H_{24}N_4O_{12}+2HO$. (Mulder).

Muscular fibrine, in contact with oil of vitriol, becomes gelatinous and dissolves. This solution, mixed with 2 vol. of water and boiled, yields sulphate of ammonia, leucine, and a syrupy substance sweet and soluble in alcohol. Gelatine, in the same circumstances, yields sugar of gelatine, and a fermentescible sugar, probably sugar of grapes.

GELATIGENOUS TISSUES.

Under this head we place several tissues which yield to boiling water a substance which on cooling forms a jelly, or may be called *gelatine*. They are chiefly found in the cellular membrane, the skin, the membranes in general, the tendons, ligaments, bones, cartilages, &c.

The cellular tissue and the membranes are chiefly formed of gelatinous matter, which is insoluble in cold water and acids. It combines with salts, as corrosive sublimate, persulphate of iron and alum, forming insoluble compounds which do not putrefy, as gelatine itself so readily does.

The gelatine of the skin, when moist, combines with tannic acid, if steeped in a solution of that acid, and is converted into leather. While the true skin is gelatinous, the epidermis is more allied to horn.

Chondrine is the name given to the gelatine of the cartilages.

Gelatine or *Glue* is that given to the gelatine of the bones and hoofs, skins, &c. of animals. Isinglass is made from the air-bladder of fishes, and is nearly pure gelatine.

1 part of pure gelatine, dissolved in 100 of hot water, forms a jelly on cooling. A solution of isinglass is completely precipitated by infusion of nut galls.

Chondrine and gelatine, in solution, are distinguished by acids, alum, and salts of lead, which precipitate chondrine but not gelatine. In regard to other tests, they agree. $\frac{1}{5000}$ of either may be detected by tannic acid.

By the action of chlorine on gelatine, there is formed what is called *chlorite of gelatine*, consisting, according to Mulder, of chlorous acid and gelatine.

By the action of potassa, gelatine is converted into sugar of gelatine, or into a mixture of sugar of gelatine and leucine.

Sugar of gelatine crystallizes in prisms, very soluble in water, and very sweet. With nitric acid it forms an acid, nitrosaccharic acid, which forms white transparent prisms, fusible and very soluble; it forms salts, which for the most part crystallize. According to Mulder, sugar of gelatine is $C_8H_9N_2O_7=C_8H_7N_2O_5+2HO$; and it forms with metallic oxides compounds of the formula $C_8H_7N_2O_5+2MO$. Nitrosaccharic acid is $(C_8H_7N_2N_5+2NO_5)+4HO$; and its salts are $(C_8H_7N_2O_5+2NO_5)+2MO+2HO$ or $(C_8H_7N_2O_5+2NO_5)+3MO+HO$. But, according to Boussingault, sugar of gelatine is $C_{16}H_{18}N_4O_{14}=C_{16}H_{15}N_4O_{11}+3HO$. The proportions are the same as in Mulder's formula, but doubled, and the compound is supposed to contain 3 eq. of basic water. But in the compounds of the sugar with bases, these 3 eq. of water are replaced by 4 of oxide, giving the formula $C_{16}H_{15}N_4O_{11}+4MO$, which is the double of Mulder's formula, plus 1 eq. water.

The nitrosaccharic acid in crystals, according to Boussingault, is $C_{16}H_{18}N_4O_{14}+4NO_5+6HO=C_{16}H_{17}N_8O_{33}+7HO$. When dried at 230° it is $C_{16}H_{17}N_8O_{33}+$

4HO, and its salts correspond, being as follows, $C_{16}H_{17}N_8O_{33}+4MO$. If we double Mulder's formula, for the sake of comparison, we obtain $C_{16}H_{14}N_8O_{30}+8HO$ for the acid, and for the salts $C_{16}H_{14}N_8O_{30}+4MO+4HO$. It will be seen that in regard to the nitrosaccharic acid, Boussingault's formula differs from Mulder's in containing 1 eq. of water less, instead of more, as in the sugar of gelatine.

The nitrosaccharates crystallize very easily. That of copper, according to the very recent experiments of Verloren, is $C_{16}H_{14}N_8O_{30}+2HO+6CuO$.

Gelatine does not yield proteine by the action of potassa, and therefore does not belong to the series of the proteine compounds. Liebig adopts for gelatine the formula $C_{48}H_{41}N_{7\frac{1}{2}}O_{18}$; and for chondrine, $C_{48}H_{40}N_6O_{20}$. The arterial membrane he supposes to be $C_{48}H_{38}N_6O_{16}$. The latter is equal to proteine, plus 2 eq. water; and chondrine is equal to proteine, plus 4 eq. water and 2 eq. oxygen. It is easy, therefore, to see that gelatine is not fitted for nutrition of the body generally, since it cannot yield blood, which is only formed by proteine compounds. Gelatine may contribute, however, to the nutrition or supply of the gelatigenous tissues.

Bone. The Gelatine and other animal matters in healthy bone constitute from 37·5 to 44 per cent.; the rest is earthy matter. In rickets and mollities ossium, the cartilaginous matter amounts to from 63 or 70 to 80 per cent., and the phosphate of lime is diminished in proportion, not exceeding, in some cases, 12 or 13 per cent.

The proportions of gelatine and earthy matter vary in different animal species.

The earthy ingredients of bone are, phosphate of lime, carbonate of lime, fluoride of calcium, phosphate of magnesia, with small quantities of common salt, soda, &c.

Bone or *Ivory Black*, obtained by calcining bones in retorts, contains all the earthy and saline matters, with a large proportion of charcoal intimately mixed with them. It probably contains nitrogen. Qu? as paracyanogen or mellone?

THE BILE.

This animal fluid, collected from the liver in the gall-bladder, is slightly alkaline, and has a viscid, oily consistence. It has, when fresh, a golden yellow colour with a tinge of green, and becomes darker when exposed to the air. Its taste is bitter and persistent, with a sweetish after-taste. It is perfectly miscible with water, and its aqueous solution froths like solution of soap.

When dried in the vapour-bath, bile leaves a yellow mass, which dissolves in alcohol, leaving undissolved a little mucus. The alcoholic solution is deep green, but may be decolorised either by animal charcoal, or by the cautious addition of baryta, which forms an insoluble compound with the colouring matter. The decolorised alcoholic solution of bile still contains cholesterine, which is separated by adding twice its volume of ether, which separates the bile as a thick syrup, retaining the cholesterine dissolved. The bile, if now dried up in the vapour-bath, leaves a transparent solid mass like gum arabic, perfectly soluble in water and in alcohol.

The solution of bile is precipitated by natural acetate of lead, but the liquid becomes acid. If the free acid be neutralized, acetate of lead produces a fresh precipitate, the liquid again becoming acid. Tribasic subacetate of lead precipi-

tates at once the whole of the organic matter of the bile, but an excess of the precipitant is apt to redissolve a part of the precipitate, which is also soluble in alcohol. Mineral acids cause a resinoid precipitate in solution of bile.

Bile in solution may be recognized by the property of striking a purple colour with solution of sugar and sulphuric acid.

Purified bile, when calcined, leaves a white ash, composed chiefly of carbonate of soda, with traces of phosphate of soda and common salt. The ash amounts to 12 per cent., of which upwards of 11 consist of carbonate of soda.

It is, therefore, evident that bile is composed of soda united to an organic compound, having the characters of an acid, although a feeble one, and in some respects analogous to the fatty and resinous acids. This compound, which is the whole organic or combustible part of the bile, is called *choleic* or *bilic acid*, and bile is the *choleate of soda.*

Choleic acid is best prepared by making an alcoholic solution of 8 parts of pure bile, and dissolving, with the aid of heat, in this, 1 part of effloresced (monohydrated) oxalic acid. The oxalate of soda separates in crystals. The filtered liquid, diluted with a little water, is digested with carbonate of lead, till all oxalic acid is removed. Any lead that may be dissolved is separated by sulphuretted hydrogen, and the filtered solution evaporated in the water heat. Choleic acid may also be obtained by the action of dry hydrochloric acid gas on a solution of pure bile in absolute alcohol, and by several other processes, of which one may be noticed. Pure bile is precipitated by subacetate of lead, and the precipitate brought with water to the boiling point. Sulphuric acid is now added, drop by drop, until the precipitate has lost its peculiar consistence. The liquid is then filtered, and any dissolved lead separated by sulphuretted hydrogen.

To purify choleic acid it is dissolved in a very small quantity of alcohol, and precipitated by ether, which retains in solution fatty matters. The probable formula of choleic acid is $C_{44}H_{36}NO_{13}=C_{44}H_{35}NO_{12},HO$.

When dried in the water-bath, or in vacuo, over sulphuric acid, choleic acid, if prepared from decolorised bile, is colourless, or nearly so, and has the aspect of gum. It is resinous and friable when dry, but its powder attracts moisture strongly, and becomes agglomerated together. Its solution is distinctly acid to test-paper. The addition of mineral acids causes a separation of choleic acid in oily drops, which are soluble in pure water.

Pure choleic acid, when heated on platinum foil, burns with flame, leaving a voluminous coal which finally burns away without residue of ashes. When choleic acid leaves an alkaline ash, it is because it contains undecomposed bile, choleate of soda; in fact, it may be called acid choleate of soda, a substance which has been described as a distinct ingredient of the bile by several chemists.

Numerous analyses of pure bile (deducting the ashes) and of choleic acid, both prepared in many different ways, by different chemists, as Demarçay, Theyer and Schlosser, Kemp, Enderlin and others, agree so well together that no doubt can be entertained in regard to this point, that the bilic or choleic acid of ox bile is a substance of uniform composition, and that the acid in bile has the same composition as that which is obtained in the separate state by the processes above given.

Further, if the choleate of lead, purified from phosphate, chloride, &c. of lead by solution in alcohol, be acted on by carbonate of soda, choleate of soda (artifi-

cial) is obtained; and this salt, when pure, is found to differ in no one respect from pure bile, or natural choleate of soda, and is, therefore, regenerated bile. Its composition is the same as that of bile.

Choleate of soda has already been described as purified bile.

Acid choleate of soda has been at different times known as *biliary matter*, and as *bilifellic acid with excess of biline.* (Berzelius.) But the biline of this chemist, and also his sugar of bile, are nothing more nor less than either pure bile or choleic acid. Platner has lately obtained the acid choleate of soda crystallized, which is a strong additional argument in favour of the opinion that the bile is a uniform and definite compound of choleic acid, and that all the numerous compounds described by Berzelius and others as constituents of bile, are products of the decomposition of choleic acid. This is a consideration of the utmost importance, with reference to the production of bile in the animal body, to its functions, and in short to chemical physiology.

Choleate of lead (basic). This salt, precipitated by subacetate of lead, has the characters of a plaster, as choleate of soda has those of a soap.

PRODUCTS OF THE DECOMPOSITION OF BILE.

1. *Choloidic acid.* This acid is formed by the action of hydrochloric acid when boiled with bile. It differs from choleic acid in containing no nitrogen. Its formula is $C_{60}H_{50}O_{11}$. Its production is attended with the formation of *taurine.* Choloidic acid is resinous or rather pitchy in aspect, softened by the heat of boiling water, insoluble in water and ether, soluble in alcohol. Probable formula $C_{60}H_{50}O_{11}=C_{60}H_{49}O_{10},HO$.

2. *Taurine,* $C_4NH_7O_{10}$. This substance is found in the liquid which has deposited the choloidic acid. When pure, it forms large prisms, neutral, with a cooling taste, soluble in water. It contains the elements of binoxalate of ammonia and of water: $2C_2O_3+NH_4O+3NO$.

[Professor Redtenbacher of Vienna, has subjected taurine to a new analysis, and has found it to contain 26 per cent. of sulphur. This remarkable result has been quite recently confirmed by Professor Gregory; who by deflagrating a portion of taurine with nitre, dissolving and neutralizing with an acid, obtained by the addition of nitrate of baryta a very copious precipitate of sulphate.]

3. *Cholinic acid.* This is another non-azotized acid, formed when bile is acted on by fusion with caustic alkalies, which disengage the nitrogen as ammonia. It resembles the fatty acids, or rather the resinous acids. It forms large transparent tetrahedra, soluble in alcohol and ether, nearly insoluble in water.

4. *Dyslisine.* This is the name given by Berzelius to a compound formed during the action of hydrochloric acid on bile. It is very sparingly soluble in hot alcohol. (Hence its name, from δυς, difficult, and λυσις, solution). It has a resinous aspect, and the formula $C_{60}H_{46}O_7$, that is, choloidic acid *minus* 4 eq. water.

The *fellic acid* and *cholinic acid* of Berzelius are mixtures of some of the above, or of other products, with unaltered choleic acid. They do not exist ready-formed in bile, according to Theyer and Schlosser.

5. *Cholic acid* (Gmelin). This is an acid, containing nitrogen, formed when choleate of lead is acted on by acetic acid. It forms fine needles of a sweet and pungent taste, very soluble in alcohol and in hot water. Its formula is unknown.

6. *Cholanic acid* is a resinoid acid, found in putrid bile, and very similar to choloidic acid, if not identical with it.

7. *Fellanic acid* accompanies the preceding. It forms transparent prisms, and may possibly be cholinic acid. At all events, it is not established as a distinct compound; but is a product, probably a mixed one, of some of the changes of so complex a substance as choleic acid.

The colouring matter of the bile when dry is reddish-brown, but dissolves in potassa with a yellow colour, becoming greenish-brown in the air. Its solution, mixed with excess of nitric acid, becomes first green, then blue, violet, red, and finally yellow. The same changes of colour are seen in serum, chyle, or urine charged with bile, as in jaundice.

COMPOSITION OF CHOLEIC ACID.

The formula of choleic acid cannot be considered as ascertained with certainty; but the most recent and very elaborate researches of Theyer and Schlosser have led these chemists to adopt the formula $C_{44}H_{36}NO_{13}=C_{44}H_{35}NO_{12}+HO$, for *choleic acid*, and for *choleate of soda*, (bile) $C_{44}H_{35}NO_{12}+NaO$.

When fused with potassa, choleic acid loses 1 eq. ammonia and 2 eq. carbonic acid, $(=C_2NH_3O_4)$ and leaves $C_{42}H_{33}O_9$. This is hydrated cholinic acid, or rather $C_{42}H_{32}O_8+HO$.

When boiled with hydrochloric acid=

3 eq. of choleic acid, hydrated	$=C_{132}H_{108}N_3O_{39}$
take up 13 eq. water	$=H_{13}O_{13}$
In all	$=C_{132}H_{121}N_3O_{52}$
and lose 3 eq. taurine, $3(C_4H_7NO_{10})$	$=C_{12}H_{21}N_3O_{30}$
leaving 2 eq. choloidic acid, $2(C_{60}H_{50}O_{11})$ . . .	$=C_{120}H_{100}O_{22}$

It has already been mentioned that 1 eq. choloidic acid, *minus* 4 eq. water, is equal to $C_{60}H_{46}O_7$, which is the formula of dyslysine.

BILIARY CONCRETIONS.

The calculi or concretions found in the gall-bladder are generally composed of cholesterine, with more or less colouring matter. Sometimes the cholesterine is so pure that alcohol dissolves it entirely, and becomes hardly coloured; at other times, colouring matter alone is found. The former case occurs in the human subject: the latter generally in the ox.

Lithofellic acid is an acid found constituting the mass of certain concretions called *bezoar orientale*, and said to be found in the stomach of certain antelopes; but which are, no doubt, biliary concretions.

Lithofellic acid is fusible, gives off when heated a fragrant vapour, and has, when cut or rubbed in the concretion, the lustre of wax. It dissolves in hot alcohol, and forms brilliant six-sided prisms, insoluble in water. Formula, $C_{42}H_{38}O_8$ (Ettling and Will) $C_{40}H_{35}O_7,HO$ (Wöhler).

Nitric acid converts it into a new acid containing nitrogen. Formula, $C_{40}H_{28}NO_{11}$.

When distilled, lithofellic acid loses 2 eq. water, and yields pyrolithofellic acid, $C_{40}H_{34}O_6$.

BRAIN AND NERVOUS MATTER.

This substance consists of water to the extent of about 80 per cent.; of albuminous matter, 7 per cent.; and of several peculiar fats, among which are cholesterine, and another beautifully crystalline fat, resembling cholesterine, but distinct from it.

Cerebric Acid. This is a fatty acid, peculiar to the nervous matter. It is purified by means of ether, which removes an oily matter, and by crystallization in hot alcobol. It forms white granular crystals, slightly soluble in water, especially when hot, although the greater part is not dissolved but swells up into a gelatinous paste. It melts when heated, and when burned leaves a very acid coal. It contains both nitrogen and phosphorus, which distinguishes it from the ordinary fat acids. Its salts are very insoluble in alcohol, as well as in water.

Oleophosphoric Acid. This acid is dissolved, in combination with soda, by the ether used in purifying cerebric acid; but it is hardly known in a state of purity, being mixed with a neutral oil, *cerebroleine*, with cholesterine, and with cerebric acid, in small quantity. With alkalies it forms soaps, exactly similar to the salts dissolved from brain by ether. When boiled with water or alcohol, it is resolved into *cerebroleine* and phosphoric acid. Of the latter it yields about 2 per cent.

Cerebroleine is purified by cold alcohol, which dissolves the oil, leaving undissolved all cholesterine and cerebric acid. Its composition is the same as that of the oleine of human fat.

The cholesterine of the brain appears to be identical with that of bile. The brain also contains traces of oleic and margaric acids. When it putrefies, the oleophosphoric acid disappears entirely.

The most important point in the chemical history of the brain is that it contains both fat and albumen, the two extremes of the animal products, and substances (cerebric and oleophosphoric acids) of a composition intermediate between that of albumen and that of fat. These bodies, however, appear to contain even a larger proportion of phosphorus than albumen. It is not yet known where the cerebric and oleophosphoric acids are produced: whether in or by a special organ, as the bile is by the liver; or whether in the circulation generally. It will be seen hereafter that the blood does contain traces of cholesterine and other fatty matters; and, indeed, as the blood also contains bile, it may be supposed that the liver does not form the bile but merely separates it from the blood, it having been previously formed. In like manner, even if there should be found an organ connected with the formation or secretion of nervous matter, still the function of that organ might be only to separate cerebric acid, previously formed, from the blood. At all events, we cannot doubt that the very remarkable composition of the acids of the brain has an important relation to the functions of that organ, and that the production of those acids forms an essential part of the vital process going on in the body.

GASTRIC JUICE.

This juice, as extracted from the stomach of executed criminals, is colourless or slightly yellow, turbid, and distinctly acid. It contains free acetic and hydrochloric acids along with chlorides of potassium and sodium.

The property of dissolving or digesting food such as albumen, fibrine, caseine, &c., is owing in part to the presence of free hydrochloric acid, and in part to the presence of part of the lining membrane of the stomach dissolved, and in a state of change. The gastric juice converts into chyme, or digests, albumen, fibrine, &c., out of the body as well as in it, if the temperature of the stomach be kept up; and water acidulated with a trace of hydrochloric acid, and afterwards left for 24 hours in contact with the lining membrane of a stomach, acquires in a very high degree the solvent power of the gastric juice. Water thus prepared, dissolves in 8 to 12 hours, at the temperature of from 86° to 104°, hard-boiled white of egg, &c., which requires 4 days at a temperature of 158° to 176° to be dissolved by water merely acidulated with the same proportion of acid, but not placed in contact with the stomach. This latter fluid, however, dissolves meat better than it does albumen, because the meat supplies some membranous matter in a state of change, by which the solution of the fibrine is finally produced.

All attempts to isolate the supposed principle—*pepsine* as it was called, which is supposed by some to be the solvent of food in the stomach—have failed. The gastric juice has only yielded traces of animal matter, and we have not yet any proof that its solvent action depends on a peculiar compound, and is not rather the effect of a kind of fermentation induced in the food by contact with the particles of the dissolved epithelium, themselves in a state of change, and consequently of motion. Indeed, since this work was commenced, the existence even of free hydrochloric acid in the gastric juice has been denied, and it is very doubtful whether any free acid, such as lactic or formic acid, ever exist in the gastric juice in its normal state. On the whole, then, taking into account the facts of artificial digestion, it appears most probable that digestion is a process analogous to fermentation in the conditions under which it takes place, namely, a certain temperature, and contact with azotized matter in a state of decomposition; but differing from the usual forms of fermentation in its phenomena, no gas being disengaged, and its chief result being the solution of an originally insoluble matter.

SALIVA.

The chief use of the saliva is to assist in digestion, whether by itself containing animal matter in a state of change, or by its remarkable power of inclosing and retaining bubbles of air, the oxygen of which commences the change necessary to digestion, on coming in contact with the food or the stomach and gastric juice. To serve this purpose, the saliva has a very great degree of viscidity, so that it froths up easily, and the froth does not fall readily. It is alkaline, and contains hardly more than 1 or 2 per cent. of solid matter, partly mucus, partly the usual salts, partly a peculiar soluble matter, *ptyaline*. The salts of the saliva are the chlorides of potassium, sodium, and calcium, some potassa, and soda, with a large proportion of bone earth. It appears also to contain a trace of sulphocyanide of potassium: at least it reddens with persalts of iron; and although acetates do this, there is reason to ascribe the effect here to sulphocyanides.

The *pancreatic juice* resembles saliva, but appears to be slightly acid, and contains 8 or 9 per cent. of solid matter, including ptyaline and a matter like caseine. This juice is added to the chyme in its passage through the duodenum, along with the bile and intestinal mucus.

The chyme, after receiving the pancreatic juice, the bile, and mucus, passes along the intestine, where the absorbents or lacteals take up the fluid part, leaving the insoluble portions. The chyle or absorbed fluid is partly conveyed into the abdominal veins, and partly made to pass through numerous glands (in which process it loses its acid reaction, becoming alkaline), from which it proceeds to the thoracic duct, and is then, with the lymph, poured into the vena cava to mix with the venous blood.

In the mean time, the insoluble parts of the chyme are rejected, and accumulate in the large intestines, various gases being disengaged, such as carbonic acid, hydrogen, carburetted hydrogen, nitrogen, and sulphuretted hydrogen.

The solid excrements of man contain very little matter soluble in water, and consist of woody fibre, with fatty, resinous, and waxy substances, and finally the insoluble salts of the food, namely, phosphate of lime and magnesia, with traces of soluble salts, and some silica.

The urine of man contains urea and uric acid, also hippuric acid, and other organic compounds very imperfectly known. It contains also phosphoric acid, magnesia, often ammonia, soda, phosphate of soda, common salt, sulphuric acid or sulphate of soda, in short, the soluble salts of the food, along with sulphuric acid formed by the oxidation of the sulphur of the tissues. The addition of ammonia to urine causes a precipitate of phosphate of lime.

Fresh urine, filtered (to separate mucus) into a perfectly clean vessel, keeps unchanged for weeks or even months; but if in contact with decomposing animal matter, the urea is speedily transformed, by putrefaction, into carbonate of ammonia, while phosphate of lime is precipitated, the urine becoming strongly alkaline.

The urine of the herbivora contains much uric acid, also hippuric acid: that of the carnivora contains more urea, and is strongly acid: uric acid predominates very greatly in the urine of birds, and that of reptiles is nearly pure urate of ammonia.

When benzoic acid is administered internally, it appears in the urine as hippuric acid, which latter acid is generally present in small quantity in urine. The acid reaction of human urine is not owing to lactic acid, as was formerly supposed, but to free uric acid dissolved by the phosphate of soda.

The salts of the urine and of the excrements, being derived directly from the food, vary according to its nature, the soluble inorganic salts of the food being found in the urine, the insoluble salts in the excrements. Thus, the ashes of the food of the carnivora contain no carbonates, but are rich in phosphates, and such also is the case with the salts (or ashes) of their excreta, liquid or solid. In fact, if we know the nature and composition of the ashes of the food, we can tell at once the salts of the urine. In an adult animal, the quantity of salts excreted is precisely equal to that contained in the ingesta, and therefore, by altering the food we can alter at pleasure the nature of the salts in the urine.

As an example, we may here adduce the case of the horse, which animal consumes, in his food, a certain quantity of mineral substances, derived ultimately from the soil:—

THE HORSE.

Consumes of Mineral Substances,			Excretes of Mineral Substances,		
	oz.			oz.	
In 15 lbs. of hay,	18·61	21·49	In the urine	3·51	21·87
In 4·54 lbs. of oats,	2·46		In the fæces	18·36	
In water	0·42				

The above result is one obtained by actual and very careful experiment, and the nature of the salts is found to be the same, as indeed must obviously be the case, as long as the animal does not change its weight. A growing animal will retain the phosphates in part to aid in forming bone, and an old or wasting animal will give out more salts than are taken in.

It is obvious that analyses of urine or excrement are unnecessary if we can examine the food; and that in general they must be useless, since we can never expect the same result twice, unless where the food is not varied.

Guano,* so highly prized as a manure, is the decayed excrement of sea fowls, which was originally, like that of reptiles, and indeed also of birds in general, mixed urine and fæces, the urine being solid or semisolid, and consisting of urate of ammonia. It varies much in the proportions of its ingredients, both because the original excrement must have varied according to the food of the birds in different places, and also because some specimens have not been so long exposed to air and moisture as others, and some are almost fresh. Thus some guano contains upwards of 30 per cent. of uric acid, while in other specimens hardly a trace of that acid is left. The better qualities of guano contain much ammonia, partly free or as carbonate, as proved by its odour, partly combined, as sal-ammoniac, oxalate, urate, and phosphate of ammonia, and phosphate of ammonia and magnesia. They also contain phosphate of soda and phosphate of lime, the latter being derived from the bones of the fish on which the birds fed. There are also found sulphate of potassa and soda, and oxalate of lime, in guano. The remainder is water, and a brown matter like humus.

It is easy to see that guano must act chiefly as a source of ammonia and of earthy and alkaline phosphates, so valuable to growing plants, especially to those cultivated for food; and that its value depends very much on the amount of phosphates it contains. But while the value of guano is unquestionable, let us not overlook the fact, that while we are ransacking the most remote islands for guano, that substance supplies us with nothing but the mineral salts and the ammonia which have formed crops of vegetables and races of animals at some former period, and that it differs in no essential point from the fresh or modern excreta of man and animals nearer home, which excreta, at least those of man, the most valuable of all, we allow to be carried into the sea in quantities which may be measured by the food we consume. In fact we take out of the sea, in the shape of guano, only part of what we throw into it in the contents of our common sewers. These valuable matters, instead of being carefully collected and preserved, as in China, are sent to form the food of sea plants: on these plants animals feed, which animals serve as food to fish. The fish are consumed by sea fowl, and we recover in their excrement a part of what we are constantly throwing away. Another part of what we lose we recover in this country, at a great expense, in the shape of bone-earth, which, however, must be taken from other countries. We shall return to this subject: meanwhile, let us express a hope that Europe will at length follow generally, as in some districts it has done, the rational example set by the eminently practical Chinese, of restoring to the soil, as nearly as possible, in the shape of excreta, what we take from it in our crops and cattle, and thus keeping up its fertility.

URINARY CALCULI.

These are of various kinds, according to the peculiar condition of the urine.

* Found in large quantities covering the surface of many of the South Sea islands, and also upon the southern coast of Africa.

Uric acid calculus is the most frequent, being the usual deposit when the urine is acid. Its origin, as a calculus or deposit, that is, in abnormal quantity, is owing to deficient aeration, much oxygen being required to resolve it into soluble compounds, such as urea, carbonate of ammonia, or even oxalic acid. Hence sedentary habits, highly carbonized food, and indulgence in strong wine, all favour its production: the first by diminishing the supply of oxygen, the two latter causes by seizing on the oxygen to the exclusion of the uric acid. It is easily recognized by the action of potassa, which dissolves it, and forms a solution from which acids precipitate uric acid: or by nitric acid, which dissolves it with effervescence, and yields on evaporation of the solution a deep red stain, becoming purple with potassa. Uric acid calculus is commonly tinged more or less red or brown. When pure it is entirely dissipated before the blowpipe.

Urate of ammonia also occurs, and is distinguished from uric acid by disengaging ammonia when dissolved in potassa.

Phosphate of lime is very frequent when the urine is neutral or alkaline. It is white and earthy, soluble in nitric acid, and precipitated by ammonia. It is fixed in the fire.

Phosphate of ammonia and magnesia is also pretty frequent. It dissolves easily in acetic acid, and when heated gives off ammonia, leaving a solid mass soluble in acids.

Fusible calculus is a mixture of the two preceding. It melts readily before the blowpipe.

Oxalate of lime constitutes the mulberry calculus, and often appears as minute crystals in the urine. When heated, it leaves carbonate of lime; or if heated in a tube with oil of vitriol, it gives off carbonic oxide. It dissolves in acids, and is precipitated by alkalies.

Carbonate of lime occasionally, but very rarely, constitutes a urinary calculus, which is easily recognized by the action of hydrochloric acid, which dissolves it with effervescence, and by a red heat, which leaves quicklime.

Cystic oxide or *cystine*, and *xanthic oxide*, are very rare calculi. Their characters and composition have been given under *Uric Acid*.

LYMPH.

This fluid may be looked on as blood devoid of its colouring matter. When drawn from the vessels, it coagulates like blood, from the separation of fibrine; and the liquid in which the coagulum has formed itself, coagulates, when heated, like the serum of the blood. Human lymph contains about 96 per cent. of water, and variable proportions of albumen, fibrine, and salts, the salts amounting to nearly 2 per cent.

BLOOD.

This important fluid, from which the whole animal body is formed, and by which it is supplied and nourished, is a thick, somewhat viscid, liquid, of a slight saline taste, and a peculiar faint odour. It is deep red and opaque, and has a density of 1·0527 to 1·057.

It is made up of an immense number of *globules* or flattened disks, floating in a limpid yellowish fluid. When drawn, it soon coagulates, forming a trembling jelly, which gradually contracts, expressing a yellowish liquid, *the serum*, which is occasionally turbid, and is always alkaline to test paper, and saline to the taste.

The coagulation consists in the separation of the fibrine previously dissolved, which, owing to some unknown cause, assumes the insoluble state, forming a fine network or jelly, in which the globules are inclosed. If the blood be beat with a rod, the fibrine separates perfectly and adheres to the rod; but it is in the form of white filaments, and the globules remain suspended in the serum, no jelly whatever being formed in this case. Or if the fresh blood be mixed with 8 times its bulk of solution of sulphate of soda, no coagulum is formed, the fibrine remains dissolved, and a sediment is deposited which contains the globules unaltered.

The *red globules* thus prepared may be collected in a filter. Pure water added to them, or to the coagulum of blood, rapidly alters their form, and in fact dissolves them into an opaque liquid. This action of water is thus explained: the globules are formed of a thin, colourless, and transparent coat, inclosing a very soluble colouring matter. They float in a saline liquid, in which there is equlibrium between the contents of the globules and the fluid surrounding them. But when the latter is diluted with water, the equilibrium is disturbed, and endosmosis takes place, by which the contents of the globules acquire so greatly increased a volume, that the globules burst and their contents are dissolved in the water. The torn membranes of the globules may be detected by the microscope.

In saline solutions, the globules do not absorb water any more than in the serum. When collected in a filter, the globules form a red mass of the consistence of honey, consisting of fibrine and albumen, the latter in combination with the colouring matter. In a concentrated solution of chloride of calcium, the globules lose water by exosmosis, and contract in volume. If now placed in pure water, the globules again swell, and burst, forming a jelly which dissolves in water. The solution, on standing, deposits fibrine in white membranous masses, and the supernatant liquid, when boiled, is coagulated, indicating the presence of albumen.

The *colouring matter* of the blood is contained in the globules in combination with albumen, but is unknown in a state of purity. The compound of albumen and colouring matter is of a deep-red colour, becoming bright in contact with air or oxygen, and being rendered nearly black by carbonic and sulphurous acids, sulphuretted hydrogen and sulphurets. Protoxide of nitrogen gives it a purple colour.

The red compound gives 2 per cent. of ashes, of which $\frac{1}{3}$ is peroxide of iron; and iron is uniformly present in red blood, which is the only animal product in which it occurs. This iron cannot be detected in the globules or their contents by the usual tests, but after passing chlorine through the red solution till the colour is destroyed, the iron may be detected by ferrocyanide of potassium.

When the red compound of albumen and colouring matter above mentioned is moistened with oil of vitriol, so gradually as not to become warm, a pasty mass is obtained, which attracts moisture from the air and forms a red jelly. If this be very gradually rubbed up with pure water, it contracts into a dark-red matter, which is surrounded with a colourless or yellowish liquid. This liquid is found to contain all the iron, and the dark matter, when calcined, leaves a white ash, entirely free from iron, if the operation has been well performed. I have repeated this interesting experiment, first devised, I believe, by Sanson, which proves that, although the red compound contains iron, yet the colour does not necessarily depend on that metal; for the colour is altogether uninjured by the com-

plete removal of the iron just described, although the colouring matter actually obtained in this experiment is not the original colouring matter of the blood, but modified.

The *Hematosine* of Lecanu is also a product of decomposition. It is prepared by means of diluted sulphuric acid, alcohol, and ammonia, by a tedious process. It is dark-brown, and forms red solutions with the alkalies, being insoluble in water, alcohol, and ether. It contains part of the iron of the blood, but as some kinds of hematosine contain $\frac{1}{4}$ or $\frac{1}{3}$ more iron than others, while its properties continue the same, it is obvious that the iron does not contribute essentially to those properties, such as the colour. Hematosine contains 6 to 8 per cent. of iron.

But the iron serves an important purpose in the blood; and we have reason to think that it is present in the form of oxide, for sulphuretted hydrogen and soluble sulphurets cause the blood to become first green and then black, owing to the formation of sulphuret of iron—a character indicating either the oxide or some corresponding compound, and not a compound like ferrocyanogen, in which the sulphurets cannot detect the iron. Moreover, we see that oil of vitriol dissolves out oxide of iron; and although alkalies and ferrocyanide of potassium do not detect it, this is owing to the blood being an alkaline liquid, and to the presence of so much animal matter.

It is from the blood that are formed the tissues, the cells, muscular fibre, nervous matter, &c. &c.; and we may, therefore, expect to find some relation between their composition and that of the blood. In fact, flesh, or muscular fibre, as it exists in the body, including vessels, nerves, fat, &c., has exactly the same composition as the blood has on an average of venous and arterial, or a mixture of both. We may, therefore, look on muscular fibre, or animal flesh, as simply blood more highly organized.

In addition to the substances mentioned above, namely, albumen, fibrine, colouring matter, and salts, blood also contains fat, apparently cholesterine, along with fatty acids and a peculiar fat, called *seroline*.

The normal proportions of serum and clot are 87 per cent. of serum to 13 of clot.

1000 parts of human blood contain 869·15 of serum, of which 790·37 are water, 67·8 albumen, and 10·98 of salts and fatty matter: along with 130·85 of clot, containing 125·63 albumen and fibrine of the globules, and 2·27 hematosine (along with a little fatty matter and traces of salts in all three), also 2·95 of fibrine, separate from the globules.

Venous blood contains more water and fewer globules than arterial blood.

The blood contains gases, chiefly carbonic acid and nitrogen, which it gives off in vacuo, or in a current of hydrogen. It is said to contain free oxygen, but this seems very improbable, when we reflect that fibrine absorbs oxygen, transforming it into carbonic acid, and that blood is instantly altered by contact with oxygen. The change from venous to arterial blood, from dark to florid, depends on the presence of oxygen, but also requires the presence of a saline solution. Indeed a similar change of colour takes place in vacuo if the clot of venous blood be there covered with a pretty strong solution of various salts.

THE NUTRITION OF PLANTS AND ANIMALS.

The animal and vegetable kingdoms of nature are connected together in a

beautiful system of mutual dependence, exhibiting a perpetual circulation of certain elements through both, the mineral kingdom being the point of departure and that also where the circulation terminates, to recommence unceasingly,

Plants derive their nourishment exclusively from the mineral world. It is clear that the first plants must have done so, and although the decaying remains of former plants now contribute to vegetation, we shall see that they do so under mineral forms, and not essentially: they promote vegetation, but are not indispensable to it.

The mineral food of plants, then, consists of carbonic acid, water, and ammonia, all of which are obtained from the atmosphere, and of sulphur (sulphuric acid), phosphorus (phosphoric acid), alkalies, earths, salts, and metals, all derived from the soil. Without the aid of the matters derived from the soil, the most abundant supply of carbonic acid, water, and ammonia, is of no use. But if a soil contain these necessary substances, plants will thrive in it, even if they have no carbonic acid or ammonia furnished in the shape of manure beyond the usual atmospheric supply.

During germination, oxygen is absorbed and carbonic acid produced: starch is transformed, probably by the action of disastase, or of an acid developed during germination, into sugar or dextrine, which being soluble, are fitted for being conveyed to all parts of the plant. Meanwhile, the azoto-sulphurized ingredients of the seed also become soluble, and with the sugar, &c., contribute to the formation of new parts, destined to collect food from the air or the soil.

The leaves and roots, as soon as formed, absorb carbonic acid from the air and from the soil. Alkalies are at the same time taken up by the roots, and with their aid the carbonic acid, under the influence of light, is decomposed, its carbon being retained, while its oxygen is given off. At the same time, water, ammonia, sulphuric acid (or a sulphate), and phosphoric acid or phosphates are taken up, and their elements, along with the carbon, give rise to fibrine, albumen, caseine, &c.

It is probable that the fixation of carbon is a gradual process, having successive stages; that the carbonic acid is first reduced or deoxidized so far as to yield oxalic acid; thus $C_2O_4 - O = C_2O_3$; that oxalic acid, with the aid of water, is farther reduced, so as to yield malic or citric or tartaric acid; thus, $C_4O_6 + 2HO = C_4H_2O_8$; and $C_4H_2O_8 - O_4 = C_4H_2O_4$; this last formula doubled is that of anhydrous malic acid, $C_8H_4O_8$. From this and similar compounds, sugar, $C_{12}H_{12}O_{12}$, starch, $C_{12}H_{10}O_{10}$, gum, $C_{12}H_{10}O_{10}$, and woody fibre, $C_{12}H_9O_9$ or $C_{36}H_{22}O_{22}$, are easily deduced, by the addition of the elements of water and the elimination of oxygen. Thus, 3 eq. hydrated malic acid, $C_{24}H_{18}O_{30}$, plus 6HO and minus O_{12}, is equal to 2 eq. dry sugar of grapes, $C_{24}H_{24}O_{24}$. There is good reason to think that the chief function of the alkalies in plants is to promote these metamorphoses.

Water not only acts by its elements, but also as the indispensable solvent through which the whole food of plants, especially that derived from the soil, can alone enter them.

From the above considerations we may draw several useful inferences.

1. The presence of decaying vegetable matter in the soil promotes vegetation by furnishing a steady supply of carbonic acid gas. The proportion of decaying matter or humus must not exceed a certain limit; otherwise there is too much carbonic acid in the air of the soil, and the plant dies in such circumstances.

2. The presence of decaying azoto-sulphurized matter in the soil is very ad-

vantageous, furnishing a supply of ammonia, which is essential to vegetation, and is scantily supplied by the atmosphere.

3. The supply of carbonic acid and of ammonia can only favour the development of vegetation in so far as alkalies and phosphates are supplied by the soil.

4. Since all the azoto-sulphurized principles, albumen, fibrine, caseine, &c., contain sulphur and phosphorus, or rather phosphates, it is evident that seeds and such other parts of plants as contain these principles can only be developed in so far as the soil contains alkaline or earthy phosphates and sulphuric acid or sulphates.

5. If the soil is rich in alkalies, sulphates, and phosphates, and if it also contain soluble silicates, essential to the stem of the grasses and cerealia, it is fertile for all nutritious crops; and such crops will, in that case, derive from the atmosphere alone all the carbon and nitrogen (carbonic acid and ammonia) they require, *provided time be allowed.* The advantage of decaying organic matter, or of manures containing ammonia, in such a soil, consists in shortening the time necessary for the development of the plant; a matter of the last importance in our uncertain climate, but of far less consequence in southern regions, where summer is perhaps twice as long.

6. The ashes of wood, straw, leaves, &c., consisting entirely of matter extracted from the soil by the plants for the purposes of vegetation, must prove a most fertilizing manure; and in all cases, the ashes of any crop must be the best manure for that vegetable.

7. But as the ashes of plants are represented by the excreta of the animals (or the ashes of these excreta) which fed on them, so the excreta of animals fed on turnips, hay, straw, potatoes, &c., must be the best manure for turnips, hay, corn, and potatoes, respectively.

8. When by the addition, to an average soil, of guano, or of bone earth, a very heavy crop is obtained, say of wheat, we are not to expect that a repetition of the same treatment will produce the same effect. We must bear in mind, that the presence of the increased supply of phosphates has enabled the plant to take up a much larger quantity than otherwise it could have done, of alkalies, silicates, and the other necessary minerals. Since we have not added those substances in our guano or bone earth, it may happen that the soil is exhausted of its whole actually available supply of them by that one crop, and that years may elapse before it becomes, in the course of nature, as fertile as before.

9. The only certain rule is this: as far as possible to restore to the soil, in the shape of manure, exactly what it has lost in the crop; if the soil were originally fertile, this will maintain its fertility, which will even be gradually augmented by the action of the weather on the subsoil.

10. With a view to this, every particle of solid or liquid manure, especially human, should be preserved with the utmost care. It is their mineral elements which are the most valuable; and since these have all come from the soil, in preserving them for manure we are only restoring what we have taken away. This has long been systematically done in China, and is also generally practised in the Netherlands; but in this country the waste of valuable manure is lamentable, and is necessarily followed by a slow but certain deterioration of our soil and crops, which we are now endeavouring to remedy by the expensive, precarious, and partial measure of importing bone earth and guano. But guano will, ere long, be exhausted, and when other countries know the real value of their

bone earth, they will not willingly part with it, at all events not except at a very high price.

11. If a soil is not fertile generally, it must be deficient in most of the substances above alluded to; but if it yields good crops of one vegetable and not of others, it must be wanting in the characteristic mineral elements of the latter, which must then be supplied.

12. The ashes of plants being known, the fact that a certain vegetable, cultivated or wild, thrives in any given spot, furnishes us with an analysis of the available or soluble elements of the soil, and enables us to direct our measures of improvement according to the crop we wish to raise.

Although certain bases characterize the ashes of certain plants, as potassa does those of turnips and potatoes, and lime those of peas, beans, &c.; yet in many cases, one base may be substituted for another, as soda for potassa, or magnesia for lime.

It is maintained by some that carbon is introduced into plants, in part, as humus, humic acid, or humate of ammonia, dissolved in the juice, and derived from the mould in the soil. But there is no evidence that fertile soils contain humus in a form soluble in water, and the sap, when first entering the plant, is colourless, while all solutions of humus, &c., are brown. Besides, in forest land, which is not manured, the proportion of humus or of carbon in the soil, instead of diminishing, rather increases, while enormous quantities of carbon are removed annually in the shape of wood. Here, as in the case of the first vegetables, it is plain that all the increase of carbon must be derived from carbonic acid: since, if the plant does absorb humus or humic acid, or humate of ammonia, which is not proved, it must give to the soil as much or more humus, &c., as an excretion from its roots.

It has also been argued by some that plants may obtain their nitrogen, either directly by absorption of the nitrogen of the atmosphere, or by causing that gas to form ammonia, combining with hydrogen derived probably from water, &c.; or, lastly, from the decomposition of nitric acid, which acid is supposed to be formed in the atmosphere by direct combination of its elements. But no evidence has ever been given, either that plants can absorb nitrogen directly, or that they can cause the nitrogen of the atmosphere to combine with hydrogen. As for nitric acid, although traces of it have been observed in thunder-storms, it does not appear to have been formed in sufficiently large quantity;* and if it were, no proof has yet been offered that plants can derive their nitrogen from it. The action of nitrate of potassa, or of soda, as manure, proves nothing, because it may be due to the alkalies alone, and probably is so, since they do not seem to act better than other salts of the same bases. Moreover, many plants, such as tobacco, and sunflower, contain much nitrate in their juices, and therefore appear rather to form nitric acid than to destroy it. On the whole, it appears nearly certain that ammonia is the only source of nitrogen in plants. It is self-evident

* In fact, the proportion of nitric acid thus formed, is so very small as to lead to the conclusion that it is formed only from the ammonia present in the atmosphere. Should this prove true, as is highly probable, then ammonia will be the source of all the nitrogen of plants, even if part of the nitrogen should be derived from nitric acid. It is generally admitted that in nitrification the whole of the nitric acid is derived from the oxidation of ammonia.

that the atmosphere must contain ammonia, derived from the putrefaction of animal and vegetable matter, and also that, however small the *proportion*, the absolute quantity in the air at any one time must be sufficient for the supply of the vegetable world, and through it of the animal world, since all animals and vegetables ultimately putrefy, giving off their nitrogen in the form of ammonia. It is quite easy to detect ammonia in rain water, by which means it is conveyed to the roots or leaves of plants; and it has also been proved that the juices of plants contain abundance of ammonia.

The nutritious principles, albumen, fibrine, and caseine, are formed by plants alone from ammonia, sugar (or gum, starch, &c.), sulphates, and phosphates. They pass into the body of animals, and are there converted into blood. As they cannot be formed nor exist without the phosphates, so by their means the animal body is supplied with bone earth, and with the soluble phosphates necessary for the other tissues.

In the animal body, the leading and characteristic action is the absorption of oxygen and the oxidation of the tissues: that is, of carbon and hydrogen, so that animals take up oxygen, and give out carbonic acid. This is the reverse of what occurs in plants, which absorb carbonic acid, and give out oxygen.

In the lungs, oxygen enters the blood, and is carried, apparently, by the agency of a compound of iron, to every part of the body. The oxidation of the effete, or worn-out tissues, which have meanwhile been replaced by the blood, takes place in the capillaries, and is, in all probability, the source of the animal heat. The final result of this oxidation is the production of a large quantity of carbonic acid and water, which are given off by the lungs and skin.

Health, in the animal body, consists in the due balance or equilibrium between the oxidizing, or destructive agency of the atmosphere, and the process of nutrition by which the other is compensated.

Since the nutritious, or blood-forming elements of food, have the same composition as the albumen, fibrine, &c. of the tissues—indeed, in the case of animal food, are identical with them—we may consider the process of oxidation and destruction, either as affecting the food directly, or, what is more probable, those portions of the tissues which, having performed their functions, are to be thrown off. But we must not forget that in the herbivora, a great part of the combustion which yields the animal heat is carried on at the expense of those parts of the food which cannot form blood: namely, sugar, starch, or gum, fat, &c.

The fat of the animal body is, at all events in great part, derived from the non-azotized elements of the food when these are in excess, and oxygen is deficient. In these circumstances, the deficiency of oxygen is supplied at the expense of sugar, starch, or gum, which, by losing oxygen, gives rise to fat; for the proportions of carbon and hydrogen in sugar, &c., and in fat, are exactly the same, that of oxygen alone being different. Hence the conditions favourable to the formation of fat are, abundant farinaceous food, and rest, that is, defective aeration, as is seen in stall-fed animals, and in the fattening of geese fed on maize and deprived of the power of locomotion. The formation of wax, a species of fat, from sugar by the bee, is another example.

It is very interesting to remark that the composition of the chief elements of the bile, and the urine, bears a close and simple relation to that of the blood or tissues. If the formula of urate of ammonia be added to half that of choleic acid, the sum represents the composition of blood or flesh, or differs from it only by a very little water and oxygen, substances which take part in almost every chemi-

cal change in the body, water being always present in the body, and oxygen being introduced through the lungs. Now, urate of ammonia is the urine of birds and reptiles, and represents that of the mammalia; for uric acid, when further oxidized, yields urea and carbonic acid, while urea with the elements of water, passes, as in putrefying urine, into carbonate of ammonia. As for the bile, the other product of the destruction of the tissues (at least this is its origin in the carnivora, and partly in the herbivora), it undergoes resorption in the intestines, and is finally oxidized into carbonic acid and water, thus contributing to keep up the animal heat. The final result is, that the tissues, which may be supposed, with the addition of a little oxygen, to be resolved into choleic acid (bile) and urate of ammonia (urine), are entirely converted, or oxidized into carbonic acid, water, and ammonia.

The food of animals may thus be said to be literally burned in their bodies, and this, as in the case of other combustibles, for the purpose of producing heat. The gaseous product of the combustion are sent off through the skin and lungs, while the smoke, soot, and ashes are represented by the excrements and urine.

The food required by animals must bear a certain relation to the waste of matter, and to the heat required. Thus, a hard-working man, in whom the change of matter is rapid, requires much more food (blood, or proteine compounds) than a sedentary person; and in cold climates, a much larger quantity of food rich in carbon, especially fat, blubber, and similar matters, is necessary than in warm climates, where, indeed, such food excites invincible repugnance. Any misproportion in the amount or nature of the food has a tendency to induce disease. Thus, Europeans, who often eat and drink as at home when they go to tropical countries, pay the penalty of their ignorance in the very frequent liver complaints observed among them. For the same reason, hepatic disease is more frequent during summer than during winter.

After death, the animal body is slowly, but surely, resolved into the ultimate products of putrefaction, namely, carbonic acid, water, and ammonia, which rise into the atmosphere, having completed the circuit through which we have traced them, in order to recommence it by once more contributing to the growth of plants on which animals will again feed.

The bones of dead animals are also by degrees restored to the soil from which they were taken; and nothing is finally lost. Even the rich manure which we recklessly cast into the sea, serves as manure for sea plants, on which are fed fish, which, in their turn, become food for sea fowl, the excrements of these last, in the shape of guano, returning to fertilize the fields from which their mineral elements were perhaps originally taken.

It is evident that there must be a balance or equilibrium kept up between the animal and vegetable worlds. For the atmosphere in which both live does not, at least perceptibly, change in its composition. There is no appearance either of increase or diminution, in the proportion of oxygen, or in that of carbonic acid. Yet we know that animal life tends directly and powerfully to increase the proportion of carbonic acid, and to diminish that of oxygen, while the tendency of vegetable life is exactly the reverse. Hence if, in any quarter, population or animal life extends, a corresponding augmentation of vegetable life must somewhere be the result; or if, by cultivation, the amount of vegetation in any quarter is increased, the inevitable consequence must be an extension of animal life, otherwise the air would become richer in oxygen. As both carbonic acid and ammonia are partly supplied to the atmosphere from the earth itself, not

merely from the decay of organic matter at the surface, but from great depths, as for example in hot springs, so we may conceive the absolute amount of carbonic acid and ammonia on the surface of the earth and in the atmosphere to be somewhat greater now than some thousand years ago. If not, then the increase of animal and vegetable life in one part of the globe must necessarily cause a diminution of one or both in some other part, since, at all events, the atmosphere becomes neither richer nor poorer in carbonic acid and ammonia. Should an addition of these substances be made, they would instantly be appropriated by the vegetable kingdom, and converted into food for animals, of which an additional number would soon be produced by the increased supply of food; and thus the aggregate amount of animal and vegetable life might be increased, while the composition of the atmosphere remained unchanged, the vegetable world exactly balancing the animal, because each produces the food of the other, as the necessary result of its own existence.

Such is a very brief and general sketch of the chemistry of animal and vegetable life, as far as we are at all acquainted with it. It is only within a very short time that this department of science has been properly cultivated, but the results already obtained are most important and highly encouraging. When we reflect that the processes by which carbonic acid, water, ammonia, and the salts of the soil are made to assume the forms, first of vegetable and then of animal tissues, as well as those by which these tissues are again resolved into the elements of which they were formed, are, and must be, purely chemical processes of combination and decomposition, governed by the laws of chemistry as ascertained by observation and experiment, but modified by the vital force, it is easy to see that from the assiduous study of the chemical changes going on in plants and animals, in health and in disease, we may confidently expect the most beneficial results. All that has hitherto been done has only pointed out the path to be followed in order to obtain valuable and permanent results. But enough has been done to satisfy all who are acquainted with the actual state of physiology that, henceforth, it is chiefly to chemistry that we must look for the extension and improvement of physiological science. Already a knowledge of chemistry is admitted to be indispensable to the physiologist, and before long this opinion will be so far acted on that no one who is not well versed in chemistry will venture to write on physiological subjects.

PART IV.

ANALYTICAL CHEMISTRY.

MINERAL ANALYSIS.*

THE subject of Chemical Analysis is so comprehensive, that to give more than a general outline of this branch of practical chemistry would be inconsistent with the plan of these Elements.

The few following observations are thrown into four sections: the first of which comprises general instructions concerning the manipulations necessary in analytical processes; the second contains a few directions for the performance of qualitative analysis; the third, for the quantitative estimation of the most common constituents of minerals; and the fourth, for the analysis of mineral waters.

An analysis may have for its object the estimation of the weights of either the ultimate or proximate constituents of a substance; that is, of the ultimate elements of which a body is composed, without reference to the manner in which those elements are arranged; or of the proximate compounds which form, by their immediate union, the substance in question. In inorganic analysis, the proximate constituents are the substances generally sought; and the elementary composition of these being already known, the ultimate elements of which the substance analyzed is composed are also ascertained.

Before the composition of a substance can be determined quantitatively, it is necessary to have the nature or quality of the constituents accurately determined: and thus a chemical analysis is resolved into two distinct examinations; first, for the nature of the constituents, which is called the *qualitative analysis;* and second, for the respective weights of these constituents, which is the *quantitative analysis.* As an example, it might be ascertained merely that crystallized sulphate of magnesia is composed of magnesia, sulphuric acid, and water; or that the salt mentioned contains, in 100 parts, 16·7 of magnesia, 32·4 of sulphuric acid, and 50·9 of water.

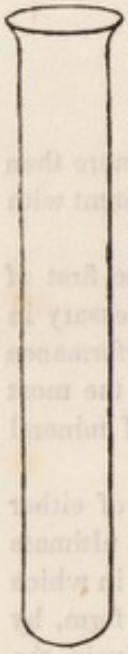
* From the pen of E. A. Parnell, author of the Elements of Chemical Analysis, &c.

SECTION I.

MANIPULATIONS IN ANALYTICAL PROCESSES.

In qualitative analysis the presence of any particular ingredient in the substance under examination is generally ascertained by mixing a test-liquid with the solution of the substance operated on, and observing, by the occurrence or non-occurrence of a precipitate, whether the suspected substance is present or not. If the test-liquid which is added produces no precipitate with any other substance whatever than that sought for, this simple operation is conclusive as to the presence or absence of the suspected body: but if, on the other hand, a test-liquid can produce a precipitate with more than a single substance, it becomes necessary to apply other tests before positive evidence of the presence of a particular substance is obtained. For example, if a neutral solution is to be tested for sulphuric acid, a solution of nitrate of baryta or chloride of barium is added to the liquid: the absence of a precipitate in that case is conclusive as to the absence of sulphuric acid. But if a precipitate occurs, it might be produced in a neutral solution by other acids besides sulphuric; namely, boracic, phosphoric, hydrofluoric, arsenic, and a few others. The precipitates, however, which are produced by these acids in solutions of salts of baryta, are soluble in nitric or hydrochloric acid, while sulphate of baryta is not. If either nitric or hydrochloric acid, therefore, is added to the mixture with the barytic salt containing the precipitate, the solubility or insolubility of the latter shows whether or not it contains sulphuric acid.

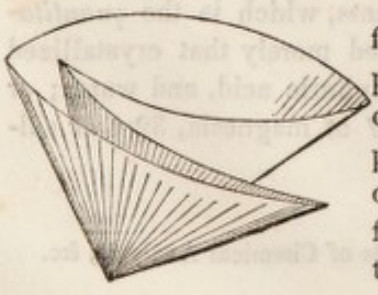
Fig. 1.



The mixture of the solution of the substance to be analyzed with the test-liquid may be made either in a conical wine-glass, or in a test-tube. The wine-glass should be provided with a spout for the convenience of pouring liquids into a tube or flask, with the view of applying heat; an operation frequently necessary. Instead of a wine-glass, a test-tube (*fig.* 1) is frequently employed, which possesses the advantage of allowing heat to be applied without transferring the liquid to another vessel. A convenient size for ordinary use is four inches in length, by two-thirds of an inch in diameter.

When it is necessary to examine the action of a test liquid on a precipitate obtained in the course of testing, that may sometimes be done in the same glass or tube; but often it is requisite to separate the precipitate wholly from the solution, which is accomplished by *filtration*. The process of filtering is one on which the success of analyses, both qualitative and quantitative, but especially of the latter, materially depends.

Fig. 2.



Filtration is effected by means of a paper filter, formed by doubling twice a circular piece of filtering paper, so as to form a quadrant, and then opening one of the folds, as shown in *fig.* 2. The filter is supported in a glass funnel, which is itself held in any convenient manner; a vessel being placed below the funnel to recive the filtered liquid. Before pouring the turbid liquor on it, the filter should be wetted

with a few drops of distilled water, which has the effect of swelling the fibres of the paper, without which precaution the liquid would not at first pass through clear. As the loss of a single drop of the liquid might, in quantitative analysis, render the operation worthless, its transference to a filter must always be directed by a glass rod, applied to the lip of the containing vessel, and held nearly perpendicular, with its extremity very near, but not touching the filter (see *fig.* 3).

Fig. 3.



In quantitative analysis, the substance, whose weight is to be determined, is generally separated from the solution in which it is contained, by precipitation in a solid form, which is capable of being weighed, and which contains a known proportion of the substance to be estimated. If, for example, the amount of copper contained in a solution is required, that metal is precipitated in the state of oxide by caustic potassa: when washed and perfectly dried, the precipitate oxide may be weighed; and as it is known to contain, in 100 parts, 79·83 parts of copper, the quantity of the metal contained in any amount of the oxide is readily learned by calculation.

The whole of the precipitate having been collected on the filter, as already described, it is washed with pure distilled water until every trace of the original liquid is removed, and then dried on the filter in a hot drying-stove at any temperature below 212°. When dry, if the substance is not decomposed by being heated to redness, it is held, being still on the filter, immediately over a porcelain or platinum crucible, the weight of which when empty is already known; the paper is set on fire, and the precipitate is allowed to fall into the crucible, together with the ash of the filter. The crucible should be placed over a piece of highly-glazed coloured paper, to retain any particles of the precipitate which may fall on it, and which are afterwards carefully put into the crucible. After the matter has been heated to redness, if the filter has been completely burned, the crucible with its contents is weighed, and the weight of the empty crucible is deducted from the entire weight. The ash of the filter also, the average weight of which is determined by previous experiments, must be subtracted from the weight of the heated mass.

In those cases in which the precipitate to be weighed cannot be heated to redness without suffering decomposition, the filter in which it is to be collected should be carefully dried, and introduced, folded, into a platinum crucible, which is then covered and weighed. The necessity of weighing the filter in a closed vessel arises from the circumstance, that dry paper rapidly absorbs hygrometric moisture from the air, which would prevent its weight being accurately determined, if placed, open, on the pan of the balance. Having weighed the filter and crucible, the filtration may be conducted as usual; and, when the precipitate is washed and dried in the drying-stove, the filter containing it is folded, introduced into the same crucible, and weighed. After the first weighing, the crucible should be uncovered and exposed to as high a temperature as paper will support without charring, to discover if any loss in weight is experienced through the escape of water, from the mass not having been previously rendered per-

fectly dry. The weight of the empty crucible and filter, deducted from the entire weight, gives that of the precipitate.

Such is an outline of the methods usually followed in determining the weights of the ingredients of compound bodies. There are, however, many cases in which a different course is pursued, varying according to the nature of the substances and the degree of nicety required; but a description of these would improperly encroach on space which is devoted to another purpose.



SECTION II.

QUALITATIVE ANALYSIS.

In analytical processes the first object is to obtain the substance in a proper state of solution. If soluble in water, that fluid is preferred to every other menstruum; but, if not, an acid, or any convenient solvent may be employed. In many instances, however, the substance to be analyzed resists the action even of acids, and in that case the following method is adopted:—The compound is first crushed by means of a hammer or steel mortar, and is afterwards reduced to an impalpable powder in a mortar of agate; it is then intimately mixed with three, four, or more times its weight of potassa, soda, baryta, or their carbonates; and, lastly, the mixture is exposed in a crucible of silver or platinum to a strong heat. During the operation, the alkali combines with one or more of the constituents of the mineral; and, consequently, its elements being disunited, it no longer resists the action of the acids.

The following brief observations on qualitative analysis have reference to the discovery of the constituents of a salt soluble in water, and which consists of a single acid and a single base, to ascertain which two distinct operations are in general necessary.

The bases, for the detection of which means are pointed out, are the following:

1. Oxide of copper.
2. Oxide of lead.
3. Protoxide of tin.
4. Peroxide of tin.
5. Peroxide of iron.
6. Protoxide of iron.
7. Oxide of chromium.
8. Protoxide of manganese.
9. Oxide of zinc.
10. Alumina.
11. Magnesia.
12. Lime.
13. Strontia.
14. Baryta.
15. Ammonia.
16. Potassa.
17. Soda.

1. A portion of the solution of the substance under examination is strongly acidified by a mineral acid, and saturated with sulphuretted hydrogen gas, or else is mixed with water strongly impregnated with that gas.

If a black or brownish precipitate is formed, the base is one of the first three in the list, namely, oxide of copper, oxide of lead, or protoxide of tin. To dis-

tinguish these three bases, add to other portions of the original solution the three following special tests:

(*a.*)—Ammonia; which gives an intense blue liquid with solutions of *copper*.

(*b.*)—Iodide of potassium; which produces a fine yellow precipitate of iodide in solutions of *lead*.

(*c.*)—Bichloride of mercury; which gives with solutions of *proto-salts of tin*, first a white precipitate of calomel, and afterwards a black precipitate of metallic mercury. The solution supposed to contain a proto-salt of tin should be added gradually to the bichloride of mercury, and not in the reverse order, so that the bichloride is at first in large excess.

If a yellow or milky-white precipitate is produced by sulphuretted hydrogen, the base may be either peroxide of tin or peroxide of iron: the precipitate in the former case being the bisulphuret of tin; and in the latter, free sulphur, proceeding from the decomposition of sulphuretted hydrogen by peroxide of iron, the latter being at the same time reduced to the state of protoxide.

(*a.*)—If the base is *peroxide of iron*, yellow prussiate of potassa gives, with the original solution, a deep blue precipitate of Prussian blue.

(*b.*)—If the base is peroxide of tin caustic potassa produces in the original solution a white precipitate of peroxide of tin, which may redissolve in an excess of the alkali, and which, if collected and ignited strongly, becomes insoluble in acids.

2. If sulphuretted hydrogen produces no precipitate in the acid solution of the substance, render another portion of the solution alkaline by ammonia, and then add an excess of hydrosulphuret of ammonia.

(*a.*)—The formation of a black precipitate by hydrosulphuret of ammonia indicates the presence of *protoxide of iron*, in which case the original solution gives a deep blue precipitate with the red prussiate of potassa.

(*b.*)—If hydrosulphuret of ammonia gives a dull green precipitate, the base is *oxide of chromium*. If the precipitate is collected and fused with a bead of microcosmic salt before the blowpipe, the bead is found to be red while hot, but green when cold.

(*c.*)—If hydrosulphuret of ammonia gives a flesh-colour precipitate, the base is *manganese*; in which case a solution of chloride of lime produces in the original solution a dark brown precipitate of hydrated peroxide of manganese.

(*d.*)—If hydrosulphuret of ammonia gives a white precipitate, the base may be either *oxide of zinc* or *alumina*. These substances may be distinguished by ammonia which added to the original solution produces a white precipitate in both cases; but oxide of zinc is soluble in excess of the alkali, while alumina is not.

3. If neither sulphuretted hydrogen nor hydrosulphuret of ammonia produces a precipitate, add a solution of carbonate of soda to another portion of the solution. The occurrence of a precipitate shows, that the base is either magnesia, lime, strontia, or baryta, to distinguish which the original solution is tested in the following manner:

(*a.*)—If a solution of oxalate of ammonia gives no precipitate, the base is *magnesia*.

(*b.*)—If oxalate of ammonia gives a precipitate, but dilute sulphate of soda does not, the base is *lime*.

(*c.*)—If dilute sulphate of soda gives a precipitate, the base is either *baryta*

or *strontia*. These earths may be distinguished by a solution of hyposulphite of soda, which precipitates baryta, but not strontia.

4. If carbonate of soda gives no precipitate, the base is then one of the three alkalies, ammonia, potassa, or soda.

(*a.*)—If *ammonia*, the odour of that alkali is recognized on adding caustic potassa.

(*b.*)—A strong solution of tartaric acid gives a white crystalline precipitate of bitartrate of potassa if the base is *potassa*.

(*c.*)—Salts of *soda* are best distinguished by the yellow colour which they communicate to the flame of alcohol.

The base of the salt having been discovered, the examination for the acid may then be performed. The acids, for the detection of which instructions are given, are the following.

1. Carbonic.
2. Sulphurous.
3. Hydrosulphuric.
4. Hydriodic.
5. Sulphuric.
6. Phosphoric.
7. Arsenic.
8. Boracic.
9. Hydrofluoric.
10. Iodic.
11. Hydrochloric.
12. Nitric.
13. Chloric.

1. To the saturated solution of the salt in water, if soluble, or to the dry salt, if insoluble, dilute sulphuric acid is applied. The effervescence of a gas may proceed from carbonic, sulphurous, or hydrosulphuric acid. A development of free iodine may proceed from hydriodic acid.

Carbonic.—The gas evolved is inodorous, and, when passed through lime-water, causes a white precipitate, which dissolves on transmitting an excess of the gas.

Sulphurous.—The evolved gas has the pungent smell of burning sulphur.

Hydrosulphuric.—The gas has a fœtid odour, and the solution of the substance produces a black precipitate in salts of lead.

Hydriodic.—To detect hydriodic acid (iodides), mix the solution of the substance with a little solution of starch, and allow chlorine gas to fall on the surface of the liquid: the blue iodide of starch is formed. (See page 237.)

2. If sulphuric acid produces neither effervescence nor development of free iodine, add a solution of nitrate of baryta to the neutral solution of the substance. The acids which may be precipitated thereby are the following:

Sulphuric.—The precipitate is insoluble in pure hydrochloric acid.

Hydrofluoric.—The powdered substance, gently heated with oil of vitriol in a platinum crucible, evolves a vapour which corrodes glass.

Arsenic (*Arsenious*).—Sulphuretted hydrogen gas, passed through the solution of the substance, strongly acidified by hydrochloric acid, gives a yellow precipitate of sulphuret of arsenic. This precipitate being dried, mixed with a black flux and heated to redness in a glass tube, gives a sublimate of metallic arsenic.

Phosphoric.—Nitrate of silver gives, with the neutral solution of the substance, a yellow precipitate of phosphate of silver, soluble in nitric acid.

Boracic.—If the dry substance is moistened with oil of vitriol, and then alcohol added, the latter burns with a green flame.

Iodic.—Sulphurous acid developes free iodine in the original solution; the presence of iodine may then be ascertained by its action on starch.

3. If dilute sulphuric acid produces no effervescence, and nitrate of barytes no precipitate, the acid may be hydrochloric, hydriodic, nitric, or chloric; in which case add nitrate of silver to the solution of the substance.

(*a.*)—If a yellow precipitate is formed, the acid may be *hydriodic*, which is known by the insolubility of the precipitate (iodide of silver) in solution of ammonia.

(*b.*)—If a white curdy precipitate is formed by nitrate of silver, the acid is *hydrochloric*; in which case the precipitate (chloride of silver) is readily dissolved by ammonia.

4. If nitrate of silver produces no precipitate, the acid is either *nitric* or *chloric*. To detect nitric, add the dry substance under examination to a mixture of protosulphate of iron and oil of vitriol; immediately, or on heating, a brown colour is developed, owing to nitric oxide.

To detect chloric acid, add oil of vitriol to the dry salt: peroxide of chlorine is evolved, and the liquid bleaches vegetable colours.

QUALITATIVE ANALYSIS OF GASES.

Table exhibiting the distinctive properties of oxygen, nitrogen, protoxide of nitrogen, deutoxide of nitrogen, hydrogen, carbonic oxide, and carbonic acid.

(From Graham's Elements of Chemistry.)

GASES.

Soluble in water	Carbonic acid	Solution disturbs lime water.
	Protoxide of nitrogen	Does not.
Support combustion	Oxygen	
	Protoxide of nitrogen	
Combustible	Carbonic oxide	Product of combustion disturbs lime-water.
	Hydrogen	Does not.
Extinguish combustion	Deutoxide of nitrogen	Forms brown fumes with oxygen.
	Nitrogen	Does not.

SECTION III.

QUANTITATIVE ANALYSIS.

The following observations on Quantitative analysis relate chiefly to those earthy minerals with which the beginner usually commences his labours, the most common constituents of which are silica, alumina, iron, manganese, lime, magnesia, potassa, soda, and carbonic and sulphuric acids.

Analysis of marble, or carbonate of lime.—The quantity of carbonic acid contained in marble and all other carbonates which are soluble in hydrochloric or sulphuric acid in the cold may be determined by the following simple method:—A known weight of the powdered substance is introduced into a flask similar to

Fig. 4.



that represented in *fig.* 4. The flask should be thin at the bottom to allow of the application of heat, and have the capacity of three or four ounces of water. It is fitted with a cork, which has a perforation to admit a small bent tube; and the latter is connected by means of another cork with a somewhat larger tube, *a*, containing fragments of dry chloride of calcium. The extremity *b* of this tube is drawn out so as to be capillary. The small tube *c* within the flask, sealed at one end, is intended to hold hydrochloric or sulphuric acid to decompose the carbonate, and is of such length that it will not fall flat on the bottom of the flask, but rest against the side at an angle of about 45° with the bottom; so that, on inclining the flask, all the acid contained in this tube can be made to flow out. The apparatus being arranged, the weighed carbonate is introduced into the empty flask with about half an ounce of water; the small tube *c*, containing sufficient hydrochloric or sulphuric acid to decompose the carbonate, is then introduced, taking care that no acid comes in contact with the carbonate, and the flask is closed by the cork attached to the chloride of calcium tube *a*. The whole apparatus is now weighed; after which the flask is inclined, in order that a little of the acid in the tube *c* may flow out and come in contact with the carbonate, which is repeated until the latter is completely decomposed. As the evolved carbonic acid gas is dried in passing through the chloride of calcium tube *a*, nothing else than this gas escapes, and the loss in weight of the apparatus at the close of the experiment is the weight of the carbonic acid required; but, as the flask is then full of carbonic acid gas, which is considerably heavier than air, it should not be weighed in its present state. To get rid of the remaining carbonic acid, the flask is very gently heated, so as to fill it with aqueous vapour, and thus drive out the gas, the steam itself not proceeding further than the chloride of calcium tube. On the condensation of the steam, air enters the flask, which, when cold, is in the same condition as it was when weighed before the decomposition of the carbonate, excepting only in the loss of carbonic acid.

Separation of Lime and Magnesia.—The more common kinds of carbonate of lime frequently contain traces of siliceous and aluminous earths, in consequence of which they are not completely dissolved in dilute hydrochloric acid. A very frequent source of impurity is carbonate of magnesia, which is often present in such quantity that it forms a peculiar compound called *Magnesian limestone.* The analysis of this substance, so far as respects carbonic acid, is the same as that of marble. The separation of the two earths may be conveniently effected in the following manner:—The solution of the mineral in muriatic acid is evaporated to perfect dryness in a flat dish or *capsule* of porcelain; and, after redissolving the residuum in a moderate quantity of distilled water, a solution of oxalate of ammonia is added as long as a precipitate ensues. The oxalate of lime is then allowed to subside, collected on a filter, dried, and decomposed by a red heat; and after moistening the resulting carbonate with a strong solution of carbonate of ammonia, in order to supply any particles of quicklime with carbonic acid, it should be dried, heated to low redness, and regarded as pure carbonate of lime. To the filtered liquid, containing the magnesia, a mixture of pure ammonia and phosphate of soda is added, when the magnesia is precipitated in the form of the ammoniaco-phosphate. Of this precipitate, heated to redness, 100 parts, according to Stromeyer, correspond to 37 of pure magnesia.

The precipitation of magnesia by means of phosphoric acid and ammonia, though extremely accurate when properly performed, requires several precautions. The liquid should be cold, and either neutral or alkaline. The precipitate is dissolved with great ease by most of the acids; and Stromeyer has remarked, that some of it is held in solution by carbonic acid, whether free, or in union with an alkali. The absence of carbonic acid should therefore always be insured, prior to the precipitation, by heating the solution to 212°, acidulating at the same time by hydrochloric acid, should an alkaline carbonate be present. Berzelius has also observed, that, in washing the ammoniaco-magnesian phosphate on a filter, a portion of the salt is dissolved as soon as the saline matter of the solution is nearly all removed; that is to say, it is dissolved by pure water. Hence the edulcoration should be completed by water, which is rendered slightly saline by hydrochlorate of ammonia.

Earthy Sulphates.—The most abundant of the earthy sulphates is that of lime, the analysis of which is easily effected. By boiling it for fifteen or twenty minutes with a solution of twice its weight of carbonate of soda, double decomposition ensues; and the carbonate of lime, after being collected on a filter and washed with hot water, is heated to low redness and weighed.

Of the dry carbonate, fifty parts correspond to twenty-eight of lime. The alkaline solution is acidulated with hydrochloric acid, and the sulphuric acid thrown down by chloride of barium. From the sulphate of baryta, collected and dried at a red heat, the quantity of acid may easily be estimated.

The method of analyzing the sulphates of strontia and baryta is somewhat different. As these salts are difficult of decomposition in the moist way, the following process is adopted:—The sulphate, in fine powder, is mixed with three times its weight of carbonate of soda, and the mixture is heated to redness in a platinum crucible for the space of an hour. The ignited mass is then digested in hot water, and the insoluble earthy carbonate collected on a filter. The other parts of the process are the same as the foregoing.

Mode of analyzing Compounds of Silica, Alumina, and Iron.—Minerals, thus constituted, are decomposed by an alkaline carbonate, at a red heat, in the same manner as sulphate of baryta. The mixture is afterwards digested in dilute hydrochloric acid, by which means all the ingredients of the mineral, if the decomposition is complete, are dissolved. The solution is next evaporated to dryness, the heat being carefully regulated towards the close of the process, in order to prevent any of the chloride of iron, the volatility of which is considerable, from being dissipated in vapour. By this operation, the silica, though previously held in solution by the acid, is entirely deprived of its solubility; so that, on digesting the dry mass in water acidulated with hydrochloric acid, the alumina and iron are taken up, and the silica is left in a state of purity. The siliceous earth, after subsiding, is collected on a filter, carefully edulcorated, heated to redness, and weighed.

To the clear liquid, containing peroxide of iron and alumina, a solution of pure potassa is added in moderate excess; so as not only to throw down those oxides, but to redissolve the alumina. The peroxide of iron is then collected on a filter, edulcorated carefully until the washings cease to have an alkaline reaction, and is well dried and ignited, as described at page 771. This operation, however, should be done with care; since any adhering particles of paper, or other combustible matter, would bring the iron into the state of black oxide, a change which is known to have occurred by the iron being attracted by a magnet.

To procure the alumina, the liquid in which it is dissolved is boiled with hydrochloric of ammonia, when chloride of potassium is formed, the volatile alkali is dissipated in vapour, and the alumina subsides. As soon as the solution is thus rendered neutral, the hydrous alumina is collected on a filter, dried by exposure to a white heat, and quickly weighed after removal from the fire.

Separation of Iron and Manganese.—A compound of these metals or their oxides may be dissolved in hydrochloric acid. If the iron is in a large proportion compared with the manganese, the following process may be adopted with advantage:—To the cold solution, considerably diluted with water, and acidulated with hydrochloric acid, carbonate of soda is gradually added, and the liquid is briskly stirred with a glass rod during the effervescence, in order that it may become highly charged with carbonic acid. By neutralizing the solution in this manner, it at length attains a point at which the peroxide of iron is entirely deposited, leaving the liquid colourless; while the manganese, by aid of the free carbonic acid, is kept in solution. The iron, after subsiding, is collected on a filter, and its quantity determined in the usual manner. The filtered liquor is then boiled with an excess of carbonate of soda; and the precipitated carbonate of manganese is collected, heated to full redness in an open crucible, by which it is converted into the red oxide, and weighed. This method is one of some delicacy; but in skilful hands it affords a very accurate result. It may also be employed for separating iron from magnesia and lime as well as from manganese.

But if the proportion of iron is small compared with that of manganese, the best mode of separating it is by succinate of ammonia or soda, prepared by neutralizing a solution of succinic acid with either of those alkalies. That this process should succeed, it is necessary that the iron be wholly in the state of peroxide, that the solution be exactly neutral, which may easily be insured by the cautious use of ammonia, and that the reddish-brown coloured succinate of peroxide of iron be washed with cold water. When the precipitate is washed clean, solution of ammonia should be poured on it to separate succinic acid, and the remaining peroxide of iron may be dried, cautiously ignited, and weighed. From the filtered liquid the manganese may be precipitated at a boiling temperature by carbonate of soda, and its quantity determined in the way above mentioned. The benzoate may be substituted for succinate of ammonia in the preceding process.

It may be stated as a general rule, that, whenever it is intended to precipitate iron by means of the alkalies, the succinates, or benzoates, it is essential that this metal be in the maximum of oxidation. It is easily brought into this state by digestion with a little nitric acid.

Separation of Manganese from Lime and Magnesia.—If the quantity of the former is proportionally small, it is precipitated as a sulphuret by hydrosulphuret of ammonia or sulphuret of potassium. The sulphuret is then dissolved in hydrochloric acid, and the manganese thrown down as usual by means of an alkali. But if the manganese is the chief ingredient, the best method is to precipitate it at once, together with the two earths, by a fixed alkaline carbonate at a boiling temperature. The precipitate, after being exposed to a low red heat and weighed, is put into cold water acidulated with a drop or two of nitric acid, when the lime and magnesia will be slowly dissolved with effervescence. Should a trace of the manganese be likewise taken up, it may easily be thrown down by hydrosulphuret of ammonia.

Stromeyer has recommended a very elegant and still better process for removing small quantities of manganese from lime and magnesia. The solution is acidulated with nitric or hydrochloric acid; bicarbonate of soda is gradually added in very slight excess, stirring after each addition, that the liquid may be charged with carbonic acid; and a solution of chlorine, or a current of the gas, is introduced. The protoxide of manganese is converted by the chlorine into the insoluble hydrated peroxide, while any traces of lime or magnesia, which might otherwise fall, are retained in solution by means of carbonic acid. A solution of chloride of soda or lime is in fact our most delicate test for small quantities of manganese.

Mode of analyzing an Earthy Mineral containing Silica, Iron, Alumina, Manganese, Lime, and Magnesia.—The mineral, reduced to fine powder, is ignited with three or four times its weight of carbonate of potassa or soda, the mass is taken up in dilute hydrochloric acid, and the silica separated in the way already described. To the solution, thus freed from silica and duly acidulated, carbonate of soda, or still better the bicarbonate, is gradually added, so as to charge the liquid with carbonic acid, as in the analysis of iron and manganese. In this manner the iron and alumina are alone precipitated, substances which may be separated from each other by means of pure potassa (page 777). The manganese, lime, and magnesia, may then be determined by the processes above described.

SECTION IV.

ANALYSIS OF MINERAL WATERS.

Rain water collected in clean vessels in the country, or freshly fallen snow when melted, affords the purest kind of water which can be procured without having recourse to distillation. The water obtained from these sources, however, is not absolutely pure, but contains a portion of carbonic acid and air, absorbed from the atmosphere. It is remarkable that this air is very rich in oxygen. That procured from snow water by boiling was found by Gay-Lussac and Humboldt to contain 34·8, and that from rain water 32 per cent. of oxygen gas. From the powerfully solvent properties of water, this fluid no sooner reaches the ground and percolates through the soil, than it dissolves some of the substances which it meets with in its passage. Under common circumstances it takes up so small a quantity of foreign matter, that its sensible properties are not materially affected, and in this state it gives rise to *spring*, *well*, and *river* water. Sometimes, on the contrary, it becomes so strongly impregnated with saline and other substances, that it acquires a peculiar flavour, and is thus rendered unfit for domestic uses. It is then known by the name of *mineral water*.

The composition of spring water is dependent on the nature of the soil through which it flows. If it has filtered through primitive strata, such as quartz rock, granite, and the like, it is in general very pure; but, if it meets with limestone or gypsum in its passage, a portion of these salts is dissolved, and communicates

the property called *hardness*. Hard water is characterized by decomposing soap, the lime of the former yielding insoluble compounds with the margaric and oleic acids of the latter. If this defect is owing to the presence of carbonate of lime, it is easily remedied by boiling, when free carbonic acid is expelled, and the insoluble carbonate of lime subsides. If sulphate of lime is present, the addition of a little carbonate of soda, by precipitating the lime, converts the hard into soft water. Besides these ingredients, the chlorides of calcium and sodium are frequently contained in spring water.

Spring water, in consequence of its saline impregnation, is frequently unfit for chemical purposes, and on these occasions distilled water is employed. Distillation may be performed on a small scale by means of a retort, in the body of which water is made to boil, while the condensed vapour is received in a glass flask, called a *recipient*, which is adapted to its beak or open extremity. This process is more conveniently conducted, however, by means of a still.

The different kinds of mineral water may be conveniently arranged for the purpose of description in the six divisions of acidulous, alkaline, chalybeate, sulphureous, saline, and siliceous springs.

1. Acidulous springs, of which those of Seltzer, Spa, Pyrmont, and Carlsbad are the most celebrated, commonly owe their acidity to the presence of free carbonic acid, in consequence of the escape of which they sparkle when poured from one vessel into another. Such carbonated waters communicate a red tint to litmus paper before, but not after being boiled, and the redness disappears on exposure to the air. Mixed with a sufficient quantity of lime water, they become turbid from the deposition of carbonate of lime. They frequently contain carbonate of lime, magnesia, and protoxide of iron, in consequence of the facility with which these salts are dissolved by water charged with carbonic acid.

2. Alkaline waters are such as contain a free or carbonated alkali, and consequently, either in their natural state, or when concentrated by evaporation, possess an alkaline reaction.

These springs are rare. The best instance I have met with is in water collected at the Furnas, St. Michael's, Azores, and sent to the Royal Society of Edinburgh by Lord Napier. These springs contain carbonate of soda and carbonic acid, and are almost entirely free from earthy substances. Of five different kinds of these waters which I examined, the greater part also contained protoxide of iron, hydrosulphuric acid, and chloride of sodium.

3. Chalybeate waters are characterized by a strong styptic inky taste, and by striking a black colour with the infusion of gall-nuts. The iron is sometimes combined with hydrochloric or sulphuric acid; but most frequently it is in the form of protocarbonate, held in solution by free carbonic acid. On exposure to the air, the protoxide is oxidized, and the hydrated peroxide subsides, causing the ochreous deposit so commonly observed in the vicinity of chalybeate springs.

To ascertain the quantity of iron contained in a mineral water, a known weight of it is concentrated by evaporation, and the iron is brought to the state of peroxide by means of nitric acid. The peroxide is then precipitated by ammonia and weighed; and, if lime and magnesia are present, it may be separated from those earths by the process described in the last section.

Chalybeate waters are by no means uncommon; but the most noted in Britain are those of Tunbridge, Cheltenham, and Brighton. The Bath water also contains a small quantity of iron.

4. Sulphureous waters, of which the springs of Aix-la-Chapelle, Harrowgate, and Moffat afford examples, contain hydrosulphuric acid, and are easily recognized by their odour, and by causing a brown precipitate with a salt of lead or silver. The gas is readily expelled by boiling, and its quantity may be roughly estimated by transmitting it through a solution of pure chloride of mercury, and weighing the sulphuret which is generated.

5. Those mineral springs are called saline, the character of which is caused by saline compounds. The salts which are most frequently contained in these waters are the sulphates and carbonates of lime, magnesia, and soda, and the chlorides of calcium, magnesium, and sodium. Potassa sometimes exists in them, and Berzelius has found lithia in the spring of Carlsbad. It has lately been discovered, that the presence of hydriodic acid in small quantity is not unfrequent. As examples of saline water may be enumerated the springs of Epsom, Cheltenham, Bath, Bristol, Barèges, Buxton, Pitcaithly, and Toeplitz.

The first object in examining a saline spring is to determine the nature of its ingredients. Hydrochloric acid is detected by nitrate of oxide of silver, and sulphuric acid by chloride of barium; and, if an alkaline carbonate be present, the precipitate occasioned by either of these tests will contain a carbonate of oxide of silver or baryta. The presence of lime and magnesia may be discovered, the former by oxalate of ammonia, and the latter by phosphate of ammonia. Potassa is known by the action of chloride of platinum (page 295). To detect soda, the water should be evaporated to dryness, the deliquescent salts removed by alcohol, and the matter insoluble in that menstruum, taken up by a small quantity of water, and be allowed to crystallize by spontaneous evaporation. The salt of soda may then be recognized by the rich yellow colour which it communicates to flame (page 300). If the presence of hydriodic acid be suspected, the solution is brought to dryness, the soluble parts dissolved in two or three drachms of a cold solution of starch, and strong sulphuric acid gradually added (page 239.)

Having thus ascertained the nature of the saline ingredients, their quantity may be determined by evaporating a pint of water to dryness, heating to low redness, and weighing the residue. In order to make an exact analysis, a given quantity of the mineral water is concentrated in an evaporating basin as far as can be done without causing either precipitation or crystallization, and the residual liquid is divided into two equal parts. From one portion the sulphuric and carbonic acids are thrown down by nitrate of baryta, and, after collecting the precipitate on a filter, the hydrochloric acid is precipitated by nitrate of oxide of silver. The mixed sulphate and carbonate is exposed to a low red heat, and weighed; and the carbonate is then dissolved by dilute hydrochloric acid, and its quantity determined by weighing the sulphate. The chloride of silver, of which 143·42 parts correspond to 36·42 of hydrochloric acid, is fused in a platinum spoon or crucible, in order to render it quite free from moisture. To the other half of the concentrated mineral water, oxalate of ammonia is added for the purpose of precipitating the lime; and the magnesia is afterwards thrown down as the ammoniaco-phosphate, by means of ammonia and phosphoric acid. Having thus determined the weight of each of the fixed ingredients excepting the soda, the loss is of course the quantity of that alkali required.

The individual constituents of the water being known, it remains to determine the state in which they were originally combined. In a mineral water containing sulphuric and hydrochloric acids, lime, and soda, it is obvious that three cases are possible. The liquid may contain sulphate of lime and chloride of

sodium, or chloride of calcium and sulphate of soda; or each acid may be distributed between both the bases. It was at one time supposed that the lime must be in combination with sulphuric acid, because the sulphate of that earth is left when the water is evaporated to dryness. This, however, by no means follows. In whatever state the lime may exist in the original spring, gypsum will be generated as soon as the concentration reaches that degree at which sulphate of lime cannot be held in solution. The late Dr. Murray, who treated this question with much sagacity, observes that some mineral waters, which contain the four principles above mentioned, possess higher medicinal virtues than can be justly ascribed to the presence of sulphate of lime. He advances the opinion, that alkaline bases are united in mineral waters with those acids with which they form the most soluble compounds, and that the insoluble salts obtained by evaporation are merely products. He therefore proposes to arrange the substances determined by analysis according to this supposition. (Edin. Phil. Trans. vii.) To this practice there is no objection; but it is probable that each acid is rather distributed between several bases than combined exclusively with either.

Sea water may be regarded as one of the saline mineral waters. Its taste is disagreeably bitter and saline, and its fixed constituents amount to about three per cent. Its specific gravity varies from 1·0269 to 1·0285; and it freezes at about 28·5° F. A very complete analysis of the water of the English Channel was executed a few years ago by Dr. Schweitzer, of Brighton, the results of which are subjoined:—

	Grains.
Water	964·74372
Chloride of Sodium	27·05948
Chloride of Potassium	0·76552
Chloride of Magnesium	3·66658
Bromide of Magnesium	0·02929
Sulphate of Magnesia	2·29578
Sulphate of Lime	1·40662
Carbonate of Lime	0·03301
	1000·00000

The water of the Dead Sea has a far stronger saline impregnation than sea water, containing one-fourth of its weight of solid matter. It has a peculiarly bitter, saline, and pungent taste, and its specific gravity is 1·211. According to the analysis of Marcet, 100 parts of it are composed of—muriate of magnesia 10·246, muriate of soda 10·36, muriate of lime 3·92, and sulphate of lime 0·054. In the river Jordan, which flows into the Dead Sea, Marcet discovered the same principles as in the lake itself.

6. Siliceous waters are very rare, and in those hitherto discovered the silica appears to have been dissolved by means of soda. The most remarkable of these are the boiling springs of the Geyser and Rykum, in Iceland, a gallon of which, according to the analysis of Black, contains the following substances; (Edinburgh Philos. Trans. iii. 95:)

	Geyser.	Rykum.
Soda	5·56	3·0
Alumina	2·80	0·29
Silica	31·50	21·83
Muriate of Soda	14·42	16·96
Sulphate of Soda	8·57	7·53

The hot springs of Pinnarkoon and Loorgootha in India are analogous to the foregoing. A gallon of the water yields about 24 grains of solid matter; and the saline contents, sent to Dr. Brewster by Mr. P. Breton, was found to consist of 21·5 per cent of silica, 19 of chloride of sodium, 19 of sulphate of soda, 19 of carbonate of soda, pure soda 5, and 15·5 of water. (Edinburgh Journal of Science, No. xvii. p. 97.)

It is remarkable that nitrogen gas very generally occurs in hot springs. It was found by Longchamp in various hot springs of France, and a similar observation has been made by Dr. Daubeny. Its source is clearly referable to atmospheric air contained in water, which air has been deprived of its oxygen by chemical changes in the interior of the earth.

ORGANIC ANALYSIS.

The Analysis of organic substances has for its object, to determine the nature and quantity of the elements which compose them; and is one of the most important departments of analytical chemistry. The method employed by the earlier chemists to obtain a knowledge of the chemical composition of organic bodies had not the smallest resemblance to the organic analysis of the present day. They subjected these bodies to destructive distillation, and judged of the difference in their composition by the products thus obtained.

It is only within the last thirty years that this department of chemistry has been cultivated on scientific principles; and all the lately proposed methods differ from one another only in the way in which those principles are carried out.

The simplest method of ascertaining the component parts of an organic compound, would seem to be, to endeavour to obtain its elements in a separate form; but it is obvious that, if we can obtain, instead of the elements in the free state, compounds, of known composition, of those elements with others, we can determine their quantity with equal accuracy.

Most vegetable substances contain carbon, hydrogen, and oxygen; a small number contain, besides these elements, nitrogen. Of these four simple substances, nitrogen alone can be obtained in a state of purity from organic compounds; but if all the carbon be converted into carbonic acid, and all the hydrogen into water, we can then calculate, with the utmost precision, the quantity of carbon and hydrogen from that of the carbonic acid and water. Even if the elements of organic substances could be separated from them in a state of purity, we should be forced to give the preference, in analysis, to the indirect method now employed, on account of its superior accuracy.

The method, then, which we employ to procure an exact knowledge of the composition of an organic compound, consists in the conversion of a known weight of the substance into carbonic acid and water; and the success of th

analysis only depends on the apparatus employed, in so far as that apparatus must allow us to collect these products without loss, and to determine their weight. When the compound contains nitrogen, this element is collected in the separate state; and the oxygen is always ascertained indirectly.

Gay-Lussac, and Thénard, the first chemists who executed organic analysis, used chlorate of potassa for the combustion of organic bodies. The substance to be analyzed was mixed with it, the mixture formed into pellets, and introduced in small quantities into a red hot tube of glass, placed vertically. The gaseous matter disengaged by the combustion was, by means of a lateral tube, collected in a jar over mercury.

The whole gas was accurately measured, and, the corrections for barometer and thermometer being made, caustic potassa was introduced into the jar. After all the carbonic acid was absorbed, there remained either pure oxygen gas, or a mixture of oxygen and nitrogen. The relative quantity of the latter was ascertained by the eudiometer. The knowledge of the weight of the substance, and that of the chlorate of potassa; of the quantity of carbonic acid formed, and of the oxygen remaining, supplied all the data necessary for calculating the composition of the body analyzed. That portion of the oxygen of the chlorate of potassa which had disappeared, had of course formed water with the hydrogen of the substance.

The only objection to the apparatus of Gay-Lussac and Thénard was, that it made the accuracy of the results to depend too much on the dexterity of the operator. The analysis of substances containing nitrogen, moreover, by means of chlorate of potassa, was not very exact, in consequence of the formation of nitrous acid; and it was obviously impossible to employ that salt in the analysis of liquid or volatile substances.

Berzelius endeavoured, and successfully, to render this method more convenient in the execution, and to diminish the number of calculations required. He placed the tube of combustion in the horizontal position, and collected the water formed. He also employed the chlorate of potassa, mixed with a large quantity of common salt, by which means the combustion was rendered slower, and at the same time the advantage was gained of introducing the whole of the substance to be burned, into the tube, before commencing the combustion.

These forms of apparatus, which were applicable only to a very limited class of bodies, were greatly and most essentially improved by the use of oxide of copper, instead of chlorate of potassa; which was first proposed by Gay-Lussac, and employed by him in the analysis of uric acid. At present, the superiority of oxide of copper is so generally admitted, that chlorate of potassa is no longer employed. Besides oxide of copper, chromate of lead has of late been used in the analysis of many substances containing a large proportion of carbon.

De Saussure and Prout have both described forms of apparatus for the analysis of organic bodies, which differ from the original one of Gay-Lussac and Thénard, only in their form, and in the substitution of oxygen gas, and oxide of copper, instead of chlorate of potassa.

The apparatus of Prout is so arranged that the substance to be analyzed is burned, either alone, or mixed with some other body, in a known volume of oxygen gas, and the volume of the gas, after the combustion, is compared with its original bulk. This method is founded on the well known fact, that, when carbon is burned in oxygen gas, the carbonic acid gas produced, occupies exactly the same space as the oxygen consumed, and consequently does not alter its

volume: as also, that when hydrogen unites with oxygen, for each volume of hydrogen, half a volume of oxygen disappears by the condensation of the water which is formed.

Consequently, if the substance to be burned consists of carbon, hydrogen, and oxygen, there are only three cases possible. Either the volume of the oxygen is unaltered; and in this case, the substance contains oxygen and hydrogen in the proportions necessary to form water; or the volume of the oxygen is diminished, or it is increased. In the latter cases, the body either contains more hydrogen, and consequently less oxygen than is sufficient to form water; or there is less hydrogen, and consequently more oxygen than is required for that purpose. The diminution or increase in the volume of the oxygen can be exactly measured, and, the quantity of the carbonic acid produced being ascertained, it is easy to express the composition of the substance in numbers.

But this apparatus cannot be applied to the anlysis of substances containing nitrogen, nor to that of many other bodies. Lately, Brunner has constructed an apparatus on a similar principle. All these forms of apparatus, however, have been employed by their inventors alone; and as they have no advantage over the one now commonly employed, it is unnecessary to describe them minutely in this place.

GENERAL METHOD OF PROCEEDING.

In the next section we shall describe the instruments and processes which are at present employed by the majority of chemists for organic analysis; and we shall here prefix some general remarks on the operations which occur in such analyses.

It will be observed, that all the parts of the apparatus used for this purpose are extremely simple, and for their employment require no especial dexterity. The essential conditions for performing a good analysis are, the greatest accuracy in weighing, and the strictest conscientiousness in the execution of all the preparatory steps of the process. Let us not flatter ourselves that we can obtain an accurate result, if any thing be neglected that can secure it. All the time and labour we bestow are thrown away, if we omit any one of the precautions which are recommended.

It is obvious that the object in view may be obtained by various means, and that the methods described in the following pages are susceptible of improvement: but all the so-called improvements, hitherto proposed, only prove that their authors are ignorant of the most general principles of what a method ought to be.

Every chemist will be able, when he has acquired some experience in organic analysis, to alter the apparatus here described, in particular cases, according to his ideas, and to adapt it to the object he has in view; but it would be going too far to consider this deviation in a special case, as an improvement of the process in general, and to recommend it as such.

There is within the human mind an innate desire for improvement—hence the efforts to improve what we possess, and to discover new means of attaining the desired object. But we frequently commit the error of neglecting to test the utility of the known methods, or even to make ourselves familiar with them. We begin by deviating from the customary path; and if our efforts be crowned with success, the satisfaction we experience in the discovery we have made,

leads us to overlook the circuitous nature of the route we have followed, and the difficulties we have had to overcome, which we should not have encountered on the beaten path.

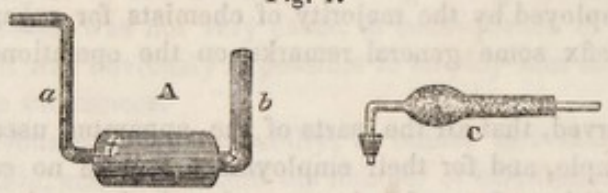
In what follows, we hold to the rule of Berzelius, the most experienced chemist of our own, and probably also of all times; and of two equally good methods, we prefer the simple to the complicated one.

The first problem to be solved, in performing an organic analysis, is, to procure the substance to be analyzed in the highest degree of purity. No means should be neglected to satisfy ourselves of the absence of foreign matters. The matter being supposed pure, we must attend to the difficulty of determining the weight of the body to be analyzed, as one source of uncertainty in the results of the analysis, and of the variations occurring in different analyses of the same substance. All organic bodies greedily absorb moisture from the air, and thus become heavier. They must, therefore, first be deprived of all hygrometric moisture, and then weighed in such a manner that it is hardly possible for them to attract moisture during the time they are in the scale.

When we consider that an excess of water, to the amount of $\frac{7}{100}$ths or $\frac{8}{100}$ths of a grain is equivalent to a loss of twice as much carbonic acid, we cannot surely bestow too much attention on the accurate determination of the weight of the substance to be analyzed.

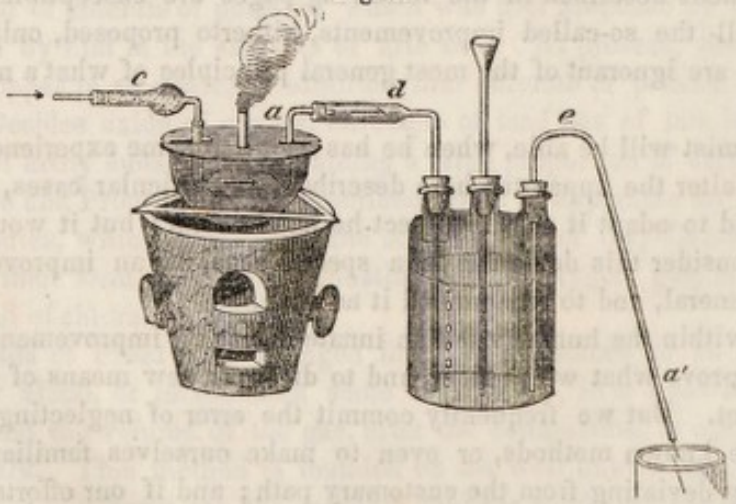
This object may be obtained in various ways. The following apparatus gives complete security on this head. It consists of the tube A, *fig.* 1. The wide

Fig. 1.



part below is about half an inch in diameter: the tubes *a* and *b* are barometer tubes, one of one-sixth, the other of one-fourth of an inch in diameter. The substance is introduced by the wide tube *b*, which is then connected by means of a cork with the tube C, containing fused chloride of calcium. The opposite tube *a* is joined with the tube *d*, *fig.* 2: *e* is an ordinary syphon. The tube *d* is about an inch shorter than *a'*, the external limb of the syphon.

Fig. 2.



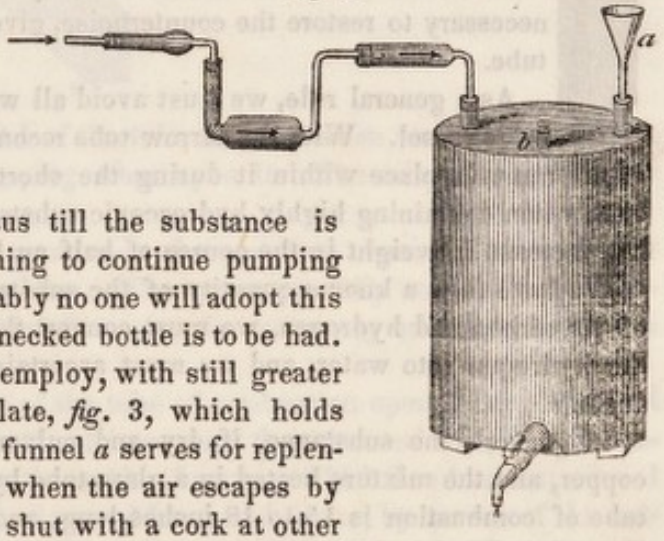
By means of this arrangement we can produce a perfectly uniform discharge of water from the three necked bottle; and since the air, which replaces the

water, must enter the bottle by the tube *d*, we can instantly perceive whether all the joinings are air-tight.

The bottle is filled with water; and, of course, when this water is made to flow out by the syphon, the continual current of dry air thus produced entirely removes all moisture from the substance.

The horizontal part of the drying apparatus is placed in a sand bath, a water bath, a bath of solution of chloride of calcium, &c., according to the temperature to which we wish to expose the substance. If we wish to determine the amount of water, the apparatus A is weighed, first empty, and then with the substance. It is then placed in the water bath, &c., and a stream of dry air is made to pass through it, as long as water condenses in the tube *d*. By weighing occasionally, we ascertain if it loses weight. When the weight becomes constant, a small portion of the substance is shaken out of *b* into a long and perfectly dry test tube, which is then heated by a spirit lamp or sand bath—of course to a degree insufficient to produce decomposition. If no trace of water bedew the side of the test tube, we may be certain that the substance is perfectly dry: if any moisture appear, the water bath must be replaced by one of a solution of salt, or of chloride of calcium, and the operation repeated at a higher temperature.

Fig. 3.

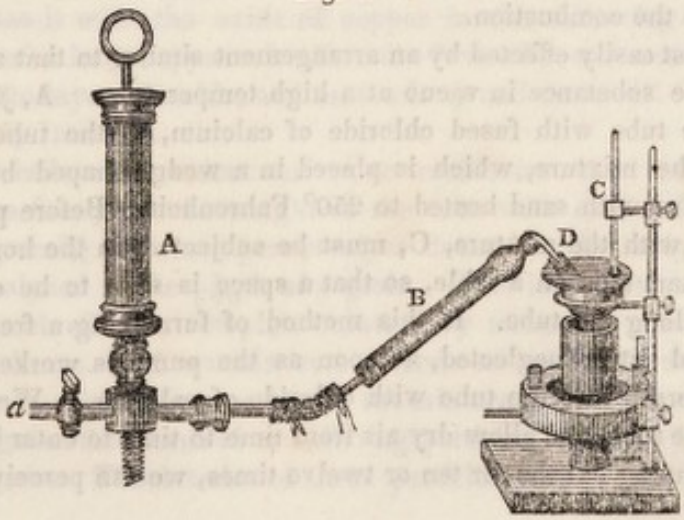


Mitscherlich employs a similar apparatus for drying organic substances; but instead of the bottle and syphon he connects with the tube *a* a hand air-pump, by means of which he draws air through the apparatus till the substance is dry. But it is extremely fatiguing to continue pumping from four to six hours; and probably no one will adopt this method, except where no three necked bottle is to be had.

Instead of the bottle we may employ, with still greater convenience, a vessel of tin plate, *fig.* 3, which holds about 4 gallons of water. The funnel *a* serves for replenishing the vessel when empty, when the air escapes by the middle opening *b*, which is shut with a cork at other times. The flow of water is regulated by the stopcock.

When the substance retains water with great obstinacy, it is dried in vacuo at a high temperature. The cut *fig.* 4, exhibits this arrangement. A is a small

Fig. 4.



hand air-pump, B a tube with chloride of calcium, D a strong cylindrical tube, sealed at one end, which contains the substance to be dried. C is a thermometer. The tube D is placed in an iron or copper vessel with a concentrated solution of chloride of zinc, and heated nearly to the temperature at which the substance is decomposed. After the moist air has been removed by the air-pump, air is from time to time admitted into the apparatus by the stopcock *a*; this air by passing through the chloride of calcium, is each time deprived of all hygrometic moisture, so that in a very short time, at most in a few minutes, we can by this means remove all water, whether hygrometric water or water of crystallization.

Fig. 5.



When the substance is dry, a certain quantity of it must be weighed out for analysis. This is best done in a small narrow tube, open at the end. The cut, *fig.* 5, exhibits it of the actual size. This tube may either be placed horizontally on the scale, or set in a conical roll of tin-plate, which rests with its broad end on the pan of the balance. A stand of tin-plate is also very convenient. The tube being weighed, a portion of the substance is introduced and the tube is weighed again. The increase of weight gives the quantity of the substance.

We may also counterpoise the tube with the substance, empty the tube, and return it into the scale with any adhering particles. The weight necessary to restore the counterpoise, gives the quantity taken out of the tube.

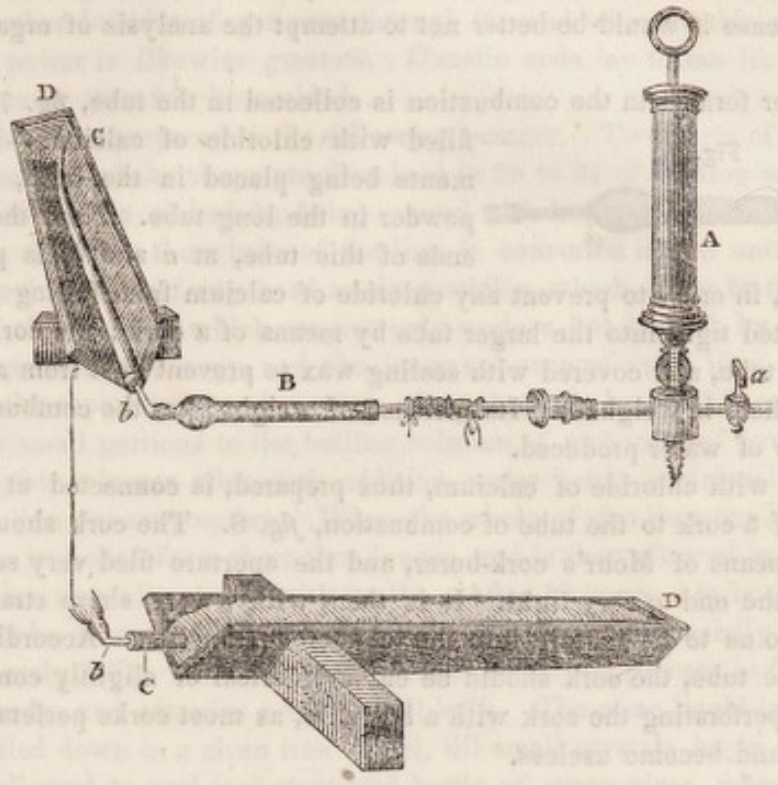
As a general rule, we must avoid all weighing in a watch-glass, or any wide vessel. With the narrow tube recommended, no appreciable change of air can take place within it during the short time it lies on the scale; and even when containing highly hydroscopic substances, this simple apparatus does not increase in weight in the course of half an hour.

We have now a known quantity of the substance. To determine the amount of its carbon and hydrogen, we must convert the carbon into carbonic acid, and the hydrogen into water, and we must ascertain the weight of both these products.

In general, the substance, if dry and pulverizable, is mixed with oxide of copper, and the mixture heated in a glass-tube by means of a charcoal fire. The tube of combustion is 15 to 18 inches long, and $\frac{1}{3}$ to $\frac{1}{2}$ of an inch in diameter. The closed end is drawn out to a point, which is bent obliquely upwards, and sealed. During the mixture of the substance with the oxide of copper, both bodies attract moisture from the air. This water would increase the weight of that formed in the combustion, and must be most carefully and completely removed before the combustion.

This is most easily effected by an arrangement similar to that above described, for drying the substance in vacuo at a high temperature. A, *fig.* 6, is the air-pump, B the tube with fused chloride of calcium, C the tube of combustion filled with the mixture, which is placed in a wedge-shaped box of wood, D, and surrounded with sand heated to 250° Fahrenheit. Before pumping out the air, the tube with the mixture, C, must be subjected, in the horizonal position, to several smart taps on a table, so that a space is seen to be empty above the mixture all along the tube. If this method of furnishing a free exit to the air when pumped out be neglected, as soon as the pump is worked, a part of the mixture is forced into the tube with chloride of calcium. We now produce a vacuum in the tube, and allow dry air from time to time to enter by the stopcock, and after pumping out the air ten or twelve times, we can perceive no further de-

Fig. 6.



position of moisture at the point *b* of the tube B, even when we surround it with cotton wool, and cool it by dropping ether upon it. The mixture may then be considered dry.

The substance is mixed with pure oxide of copper in a clean and warm mortar of Wedgewood's ware or porcelain. The more carefully we divide the substance and mix it with the oxide of copper, the more easy and complete is the combustion.

Mitscherlich leaves the point of the tube of combustion open, joins either end with a tube containing chloride of calcium, with the other end of which is connected a pair of bellows; heats the oxide of copper, which has been introduced so as to fill half of the tube, to a low red heat, and forces, by means of the bellows, dry air over the hot oxide. The point is then sealed up. He now counterpoises the tube with the oxide of copper, and shakes out of the tube in which it has been dried, a portion of the substance to be analyzed, into the counterpoise tube. The increase of weight gives the quantity of the substance.

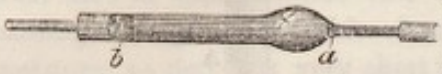
He now mixes it with the oxide of copper in the following manner:—He bends one end of a long copper wire into the form of a corkscrew, screws this half way into the layer of oxide, and moves it up and down till the mixture appears sufficiently intimate.

This method is less convenient and more troublesome than the one above described. In the first place the weight of the tube with oxide of copper, (from 1800 to 2100 grains,) does not permit us to determine the weight of the substance to be analyzed to the $\frac{1}{500}$th of a grain. This is a source of uncertainty. Again, we cannot effect a complete mixture by means of a corkscrew wire. This is easily shown. If we mix some starch as intimately as possible with oxide of copper in this manner, and press the mixture in a mortar with the pestle, we easily recognize the unmixed or cohering particles of starch by a number of round white spots. The interior of these particles would only be charred, not

burned. Berzelius recommends this method, when we have not an air-pump; but in that case it would be better not to attempt the analysis of organic bodies at all.

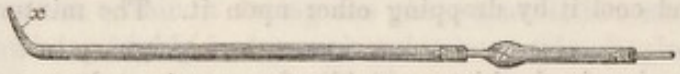
The water formed in the combustion is collected in the tube, *fig.* 7, which is filled with chloride of calcium—large fragments being placed in the bulb, and coarse powder in the long tube. Near the two open ends of this tube, at *a* and *b*, is put a little cotton-wool, in order to prevent any chloride of calcium from falling out. The tube *b* is fitted tight into the larger tube by means of a cork: the cork is cut off close to the tube, and covered with sealing wax to prevent dust from adhering to it. The whole is weighed. Its increase of weight after the combustion gives the quantity of water produced.

Fig. 7.



The tube with chloride of calcium, thus prepared, is connected at the end *a* by means of a cork to the tube of combustion, *fig.* 8. The cork should be perforated by means of Mohr's cork-borer, and the aperture filed very smooth, and made to fit the end *a* very tight. It is then, with a very sharp straight-edged knife, cut so as to fit closely into the tube of combustion. According to the shape of the tube, the cork should be cut cylindrical or slightly conical. We must avoid perforating the cork with a hot wire, as most corks perforated in this way crack, and become useless.

Fig. 8.



The carbonic acid formed in the combustion is collected in the apparatus, *fig.* 9. which is filled with a solution of caustic potassa, in such a manner that a small bubble of air remains in each bulb. This apparatus consists of a glass tube, in which 5 bulbs are blown. To fill this apparatus with caustic ley, one end must be connected by a cork with the sucker, *fig.* 10; the other end of the potassa apparatus is then dipped into a glass containing the ley, and the liquid drawn by suction with the mouth into the apparatus. The end of the tube which has been moistened with the ley is to be dried externally, and internally: the latter is easily accomplished by means of a small roll of filtering paper. The apparatus, when quite dry and clean, is weighed, and then joined to the tube with the chloride of calcium by means of a small tube of caoutchouc.

Fig. 9.

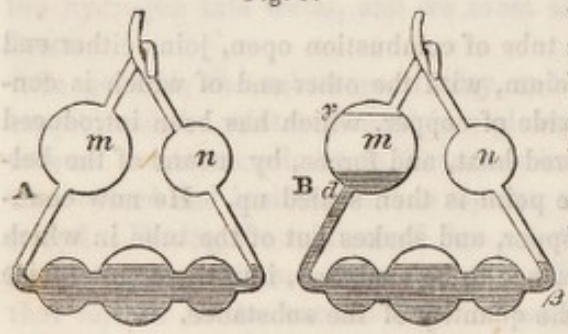
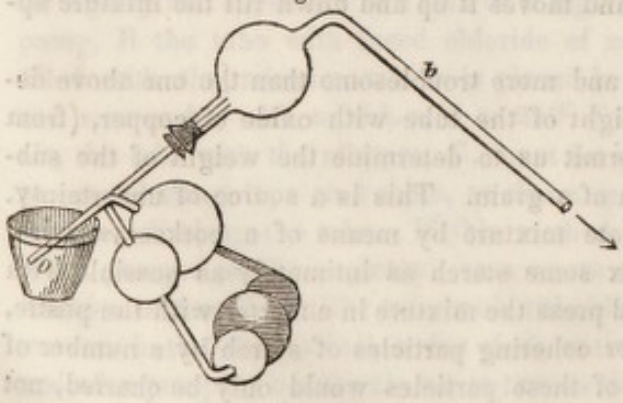


Fig. 10.



The potassa apparatus, when filled with ley, commonly weighs

from 750 to 900 grains. If the ley have the sp. gr. 1·25 to 1·27, it does not produce foam when bubbles of gas pass through it; and when of this strength, its absorptive power is likewise greatest. Caustic soda ley foams like soap and water, and must therefore be avoided.

[The ley is best prepared in the following manner. Two parts of the subcarbonate of potassa of the shops are dissolved in 20 to 24 of boiling water. One part of quicklime is slaked by being *covered* with hot water in any convenient vessel. In this way the whole of the lime is converted into a uniform cream, without the formation of any hard sandy particles, which occur in the ordinary method of slaking, and which are not only useless but hurtful, by preventing, from the space they occupy, and the increased proportion of lime they render necessary, the separation, by decanting, of much of the ley. The cream of lime is added in small portions to the boiling solution of carbonate of potassa, which is boiled a few minutes after each addition, water being occasionally added to supply the loss by evaporation. When the whole of the lime has been added, the mixture is boiled for a short time longer, and is then allowed to cool in the pan or goblet, carefully closed with its lid. After 12 hours, nearly the whole of the ley may be decanted perfectly clear, and quite caustic, especially if the vessel has been nearly full. The carbonate of lime, when this process is followed exactly, is sandy, and occupies a very small bulk. The clear liquid is now to be rapidly boiled down in a clean iron vessel, till small crystals begin to separate. It is then allowed to cool in a stoppered bottle of green glass, when it deposits the whole of the sulphate of potassa originally present in the subcarbonate; that salt being absolutely insoluble in a clear solution of caustic potassa. For the above essential improvements in the preparation of caustic potassa, we are indebted to the author of this treatise and to Dr. F. Mohr of Coblentz. I find that the solution which has deposited the sulphate of potassa possesses the sp. gr. 1·25, and is perfectly adapted for organic analysis. As all contact with organic matter has been avoided, it is also in general colourless, and yields solid caustic potassa almost white, containing no impurity except a little chloride of potassium; which of course may be avoided by using genuine salt of tartar; but which does not in the least affect the use of the potassa for most purposes. The necessity for using at least 10 or 12 parts of water to 1 of carbonate of potaasa arises from the curious fact, noticed by Professor Liebig, that when less water is present, the potassa takes back the carbonic acid from the carbonate of lime.—W. G.]

The tubes of caoutchouc are made out of thin sheets of that substance. A portion, $1\frac{1}{2}$ inch long, is doubled up so as to form a tube of the size of those which it is to connect. About a line in width is now to be cut off with a very clean and sharp pair of scissors, along the length of the caoutchouc where the two sides meet. We thus obtain two smooth cut surfaces, which, if pressed together by the thumb nails, adhere so as to form a perfect junction. The tube is now pulled lengthways, so as to stretch it several times. If we touch the fresh cut surfaces with the fingers, they do not cohere where they have been touched. It is right also to moisten the inside of the caoutchouc, before forming the tube, that its sides may not cohere. The caoutchouc tubes are fastened over the glass tubes by strong threads of silk, knotted at the ends, to prevent them from slipping.

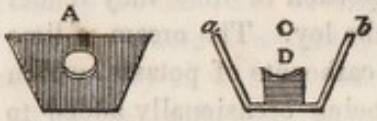
[It is more effectual to dust the inside of the tube with any fine powder, such as flour or starch—removing all that is superfluous.—W. G.]

The furnace in which the combustion is carried on, is exhibited by *fig.* 11. It is made of sheet iron, 22 to 24 inches long, and 3 inches high. The bottom is 3 inches wide, and furnished with apertures which form a sort of grate; these apertures are narrow slits, running across, at an half inch distance from each other. The sides of the furnace are inclined outwards so that at the top they are $4\frac{1}{2}$ inches apart. The whole rests on a large tile or paving stone, *e*, *fig.* 14, in such a manner that the two slits nearest the front are left open, while the remainder are closed by the tile. Within the furnace are placed at intervals supports of strong sheet iron, of the form D, *fig.* 12. They must be of equal height, and must correspond with the round aperture in the front of the furnace, A, *fig.* 12. Their use is to support the tube of combustion.

Fig. 11.



Fig. 12.



When we wish to increase the heat, the furnace is raised a little on one side, and a thin bit of tile is introduced at two places. This allows air to enter by all the slits in the bottom of the furnace. Good charcoal is the only fuel employed in this furnace.

SPECIAL DETAILS OF THE METHOD.

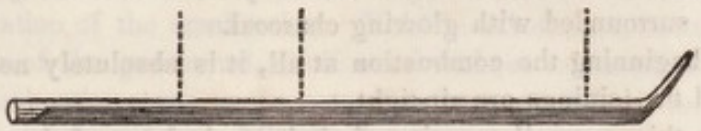
The tube of combustion, if necessary, is washed out with water, and dried by means of bibulous paper tied round a whalebone. When the point has been drawn out and sealed, the tube is made very hot, and a long narrow tube introduced as far as the closed end. By drawing air through the narrow tube with the mouth, the last traces of moisture are soon removed. The dry tube is rinsed out with a little hot oxide of copper, which is then put aside. In order to have some measure of the quantity of oxide which is to be mixed with the substance we wish to analyze, the tube is now to be filled to three-fourths of its length with pure oxide of copper, out of the crucible in which it has been just ignited, and while it is yet hot. We must carefully avoid bringing this oxide, which is destined for the combustion, in contact with any foreign matter.

The mixture of solid substances, not volatile, with the oxide of copper, must always be made in a mortar of porcelain, (Wedgewood's ware,) of a smooth, but not polished surface, and a deep shape. The mortar is previously rubbed out with pure oxide of copper, which is put aside. The weighed substance is now shaken out into the mortar, and the tube in which it was contained rinsed out with a little oxide of copper, which is added to the substance. The latter is first rubbed with a little oxide, with which it is intimately mixed, and by degrees the whole oxide of copper is added, which had been measured in the tube.

The mixture must be made without applying any great force, for which reason the substance, before being weighed, and the oxide of copper, before the gentle ignition which must always precede its use, must be reduced to a fine powder. If the oxide of copper contain hard particles, the mixture cannot be made sufficiently intimate; and it often happens that the pestle, when pressed on such particles, springs off, whereby portions of the mixture may be thrown out of the mortar. If the mortar be placed on a sheet of glazed writing paper, it is easy to see whether any part of the mixture has been lost or not.

Having first introduced pure oxide of copper, so as to fill about half an inch at the closed end of the tube of combustion, we now transfer the mixture from the mortar to the tube. The mortar is rubbed out with pure oxide of copper, which is also introduced into the tube, and above the whole is put pure oxide of copper, till within one inch of the open end of the tube. In *fig.* 13 are shown

Fig. 13.

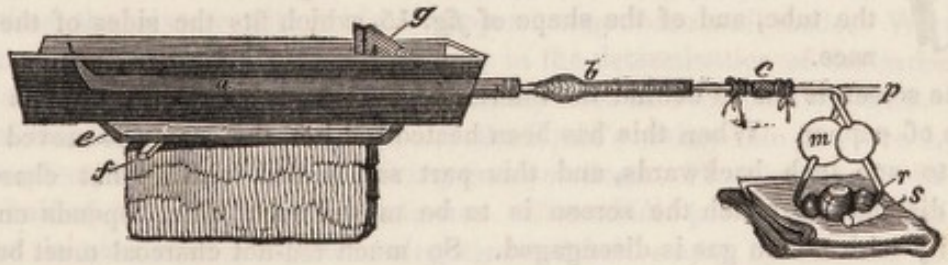


the lengths of the different layers of pure oxide, mixture, rising from the mortar, and again pure oxide. They are marked by the dotted lines, and serve to show nearly the usual proportions.

The cork which joins the tube of chloride of calcium to the tube of combustion, is struck with a light hammer, till it becomes soft and elastic. When the perforation for the small tube is finished, and the cork accurately fitted to the tube of combustion, the cork is placed in a covered crucible in hot sand, in order to expel from it all hygrometric moisture. It must fit very tight into the tube of combustion; but its softness allows the employment of the necessary force, without the risk of breaking the apparatus.

The tube of combustion, and that with the chloride of calcium, must be horizontal, or very slightly inclined towards the potassa apparatus, so that the water which collects in the narrow end of the tube with chloride of calcium, may flow forward of itself to the chloride of calcium. For this purpose, the farther end of the furnace is made a little higher than the other, by introducing a thin bit of wood or iron below the tile at that end. *Fig.* 14 shows the whole apparatus

Fig. 14.



arranged for the combustion; *a* is the tube of combustion, *b* the tube with chloride of calcium, *c* the caoutchouc tube, *m* the larger bulb of the potassa apparatus, which is joined to the tube *b*, *e* is the tile, *f* a small wedge of iron introduced to give the furnace a slight inclination towards the potassa apparatus.

The tube of combustion, before being joined with the tube *b*, or introduced into the furnace, must be tapped smartly in the horizontal position on a flat table, in order to produce, above the mixture, (*fig.* 13) through the whole length of the tube, a vacant space to afford a passage to the gaseous products of the combustion. Without this precaution, it often happens that the oxide of copper is thrown forwards, or that the tube at the farther end becomes choked. Innumerable analyses have shown that, with this arrangement, the combustion is not less complete than when no vacant space is left, however rich in carbon the substance may be.

Mitscherlich screws a spiral of copper wire through the whole length of the mixture, and leaves it in the tube during the operation, with the design of interrupting the continuity of the mass; but we cannot depend on its efficiency. I repeat, that the arrangement described gives the only security for the uniform success of the analysis.

The anterior portion of the tube of combustion contains pure oxide of copper, which must be raised to a red heat before that part of the tube which contains the mixture is surrounded with glowing charcoal.

But, before beginning the combustion at all, it is absolutely necessary to be assured that all the joinings are air-tight.

To ascertain this, a small quantity of air is sucked out of the apparatus, by means of the suction-tube *b*, (*fig.* 10,) and the mouth; this naturally causes the ley to rise in the tube of the bulb, *m*. It is, consequently, from 1 to $1\frac{1}{2}$ inch higher in that than in the opposite tube, as may be seen in B, (*fig.* 9,) where α and β mark the level of the ley in both tubes. If this level does not remain unchanged; that is, if the liquid falls back into the middle part of the apparatus, A, *fig.* 9, air must enter the apparatus either by the caoutchouc tube, *c*, or the cork. One or both must be changed, till the liquid raised by suction to α, remains steadily at the same point.

The anterior portion of the tube of combustion is now surrounded with red-hot charcoal. If the tube be quite dry, and the glass free from knots, there is no danger of its being cracked by the heat. If the oxide of copper has not been thoroughly dried, the first action of the heat causes a more or less distinct deposition of dew on the cold empty part of the tube *a*, which projects one inch out of the furnace. In this case, we may be quite certain that the determination of the hydrogen will give an excess.

Fig. 15.



To keep the fragments of charcoal in their place, and to prevent the heat from spreading to the remaining parts of the tube *a*, the screen *g*, *fig.* 14, is employed. It is made of strong sheet-iron, with a slit for the tube, and of the shape of *fig.* 15, which fits the sides of the furnace.

The screen is set up behind the interior part of the tube, which contains pure oxide of copper. When this has been heated red-hot, the screen is moved one-half to one inch backwards, and this part surrounded with red-hot charcoal. The distance to which the screen is to be moved each time, depends on the rapidity with which gas is disengaged. So much red-hot charcoal must be put on each time, that the part of the tube, which must be completely surrounded with glowing coals, shall be quickly raised to a red heat. Even when the disengagement of gas is at first more rapid than is desirable, we must not remove the charcoal we have put on. To do so would rarely moderate the disengagement of gas, but might easily render the combustion imperfect. We must, therefore, endeavour to regulate the current of gas, by heating shorter portions of the tube at once.

The fore-end of the tube, which is empty, and projects one inch out of the furnace, must be kept during the whole operation, so hot that not the smallest quantity of water can condense within it. In this way, we can avoid any loss of water with certainty.

The combustion would proceed with perfect regularity, if we could deprive the glass of all conducting power. This is impossible, but we cannot be too careful only to heat small portions of the tube at once. The bubbles of gas must form an uninterrupted and rapid current, yet not too rapid.

When there are too few supports in the furnace, the tube sometimes bends by its own weight; but there is no danger of its being blown into holes, as the pressure of the liquid which the gas has to overcome in escaping, is too small to act on the glass, even when softened by the heat.

Mitscherlich places the tube of combustion in a gun-barrel, filed open the long way so as to admit the tube. He thus endeavours to secure a uniform heating, without melting of the tube; but in this way, we lose all the advantages of an accurate regulation of the combustion. Volatile substances, heated by the conducting power of the gun-barrel, distil over without interruption, and without undergoing combustion; and in the case of substances difficult to burn, we cannot apply the necessary heat. Mitscherlich tries to prevent the conduction of the heat along the gun-barrel by blowing on it, or surrounding it with moist cloths. But, during the combustion, our attention is taken up with matters of too great importance to permit of our occupying ourselves with attempting to keep the gun-barrel cool by blowing on it. To surround it with moist cloths is altogether inadmissible, for obvious reasons.

The position of the potassa apparatus during the combustion, is shown in *fig.* 14. A bit of cork is introduced under *r*, so that this part lies a little higher than the opposite end. It is best supported on a folded towel.

When the whole tube of combustion, at the end of the operation, is surrounded with red-hot charcoal, the heat is to be increased along the whole length of the furnace. This is done below, by admitting air through all the slits, and above, by blowing the fire with a sheet of pasteboard, which is rapidly moved backwards and forwards. As soon as the disengagement of gas becomes very slow, the bit of cork is removed from the potassa apparatus, which is restored to its horizontal position. *Fig.* 9, A, *page* 790.

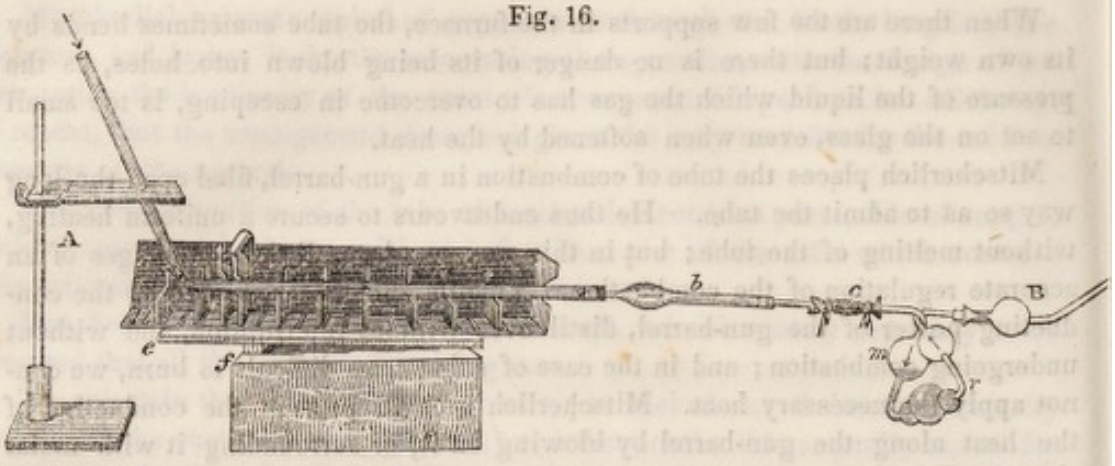
We can now see whether the combustion has been completely successful or not. If the disengagement of gas cease all at once, we are sure that the combustion has been complete. If it continue, on the contrary, at intervals for a long time, the mixture with oxide of copper has not been well made. We may then reckon with certainty on a deficiency in the determination of the carbon.

As soon as no more gas comes over, the ley rises into the bulb *m*, *fig.* 9. The size of this bulb prevents all chance of the liquid's rising into the tube *b*, and allows plenty of time for the remaining manipulations. For when the liquid has filled half of the bulb *m*, it ceases to rise. The middle part of the potassa apparatus is now horizontal, and being rendered half empty by the rise of the liquid in *m*, air passes into the interior. In *fig.* 9, γ points out the height to which the liquid can ascend. When it has reached this point there is no further obstacle to the entrance of air.

The charcoal which surrounds the farther end of the tube of combustion with its sealed point, is now removed, and the point is cut across with small pliers, at the point *x*, *fig.* 8. Over the point, when opened, is placed a tube, *h*, 15 to 20 inches long, open at both ends, supported by a stand, *fig.* 16.

The suction tube is now placed on the end of the potassa apparatus, and a certain quantity of air is drawn with the mouth through the potassa apparatus, whch is now placed in the same position as during the combustion; by this means, all the carbonic acid and watery vapour which have remained in the apparatus are now absorbed by the ley and the chloride of calcium. *Fig.* 16 shows the apparatus at this period. The left hand holds the potassa apparatus at *r*, raising this part a little: the right hand holds the suction tube B.

Fig. 16.



When the combustion has been complete, no taste is perceived in the air drawn through. When it has been imperfect, a more or less distinctly empyreumatic taste is perceived. The latter circumstance is not always a proof that the analysis has failed; for it very often happens that two analyses agree perfectly, in one of which an empyreumatic taste is perceived, in the other not. This proves how minute a quantity of empyreumatic matter suffices to communicate a taste to the air.

Berzelius proposes to avoid the suction with the mouth by employing the apparatus formerly described for producing a current of air. *See figs.* 2 *and* 3. This arrangement is inconvenient, gives unnecessary trouble, and is far from supplying the manageable delicacy of the human organ.

The air which is drawn through the apparatus contains water and carbonic acid; and both are added to the products of the combustion, unless we take means to remove them from the air before it enters the apparatus.

For this purpose, Berzelius connects the point of the combustion tube, after it has been cut, with a tube filled with dry caustic potassa. This may be done, but it is a disagreeable operation, since the tube of combustion must be kept red hot while the air passes through it, in order to oxidize any traces of carbon which may be deposited on the reduced copper: while in order to attach the caoutchouc connector to the point, it must no longer be very hot. Besides, the air, which is made to pass through the potassa apparatus, if dried, absorbs moisture from the ley, which it carries away; giving rise to an apparent loss of carbon. Now, if the current of dry air, as recommended by Berzelius, be continued for a quarter of an hour, it is impossible to neglect this loss, which must then be prevented by attaching to the potassa apparatus another tube for collecting this moisture, and adding its weight to that of the potassa apparatus.

All these troublesome and complicated arrangements may be avoided by proceeding as follows:—

The combustion being over, and the caustic ley ascending to γ, *fig.* 9, B, the potassa apparatus is so inclined that the angle B is closed by the liquid; the point of the combustion tube is now cut off, and air enters. The natural result of this is, that the liquid sinks in the bulb *m*, and rises in *n*, till an equilibrium is established, and a portion of liquid remains in each bulb. The bulb *m* is full of carbonic acid gas, which is absorbed by the caustic ley; the carbonic acid gas in the tube *b* takes the place of that which is absorbed, and thus all the carbonic acid gas in the apparatus is by degrees brought into the bulb *m*, where it is so completely absorbed that not a single bubble of gas passes through the ley.

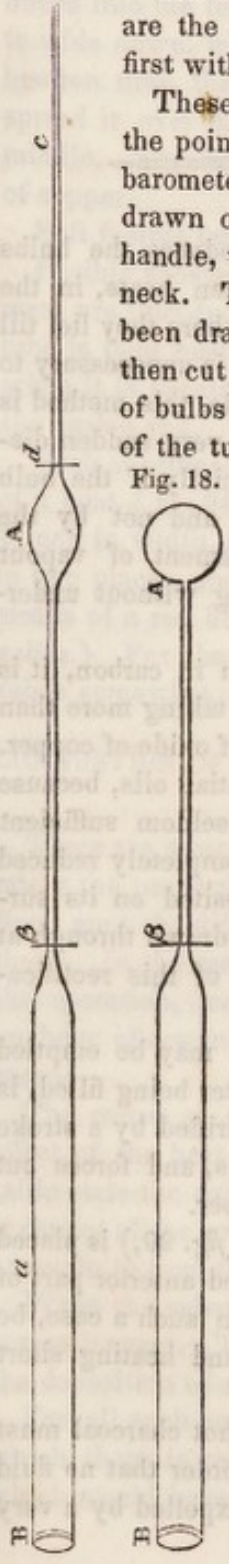
When the apparatus has stood thus for a few minutes, the air in the apparatus contains no more carbonic acid. To make all sure, however, air is drawn through

by the suction tube for a few seconds; till so much has passed as is about equal in volume to the contents of the tube of combustion, *a*, and the tube with chloride of calcium, *b*.

When, as sometimes occurs in the combustion of substances very rich in carbon, a trace of carbon has been deposited on the reduced copper, and has thus escaped oxidation, it is completely oxidized by the small quantity of air now drawn through the red hot tube; and the loss of carbon from this source is avoided.

COMBUSTION OF VOLATILE LIQUIDS.

Fig. 17.



The analysis of such bodies is the most simple and easy; the results are the most exact; and beginners will do well to occupy themselves first with the combustion of such substances.

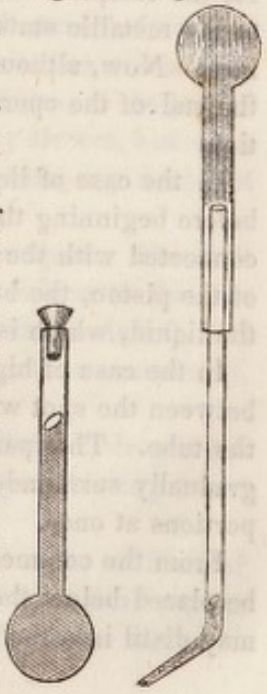
These liquids are weighed in small bulbs of glass, with a long neck, the point of which is sealed. These bulbs are easily prepared. A barometer tube, *a*, *fig.* 17, 12 inches long and $\frac{1}{4}$ inch in diameter, is drawn out before the blowpipe. The portion drawn out serves as a handle, wherewith to draw out a small portion of *a* with a long narrow neck. The point *c* is then sealed off at *d*; the portion of *a* which has been drawn off, A, is softened and blown into a bulb, (*fig.* 18.) It is then cut off at β, and the same process is repeated till a sufficient number of bulbs is procured. The moisture from the mouth, owing to the length of the tube from A to B, never penetrates into the bulb.

Fig. 18.

It is obvious that the portion of tube A, if wide enough, need not be blown out. Its neck is 1 to $1\frac{1}{2}$ inches long; and the sharp edges where it has been cut off must be rounded in the flame of a spirit lamp; otherwise we are in danger of breaking off little splinters after the bulb has been weighed, and while we are introducing the liquid.

To fill the bulb with liquid, it is warmed, and the open end of the neck introduced into the liquid. When by cooling a certain quantity of liquid has entered, the bulb is again warmed; the vapour which is formed expels almost the whole of the atmospherical air, and when the point is again dipped in the liquid, the bulb fills to three fourths of its bulk. The point is now sealed up, the whole is weighed, and subtracting the weight of the bulb, when empty, we have the weight of the liquid.

Fig. 19. Fig. 20.



Before weighing the bulbs, the oxide of copper has been ignited, and, while still red-hot, introduced into the tube (*fig.* 19,) which is closed with a dry cork, and allowed to become quite cold. It is not so convenient to allow the crucible to cool under a bell jar along with oil of vitriol.

The tube, *fig.* 19, is so wide, that the tube of combustion slides easily into it. We first allow, as shown in *fig.* 20, one to one and a half inch of the perfectly dry oxide to fall into the tube of combustion,

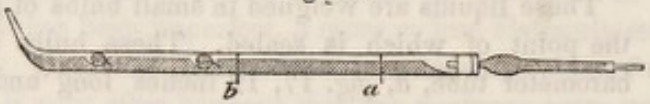
and then introduce the bulbs alternately with more oxide, so that the latter can attract no moisture. The bulbs are scratched with a sharp file on the middle of the neck, as in *fig.* 21, at *a*. They are held by the point, and when introduced into the mouth of the tube, broken across, both bulb and neck being allowed to slide down into the tube.

Fig. 21.



The two bulbs, holding from 6 to 8 grains of liquid are sufficient; they are separated in the tube by a layer of oxide of copper, of 2 to 3 inches long. If the tube of combustion be 18 inches long, then there is above the uppermost bulb a layer of oxide 11 to 12 inches long. *Fig.* 22 shows the bulbs with the layers of oxide of copper.

Fig. 22.



Mitscherlich is the only chemist who introduces the bulbs into the tube of combustion sealed up. He then heats, in the course of the operation, the part of the tube where they lie, till they burst. If the liquid be not very volatile, it is unnecessary to leave the bulbs closed; and if it be very volatile, this method is ill adapted to practice—for with such liquids a very sudden disengagement of vapour cannot be avoided, especially if the bulb be burst by the elastic force of the vapour, and not by the expansion of the liquid. Now when this sudden disengagement of vapour occurs, it is impossible to prevent a portion of it from escaping without undergoing combustion.

When the liquid boils at a high temperature, and is also rich in carbon, it is divided into three portions in separate bulbs, without however, taking more than from 7 to 9 grains in all. The bulbs are separated by layers of oxide of copper.

This precaution must be attended to in analyzing the essential oils, because the oxide of copper, which immediately surrounds a bulb, is seldom sufficient for the complete oxidation of the vapour, and, being itself completely reduced to the metallic state, a thin layer of carbon is sometimes deposited on its surface. Now, although this carbon may be oxidized by the air drawn through at the end of the operation, yet it is better to avoid the necessity of this rectification.

In the case of liquids which are not very volatile, the bulbs may be emptied before beginning the combustion. The tube of combustion, after being filled, is connected with the air-pump, as in *fig.* 7. When the air is rarified by a stroke of the piston, the bubble of air contained in each bulb expands, and forces out the liquid, which is absorbed by the surrounding oxide of copper.

In the case of highly volatile liquids, a second screen at *b*, (*fig.* 29,) is placed between the spot where the uppermost bulb lies, and the heated anterior part of the tube. This part, containing pure oxide of copper, must, in such a case, be gradually surrounded with red hot charcoal, beginning at *a*, and heating short portions at once.

From the commencement of the operation, some bits of red-hot charcoal must be placed below the closed point of the tube of combustion in order that no fluid may distil into the closed end, from which it could only be expelled by a very

strong heat; the liquid then boils by starts, and in little explosions, whereby some of it may readily pass away unoxidated with the gaseous products, forming a visible white cloud.

When the anterior part of the tube is red-hot, the screen *b* is removed, and a piece of burning charcoal from time to time brought near the spot where the first bulb lies. In other respects the combustion is to be carried on as formerly described.

Fixed oils are weighed in the small tube, (A, *fig.* 23,) which is supported during the weighing on the stand (B, *fig.* 23,) of tinned iron. When 2 inches of oxide of copper have been introduced into the tube of combustion, the tube with the oil is allowed to slide down, with the open end upwards. By inclining the combustion tube, the oil is allowed to flow out, and we endeavour to spread it over the sides of the combustion tube as far up as the middle. The tube is then filled, as formerly directed, with oxide of copper.

Fig. 23.



Soft fusible matters may be treated exactly in the same way.

Fusible substances which, though solid, cannot be reduced to powder, such as wax, are introduced into the empty combustion tube in weighed fragments. The tube is then heated, after being closed with a cork, till the substance melts, when it is spread along three fourths of the length of the tube, reckoning from the sealed end. When cold, the tube is filled with oxide of copper.

Such substances may also be weighed in a little glass vessel having the shape of a boat, (*fig.* 24,) which is easily made by taking a tube $\frac{1}{4}$ inch in width, softening it, and drawing it out upwards in two places, and then splitting the tube lengthways by means of a red hot point of charcoal,—(*Sprengkohle*, *Berzelius.*) For the combustion of such substances we must select combustion tubes somewhat wider and longer than for ordinary combustions.

Fig. 24.



COMBUSTION OF SUBSTANCES VERY RICH IN CARBON, OR OF SUBSTANCES CONTAINING CHLORINE.

There are some substances in which it is almost impossible to determine accurately the proportion of carbon by means of combustion with oxide of copper. Such are: the different kinds of coal, indigo, ulmine, and all bodies resembling these. In the case of coal, for example, the disengagement of gas, at the end of the operation, does not cease. It becomes, indeed, gradually slower, but even an hour afterwards, when the heat has been strong, the caustic ley does not ascend.

The cause of this is, doubtless, that the combustion is unequal. The first effect of the heat is to disengage combustible gases, which reduce to the metallic state the oxide surrounding each particle; and so much carbon is left, that it cannot all be oxidized by cementation. The loss of carbon, thus occasioned, amounts to from three to five per cent.

When the substance contains chlorine, the determination of the hydrogen becomes inexact. The chloride of copper being volatile, it is impossible to prevent the deposition of some of it in the chloride of calcium tube.

For all such combustions, it is necessary to employ the chromate of lead, of which there is required rather more than half the bulk of the oxide of copper which would have been required. In other respects the process is the same.

When the chromate of lead is used, it is necessary to give a strong heat at the end of the process. Pure oxygen is then disengaged, in which the remaining charcoal undergoes perfect combustion. But the increased heat renders it necessary to protect the tube by covering it with a thin sheet of copper, which, from its flexibility, may be easily wrapped round the tube, and which may be kept in shape by a few rings of iron wire bent round it.

The same object may be less conveniently attained, when oxide of copper is employed, by placing, in the closed end of the tube, a mixture of 1 part of chlorate of potassa, and 8 parts oxide of copper. When, at the end of the operation, this part of the tube is heated, the remaining charcoal is burnt by the oxygen which is disengaged.

For substances containing chlorine, the chromate of lead is a precious, nay, indispensable means of combustion. Chloride of lead is formed, which is not at all volatile, at a red heat.

It is necessary to bestow some attention on the preparation of the oxide of copper, and the chromate of lead, as also on the choice of combustion tubes.

OXIDE OF COPPER.

This oxide may be prepared by mixing hot solutions of sulphate of copper and carbonate of soda. The pale blue precipitate of carbonate of copper is left, during from eight to fourteen days, in the liquid, and in a warm situation. At the end of that time it loses its gelatinous consistence, becoming green and crystalline, in which state it is easily washed and dried. Before being used, it must be strongly, ignited, and carefully tested for sulphuric acid and soda. If it contain even a minute quantity of these, it is unfit for analyses.

The oxide thus obtained is brownish black, and forms an extremely loose, light powder, which is in the highest degree hygroscopic. Organic substances, when mixed with it, are burnt with great facility; but occasionally the mixture in the tube, when one part of it has been ignited, continues to burn spontaneously, in which case the analysis is good for nothing.

It is better to use the oxide of copper prepared from the nitrate by calcination. Its preparation is both easier and cheaper, and we are never doubtful of its purity.

To prepare it, sheet copper is ignited, and thrown, while red-hot, into cold water. All impurities on the surface peel off with the crust of oxide formed. The clean, well-washed metal is now dissolved in pure nitric acid, and the solution evaporated to dryness in a porcelain capsule. The dry salt is next ignited in a well covered hessian crucible, (care being taken not to introduce too much at once, as the salt froths up,) and the calcined mass is frequently stirred with a hot glass rod, or copper-wire, in order that no part of the nitrate may escape decomposition. Platinum crucibles must not be employed for this operation, as they are by degrees attacked and worn away when oxide of copper is ignited in them.

The ignited oxide is reduced to fine powder, and preserved in a well-stopped vessel. It is compact, heavy, coal-black. Its hygroscopic condition depends on the temperature to which it has been exposed. When very strongly ignited, the oxide shrinks in bulk, becomes very hard, and loses almost all hygrometric properties. In this form, if broken into small fragments, it answers admirably, when the finer parts are removed by sifting, for the combustion of liquids, and of difficultly combustible, fatty, fusible, substances. The tube may be completely

filled with it, and no tapping is required, as there are sufficient pores in the mass to yield a free passage to the gases.

To attain the same end, Dumas employs the oxide obtained by calcining copper turnings on a muffle. This oxide retains the form of the turnings, and is equally well adapted for the purpose above mentioned.

The oxide of copper, which has been used for a combustion, may be again rendered fit for use by moistening it with pure nitric acid, and igniting it afresh. Should the copper originally have been contaminated by brass solder, the oxide cannot be used for the determination of nitrogen, as the nitrate of zinc is only partially decomposed by ignition, but readily yields nitrogen or nitric oxide when heated with organic matter.

If the substance analyzed have been a compound of an organic substance with a fixed base, the oxide, after the combustion, must be digested in cold dilute nitric acid, well washed and ignited.

After the combustion of a compound containing chlorine, the oxide must be redissolved in nitric acid, and the chlorine precipitated by nitrate of silver. Any excess of silver in the filtered solution is reduced by the ignition, and its presence is not injurious.

CHROMATE OF LEAD.

This substance is obtained in a state of perfect purity by precipitating acetate or nitrate of lead with bichromate or potassa, and washing the precipitate carefully with distilled water. But in the state in which it is obtained by mere drying, it is not adapted for analyses. It must be strongly ignited till it begins to melt, and then reduced to a very fine powder. The ignition changes its beautiful yellow colour to a dirty brownish red, which it retains on cooling.

The chromate of lead may be used in every kind of combustion as well as the oxide of copper. The combustion takes place easily, and at a moderate heat. It is always complete, for the gases after the combustion are invariably tasteless.

Compared with an equal weight of oxide of copper, it does not contain so much oxygen available for combustion; but compared with an equal bulk, it contains nearly one half more, since its density is more than twice as great as that of the oxide of copper.

It is highly probable that the chromate of lead will be preferred to the oxide of copper in many cases, where it is desirable to determine the proportion of hydrogen with extreme accuracy. The chromate is not in the slightest degree hygroscopic, and the trace of moisture, which the substance may have attracted during the mixture, can be afterwards removed with much greater facility than in the case of oxide of copper.

COMBUSTION TUBES.

The glass of which these tubes are made must be chosen with great care. The Bohemian potassa glass, which contains no lead, is the best. Tubes of this glass never crack, even when suddenly surrounded with red-hot charcoal. It is extremely difficult to melt, and when softened, it is extremely tough. The green bottle glass of Germany cracks easily in the fire, is difficult to melt, but, when once softened, very liquid. The softened parts are blown out by the slightest pressure, and holes are formed instantly when this occurs.

The French white and green bottle glass must be rejected. The French green

glass can be melted in a tube of Bohemian glass, without the form of the latter being altered.

Having now described all the precautions and manipulations which insure the performance of a trustworthy analysis, as far as concerns the determination of carbon and hydrogen by weighing, it remains for us to describe the method of determining the carbon by the volume of the carbonic acid produced, as well as that of the nitrogen, which latter is always done by measurement. I have also to consider the degree of accuracy which is attainable in the determination of the carbon and hydrogen.

CARBON.

The determination of the carbon by the process and apparatus above described may be rendered inexact by several sources of error. The first and most important is incomplete combustion. In repeating the analysis, this may be avoided by using a longer combustion tube and increasing the proportion of oxide of copper. The latter precaution insures a greater degree of division, and a slower combustion, which generally suffices.

A second source of uncertainty, as formerly mentioned, arises from the circumstance that the gaseous matter which, during and after the combustion, passes through the potassa apparatus, carries with it a portion of water, from the caustic ley, the weight of which is thus diminished. But it is obvious that this loss of water is, in part at least, compensated by the carbonic acid of the air, so that the loss of weight varies, according to the quantity of carbonic acid present in the atmosphere.

This point has been satisfactorily cleared up by direct experiments. When the combustion tube is surrounded with red-hot charcoal, and the point broken off, *fig.* 16, without the tube *h*, the open point being also surrounded with charcoal, the potassa apparatus, after 2000 cubic centimetres of air have passed through it, not only does not lose weight, but gains 18½ milligrammes (0·275 grain nearly.)

To determine the amount of water carried away by the current of air, there was connected with the potassa apparatus a second similar one filled with strong sulphuric acid. It is clear, that the water carried in the form of vapour by the current of air from the caustic ley must have been condensed by the sulphuric acid.

Now the weight of the apparatus containing the sulphuric acid had increased by 14 milligrammes (0·21 grain nearly,) so that, instead of a deficiency in the carbon, there was, in this experiment, an excess; for the caustic ley has absorbed 32½ milligrammes (0·48 grain nearly) of carbonic acid from the air, and had given off 14 milligrammes of water.

When the tube *h*, 12 or 15 inches long, was placed on the point of the combustion tube as in *fig.* 16, and the experiment repeated with the same quantity of air, the apparatus with sulphuric acid again gained in weight 13.6 milligrammes, and the potassa apparatus lost 5 milligrammes, (0·075 grain nearly.)

It is obvious that by this arrangement the error in the determination of carbon arising from the loss of water is completely compensated by the absorption of carbonic acid from the air.

When 200 cubic centimeters (the quantity commonly occurring in a combustion) of carbonic acid pass through the potassa apparatus, the loss amounts only

to half a milligramme (0·0075 grain nearly) in the weight of carbonic acid. Reduced to carbon, this amounts only to 0·000138 gramme, (0·002 grain nearly); and this loss is extended over from 0·4 to 0·8 gramme (6 to 12 grains) of the substance analyzed.

Those who, at the end of the combustion, connect the point of the combustion tube with a tube of fused potassa, to deprive the air of its carbonic acid, must therefore add to the weight of the potassa apparatus on an average 0.0013 gramme, (0·0295 grain nearly,) for every 100 cubic centimetres of gaseous matter which pass through.

But the experiments above detailed, show that it is unnecessary to have recourse to that method; and that, in all circumstances, it is safer to follow the process I have recommended.

When the quantity of carbonic acid produced in the combustion is very large, and the bubbles follow each other with rapidity, the caustic ley becomes warm, and the loss of water is increased.

In weighing the potassa apparatus, it must be observed, that when it is warm less moisture condenses on the surface of the glass than before the combustion, when it was weighed cold. This difference amounts to 0·003, or 0·004 gramme. When the air is very moist it may even reach 0·006 gramme, (0·045, 0·06, 0·09 grain nearly). It is better therefore to wait until the apparatus has cooled down.

An examination of the analysis of one or two substances possessing high atomic weights, will give the clearest idea of the accuracy with which the apparatus described enables us to determine the carbon.

It is known with sufficient certainty, that the atomic weight of the amygdalate of baryta is =6738·829. Three analyses of this salt gave of carbonic acid 163 8, 163.5, 163.3 per cent. The mean is 163·5. The quantity calculated according to the theoretical composition of the salt is 163·7. The loss of carbonic acid is, consequently 0·002 carbonic acid, (0·2 per cent.) which is equal to 0·00055 carbon, (0·055 per cent.) There is no kind of analysis, in which greater accuracy is attainable.

This is the proper place for some remarks on the true atomic weight of carbon. The earlier determinations of Berzelius give the number 75·33. His latest experiments give 76·437. I consider the latter as the true atomic weight, determined with astonishing accuracy. Every day's experience confirms its exactness, and the following considerations will give to all chemists the same conviction.

The mean of 5 analyses of stearine give, in 100 parts of this substance, 76.084 carbon. The three highest results gave a mean of 76·306.

From the products of the decomposition of stearine we know with certainty that one equivalent of it contains 146 atoms of carbon; which, taking the atomic weight of carbon at 76·437, would give of carbon in stearine 76·21 per cent. Were the atom of carbon, as Thomson considers it, exactly 75; or 75·33, as the first experiments of Berzelius made it, the analysis, supposing stearine to contain 146 atoms of carbon, should have yielded not more than 75·85 and 75.98 per cent of carbon.

The difference, 0·36 per cent. carbon, amounts to one atom less. But if we assume stearine to contain only 145 atoms carbon, all coincidence between the composition of stearine and that of stearic acid and glycerine, the products of its decomposition, disappears; and we must then suppose that the analysis of one

or of both of these substances is inaccurate; a supposition for which there is no foundation.

In the combustion of substances which contain sulphur, as xanthates, sulphosinapisine, &c., the weight of the carbon generally turns out too high. This proceeds from the formation of sulphurous acid, which always occurs when the mixture with oxide of copper has not been made sufficiently intimate. The sulphurous acid is absorbed by the caustic ley, and increases its weight. When we have reason to fear this source of error, we must place between the chloride of calcium tube and the potassa apparatus a tube with peroxide of lead.

A concentrated solution of chloride of calcium, such as is formed in the chloride of calcium tube, does not retain any sulphurous acid, particularly when it is allowed to lie till all the liquid in it has solidified, that is, till the chloride of calcium has crystallized. The sulphurous acid which has passed through the chloride of calcium is absorbed by the peroxide of lead. The latter must not be placed between the chloride of calcium and the combustion tube, unless we mean to neglect the water in that particular analysis; as some water would be absorbed by it.

HYDROGEN.

The only error inherent to the method of analysis recommended, which affects the determination of the hydrogen, arises from the moisture of the atmospheric air which is drawn through the apparatus at the end of the combustion, with the view of bringing the whole carbonic acid in contact with the absorbing liquid.

Innumerable experiments have shown, that the amount of moisture absorbed by the chloride of calcium, when 200 cubic centimetres have passed through, never amounts to more than 0·005 or 0·006 gramme (0·075 to 0·09 grain, nearly.) This corresponds to 0·00055 or 0·00066 gramme (0·0075 to 0·009 grain, nearly) of hydrogen. This excess is divided over 0·3 to 0·5 gramme (4·5 to 7·5 grains nearly) of the substance analyzed; and it is equally great, whether the substance contain much or little hydrogen. If the substance analyzed be rich in hydrogen, and have a small atomic weight, this error becomes proportionally smaller. In such cases we are in no doubt as to the number of atoms of hydrogen. An example will illustrate this.

100 parts of pyroacetic spirit (acetone) when burned with oxide of copper, yield as a mean result 94·23 parts of water. The amount, calculated from theoretical composition, is 92·45 parts of water per cent. The analysis, therefore, gives 1.8 per cent. of water, or 0·2 per cent. of hydrogen, in excess. Now, the atomic weight of acetone is 366·750. Had this quantity been burned, we should have had an excess of hydrogen over the theoretical quantity, amounting to 0·7335; but since the atom of hydrogen weighs 6·23978, it is obvious that the error is far short of one atom of hydrogen; and that it may safely be neglected in such cases, especially as we know the source of it, and the limits within which it is confined.

But this error cannot be neglected in substances of high atomic weight which contain much hydrogen. We must subtract from the amount of water obtained 0·005 to 0·006 gramme, (0·075 to 0·09 grain nearly;) or, if we are unwilling to trust to this correction, we must break off the point before the caustic ley begins to ascend, remove the hot charcoal from about the point, and, when it has

cooled sufficiently, connect it, by a tube of caoutchouc, with a tube containing chloride of calcium, or with a potassa apparatus filled with sulphuric acid.

An example will render obvious the necessity for this correction. 0·3054 gramme of stearine, without correction, and without any means having been taken to desiccate the air, yielded 0·343 gramme of water: 100 parts, consequently, would have given 112·31. According to the theoretical composition of stearine, 100 parts should yield only 109·63 of water. There is, therefore, here an excess of 2·68 per cent. of water, or 0·297 per cent. of hydrogen. Now, this slight excess, calculated on the atomic weight of stearine, corresponds to somewhat more than three atoms of hydrogen.

If, however, we deduct, previously to the calculation, 0·006 gramme as hygrometric moisture, there remain for 100 parts of stearine 110·35 of water, or an excess over theory of 0·72 per cent. water, or 0·08 per cent. hydrogen; which excess, calculated on the atomic weight, amounts to less than one atom of hydrogen.

By following, therefore, the process of analysis recommended in this work, we must always be prepared for an excess of hydrogen over the truth, amounting to from 0·14 per cent. to 0·2 per cent.; and we can only consider the determination of the hydrogen as exact, when this excess does not exceed 0·2 per cent. When the analysis, without the above correction, gives exactly the theoretical quantity of hydrogen, there is much reason to doubt the accuracy of the experiment; and the formula found for the composition of the substance is erroneous, when the results of repeated analyses yield constantly less hydrogen than the formula indicates.

In publishing the weights obtained in an analysis, we must not make the above deduction, but give the numbers as they occur, since the amount of excess, due to hygrometric water, furnishes to the reader a valuable means of judging of the accuracy of the determination of the hydrogen. It is only in calculating the composition with a view to discover the formula that we are to make the correction above mentioned.

The determination of the hydrogen becomes inaccurate when a compound of chlorine is burnt with oxide of copper. The chloride of copper which is formed, sublimes with the current of gaseous matter, condenses in the chloride of calcium tube, and increases its weight. The more slowly the combustion goes on, the smaller is this excess of weight; but it must never be neglected. It amounts in all to from 0·01 to 0·015 gramme, (0 15 to 0·225 grain nearly.) By dissolving the chloride of calcium, precipitating the copper with sulphuretted hydrogen, and determining its quantity, this source of error may be corrected.

In the analysis of such bodies we must be particularly cautious in moderating the current of air which is drawn through the apparatus after the combustion; for if the current be made rapid, the chloride of copper may be seen passing through the caustic ley in the form of white vapours, and the nauseous metallic taste of the salts of copper is perceived in the mouth.

By the use of the chromate of lead, this source of error may be entirely avoided.

The chloride of calcium tube must be emptied immediately after we have weighed it, if we would not lose it. If this be not done, the saturated solution of chloride of calcium which has been formed, crystallizes, and infallibly bursts the tube.

DETERMINATION OF NITROGEN.

When substances containing nitrogen are analyzed, the carbon and hydrogen are ascertained by the method already described, and the determination of the nitrogen becomes then the subject of a separate experiment, in which every thing else is neglected.

We see at once, and clearly, whether a substance contain nitrogen or not, in determining the carbon. If nitrogen be present, bubbles of gas, during the whole combustion, escape through the potassa ley. If these bubbles towards the end of the combustion, are larger than an ordinary pin's head, we may be sure that the substance contains nitrogen.

We may also ascertain whether a substance contain nitrogen by melting a portion of it in a test tube with 4 to 10 times its weight of fused caustic potassa. Nitrogenized substances are thus decomposed without blackening, and the whole nitrogen is disengaged in the form of ammonia, which in all cases may be easily recognized by the smell. If we are obliged to have recourse to turmeric and other tests to detect the ammonia, then the presence of nitrogen is doubtful.

In the combustion of most nitrogenized substances, the nitrogen is disengaged in the free state, and in the form of gas, mixed with the carbonic acid and watery vapour. In other cases deutoxide of nitrogen is formed; the production of which renders the determination of the nitrogen difficult, and is certain to render it inaccurate, if the utmost care be not taken to reduce the deutoxide again to the state of nitrogen.

The nitrogen is always determined by measurement. Now, since nitrogen, by passing into deutoxide of nitrogen, doubles its volume, we are thus exposed to a source of error, which increases the apparent quantity of nitrogen. This error is obviated by using a combustion tube 3 or 4 inches longer than in the determination of carbon, and placing, above the anterior layer of pure oxide of copper, a layer of copper turnings, which have been ignited till their surface became black, and afterwards heated in a current of hydrogen till the crust of oxide on the surface has been completely reduced. Besides this, oxide of copper may be used for the combustion, which has already served for an analysis, and which consequently contains a considerable quantity of metallic copper.

The following rule must be attended to in the determination of nitrogen:— *The more carefully and intimately the mixture with the oxide of copper has been made, and the more slowly the combustion is made to proceed, the less danger is there of the formation of the deutoxide of nitrogen.* To give an idea of how we ought to proceed, it may here be remarked, that the combustion of a nitrogenized substance requires twice as much time as that of a substance containing no nitrogen.

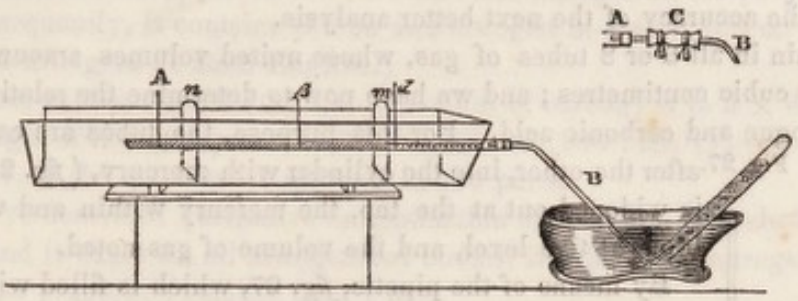
The methods to be pursued in the determination of nitrogen are various, and more or less simple according to the amount of nitrogen present in the substance.

The qualitative analysis of the gaseous mixture produced in the combustion, must in all cases precede the quantitative determination of the nitrogen; for the knowledge of the relative volumes of carbonic acid and nitrogen suffices, in most cases, to enable us to calculate the amount of nitrogen, that of carbon having been previously ascertained. In these cases the employment of a special process becomes superfluous. The apparatus employed for this qualitative analysis is extremely simple; the whole operation lasts, including all the preparations, about

two hours; and what we thereby ascertain determines our choice of another process, or renders all further operations unnecessary.

The substance (weighed or not weighed, this is indifferent) is mixed with forty to fifty times as much oxide of copper as would suffice for its complete oxidation. The mixture is introduced into the tube of combustion, A, *fig.* 25, so as

Fig. 25.



to occupy half its length. Of the two remaining quarters of the length of the tube, one is filled with oxide of copper from β to α, the other with copper turnings from α to the mouth of the tube. The combustion tube being connected with the tube B, for collecting the gas, is placed in the furnace. The tube B may be rendered moveable by a caoutchouc connecter, C; it reaches into the mercurial trough, and is barely covered with mercury.

The screen *m* is put on at α, and then both the metallic copper and the oxide of copper are raised to a full red heat; the slits in the bottom of the furnace as far as α, being exposed, so that the heat may be strongest in the anterior half of the tube. If the tube be not of Bohemian glass, this part of the tube must be wrapped in thin sheet copper, tied on with copper wire: otherwise, the pressure, even of a small column of mercury, blows out the heated part, and causes a hole in the tube.

As soon as the copper and oxide are fully red hot, the second screen, *n*, is so placed, that a length of one inch of the tube, *from the closed end*, is exposed, and this is surrounded with red hot charcoal. The combustion is thus begun at the closed end; the gaseous matter disengaged expels all the atmospheric air from the apparatus, and by this means the whole is filled with the gaseous products of the combustion alone. The combustion is now carried on as usual, beginning at α, and proceeding gradually towards the closed end, by moving the screen, *m*, backwards half an inch at a time, surrounding each $\frac{1}{2}$ inch with glowing charcoal, &c. The gas, produced at this period, is collected in graduated tubes $\frac{1}{2}$ inch in diameter, and 12 to 15 inches long, accurately graduated into equal parts, whether cubic inches, or cubic centimetres, or arbitrary measures, but all strictly uniform in each individual tube.

When the first tube is three-fourths full of gas, it is to be lifted out of the mercury, and air allowed to enter it. As this air, in a few seconds, mixes with the gas, it furnishes a very delicate test of the presence of deutoxide of nitrogen. Should $\frac{1}{1000}$th of this gas be present, the well-known red vapours of nitrous acid are instantly seen, which, if in very small proportion, give a yellow colour to the gas, when viewed through a great thickness, as by looking through the tube horizontally from end to end.

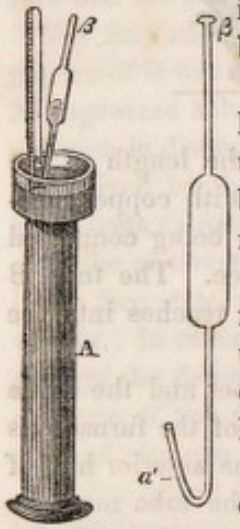
Sometimes deutoxide of nitrogen occurs at the beginning, and not after some time, because the oxide at α is reduced and assists the deoxidizing agency of the

turnings. The above-described test of the purity of the gas must be tried at the beginning, middle, and end of the combustion. If the formation of deutoxide of nitrogen has been observed throughout the whole operation, either the mixture of the substance with the oxide has been imperfect, or the combustion has been too rapid, or else it is necessary to increase the proportion of copper turnings.

It is not worth while in this case to finish the experiment: it teaches nothing, gives rise to false notions of the composition of the substance, and only raises doubts of the accuracy of the next better analysis.

We obtain in all 6 or 8 tubes of gas, whose united volumes amount to from 300 to 600 cubic centimetres; and we have now to determine the relative volume of the nitrogen and carbonic acid. For this purpose, the tubes are carried, one after the other, into the cylinder with mercury, (*fig.* 26,) which is widened out at the top, the mercury within and without is brought to a level, and the volume of gas noted.

Fig. 26. Fig. 27.



By means of the pipette, *fig.* 27, which is filled with caustic ley, and closed at α with mercury, the ley is introduced into the tube to the depth of some lines. This is generally done by applying the mouth to β, and producing a slight pressure, not more than sufficient to force out some of the ley.

When the bent point of the pipette is $1\frac{1}{2}$ inch long, and reaches above the mercury into the tube, we have only to raise the graduated tube in the mercury, so as to cause a slight vacuum within, when the pressure of the atmosphere causes the ley to flow into the graduated tube.

By gently moving up and down the graduated tube, all the carbonic acid is rapidly absorbed, and nothing but nitrogen is left. The open end of the tube is easily broken, owing to the weight of the mercury. This accident may be entirely avoided, by holding the tube so that its mouth is constantly in contact with the side of the cylinder while we are moving it up and down. The mercury without and within is now again brought to a level, and the volume of gas noted.

Let the volume of gas in the 6 tubes be = 620, and let the remainder, after the action of the caustic ley, be = 124; 496 vol. of carbonic acid have consequently disappeared. Hence, in this case, the volume of the nitrogen is to that of the carbonic acid, as 124 : 496, or as 1 to 4.

We may now proceed, in a variety of ways, to calculate the nitrogen contained in the substance from the relative volumes, *it being presupposed, that the quantity of carbonic acid yielded by a given weight of the substance is known.* Either we convert the weight of the carbonic acid into volume, and divide this by the number expressing the relative proportion; the quotient gives the corresponding quantity of nitrogen by volume. For example, 0·100 gramme of caffeine yield by combustion, by weight, 0·180 grammes of carbonic acid. The gaseous mixture which caffeine yields by combustion, contains nitrogen and carbonic acid in the proportion by volume of 1 to 4. Now, 1000 cubic centimetres of carbonic acid gas weigh 1·97978 gramme,—0·180 gramme of carbonic acid, therefore, corresponds to 91·85 cubic centimetres. Dividing this number by 4, we obtain the number 22·85 cubic centimetres, which are to 91·85 as 1 to 4. These 22·85 cubic centimetres are calculated as nitrogen. We know that 1000 cubic centimetres of nitrogen weigh 1·26 gramme. Hence, 100 parts of caffeine contain 28·834 of nitrogen, and 49·796 carbon.

Or, to avoid this tedious calculation, if we remember that 1 vol. carbonic acid represents 1 atom of carbon, and 1 vol. nitrogen gas, 2 atoms of nitrogen, (1 atom English,) since the quantity of carbon, and the relative volumes of carbonic acid and nitrogen are known, we calculate the nitrogen from the atomic weights.

Caffeine, according to the determination of the carbon, contains 49·796 per cent. of carbon. It also yields carbonic acid and nitrogen in the proportion of 4 to 1; consequently, it contains carbon and nitrogen in the proportion of 4 atoms carbon to 2 nitrogen. (1 atom English.)

Therefore, as $4 \times 76{\cdot}437$ (the atomic weight of carbon) is to $2 \times 88{\cdot}518$ (the atomic weight of nitrogen,) so is $49{\cdot}796 : x$. That is, $305{\cdot}748 : 177{\cdot}036 :: 49{\cdot}796 : x = 28{\cdot}834$, = the quantity of nitrogen in 100 parts.

The above described qualitative determination of nitrogen furnishes complete security, and is exact for all nitrogenized bodies, in which the nitregen is to the carbon in no proportion smaller than 1 to 8.

We now know the sum of the volumes of nitrogen gas and carbonic acid gas yielded by a given weight of the substance. We know, further, from a previous analysis, the weight of the carbonic acid. The latter, being reduced to volume, is deducted from the mixed gases to obtain the volume of the nitrogen, which is then reduced to weight. The volume of nitrogen must bear to the volume of carbonic acid a simple ratio, and, indeed, the same indicated by the qualitative analysis. If the two do not agree, one or other of the analyses is erroneous, and must be repeated.

For example, 0·100 gramme of caffeine burnt in this apparatus, yield at 0° C. and 28″ bar. 114·06 cubic centimetres of gases. The same quantity of caffeine, burned in the apparatus, *fig.* 14, gives 0·180 gramme of carbonic acid, corresponding, at 0° and 28″ bar., to 91·21 cubic centimetres of carbonic acid gas. Hence, 0·100 gramme of caffeine yields $114{\cdot}06 - 91{\cdot}21 = 22{\cdot}85$ cubic centimetres of nitrogen=28·836 per cent.

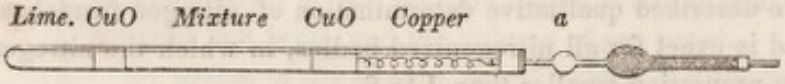
The quantity of substance which may be analyzed in this apparatus, depends on the size of the bell-jar. For each per cent. of nitrogen and carbon we must calculate one cubic centimetre in the bell-jar, and, over and above, a free space, of from 15 to 20 cubic centimetres, to allow for changes of volume from changes of temperature. If the bell-jar, for example, holds only 100 cubic centimetres, we can only measure in it the gases from 0·060 gramme (0·9 grain nearly) of caffeine, or of 0·09 to 0·1 gramme of morphine (1·35 to 1·5 grain nearly,) if the jar contain at first 15 cubic centimetres of air. These jars commonly hold from 200 to 250 cubic centimetres; but it is easy to see that in all these cases, the quantity analyzed is very small, and that the errors of manipulation or of observation have, under all circumstances, a great influence on the amount of nitrogen obtained; so that, when the quantity of nitrogen in the substance is very small, this apparatus ceases altogether to give exact and trustworthy results.

One principal source of error here is the softening of the combustion tube by the strong heat employed, whereby it loses its shape, which of course affects the volume of gas in the bell-jar. This occurs very readily, where the level of the mercury has not been very carefully regulated. It is advantageous to enclose the lower half of the tube along its whole length in a half cylinder of thin sheet copper, lined with fine charcoal powder to prevent adhesion. A sheet of platinum as long as the tube, and only just broad enough to keep it from bending, answers still better.

DIRECT DETERMINATION OF THE NITROGEN.

In the analysis of substances containing a very small proportion of nitrogen, the whole amount of the nitrogen gas is ascertained by a special operation. For this purpose we employ an apparatus, arranged in the following manner. Into the closed end of a combustion tube, 18 inches long, is introduced a layer of dry hydrate of lime, (slaked lime) of 2 to $2\frac{1}{2}$ inches. There must be at least 60 to 80 grains of it. Above it is placed 1 inch of oxide of copper, then the mixture of the substance with oxide of copper; the other divisions, *fig.* 28, point out

Fig. 28.



the oxide of copper used for rinsing out the mortar after the mixture; above this, pure oxide of copper; and, lastly, copper turnings.

The combustion tube is connected with another in the shape of a large chloride of calcium tube with two bulbs; the bulb *a* is empty, and the other bulb and the wide part of the tube are filled with fused hydrate of potassa. By means of a tube of caoutchouc, this apparatus, after the combustion tube has been placed in the furnace, is connected with the gas tube and gasometer, and the combustion carried on as usual. When the absorption tube is 12 inches long, and the wide part of it $\frac{1}{3}$ of an inch in diameter, it holds about thirty times as much potassa as is sufficient to absorb the whole carbonic acid produced, so that nitrogen alone enters the gasometer.

If the hydrate of lime be gently ignited at the end of the combustion, the water it contains is converted into vapour, and drives all the carbonic acid before it into the graduated tube. After the cooling, the combustion tube contains only watery vapour which condenses; any traces of carbonic acid being absorbed by the quick lime.

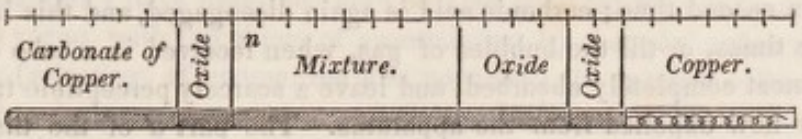
Before the combustion there was in the gasometer a known volume of air, after the combustion that volume is increased, and the increase gives exactly the volume of nitrogen that has entered the gasometer. This is measured, and after being corrected to the normal temperature and pressure, is reduced to weight.

This apparatus is exposed to a constant error, which is unavoidable. We always obtain by it too little nitrogen, which obviously arises from this, that the oxygen of the air in the tube takes part in the combustion, and the volume of gas in the gasometer is thus diminished. By a series of the most careful analyses of nitrogenized substances of known composition, the limits of this error have been ascertained, and when we add 1 per cent. to the nitrogen obtained in this way, the sum expresses exactly the true quantity of nitrogen in the substance.

When the apparatus next to be described is employed, there is always obtained an excess of nitrogen, and this excess, in good analyses, amounts to 1 to $1\frac{1}{2}$ cubic centimetres of the whole volume obtained; when deutoxide of nitrogen occurs, this excess is greater. But when a nitrogenized substance is analyzed, both in the manner last described and in that about to be mentioned, the mean of the results (one giving an excess and the other a deficiency) approaches as nearly to the true amount of nitrogen as it is possible to do at present, in cases when its

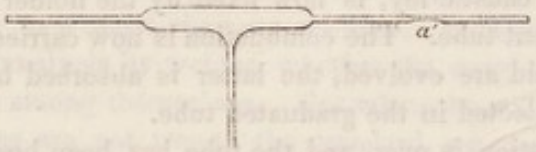
quantity is small. A combustion tube being chosen, 24 inches long, 6 inches at the closed end are filled with carbonate of copper; above this two inches are filled with pure oxide of copper; next the mixture of the substance with oxide of copper; next, another layer of pure oxide; and lastly, a layer of copper turnings. In *fig.* 29 these layers are marked. The combustion tube is connected

Fig. 29.



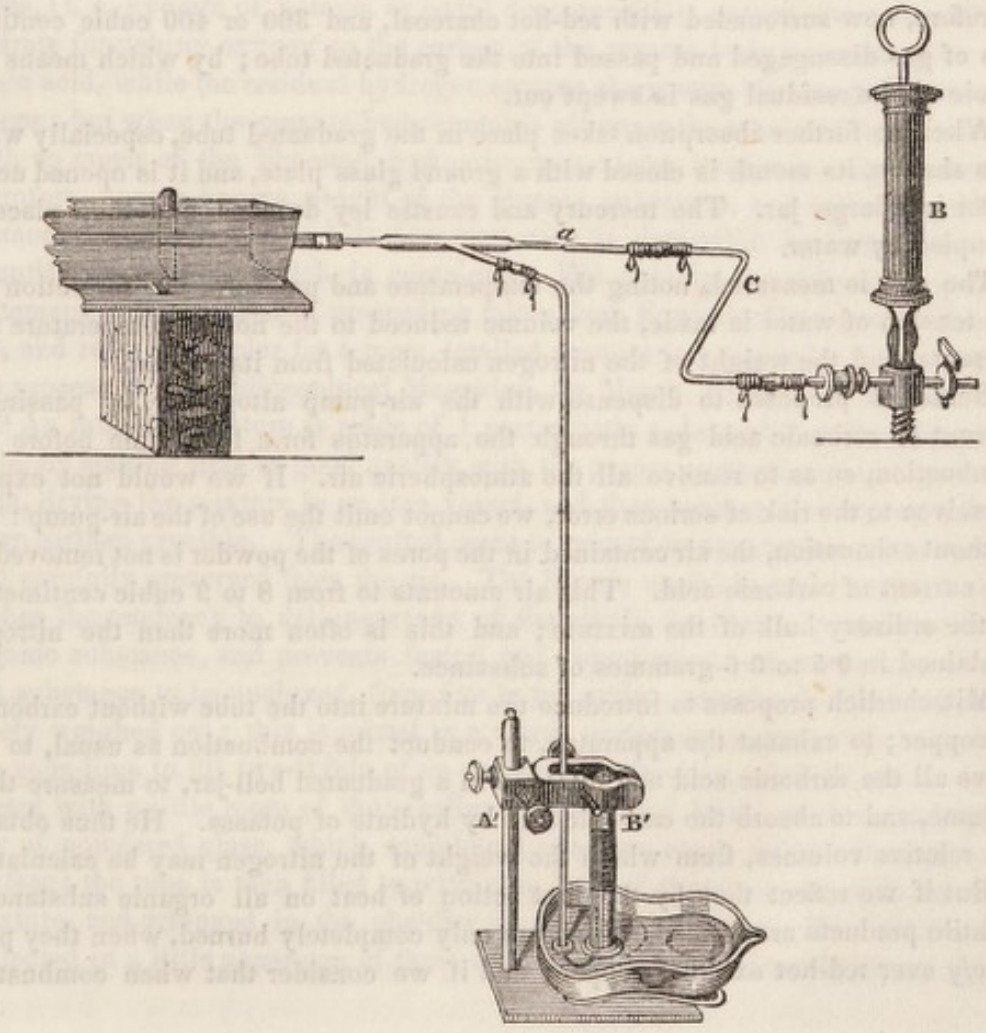
by a cork with the three-limbed tube, *fig.* 30, the cork being covered with melted

Fig. 30.



sealing wax. One limb of the tube is joined to the small air pump, *fig.* 31, B, the other with a bent tube 31 inches long, A, which dips into a small mercurial

Fig. 31.



trough, D. Both joinings are made with caoutchouc tubes. The three-limbed tube, *fig.* 30, is somewhat drawn out at *a*. The apparatus is now exhausted, the mercury rises to 27 inches. If it falls, some one of the joinings is not air tight. A screen is now placed behind the oxide of copper at *n*, *fig.* 29, and the half of the carbonate of copper farthest from the closed end of the tube is surrounded with a few red hot bits of charcoal. Pure carbonic acid is instantly disengaged, the mercury sinks, gas escapes at the end of the tube. The apparatus is now exhausted a second time; carbonic acid is again disengaged, and this is repeated four or five times, or till the bubbles of gas, when received in a tube of caustic ley, are almost completely absorbed, and leave a scarcely perceptible trace of air. The air is now expelled from the apparatus. The part *a'* of the three-limbed tube, *fig.* 30, previously drawn out, is now sealed with a spirit lamp flame, and the air pump, together with the S formed tube of connection C, removed. A graduated tube B, of about 100 cubic centimetres capacity, half filled with mercury, and half with caustic ley, is now fixed by the holder A, *fig.* 31, over the mouth of the long bent tube. The combustion is now carried on as usual; nitrogen and carbonic acid are evolved, the latter is absorbed by the ley, and thus nitrogen alone is collected in the graduated tube.

When the combustion is over, and the tube has been heated as far as *n*, *fig.* 29, the gas remaining in the apparatus still contains some nitrogen, which must be brought into the graduated tube, *fig.* 31, B'. One half of the carbonate of copper has served to expel the atmospheric air, the other half now serves to force all the residual gas into the graduated tube. The closed end of the tube is, therefore, now surrounded with red-hot charcoal, and 300 or 400 cubic centimetres of gas disengaged and passed into the graduated tube; by which means the whole of the residual gas is swept out.

When no further absorption takes place in the graduated tube, especially when it is shaken, its mouth is closed with a ground glass plate, and it is opened under water in a large jar. The mercury and caustic ley descend, and their place is occupied by water.

The gas is measured, noting the temperature and pressure, the correction for the tension of water is made, the volume reduced to the normal temperature and pressure, and the weight of the nitrogen calculated from its volume.

Berzelius proposes to dispense with the air-pump altogether, by passing a current of carbonic acid gas through the apparatus for a long time before the combustion, so as to remove all the atmospheric air. If we would not expose ourselves to the risk of serious error, we cannot omit the use of the air-pump: for, without exhaustion, the air contained in the pores of the powder is not removed by the current of carbonic acid. This air amounts to from 8 to 9 cubic centimetres in the ordinary bulk of the mixture; and this is often more than the nitrogen contained in 0·5 to 0·6 grammes of substance.

Mitscherlich proposes to introduce the mixture into the tube without carbonate of copper; to exhaust the apparatus, to conduct the combustion as usual, to receive all the carbonic acid and nitrogen in a graduated bell-jar, to measure their volume, and to absorb the carbonic acid by hydrate of potassa. He thus obtains the relative volumes, from which the weight of the nitrogen may be calculated.

But if we reflect that by the first action of heat on all organic substances, volatile products are formed, which are only completely burned, when they pass *slowly* over red-hot oxide of copper; and if we consider that when combustion

occurs in vacuo, the gases evolved expand rapidly therein, we must expect incomplete combustion at the beginning of this process. Besides, there remains at the end a certain quantity of nitrogen in the tubes which is not measured; and, farther, the volume of the hydrate of potassa must be estimated and deducted from that of the gas. This method was suggested by the analysis of uric acid; but for this substance, so rich in nitrogen, it is not required; and it is hardly to be recommended for substances which contain very little nitrogen.

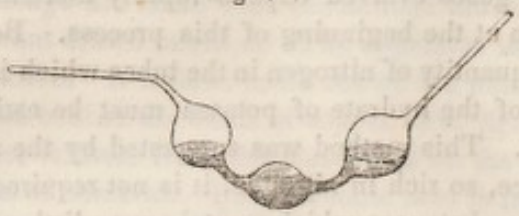
The apparatus I have described may be also used for the combustion of substances in vacuo, with the object of ascertaining, by the qualitative analysis of the gases, (rejecting, of course, the first portions,) the relative volumes of carbonic acid and nitrogen—and this with the exclusion of the air of the apparatus. Here the carbonate of copper is not required. But in substances which contain very little nitrogen, we cannot depend on the determination of the relative volumes, even when we operate with the utmost care.

We must never neglect, in all determinations of nitrogen, to subject the accuracy of our weights to a most rigorous scrutiny. It is indifferent, as is well known for ordinary analysis by weight, whether the weights be accurate or not, provided they agree among themselves. But when the weights with which we weigh our substances are not true to the standard, we are exposed to serious errors in reducing the volumes of the gases to weights.

[MM. Varrentrapp and Will have lately put in practice a new and admirable process for estimating the nitrogen in organic compounds. It has been already stated (page 535), that when neutral organic substances are heated with hydrated bases, (i. e. hydrate of potassa or soda) decomposition occurs, the water of the hydrate furnishing oxygen to the carbon of the organic body so as to form carbonic acid, while the residual hydrogen escapes along with that proper to the substance; but when the organic body contains nitrogen, the whole of this combines with so much of the liberated hydrogen as to form ammonia. By operating, therefore, upon a known weight of the organic substance, and collecting all the ammonia which is evolved, it becomes easy to determine by calculation the quantity of nitrogen which it contained. We subjoin the following general statement of the method of proceeding taken from Fowne's Elementary Chemistry, and refer the reader for a more detailed account to a paper by the authors of the process in the Philosophical Magazine, for March, 1842.

"An intimate mixture is made of 1 part caustic soda, and 2 or 3 parts quicklime, by slaking lime of good quality with the proper proportion of strong caustic soda, drying the mixture in an iron vessel, and then heating it to strong redness in an earthen crucible. The ignited mass is rubbed to powder in a warm mortar, and carefully preserved from the air. The lime is useful in many ways, it diminishes the tendency to deliquescence of the alkali, facilitates mixture with the organic substance, and prevents fusion and liquefaction. A proper quantity of the substance to be analyzed, from five to ten grains, namely, is dried and accurately weighed out; this is mixed in a warm porcelain mortar, with enough of the soda-lime to fill two-thirds of an ordinary combustion tube, the mortar being rinsed with a little more of the alkaline mixture, and lastly, with a small quantity of powdered glass, which completely removes every thing adherent to its surface; the tube is then filled to within an inch of the open end with the lime-mixture, and arranged in the chauffer in the usual manner. The ammonia is collected in a little apparatus of three bulbs containing moderately strong hydro-

Fig. 32.



chloric acid, attached by a cork to the combustion tube. Matters being thus adjusted, fire is applied to the tube, commencing with the anterior extremity. When ignited throughout the whole length, and when no more combustible gas issues from the apparatus, the point of the tube is broken and a little air drawn through the whole. The acid liquid is then emptied into a capsule, the bulbs rinsed into the same with a little alcohol, and then repeatedly with distilled water; an excess of pure chloride of platinum is added, and the whole evaporated to dryness in a water-bath. The dry mass, when cold, is treated with a mixture of alcohol and ether, which dissolves out the superfluous chloride of platinum, but leaves untouched the yellow crystalline double chloride of platinum and ammonium. The latter is collected upon a small weighed filter, washed with the same mixture of alcohol and ether, dried at 212°, and weighed; 100 parts correspond to 6·306 parts of nitrogen; or, the salt with its filter may be very carefully ignited, and the filter burned in a platinum crucible, and the nitrogen reckoned from the weight of the spongy metal, 100 parts of that substance corresponding to 14·25 parts of nitrogen;—the former plan is to be preferred in most cases.

Bodies very rich in nitrogen, as urea, must be mixed with about an equal quantity of pure sugar, to furnish incondensable gas, and thus diminish the violence of the absorption which otherwise occurs; and the same precaution must be taken, for a different reason, with those which contain little or no hydrogen."]

METHODS OF CONTROL FOR ORGANIC ANALYSES.

All the precautions which insure an accurate result having now been described, we have yet to consider some methods which are occasionally employed to check the determinations of the carbon and the hydrogen.

In the case of substances having a small atomic weight, and in which, consequently, the numbers of atoms of the elements stand in a very simple relation to one another, no further control is necessary than the accurate determination of the atomic weight. The case, however, is very different with bodies of considerable atomic weight—in which a trifling difference in the determination of the atomic weight sometimes corresponds to more than half an equivalent of carbon, and often to more than 3 atoms, or $1\frac{1}{2}$ equivalent of hydrogen. With such bodies we must not neglect the following methods of checking the result:—

Control for the Carbon.—If the substance enter into combination with a nitrogenized body, as, for example, with ammonia or nitric acid, the combustion of such compounds, when the proportion of the nitrogenized substance is known, gives, through the relative volumes of carbonic acid and nitrogen gases obtained, a strict control for the carbon. The volumes of the two gases are to each other as the equivalents of carbon and nitrogen in the compound.

A second method of checking the carbon in acids of high atomic weight, consists in the combustion of one of their salts, whose base retains carbonic acid, although ignited with oxide of copper, as, for example, baryta does. We obtain

less carbonic acid than when the substance itself is burned with oxide of copper, and, of course, exactly one atom less. The quantity of carbonic acid retained by the base may be determined, and its weight should be to that of the carbonic acid obtained in the same experiment as 1 to the remaining atoms of the carbon of the acid analyzed. Both taken together should give the number of atoms of carbon in the substance. For example, the acid in the amygdalate of baryta contains 40 atoms of carbon. This salt, by combustion with oxide of copper, yields a certain quantity of carbonic acid, which is to that retained by the baryta 39 to 1. Added together they give 40. In a similar manner must the atomic weights of all fatty acids be checked.

Control for the Hydrogen.—The hydrogen of the organic alkalies may be checked by the analysis of the salts they form with muriatic acid. Since muriatic acid undergoes no decomposition in combining with these bases, the quantity of hydrogen obtained should always be, if calculated on the weight of the base, greater by 2 atoms, or 1 equivalent, (the quantity contained in the muriatic acid,) than that furnished by the analysis of the base separately. With substances like stearic and oleic acids, there is always some uncertainty in the determination of the hydrogen; and we must here choose that number of atoms which corresponds most closely with the minimum of hydrogen obtained. The surest means of acquiring certainty in such cases, consists in the separation of the substance into new products, and the analysis of such products. The hydrogen of these must bear a distinct and obvious relation to that of the substance from which they proceed. If we cannot point out such a relation, some doubt must still remain.

DETERMINATION OF THE NUMBER OF ATOMS OF THE ELEMENTS OF AN ORGANIC COMPOUND.

The methods hitherto described give the composition of the substances analyzed in a known weight, but do not decide on the number of atoms of the elements of the compound. We may indeed ascertain their relative number, when we are able to decompose the substance into products of known composition. But this has been hitherto possible with but few; and the determination of the proportion in which the substance combines with the known atomic weight of another body, remains, as yet, the most important step towards ascertaining the true composition, and checking the numerical results of the analysis.

If the substance be an acid, its atomic weight is ascertained by the analysis of one of its salts. Its combination with oxide of silver, oxide of lead, or baryta, is best adapted for this purpose. Salts of silver, when they can be formed, are preferable to all others; they are always anhydrous, and leave, when ignited, pure metallic silver, from which the atomic weight may be easily calculated. Many salts of silver, when heated, are decomposed with a slight explosion; in these the silver must be determined by converting the oxide into chloride. Some have recommended to moisten the salt with oil of turpentine, and set it on fire, which prevents explosion; but oxalate and fumarate of silver, besides other salts, explode in spite of this precaution, which can only serve its purpose in few cases.

Berzelius analyzes salts of lead in a very convenient and expeditious way. He places the salt in a small thin capsule of porcelain, and heats it sharply at the edge, where the salt commonly takes fire, and continues to glow till nothing is left but a mixture of oxide of lead and metallic lead. The weight being taken,

it is moistened with acetic acid, and washed by decantation, first with water, and lastly with alcohol, and again dried. The loss is oxide of lead, the final increase of weight in the capsule is metallic lead.

In forming compounds of lead, we must bear especially in mind the property possessed by insoluble salts of lead, of combining with salts otherwise soluble, which may be present, and are apt to be precipitated at the same time.

If the acid form an acid and a neutral, or a neutral and a basic compound, the analysis of such compounds gives a new means of fixing the true atomic weight; but all that could be said on this head must be obvious to every one acquainted with general analysis.

Compounds of baryta answer very well. With bodies of high atomic weight the analysis of salts of lime is exposed to serious errors, from the low atomic weight of that base.

The combustion of the acid, and of one of its anhydrous salts, determines the amount of water present in the form of hydratic water.

The determination of the water of crystallization of the salts analyzed, is of great importance in organic analysis, and must never be neglected where it can be performed.

The capacity of saturation of the organic alkalies may be ascertained by means of the drying apparatus formerly described—(*figs.* 1 and 2, pages 786 and 787.) The organic base is placed in the middle portion of the vessel, and, its weight in the dry state being known, dry muriatic acid gas is introduced through *a*. The combination takes place easily, rapidly, and with disengagement of heat. Several of the bases melt, others remain porous; in all cases a certain quantity of muriatic acid, not essential to the compound, remains, and must be removed. For this purpose we proceed, just as if we wished to dry the compound. The apparatus is surrounded with boiling water, and dry air passed through till the weight becomes constant. The increase of weight in the apparatus gives the quantity of muriatic acid which has entered into combination.

If it be thought necessary to ascertain whether, during the combination, water may not have been given off, which would diminish the apparent quantity of the muriatic acid, a known weight of the salt must be dissolved in water, and the muriatic acid determined as chloride of silver.

[Note.—In a paper lately published by Professor Liebig, (Annalen der Pharmacie XXVI.) he has proposed a new method of determining the atomic weight of organic bases, which appears decidedly preferable to the above. All the vegetable alkalies in the state of muriates, form double salts with bichloride of platinum, analogous to the compounds of bichloride of platinum with muriate of ammonia, and with the chlorides of potassium and sodium; with this difference from the latter, that the salts formed by muriatic acid with the vegetable bases are true muriates, containing all the oxygen of the base, and all the hydrogen of the muriatic acid, thus adding one more to the numerous analogies existing between the vegetable alkalies and ammonia. These double salts, which are easily obtained pure, are readily analyzed by ignition. They leave metallic platinum, from which their composition may easily be calculated. This is only one of the numerous improvements in organic analysis for which we are indebted to the author of this work, and which have been the main cause of the astonishingly rapid progress lately made in this department of chemistry.—W. G.]

Many organic substances, without being exactly acids, combine with oxide of lead; and by this combination a certain portion of water is occasionally sepa-

rated, which would not have been separated by heat. By the analysis of the pure substance and of these compounds with oxide of lead, we may learn all that we wish to know of the number of atoms of the elements of the substance.

Other substances combine neither with acids nor with oxides, but they crystallize with water. In such cases the water of crystallization must be determined with the utmost care. We can calculate from it, with the same precision, the single, double, or half atomic weight of the substance, &c.—which, of course, depends on the number of atoms of water with which the substance combines.

EXAMPLES.

COMPOSITION OF AMYGDALIC ACID—DETERMINATION OF ITS ATOMIC WEIGHT.

1·089 amygdalate of baryta, decomposed by sulphuric acid, yield 0·234 sulphate of baryta. The atomic weight of the sulphate of baryta is 1458·05. That of amygdalate of baryta is therefore obtained by the proportion

0·234 : 1·089 :: 1458·05 : 6783·37.

Control.—1·002 amygdalate of baryta yield, by calcination, 0·182 carbonate of baryta. Calculated from this, the atomic weight is 6790·00. Mean of the two = 6786·68.

0·668 of the same salt yield 1·068 carbonic acid, or 159·88 per cent. 0·7235 yield 1·148 carbonic acid, or 158·60 per cent. 100 parts therefore yield, as a mean result 159·24 carbonic acid.

Further, 0·668 amygdalate of baryta yield 0·302 water, and 0·7235 yield 0·326 water.

When a salt of baryta is burned with oxide of copper, carbonate of baryta is left, the carbonic acid of which must be taken into the calculation. From one of the above experiments it appears that 100 parts of amygdalate of baryta leave, after calcination, 18·17 carbonate of baryta. These 18·17 parts contain 4·0718 carbonic acid. 100 parts of amygdalate of baryta yield, therefore, in all, 159·24 + 4·0718 = 163·3118 carbonic acid.

We calculate now the results for 100 parts amygdalate of baryta—what is wanting of the 100 is oxygen. The above experiments show that 100 parts of the salt contain,

Carbon, ...	45·157
Hydrogen, ...	5·014
Baryta, ...	14·098
Oxygen, ...	35·731
	100·000

Next, in order to find the composition of the acid, and the number of atoms of its elements, we calculate how much carbon, hydrogen, baryta, and oxygen are contained in the sum of the atoms of all the elements, that is, in the atomic weight already found.

100 parts contain				
45·157 ;	consequently	6786·68	contain	3064·660 Carbon.
5·014 ;	"	6786·68	"	340·284 Hydrogen.
14·098 ;	"	6786·68	"	956·706 Baryta.
35·731 ;	"	6786·68	"	2424·948 Oxygen.
100·000				6786·598

3064·660 is the *sum of the weights* of the atoms of carbon in 1 atom of the

salt. This number, divided by the weight of 1 atom of carbon, must give the *number* of atoms of carbon; and so on for the other elements.

$\frac{3064{\cdot}660}{76{\cdot}437}$ . . = 40·09 atoms Carbon.

$\frac{340{\cdot}284}{6{\cdot}2398}$ . . = 54 atoms Hydrogen.

$\frac{956{\cdot}706}{956{\cdot}88}$ . . = 1 atom Baryta.

$\frac{2424{\cdot}948}{100}$ . . = 24 atoms Oxygen.

Consequently the formula for the salt, as deduced from the above analysis, is

$$C_{40}H_{54}O_{24}BaO.$$

The comparison of the composition in 100 parts, given by the formula, with the numbers obtained experimentally, will now show how near the result of the analysis comes to the theoretical composition.

		In 100 parts.
40 atoms Carbon	= 3057·48	45·28
54 atoms Hydrogen	= 336·949	4·99
1 atom Baryta	= 956·880	14·17
24 atoms Oxygen	= 2400·000	35·56
Atomic weight of the formula	= 6731·309	100·00

The usual method of calculating the number of atoms in the organic substances analyzed, is exactly that now explained; the formula thus obtained being the closest expression of the numbers found by experiment. The accuracy of the formula must now be subjected to a strict examination.

In the example above given, the actual result of experiment agrees as closely as can be expected with the theoretical result, according to the formula adopted. As far as regards the carbon, oxygen, and baryta, or in short, all the elements, except the hydrogen, this is sufficient security for the correctness, both of the formula and the analysis; but if we bear in mind what has been said of the determination of hydrogen, we perceive that this *exact* coincidence proves the substance to contain *less* hydrogen than that formula indicates.

It was formerly stated that, in bodies of high atomic weight, a correction is required for the hydrogen; this, in the above calculation, has been omitted.

But if we now deduct, from the water actually obtained in each analysis, 6 milligrames (0·09 grain, nearly) as foreign to the substance, we have, from 0·668 amygdalate of baryta, 0 296 water, and from 0·7235, 0·320 water; or adding both together, from 1·3915 of the salt, 0·616 water. Hence 100 parts of the salt yield 4·91 hydrogen, that is, less than the formula requires. Adopting now the formula $C_{40}H_{52}O_{24}BaO$, the salt will contain 4·81 hydrogen per cent.; and this calculated result agrees with the *corrected* experimental one as nearly as can be expected in experiments of this nature.

From what has been said, we may conclude, with sufficient certainty, that the amygdalic acid does not contain more than 52 atoms of hydrogen, and that, consequently, the atomic weight of the salt is really only 6738·829.

It is obvious that the errors of observation in this analysis tend to diminish the apparent quantity of carbon. Now if the salt, with an atomic weight of 6786·68, only contained 39 atoms of carbon, its composition must be expressed by the formula $C_{39}H_{54}O_{25}BaO$; which would give for the atomic weight of the salt the number 6874·872; a number approaching even more nearly to that found by experiment than the above calculated one, 6738·829. But in this case, the

salt would contain only 43·35 per cent. carbon; whereas the quantity obtained, 45·157 per cent., is undoubtedly below the truth.

Here, then, a difference of $1\frac{3}{4}$ per cent. in the carbon is equal to a difference of 1 atom of that element, and it is easy to see that the loss of carbon must not, in a substance like this, exceed 0·87 per cent., if we wish the result to be free from doubt.

If we subtract, from the atomic weight of the salt that of one atom of baryta, we obtain the atomic weight of the acid; thus 6738·829—956·88=5781·949; from which number we can calculate the composition of the acid in 100 parts.

In the calculation and control of an organic base, its atomic weight is ascertained by the quantity of acid with which the base forms a definite compound; in other respects, the calculation is the same.

The number of organic substances which do not combine with some other substance of known atomic weight, and whose composition, therefore, cannot be subjected to any control, is exceedingly small. With such substances, we must be contented to ascertain the relative proportions of the atoms of their elements, and to express these in the simplest form. Mannite, for example, belongs to this class of bodies. 2·735 parts yielded by combustion 4·097 carbonic acid, and 1·770 water; which gives for 100 parts,

Carbon	39·7259
Hydrogen	7·7210
Oxygen	52·5531
	100.0000

If the atomic weight of mannite were 100, then

$\frac{39\cdot7259}{76\cdot437}$ would give the number of atoms of Carbon.

$\frac{7\cdot7210}{6\cdot2398}$ the number of atoms of hydrogen, and

$\frac{52\cdot5531}{100\cdot000}$ the number of atoms of oxygen.

But, as its atomic weight is unknown, the quotients express the relative proportions of the numbers of atoms of these elements in mannite. The quotients are,

0·518	Carbon
1·238	Hydrogen
0·525	Oxygen

We see at once, that the number of atoms of carbon in mannite must be equal to the number of atoms of oxygen; for the numbers 0·518, and 0·525 differ very slightly. We observe likewise, that the number of atoms of hydrogen must be greater than that required to make up, with the oxygen, the composition of water. For if hydrogen and oxygen were present in the proportion which constitute water, 525 of oxygen would require 1050 of hydrogen; but we have 1238, that is, very nearly one-sixth more. For one atom of oxygen, therefore, there are present 2·36 atoms of hydrogen; or, expressing this proportion in the nearest whole numbers, mannite contains, for 3 atoms oxygen, 7 hydrogen and 3 carbon.

The analysis of crystallized cane sugar gave the following results for 100 parts:—

Carbon . .	42·301 . .	$\frac{42\cdot301}{76\cdot437}=0.553$
Hydrogen . .	6·454 . .	$\frac{6\cdot454}{6\cdot2398}=1.034$
Oxygen . .	51·501 . .	$\frac{51\cdot501}{101\cdot000}=0.515$

Here we see that the number of atoms of hydrogen is exactly twice as great as the number of atoms of oxygen; and consequently, that sugar contains these elements in the proportion to form water. The number of atoms of oxygen is to the number of atoms of carbon, as 0·515 to 0·553; in whole numbers, as 11 to 12. If then, we assume sugar to contain 11 atoms of oxygen, (the smallest whole number) its composition will be expressed by the formula $C_{12}H_{22}O_{11}$.

A great many organic bodies, the atomic weight of which cannot be directly determined, are decomposed, when brought in contact, under certain circumstances, with other substances, such as acids or alkalies, into new products, whose composition either is already known, or can be easily ascertained. These decompositions furnish valuable means of determining the constitution and controlling the analysis of such bodies. Sugar, for example, in contact with ferment, is resolved into carbonic acid and alcohol; oxamide, in contact with acids or alkalies, is resolved into oxalic acid and ammonia. It is obvious, that when we have determined, in these instances, the quantity of carbonic acid and oxalic acid produced, and have satisfied ourselves that in the former case no other product besides alcohol, and in the latter none except ammonia, is formed; we can, from these data, determine the composition of these substances with absolute certainty.

A very important means of testing the composition of an organic compound of unknown atomic weight, is furnished by the hypermanganate of potash. This salt, gently heated with a soluble organic substance, is resolved into peroxide of manganese, oxygen, and potash. The oxygen enters into combination with the organic matter, and when the latter is in excess, it rarely happens that the carbon is oxidized so as to form carbonic acid. But organic acids are produced, and invariably in the proportion necessary to neutralize the potash; for the solution remains neutral. The acid chiefly formed is the oxalic; in many cases the formic. Both are easily determined; and from their quantity and that of the hydrated peroxide of manganese, the composition may be ascertained. For example, a pure solution of sugar, warmed with this salt, yields neutral oxalate of potash, and peroxide of manganese, in the proportion of 1 atom of the former to 2 of the latter; from which it is easily demonstrated that sugar contains oxygen and hydrogen in the proportion to form water.

[Note.—This experiment was first made by the Translator and M. Horace Demarçay, in 1835, and has since been confirmed by the author of this work, and by M. Pelouse. As the hypermanganate of potassa has thus become a useful re-agent in organic analysis, an account of the process by which the translator prepares this salt will not be considered out of place; more especially as a number of experimenters have found some difficulty in preparing it from the account inserted in the "Records of Science" for 1836.

Native peroxide of manganese *in very fine powder*, and fused potassa, are taken in the proportion of three atoms of each; and chlorate of potassa in the proportion of one atom. The fused potassa is dissolved in a small quantity of water, and the other substances added to the solution. The whole is dried up by a moderate heat, and the dark green mass is then powdered, and heated for half an hour to a *very low red heat* in a platinum crucible. The heated mass is then dissolved in a very large quantity of boiling water, and when the solution has become of a pure deep red, it is decanted from the hydrated peroxide which separates, and evaporated rapidly till small black crystals appear on the surface. On cooling, a large number are deposited. They are easily purified by recrys-

tallization, when they become larger and acquire a bronze colour. In the hands of the translator this process never fails, and from good oxide of manganese a quantity of crystals equal to half the weight of the oxide employed may easily be obtained. The principal causes of failure would appear to be, impurity of the oxide of manganese, or using it in a coarse powder, or, finally, applying too strong a heat.—W. G.]

Many indifferent azotized substances, in contact with alkalies, are resolved into ammonia and an acid, whose atomic weight can be determined. Such bodies are caffeine, asparagine, amygdaline, &c., the atomic weight of which may easily be deduced from the quantity of the acid, or of a salt of the acid, of known atomic weight, which is produced. For example, 1·357 parts of amygdaline produce 1·592 amygdalate of baryta. The atomic weight of this salt is 6738·829. Hence 1·592 : 6738·829 :: 1·357 : 5797 = the atomic weight of amygdaline.

DETERMINATION OF THE SPECIFIC GRAVITY OF THE VAPOURS OF VOLATILE SUBSTANCES, AS A MEANS OF ASCERTAINING THE NUMBER OF ATOMS OF THEIR ELEMENTS.

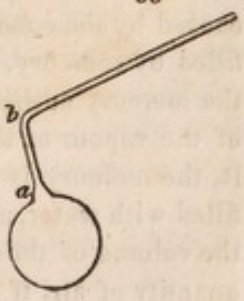
In the analysis of a volatile substance, the determination of the specific gravity of the vapour is a most valuable means of control over the analysis by combustion. The process, which is followed for this purpose, is that of Dumas, first rendered practical by that distinguished chemist, and by him also first applied, with the happiest results, to this object. The description of it, given by Dumas, in his "Traité de Chimie," embraces all the precautions which can ensure an accurate result.

The apparatus is simple in a high degree, and the whole operation is easily performed without requiring any great expenditure of time, or any peculiar dexterity in the operator. The problem to be solved is to ascertain the weight of a known volume of the vapour.

For this purpose, a convenient vessel, filled with dry air, at a known temperature and pressure, is weighed: the fluid or volatile substance, the specific gravity of whose vapour we wish to ascertain, is then introduced, and heated to from 50° to 75° beyond its boiling point, till it is entirely converted into vapour; the temperature is noted, the vessel hermetically sealed, and again weighed. We know now the weight of the vessel, when filled, both with air and with vapour. After reducing both to the same temperature and pressure, the weights of both are easily calculated, if the volume, that is, the capacity of the vessel, be ascertained. The specific gravity of the vapour is ascertained by dividing the weight of a known volume by that of an equal volume of air at the same temperature and pressure.

The following is the process in detail:—A flask of the capacity of 20 to 35 cubic inches, *fig.* 33, (10 to 18 fluid ounces), clean and dry, is chosen. It is connected with the air pump and the apparatus, *fig.* 4, *p.* 787. Air is now alternately pumped out, and re-admitted, by which means it is soon filled with dry air.

33



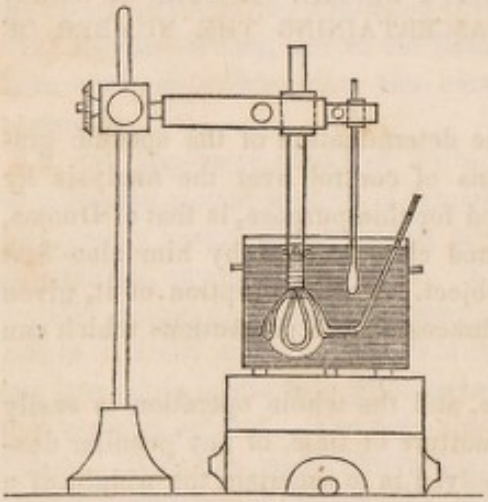
The neck of the flask is now drawn out at *a*, before the blow-pipe, to a narrow tube, 6 or 8 inches long, which is bent at *b*; the point is cut across with a sharp file, and the cut edge rounded in the flame. The glass must not split when softened, otherwise it is nearly impossible to seal it up

quickly when required. We have now got a bulb or balloon with a drawn out point. It is now weighed, and allowed to lie on the scale till its weight no longer increases by the deposition of moisture on the external surface of the glass.

To introduce the liquid or the melted volatile solid, the bulb is gently warmed, so as to expel a portion of air, and the point immersed in the fluid substance. As the heated air contracts, the liquid rises into the bulb; this may always be quickly accomplished by moistening the bulb with a little ether. The quantity of liquid introduced varies with the size of the bulb: 80 grains may be mentioned as the minimum, 160 as the maximum quantity required. If the substance should solidify in the neck or the narrow tube, these must of course be previously warmed.

The balloon is now placed in a bath of water, chloride of calcium, chloride of zinc, &c., which must always be heated to a temperature 50° to 75° beyond the boiling point of the substance. The bath may be previously heated to the required degree; there is no fear of cracking the bulb. A very exact thermometer shows the temperature of the bath.

34



35



The bulb may be supported in the bath in a variety of ways. *Fig.* 34 shows one method. *Fig.* 35 is the support for the bulb.

As soon as the temperature of the bath rises a few degrees above the boiling point of the substance, a stream of its vapour issues from the point of the tube. This gradually diminishes, and after 15 or 20 minutes, a flame brought near the point is not moved in the least. Should any drops of liquid have condensed on the neck of the tube where it is out of the bath, they must be removed. This is easily done by approaching a glowing coal; and then, by means of a spirit-lamp and blow-pipe, the point is suddenly softened, while the vessel remains in the bath; it closes hermetically with facility.

The iron vessel containing the bath is now removed from the fire, the closed bulb is taken out, washed, dried, and weighed with the precautions formerly described.

The vapour has expelled all the atmospherical air, except a small quantity, which must be ascertained. The volume of the vapour must likewise be determined.

For this purpose the point is immersed in mercury, and is cut near the neck, under the mercury, with a sharp file. When the tube is broken off, the vacuum caused by the condensation of the vapour at the ordinary temperature, is instantly filled by mercury. In general a small bubble of air is left, but in many cases the mercury entirely fills the bulb. The volume of the mercury is equal to that of the vapour at the temperature at which the bulb was sealed. To determine it, the mercury is measured in a graduated vessel. The bulb is now entirely filled with water, and the water measured in like manner. The difference between the volume of the water, and that of the mercury, gives the volume of the small quantity of air, if any, which remained.

From the data thus obtained, the specific gravity of the vapour may be calculated. The following example will illustrate this calculation. It is taken from the Analysis of Carbonic Ether, by Professor Ettling :—

Boiling point of carbonic ether, 258° F. The balloon with dry air weighed 47·77 grammes; the temperature of the air was 65·5 F.; the height of the barometer 331·8 centimetres. The bulb, after the experiment, was found, when filled with water, to have a capacity of 290 cubic centimetres, = the volume of air contained in it. 290 cubic centimetres of air at 65·5° and 331·8 B. give, at 32° and 336 bar., 267·7 cubic centimetres of air, which weigh 0·34776 gramme. Subtracting this weight from the weight of the bulb with dry air, there remains 47·42224 grammes for the weight of the bulb alone. The bulb was heated in a bath of chloride of zinc, and sealed at the temperature of 292° F. and 331·8 bar., and it now weighed 48·431 grammes. The mercury which entered the bulb after the experiment, measured 289·5 cubic centimetres at the temperature of 65·5° F. and 332 bar. Subtracting the weight of the empty bulb from that of the bulb when filled with the vapour, we have for the weight of the vapour 1·00876 grammes. If its volume, at 292° and 331·8 bar., be assumed to have been 289·5 cubic centimetres, this would give, at 32° and 336 bar., 182·98 cubic centimetres. This volume of vapour, then, weighs 1·00876 grammes; consequently, 1000 cubic centimetres would weigh 5·5129 grammes. Now, 1000 cubic centimetres of air, at 32° and 336 bar., weigh 1·299075 grammes. Hence, the specific gravity of the vapour of carbonic ether is $= \frac{5{\cdot}5129}{1{\cdot}299075} = 4{\cdot}243$.

This determination is certainly exact enough for controlling the analysis of carbonic ether; but the calculation may yield a false result under certain circumstances: for example, if a correction be not made for the small quantity of air left behind. Since the mercury which entered the bulb in the above experiment was only 289·5 cubic centimetres, while the capacity of the bulb was 290 c. c., there was left 0·5 c. c. of air, which was weighed along with the vapour. The true weight of the vapour is therefore got by subtracting from 1·00876 gramme the weight of 0·5 c. c. air, at 32° and 336 bar., which is 0·00062 gramme. The remainder is 1·008135 gramme.

But the volume of the mercury which entered the bulb does not, moreover, express the true volume of the vapour at 292° : for the 0·5 c. c. air at 292° expanded by 0·23 c. c., and, therefore, occupied at that temperature the volume of 0·73 c. c. The volume of the vapour in the above calculation, was, therefore, taken too high by 0·23 c. c. Its true volume was, 289·5 — 0·23 = 289·27 c. c. It is easy to see that, in the above example, these corrections hardly affect the result: but where the air left exceeds 2 c. c., it must be taken into the calculation as now explained.

The process just described is not susceptible of perfect accuracy. The volumes which are measured and weighed are too small. If we take very large bulbs, the apparatus becomes difficult to manage, and requires large and perfectly exact balances. But all this is unnecessary for the object in view. It is enough if the two first decimals agree with the calculated theoretical specific gravity. In no case can we reckon on the accuracy of the third decimal. For this reason it is superfluous to take into account the expansion of glass and a correction of the mercurial thermometer. The determination of the specific gravity of the vapour of camphor by Dumas, will show how slight are the changes made by these corrections on the result of experiment.

Dumas found that specific gravity, without these corrections, to be 5·356, and

after making the corrections, to be 5·337. The difference between the results of two experiments is, however, always greater than this, so that we may save ourselves the trouble of these calculations.

APPLICATION OF THE KNOWLEDGE OF THE SPECIFIC GRAVITY OF A BODY OF UNKNOWN ATOMIC WEIGHT AS A CONTROL OVER THE ANALYSIS.

The composition of carbonic ether was ascertained in the usual way. The highest numbers gave in 100 parts 51·3075 carbon, 8·5802 hydrogen, and 40·1121 oxygen. These numbers correspond to the formula $C_5H_{10}O_3$.

The specific gravities of carbon vapour, hydrogen, and oxygen, are to each other as their atomic weights. It is obvious, therefore, that in one volume of carbonic ether vapour, the volumes of carbon, hydrogen, and oxygen, must be found in the ratio of 5, 10, and 3, or in multiples or submultiples of these numbers, according to the condensation; the proportions cannot vary.

We now inquire how much carbon, hydrogen, and oxygen are contained in 4·243, the weight of one volume of carbonic ether vapour.

100 parts contain

51·3075 Carbon	therefore	4·243	contain 2·1769.
8·5802 Hydrogen,	.	4·243	. 0·3645.
40·1121 Oxygen,	.	4·243	. 1·7018.

The number 2·1769 expresses the sum of the weights of the volumes (the specific gravities) of carbon vapour in one volume of the vapour of carbonic ether. Dividing this number by the weight of one volume of carbon vapour (its specific gravity) = 0·84297, we obtain the number of volumes, namely, $2\frac{1}{2}$.

The specific gravity of hydrogen is 0·0688. Hence $\frac{0{\cdot}3645}{0{\cdot}0688} = 5$ is the number of volumes of hydrogen; and as the specific gravity of oxygen is 1·1026, $\frac{1{\cdot}7018}{1{\cdot}1026} = 1\frac{1}{2}$ is the number of volumes of oxygen in one volume of carbonic ether vapour. It is easy to see that $2\frac{1}{2}$, 5, and $1\frac{1}{2}$, are to each other as 5, 10, and 3, whence it may be inferred that the analysis and the formula deduced from it are correct:

5 volumes Carbon	$= 5 \times 0{\cdot}84279$	$= 4{\cdot}2139.$
10 volumes Hydrogen,	$= 10 \times 0{\cdot}0688$	$= 0{\cdot}6880.$
3 volumes Oxygen,	$= 3 \times 1{\cdot}1026$	$= 3{\cdot}3078.$
The sum of all is	. .	8·2097.

The number 8·2097 is to the specific gravity found by experiment, very nearly as 2 to 1. Hence in one volume of the vapour of carbonic ether, there must be contained $\frac{5}{2}$ volumes carbon, $\frac{10}{2}$ volumes hydrogen, and $\frac{3}{2}$ volumes oxygen; this is the proportion of $2\frac{1}{2}$, 5, $1\frac{1}{2}$, above obtained. The weight of one volume of carbonic acid is 1·524: that of one volume of ether is 2·58088. The sum of both is 4·10488. Hence one volume of carbonic ether vapour contains one volume carbonic acid, and one volume of the vapour of ether, condensed into one volume.

APPENDIX.

TABLE I.

Table of Chemical Equivalents of Elementary Substances with their Symbols.

Elements.	Symbols.	Equiv't.	Elements.	Symbols.	Equiv't.	Elements.	Symbols.	Equiv't.
Aluminium .	Al	13·7	Hydrogen .	H	1	Rhodium .	R	52·2
Antimony (Stibium)	Sb	64·6	Iodine . .	I	126·3	Selenium .	Se	39·6
Arsenic . .	As	37·7	Iridium . .	Ir	98·8	Silicium . .	Si	22·5
Barium . .	Ba	68·7	Iron,(Ferrum)	Fe	28	Silver, (Argentum,)	Ag	108
Bismuth . .	Bi	71	Lead, (Plumbum) . .	Pb	103·6	Sodium, (Natronium) .	Na	23·3
Boron . .	B	10·9	Lithium . .	L	6	Strontium .	Sr	43·8
Bromine .	Br	78·4	Magnesium .	Mg	12·7	Sulphur . .	S	16·1
Cadmium .	Cd	55·8	Manganese .	Mn	27·7	Tellurium .	Te	64·2
Calcium . .	Ca	20·5	Mercury,(Hydrargyrum)	Hg	202	Thorium .	Th	59·6
Carbon . .	C	6·12	Molybdenum	Mo	47·7	Tin, (Stannum) . .	Sn	57·9
Cerium . .	Ce	46	Nickel . .	Ni	29·5	Titanium .	Ti	24·3
Chlorine .	Cl	35·42	Nitrogen .	N	14·15	Tungsten, (Wolfram)	W	99·7
Chromium .	Cr	28	Osmium . .	Os	99·7	Vanadium .	V	68·5
Cobalt . .	Co	29·5	Oxygen . .	O	8	Uranium .	U	217
Columbium, (Tantalum)	Ta	185	Palladium .	Pd	53·3	Yttrium . .	Y	32·2
Copper, (Cuprum) . .	Cu	31·6	Phosphorus	P	15·7	Zinc . . .	Zn	32·3
Fluorine, .	F	18·68	Platinum .	Pt	98·8	Zirconium .	Zr	33·7
Glucinium .	G	26·5	Potassium, (Kalium)	K	39·15			
Gold(Aurum)	Au	199·2						

TABLE II.

Table of the elastic Force of Aqueous Vapour at different Temperatures, expressed in Inches of Mercury.

Temp.	Force of Vapour.		Temp.	Force of Vapour.		Temp.	Force of Vapour.	
	Dalton.	Ure.		Dalton.	Ure.		Dalton.	Ure.
32°F	0·200	0·200	79°F	0·971		126°F	3·89	
33	0·207		80	1·00	1·010	127	4·00	
34	0·214		81	1·04		128	4·11	
35	0·221		82	1·07		129	4·22	
36	0·229		83	1·10		130	4·34	4·366
37	0·237		84	1·14		131	4·47	
38	0·245		85	1·17	1·170	132	4·60	
39	0·254		86	1·21		133	4·73	
40	0·263	0·250	87	1·24		134	4·86	
41	0·273		88	1·28		135	5·00	5·070
42	0·283		89	1·32		136	5·14	
43	0·294		90	1·36	1·360	137	5·29	
44	0·305		91	1·40		138	5·44	
45	0·316		92	1·44		139	5·59	
46	0·328		93	1·48		140	5·74	5·770
47	0·339		94	1·53		141	5·90	
48	0·351		95	1·58	1·640	142	6·05	
49	0·363		96	1·63		143	6·21	
50	0·375	0·360	97	1·68		144	6·37	
51	0·388		98	1·74		145	6·53	6·600
52	0·401		99	1·80		146	6·70	
53	0·415		100	1·86	1·860	147	6·87	
54	0.429		101	1·92		148	7·05	
55	0·443	0·416	102	1·98		149	7·23	
56	0·458		103	2·04		150	7·42	7·530
57	0·474		104	2·11		151	7·61	
58	0·490		105	2·18	2·100	152	7·81	
59	0·507		106	2·25		153	8·01	
60	0·524	0·516	107	2·32		154	8·20	
61	0·542		108	2·39		155	8·40	8·500
62	0·560		109	2.46		156	8·60	
63	0·578		110	2·53	2·456	157	8·81	
64	0·597		111	2·60		158	9·02	
65	0·616	0.630	112	2·68		159	9·24	
66	0·635		113	2·76		160	9·46	9.600
67	0·655		114	2·84		161	9·68	
68	0·676		115	2·92	3.820	162	9·91	
69	0·698		116	3·00		163	10·15	
70	0·721	0·726	117	3·08		164	10·41	
71	0·745		118	3·16		165	10·68	10·800
72	0·770		119	3·25		166	10·96	
73	0·796		120	3·33	2·300	167	11·25	
74	0·823		121	3·42		168	11·54	
75	0·851	0·860	122	3·50		169	11·83	
76	0·880		123	3·59		170	12·13	12·050
77	0·910		124	3·69		171	12·43	
78	0·940		125	3·79	3·830	172	12·73	

Temp.	Force of Vapour.		Temp.	Force of Vapour.		Temp.	Force of Vapour.	
	Dalton.	Ure.		Dalton.	Ure.		Dalton.	Ure.
173°F	13·02		224°F	37·53		275°F	83·13	93·480
174	13·32		225	38·20	39·110	276	84·35	
175	13·62	13·550	226	38·89	40·100	277	85·47	97·800
176	13·92		227	30·59		278	86·50	
177	14·22		228	40·30		279	87·63	101·600
178	14·52		229	41·02		280	88·75	101·900
179	14·83		230	41·75	43·100	281	89·87	104·400
180	15·15	15·160	231	42·49		282	90·99	
181	15·50		232	43·24		283	92·11	107·700
182	15·86		233	44·00		284	93·23	
183	16·23		234	44·78	46·800	285	94·35	112·200
184	16·61		235	45·58	47·220	286	95·48	
185	17·00	16·900	236	46·39		287	96·64	114·800
186	17·40		237	47·20		288	97·80	
187	17·80		238	48·02	50·300	289	98·96	118·200
188	18·20		239	48·84		290	100·12	120·150
189	18·60		240	49·67	51·700	291	101·28	
190	19·00	19·000	241	50·50		292	102·45	123·100
191	19·42		242	51·34	53·600	293	103·63	
192	19·86		243	52·18		294	104·80	126·700
193	20·32		244	53·03		295	105·97	129·000
194	20·77		245	53·88	56·340	296	107·14	
195	21·22	21·100	246	54·68		297	108·31	133·900
196	21·68		247	55·54		298	109·48	137·400
197	22·13		248	56·42	60·400	299	110·64	
198	22·69		249	57·31		300	111·81	139·700
199	23·16		250	58·21	61·900	301	112·98	
200	23·64	23·600	251	59·12	63·500	302	114·15	144·300
201	24·12		252	60·05		303	115·32	147·700
202	24·61		253	61·00		304	116·50	
203	25·10		254	61·92	66·700	305	117·68	150·560
204	25·61		255	62·85	67·250	306	118·86	154·400
205	26·13	25·900	256	63·76		307	120·03	
206	26·66		257	64·82	69·800	308	121·20	157·700
207	27·20		258	65·78		309	122·37	
208	27·74		259	66·75		310	123·53	161·300
209	28·29		260	67·73	72·300	311	124·69	164·800
210	28·84	28·880	261	68·72		312	125·85	167·000
211	29·41		262	69·72	75·900	313	127·00	
212	30·00	30·000	263	70·73		314	128·15	
213	30·60		264	71·74	77·900	315	129·29	
214	31·21		265	72·76	78·040	316	130·43	
215	31·83		266	73·77		317	131·57	
216	32·46	33·400	267	74·79	81·900	318	132·72	
217	33·09		268	75·80		319	133·86	
218	33·72		269	76·82	84·900	320	135·00	
219	34·35		270	77·85	86·300	321	136·14	
220	34·99	35·540	271	78·89	88·000	322	137·28	
221	35·63	36·700	272	79·94		323	138·42	
222	36·25		273	80·98	91·200	324	139·56	
223	36·88		274	82·01		325	140·70	

TABLE III.

Dr. Ure's Table, showing the elastic Force of the Vapours of Alcohol. Ether, Oil of Turpentine, and Petroleum or Naphtha, at different Temperatures, expressed in Inches of Mercury.

Ether.		Alcohol sp. gr. 0·813.		Alcohol sp. gr. 0·813.		Petroleum.	
Temp.	Force of Vapour.	Temp.	Force of Vapour.	Temp.	Force of Vapour.	Temp.	Force of Vapour.
34°	6·20	32°	0·40	193·3°	46·60	316°	30·00
44	8·10	40	0·56	196·3	50·10	320	31·70
54	10·30	45	0·70	200	53·00	325	34·00
64	10·00	50	0·86	206	60·10	330	36·40
74	16·10	55	1·00	210	65·00	335	38·90
84	20·00	60	1·23	214	69·30	340	41·60
94	24·70	65	1·49	216	72·20	345	44·10
104	30·00	70	1·76	220	78·50	350	46·86
105	30·00	75	2·10	225	87·50	355	50·20
110	32·54	80	2·45	230	94·10	360	53·30
115	35·90	85	2·93	232	97·10	365	56·90
120	39·47	90	3·40	236	103·60	370	60·70
125	43·24	95	3·90	238	106·90	372	61·90
130	47·14	100	4·50	240	111·24	375	64·00
135	51·90	105	5·20	244	118·20		
140	56·90	110	6·00	247	122·10	Oil of Turpentine.	
145	62·10	115	7·10	248	126·10		
150	67·60	120	8·10	249·7	131.40	Temp.	Force of Vapour.
155	73·60	125	9·25	250	132·30		
160	80 30	130	10·60	252	138·60		
165	86·40	135	12·15	254·3	143·70	304	30·00
170	92·80	140	13·90	258·6	151·60	307·6	32·60
175	99.10	145	15·95	260	155·20	310	33·50
180	108·30	150	18·00	262	161·40	315	35·20
185	116·10	155	20·30	264	166·10	320	37·06
190	124·80	160	22·60			322	37·80
195	133·70	165	25·40			326	40·20
200	142·80	170	28·30			330	42·10
205	151·30	173	30·00			336	45·00
210	166·00	178·3	33·50			340	47·30
		180	34·73			343	49·40
		182·3	36·40			347	51·70
		185·3	39·90			350	53·80
		190	43·20			354	56·60
						357	58·70
						360	60·80
						362	62·40

TABLE IV.

For the conversion of Degrees on the Centigrade Thermometer into Degrees of Fahrenheit's Scale.

Cent.	Fahr.	Cent.	Fahr.	Cent.	Fahr.	Cent.	Fahr.
—50°	—58°0	—6°	21°2	38°	100°4	82°	179°6
—49	—56.2	—5	23.0	39	102·2	83	181·4
—48	—54.4	—4	24.8	40	104·0	84	183·2
—47	—52.6	—3	26.6	41	105·8	85	185·0
—46	—50.8	—2	28.4	42	107·6	86	186·8
—45	—49.0	—1	30.2	43	109·4	87	188·6
—44	—47.2	0	32.0	44	111·2	88	190·4
—43	—45.4	+1	33.8	45	113·0	89	192·2
—42	—43.6	2	35.6	46	114·8	90	194·0
—41	—41.8	3	37.4	47	116·6	91	195·8
—40	—40.0	4	39.2	48	118·4	92	197·6
—39	—38.2	5	41.0	49	120·2	93	199·4
—38	—36.4	6	42.8	50	122·0	94	201·2
—37	—34.6	7	44.6	51	123·8	95	203·0
—36	—32.8	8	46.4	52	125·6	96	204·8
—35	—30.0	9	48.2	53	127·4	97	206·6
—34	—29.2	10	50.0	54	129·2	98	208·4
—33	—27.4	11	51.8	55	131·0	99	210·2
—32	—25.6	12	53.6	56	132·8	100	212·0
—31	—23.8	13	55.4	57	134·6	101	213·8
—30	—22.0	14	57.2	58	136·4	102	215·6
—29	—20.2	15	59.0	59	138·2	103	217·4
—28	—18.4	16	60.8	60	140.0	104	219·2
—27	—16.6	17	62.6	61	141.8	105	221·0
—26	—14.8	18	64.4	62	143.6	106	222·8
—25	—13.0	19	66.2	63	145.4	107	224·6
—24	—11.2	20	68.0	64	147·2	108	226·4
—23	— 9.4	21	69.8	65	149.0	109	228·2
—22	— 7.6	22	71.6	66	150.8	110	230·0
—21	— 5.8	23	73.4	67	152.6	111	231·8
—20	— 4.0	24	75.2	68	154.4	112	233·6
—19	— 2.2	25	77.0	69	156.2	113	235·4
—18	— 0.4	26	78.8	70	158.0	114	237·2
—17	+ 1.4	27	80.6	71	159.8	115	239·0
—16	3.2	28	82.4	72	161.6	116	240·8
—15	5.0	29	84.2	73	163.4	117	242·6
—14	6.8	30	86.0	74	165.2	118	244·4
—13	8.6	31	87.8	75	167.0	119	246·2
—12	10.4	32	89.6	76	168.8	120	248·0
—11	12.2	33	91.4	77	170.6	121	249·8
—10	14.0	34	93.2	78	172.4	122	251·6
— 9	15.8	35	95.0	79	174.2	123	253·4
— 8	17.6	36	96.8	80	176.0	124	255.2
— 7	19.4	37	98.6	81	177.8	125	257.0

Cent.	Fahr.	Cent.	Fahr.	Cent.	Fahr.	Cent.	Fahr.
126°	258°8	175°	347°0	224°	435°2	273°	523°4
127	260·6	176	348·8	225	437·0	274	525·2
128	262·4	177	350·6	226	438 8	275	527·0
129	264·2	178	352·4	227	440.6	276	528·8
130	266·0	179	354·2	228	442.4	277	530·6
131	267·8	180	356·0	229	444.2	278	532·4
132	269·6	181	357·8	230	446.0	279	534·2
133	271·4	182	359 6	231	447.8	280	536·0
134	273·2	183	361.4	232	449.6	281	537·8
135	275·0	184	363·2	233	451.4	282	539·6
136	276·8	185	365·0	234	453.2	283	541·4
137	278·6	186	366.8	235	455.0	284	543·2
138	280·4	187	368·6	236	456.8	285	545·0
139	282·2	188	370·4	237	458.6	286	546·8
140	284·0	189	372.2	238	460.4	287	548·6
141	285·8	190	374.0	239	462.2	288	550.4
142	287·6	191	375.8	240	464.0	289	552·2
143	289·4	192	377·6	241	465.8	290	554·0
144	291·2	193	379.4	242	467.6	291	555.8
145	293·0	194	381.2	243	469.4	292	557·6
146	294.8	195	383.0	244	471.2	293	559·4
147	296·6	196	384.8	245	473.0	294	561.2
148	298·4	197	386.6	246	474.8	295	563.0
149	300·2	198	388·4	247	476,6	296	564·8
150	302·0	199	390.2	248	478.4	297	566·6
151	303.8	200	392.0	249	480.2	298	568.4
152	305.6	201	393.8	250	482.0	299	570.2
153	307.4	202	395.6	251	483.8	300	572.0
154	309.2	203	397.4	252	485.6	301	573.8
155	311.0	204	399·2	253	487.4	302	575.6
156	312.8	205	401.0	254	489.2	303	577.4
157	314.6	206	402.8	255	491.0	304	579.2
158	316.4	207	404.6	256	492.8	305	581.0
159	318.2	208	406.4	257	494.6	306	582.8
160	320.0	209	408.2	258	496.4	307	584.5
161	321.8	210	410.0	259	498.2	308	586.4
162	323.6	211	411.8	260	500.0	309	588.2
163	325.4	212	413.6	261	501.8	310	590.0
164	327.2	213	415.4	262	503.6	311	591.8
165	329.0	214	417.2	263	505.4	312	593.6
166	330.8	215	419.0	264	507.2	313	595.4
167	332.6	216	420.8	265	509.0	314	597.2
168	334.4	217	422.6	266	510.8	315	599.0
169	336.2	218	424.4	267	512.6	316	600.8
170	338.0	219	426.2	268	514.4	317	602.6
171	339.8	220	428.0	269	516.2	318	604.4
172	341.6	221	429.8	270	518.0	319	606 2
173	343.4	222	431.6	271	519.8	320	608.0
174	345.2	223	433.4	272	521.6		

TABLE V.

Dr. Ure's Table of the Quantity of Oil of Vitriol, of sp. gr. 1.8485, *and of Anhydrous Acid, in* 100 *Parts of dilute Sulphuric Acid, at different Densities.*

Liquid.	Sp. Gr.	Dry.	Liquid.	Sp. Gr	Dry.	Liquid.	Sp. Gr.	Dry.
100	1·8485	81·54	66	1·5503	53·82	32	1·2334	26·09
99	1·8475	80·72	65	1·5390	53·00	31	1·2260	25·28
98	1·8460	79·90	64	1·5280	52·18	30	1·2184	24·46
97	1·8439	79·09	63	1·5170	51·37	29	1·2108	23·65
96	1·8410	78·28	62	1·5066	50·55	28	1·2032	22·83
95	1·8376	77·46	61	1·4960	49·74	27	1·1956	22·01
94	1·8336	76·65	60	1·4860	48·92	26	1·1876	21·20
93	1·8290	75·83	59	1·4760	48·11	25	1·1792	20·38
92	1·8233	75·02	58	1·4660	47·29	24	1·1706	19·57
91	1·8179	74·20	57	1·4560	46·48	23	1·1626	18·75
90	1·8115	73·39	56	1·4460	45·66	22	1·1549	17·94
89	1·8043	72·57	55	1·4360	44·85	21	1·1480	17·12
88	1·7962	71·75	54	1·4265	44·03	20	1·1410	16·31
87	1·7870	70·94	53	1·4170	43·22	19	1·1330	15·49
86	1·7774	70·12	52	1·4073	42·40	18	1·1246	14·68
85	1·7673	69·31	51	1·3977	41·58	17	1·1165	13·86
84	1·7570	68·49	50	1·3884	40·77	16	1·1090	13·05
83	1·7465	67·68	49	1·3788	39·95	15	1·1019	12·23
82	1·7360	66·86	48	1·3697	39·14	14	1·0953	11·41
81	1·7245	66·05	47	1·3612	38·32	13	1·0887	10·60
80	1·7120	65·23	46	1·3530	37·51	12	1·0809	9·78
79	1·6993	64·42	45	1·3440	36·69	11	1·0743	8·97
78	1·6870	63·60	44	1·3345	35·88	10	1·0682	8·15
77	1·6750	62·78	43	1·3255	35·06	9	1·0614	7·34
76	1·6630	61·97	42	1·3165	34·25	8	1·0544	6·52
75	1·6520	61·15	41	1·3080	33·43	7	1·0477	5·71
74	1·6415	60·34	40	1·2999	32·61	6	1·0405	4·89
73	1·6321	59·52	39	1·2913	31·80	5	1·0336	4·08
72	1·6204	58·71	38	1·2826	30·98	4	1·0268	3·26
71	1·6090	57·89	37	1·2740	30·17	3	1·0206	2·446
70	1·5975	57·08	36	1·2654	29·35	2	1·0140	1.63
69	1·5868	56·26	35	1·2572	28·54	1	1·0074	0.8154
68	1·5760	55·45	34	1·2490	27·72			
67	1·5648	54·63	33	1·2409	26·91			

TABLE VI.

Dr. Ure's Table of the Quantity of Real or Anhydrous Nitric Acid in 100 Parts of Liquid Acid, at different Densities.

Specific Gravity.	Real acid in 100 parts of the Liquid.	Specific Gravity.	Real acid in 100 parts of the Liquid	Specific Gravity.	Real acid in 100 parts of the Liquid.
1·5000	79·700	1·3783	52·692	1·1895	26·301
1·4980	78·903	1·3732	51·805	1·1833	25·504
1·4960	78·106	1·3681	51·068	1·1770	24·707
1·4940	77·309	1·3630	50·211	1·1709	23·910
1·4910	76·512	1·3579	49·414	1·1648	23·113
1·4880	75·715	1·3529	48·617	1·1587	22·316
1·4850	74·918	1·3477	47.820	1·1526	21.519
1·4820	74·121	1·3427	47·023	1·1465	20·722
1·4790	73·324	1·3376	46·226	1·1403	19·925
1·4760	72·527	1·3323	45·429	1·1345	19·128
1·4730	71·730	1·3270	44·632	1·1286	18·331
1·4700	70·933	1·3216	43·835	1·1227	17·534
1·4670	70·136	1·3163	43·038	1·1168	16·737
1·4640	69·339	1·3110	42·241	1·1109	15·940
1·4600	68·542	1·3056	41·444	1·1051	15·143
1·4570	67·745	1·3001	40·647	1·0993	14·346
1·4530	66·948	1·2947	39·850	1·0935	13·549
1·4500	66·155	1·2887	39·053	1·0878	12·752
1·4460	65·354	1·2826	38·256	1·0821	11·955
1·4424	64·557	1·2765	37·459	1·0764	11·158
1·4385	63·760	1·2705	36·662	1·0708	10·361
1·4346	62·963	1·2644	35·865	1·0651	9·564
1·4306	62·166	1·2583	35·068	1·0595	8·767
1·4269	61·369	1·2523	34·271	1·0540	7·970
1·4228	60·572	1·2462	33·474	1·0485	7·173
1·4189	59·775	1·2402	32·677	1·0430	6·376
1·4147	58·978	1·2341	31·880	1·0375	5·579
1·4107	58·181	1·2277	31·083	1·0320	4·782
1·4065	57·384	1·2212	30·286	1·0267	3·985
1·4023	56·587	1·2148	29·489	1·0212	3·188
1·3978	55·790	1·2084	28·692	1·0159	2·391
1·3945	54·993	1·2019	27·895	1·0106	1·594
1·3882	54·196	1·1958	27·098	1·0053	0·797
1·3833	53·399				

TABLE VII.

Table of Lowitz showing the Quantity of absolute Alcohol in Spirits of different Specific Gravities.

100 Parts.		Sp. Gravity.		100 Parts.		Sp. Gravity.		100 Parts.		Sp. Gravity.	
Alc.	Wat.	At 68°.	At 60°.	Alc.	Wat.	At 68°.	At 60°.	Alc.	Wat.	At 68°.	At 60°.
100	0	0·791	0·796	66	34	0·877	0·881	32	68	0·952	0·955
99	1	0·794	0·798	65	35	0·880	0·883	31	69	0·954	0·957
98	2	0·797	0·801	64	36	0·882	0·886	30	70	0·956	0·958
97	3	0·800	0·804	63	37	0·885	0·888	29	71	0·957	0·960
96	4	0·803	0·807	62	38	0·887	0·891	28	72	0·959	0·962
95	5	0·805	0·709	61	39	0·889	0·893	27	73	0·961	0·963
94	6	0·808	0·812	60	40	0·892	0·896	26	74	0·963	0·965
93	7	0·811	0·815	59	41	0·894	0·898	25	75	0·965	0·967
92	8	0·813	0·817	58	42	0·896	0·900	24	76	0·966	0·968
91	9	0·816	0·820	57	43	0·899	0·902	23	77	0·968	0·970
90	10	0·818	0·822	56	44	0·901	0·904	22	78	0·970	0·972
89	11	0·821	0·825	55	45	0·903	0·906	21	79	0·971	0·973
88	12	0·823	0·827	54	46	0·905	0·908	20	80	0·973	0·974
87	13	0·826	0.830	53	47	0·907	0·910	19	81	0·974	0·975
86	14	0·828	0·832	52	48	0·909	0·912	18	82	0·976	0·977
85	15	0·831	0·835	51	49	0·912	0·915	17	83	0·977	0·978
84	16	0·834	0·838	50	50	0·914	0·917	16	84	0·978	0·979
83	17	0·836	0·840	49	51	0·917	0·920	15	85	0·980	0·981
82	18	0·839	0·843	48	52	0·919	0·922	14	86	0·981	0·982
81	19	0·842	0·846	47	53	0·921	0·924	13	87	0·983	0·984
80	20	0·844	0·848	46	54	0·923	0·926	12	88	0·985	0·986
79	21	0·847	0·851	45	55	0·925	0·928	11	89	0·986	0·987
78	22	0·849	0·853	44	56	0·927	0·930	10	90	0·987	0·988
77	23	0·851	0·855	43	57	0·930	0·933	9	91	0·988	0·989
76	24	0·853	0·857	42	58	0·932	0·935	8	92	0·989	0·990
75	25	0·856	0·860	41	59	0·934	0·937	7	93	0·991	0·991
74	26	0·859	0·863	40	60	0·936	0·939	6	94	0·992	0·992
73	27	0·861	0·865	39	61	0·938	0·941	5	95	0·994	
72	28	0·863	0·867	38	62	0·940	0·943	4	96	0·995	
71	29	0·866	0·870	37	63	0·942	0·945	3	97	0·997	
70	30	0·868	0·872	36	64	0·944	0·947	2	98	0·998	
69	31	0·870	0·874	35	65	0·946	0·949	1	99	0·999	
68	32	0·872	0·875	34	66	0·948	0·951	0	100	1·000	
67	33	0·875	0·879	33	67	0·950	0·953				

TABLE VIII.

Tables showing the Specific Gravity of Liquids, at the Temperature of 35° *Fahr. corresponding to the Degrees of Beaumé's Hydrometer.*

FOR LIQUIDS LIGHTER THAN WATER.

Deg.	Sp. Gr.	Deg.	Sp. Gr.	Deg.	Sp. Gr.	Deg.	Sp. Gr.	Deg.	Sp. Gr.
10	=1·000	17	= ·949	23	= ·909	29	= ·874	35	= ·842
11	·990	18	·942	24	·903	30	·867	36	·837
12	·985	19	·935	25	·897	31	·861	37	·832
13	·977	20	·928	26	·892	32	·856	38	·827
14	·970	21	·922	27	·886	33	·852	39	·822
15	·963	22	·915	28	·880	34	·847	40	·817
16	·955								

FOR LIQUIDS HEAVIER THAN WATER.

Deg.	Sp. Gr.	Deg.	Sp. Gr.	Deg.	Sp. Gr.	Deg.	Sp. Gr.	Deg.	Sp. Gr.
0	=1·000	15	=1·114	30	=1·261	45	=1·455	60	=1·717
3	1·020	18	1·140	33	1·295	48	1·500	63	1·779
6	1·040	21	1·170	36	1·333	51	1·547	66	1·848
9	1·064	24	1·200	39	1·373	54	1·594	69	1·920
12	1·089	27	1·230	42	1·414	57	1·659	72	2·000

INDEX.

A.

Absinthine, 687
Absolute alcohol, 610
Acetal, 619
Acetates, 629
  products of decomposition of, 629
Acetone, 629
  its compounds and products, 629
Acetic acid, 722, 620
  products of decomposition of, 629
Acetyle, 618
  oxychloride of, 624
  combinations of, 618
Acids, definition of, 439
  nomenclature of, 113
  organic, 541
  coupled, 542
Acid, acetic and acetylous, 620
  acetylous, 620
  acetylic, 620
  aconitic, 650
  adipic, 673
  aldehydic, 620
  aloeretinic, 702
  aloetic, 702
  althionic, 618
  alloxanic, 584
  ambreic, 677
  amygdalinic, 598
  anilic, 699
  anisic, 666
  anthranilic, 700
  antimonic and antimonious, 375
  arsenic, 369
  arsenious, 364
  aspartic, 688
  atropic, 678
  azelaic, 673
  azoleic, 673
  auric, 418
  benzilic, 596
  benzoic, 690
  bibromisatic, 695
  bichlorisatic, 695
  bilifellic, 753
  boletic, 678
  boracic, 209
  boro-hydrofluoric, 253
Acid, brombenzoic, 593
  bromic, 247
  bromosalicylic, 603
  butyric, capric, and caproic, 663, 664
  caffeic, 678
  caincic, 678
  camphoric, 664
  capric, 664
  carbazotic, 699
  carbolic, 727
  carbonic, 188
  mode of obtaining in a solid state, 52
  low temperature of, in the solid state, 53
  cerebric, 755
  cetylic, 669
  chelidonic, 678
  chloranilic, 698
  chloric, 226
  chlorinized chlorindoptenic, 698
  chlorindoptenic, 697
  chlorisatic, 695
  chloroacetic, 626
  chlorocarbonic, 230
  chlorosalicylic, 603
  chlorophenesic, 700
  chlorophenusic, 700
  chlorous, 225
  chlorovalerosic, 666
  chlorovalerisic, 666
  choleic, 754
  choloidic, 753
  cholesteric, 677
  cholic, 753
  chromic, 378
  chrysanilic, 700
  chrysammic, 702
  chrysolepic, 703
  cinnamic, 605
  citraconic, 651
  citric, 648
  columbic, 396
  crameric, 678
  crenic and apocrenic, 721
  croconic, 552
  crotonic, 664
  cuminic, 667
  cyanic, 558
  cyanilic, 579
  cyanuric, 579
Acid, cynoxalic, 589
  draconic, 681
  elaidic, 678
  ellagic, 659
  equisetic, 650
  erytholeic, 690
  ethionic, 617
  ferrocyanic, 567
  fluoboric, 252
  fluochromic, 383
  fluoric, 251
  fluosilicic, 253, 250
  formic, 644
  fulminic, 561
  fumaric, 656
  fungic, 678
  gallic, 658
  glacial phosphoric, 207
  glucic, 635
  hippuric, 593
  hircic, 664
  hydrated salicylous, 601
  hydriodic, 237
  hydrobromic, 245
  hydrochloric, 219
  hydro-cobalto-cyanic, 570
  hydrocyanic, 555
  hydro-ferrid-cyanic, 570
  hydroferrocyanic, 567
  hydrofluoric, 250
  hydroleic, 675
  hydromargaric, 675
  hydromargaritic, 675
  hydromellonic, 575
  hydropersulphuric, 265
  hydroselenic, 267
  hydrosulphocyanic, 574
  hydrosulphuric, 263
  hydrotelluric, 405
  hypochlorous, 223
  hyponitrous, 178
  hypophosphorous, 204
  hyposulphobenzidic, 594
  hyposulphobenzoic, 593
  hyposulphoindigotic, 693
  hyposulphuric, 200
  hyposulphurous, 199
  indigotic, 699

Acid, iodic, 239
iodosalicylic, 603
iodous, 239
isatinic, 694
isethionic, 617
itaconic, 651
japonic, 659
kakodylic, 631
kinic, 661
komenic, 661
lactic, 639
lampic, 620
lipic, 673
lithic, *see Uric*
lithofellic, 754
maleic, 656
malic, 655
manganic, 328
margaric, 669
margaritic, 674
meconic, 660
mechloic, 689
melanic, 602
melassic, 635
mellitic, 553
mesoxalic, 584
metagallic, 658
metamargaric, 675
metaphosphoric 205,207
methionateofbaryta,617
methionic, 617
metoleic, 675
molybdic, molybdous, 392
mucic, 636
muriatic, 219
mykomelinic, 584
naphalic, 736
nitric, 181
nitro-muriatic, 222
nitronaphalesic, 736
nitronaphthalic, 736
nitro-picric, 699
nitro-salicylic, 699
nitrous, 179
œnanthic, 666
oleic, 672
oleophosphoric, 755
osmic, 428
oxalic, 549
oxalovinic, 615
oxaluric, 585
oxymuriatic, 216
palmic, 674
palmitic, 662
parabanic, 585
paraphosphoric, 205
paratartaric, 624
perchloric, 227
periodic, 241
permanganic, 328
phocenic, 664
phosphatic, 264
phosphoric, 205
phosphorous, 204
phosphovinic, 613
picric, 699
pimelic, 673
pinic, 685
prussic, 555
pyrocitric, 648
pyrogallic, 658
Acid, pyroligneous, 620
pyromalic, 655
pyromucic, 637
pyrophosphoric,207,205
racemic, 654
ricinic, 674
rhodizonic, 552
rocellic, 667
rubinic, 659
saccharic, 635
saccharosulphuric, 634
sacchulmic, 634
salicylous and salicylic, 601, 602
sebacic, 673
selenic, 214
selenious, 213
silicic, 211
silico-fluoric, 254
stearic, 669
suberic, 671
succinic, 671
sulphocyanic, 574
sulphoindigotic, 693
sulphomesitylic, 629
sulphonaphthalic, 735
sulphopurpuric, 694
sulphosaccaric, 634
sulphovinic, 613
sulphur, 192
sulphuric, 195
fuming, 196
sulphurous, 194
sylvic, 684
tannic, 657
tartaric, 651
tartralic, 653
telluric, 404
tellurous, 404
thionuric, 585
titanic, 402
tungstic, 394
uramilic, 586
uric, 580
valerianic, 666
vanadic, 388
veratric, 664
xanthic, 615
xanthoproteic, 750
Acids, organic, 541
a table of those for the detection of which directions are given in section on chemical analysis, 774
theory of, 541
Acidulous waters, 780
Aconitine, 712
Acroleine, 674
Aëriform bodies, 23, 41
Affinity, chemical, 115
table of, 116
single elective, 116
double elective, 117
disposing, 161
by what circumstances modified, 120
quiescent and divellent, 118
measure of, 125
changes that accompany, 118
Agriculture, chemistry of, 761
Air, atmospheric, 166
alkaline, 255
fixed, 188
Alabaster, 464
Albumen, animal, 744
vegetable, 740
composition of, 747
Alcohol, 609
absolute, 610
action of chlorine, &c. on, 626
action of bichloride of platinum on, 628
comp'ds derived from oxidation of, 618
Aldehydic acid, 620
Aldehyde, 618
resin of, 619
Alembroth, salt of, 509
Algaroth, powder of, 373
Alizarine, 686
Alkalies, 289
metallic bases of, 289
volatile, 255
silicated, 211
vegetable, 703
Alkalimeter, 493
Alkaline air, 255
bases, 289
Alkaline earths, 289
metallic bases of, 289
Alkaline waters, 780
Alkaloids, 703
Alkarsine, 630
Allanite, 399
Allantoine, 581
Alloxan, 582
Alloxanates, 584
Alloxantine, 586
Alloys, 431
of arsenic, 433
of tin, lead, antimony, and bismuth, 434
of copper, 434
of steel and silver, 435
of gold, 435
Almond oil, 672
Aloes, bitter of, 702
Althionic acid, 617
Alum, 468
stone, 468
Alumen ustum, 468
Alumina, or aluminous earth, 316
tests of, 317
mellitate of, 553
sulphates of, 465
sulphates, double, of, 468
acetate, of, 622
Aluminite, 465
Aluminium and its compounds, 315
Amalgam, 431, 433
for looking-glasses, 433
for electrical machine, 433
Amalgamation of silver ores, 412
Amule, or amyle, 646

Amule, compounds of, 647
Amarythrine, 690
Amber, 671
Ambergris and ambreine, 677
Amide, 258
combinations of, 543
Amilene, 648
Ammelide, 577
Ammeline, 577
and acids, 577
Ammonia, 255
Ammonia, liquid, table of the strength of solutions of, 257
character of the salts of, 256
sulphate of, 463
sulphates, double of, 470
sulphite of, 470
nitrate of, 473
phosphates of, 483
arseniates of, 487
carbonates of, 495
hydrosalts of, 499
sulphur salts of, 502
haloid salts of, 509
chlorides with, 514
oxalate of, 550
acetate of, 622
subcarbonate of, 495
bimalate of, 656
citrate of, 649
succinate of, 672
urate of, 581, 759
mellitate of, 553
cyanates of, 560
oxalurate of, 585
thionurate of, 586
benzoate of, 599
salicylite of, 602
table of salts of, 499
Ammoniacal gas, 255
Ammoniacal salts, 499
Ammoniaco-magnesian phosphate, 484
Ammonium, 256
sulpho-cyanide of, 576
oxide of, 256
Ammoniuret of copper, 467
Amygdaline, 598
Analysis qualitative, 772
quantitative, 775
Analytical chemistry, 769
division of the subject, 770
Anhydrite, 464
Aniline, 692, 700, 704
Animals, changes which occur during the life, growth, and nutrition of, 761
Anthracene, 737
Antiarine, 688
Antimonialis, pulvis, 375
Antimoniates, 375
Antimonio-sulphurets, 508
Antimonites, 375
Antimony and its comp'ds, 372
Antimony, butter of, 375
regulus of, 372
argentine flowers of, 373
glass, crocus, and liver of, 376
alloys of, *vide* Alloys
golden sulphuret of, 377
oxychloride of, 376
tartrate of, and potassa 652
Apatite, 483
Apparatus, Nooth's, 189
Aqua fortis, 182
regia, 222
Aqueous vapour, elastic force of at different temperatures, table of, 826
Arbor Dianæ, 414
Saturni, 361
Archil, 689
Aricine, 706
Arrangement of the work, 5
Arrow-root, 716
Arseniates, 486
Arsenites, 488
Arsenic and its compounds, 364
white oxide of, 364
tests of, 366
alloys of, *vide* Alloys
fuming liquor of, 370
Arsenio-sulphurets, 505
Arseniuretted hydrogen, 370
Asparagine, 688
Atmospheric air, 166
chemical properties of, 170
physical properties of, 166
analysis of, 169
weight of, 166
Atom, definition of, 136
Atomic theory, Dalton's view of, 135
weights, 136
Atropine, 711
Attraction, chemical, *vide* Affinity, 115
cohesive, 2
terrestrial, or gravity, 2
electric, 67
Aurates, 418
Auro-chlorides, 510
Azobenzide, 594
Azobenzoide, 596
Azobenzyle, 595
Azolitmine, 690
Azote, 165
Azotized substances common to the vegetable and animal world, 748

B.

Baldwin's phosphorus, 64
Balsam of Peru, 606
of Tolu, 685
Barilla, 494
Barley, malting, 742
Barium and its compounds 303
sulphur salts of, 438,502
haloid salts of, 509
hydrate of, 304
ferrocyanide of, 569
Baryta or barytes, 303
tests of, 304
Baryta, alloxanate of, 584
sulphate of, 464
nitrate of, 473
nitrite of, 475
chlorate of, 476
arseniate of, 487
carbonate of, 496
metaphosphate of, 486
Baryto-calcite, 498
Bases, a table of those for the discovery of which directions are given in section on chemical analysis, 772
tests used for the discovery of, and the modes of applying them, 773
volatile, 704
Beer, 742
Bell-metal, 434, *vide* Alloys
Benzamide, 592
Benzhydramide, 595
Benzilates, 596
Benzile, 596
hydrocyanate of, 596
Benzimide, 595
Benzoates, 591
Benzoic ether, 615
Benzoinamide, 595
Benzoine, 595
hydrocyanate of, 596
Benzole, 594
chloride of, 594
Benzone, 594
Benzoyle, 590
constitution of the compounds of, 590
hyduret of, 591
formation of, from bitter almonds, 591
chloride of, 592
bromide of, 592
iodide of, 592
sulphuret of, 592
benzoate of hyduret of, 593
table of compounds of, 590
appendix of, 598
Berberine, 713
Berlin or Prussian blue, 569
Bibromisatine, 695
Bromisatine, 695
Bile and biliary calculi, 751, 754
Bismuth or wismuth and its compounds, 399
magistery of, 400
butter of, 401
alloys of, *vide* Alloys
Bitter almonds, oil of, 591
Bitumen, 739

Black dyes, 687
Black lead, 639
Black oxide of iron, 334, 335
copper, 256
Bleaching, 218
Bleaching powder, 218
Blende, 341
Block tin, 350
Blood, 759
analysis of, 761
coagulation of, 759
serum of, 759
fibrin of, 760
Blowpipe, with oxygen and hydrogen, 158
Blue, Prussian or Berlin, 569
Blue dyes, 687
Blue vitriol, 466
Bodies, isomorphous, 454
isomeric, 150
plesiomorphous, 457
Boiling point of liquids, 42
Bone earth, 483
Borates, 491
Borax, 209, 491
Boro-fluorides, 517
Boron and its acid, 208
terchloride of, 232
Brain, analysis of, 755
Brass, 434
brazing, 434
Bromates, 480
Bromides, 245
double, 516
of cyanogen, 565
Bromine, 243
its compounds, 245
chloride of, 247
its attraction for metals, 283
Brucine, 713
Brunswick green, 513
Bryonine, 688
of antimony, 375
of zinc, 342

C.

Cadmium and its comp'ds, 343
Caffeine, 715
Calamine, 341
Calcination, 280
Calcium and its compounds, 308
sulphur salts of, 503
haloid salts of, 509
Calculi, urinary, 758
biliary, 754
Calculus, mulberry, 759
bone earth, 759
ammoniaco-magnesian fusible, 759
cystic oxide, 759
xanthic, 759
Calomel, 408
Caloric, *vide* Heat
Calorimeter of Lavoisier and Laplace, 33
Calx, 280
Camera obscura, 58
Camphone, 665
Camphor, 665
Camphor, oil of, 665
Camphorates, 665
Cannel coal, *vide* Coal
Cantharadine, 683
Canton's phosphorus, 64
Caoutchouc, 684
volatile liquid of, 684
Capnomor, 725
Caramel, 635
Carbon, 185
chlorides of, 229, 230
its compounds with oxygen, 187
with hydrogen, 258
with nitrogen, 271
with sulphur, 273
Carbo-sulphurets, 504
Carbonates, general properties of, 492
double, 498
Carbonic oxide, 190
ether, 614
Carbovinate of potassa, 614
Carburetted hydrogen, 258
Carmine, 702
Cartilage, 750
Caseine, 745
identical with legumine, 741
occurs in many vegetables, 741
Cassius, purple of, 410
Castor oil, 674
Castorine, 677
Catechine, 659
Catechu, 659
Cathartine, 688
Cedriret, 726
Celestine, 464
Cetrarine, 688
Cerine, 677
Cerium, and its compounds, 399
Cerosine, 678
Ceruse, 497
Cetene, 646
Cetyle, 646
combinations of, 647
Chalk, 496
stones, 580
Chalybeate waters, 780
Charcoal, 185
animal, or ivory black, 185
property of absorbing gases, 186
antiseptic property of, 187
destroys colours in fluids, 187
Chelidonine, 710
Chemical analysis, the different objects proposed in, 769
exemplification of, 769
quantitative and qualitative, 769
directions for conducting, 770
Chemical decomposition, theory of, 110
Chemical action, changes that accompany it, of density, temperature, form and colour, 118
affinity or attraction, 115
symbols, 146
equivalents, 128
mode of ascertaining, 134
scale of, 135
formulæ, 146
symbols, table of, 146
Chemical equivalents of elementary substances, table of, 147
Chemistry, organic, 521
inorganic, 111
Cheese, *vide* Caseine
Chinoidine, 706
Chinoiline, 705
Chlorates, 226, 476
Chloral, 626
Chloranilam, 698
Chloranilammon, 698
Chloranile, 698
Chlorides or chlorurets, 218
metallic, 282
Chlorides with ammonia, 514
with phosphuretted hydrogen, 515
Chlorides of carbon, 229
oxy-, 512
with double iodides, 515
Chloride of sulphur, 231
phosphorus, 231
boron, 232
iodine, 241
bromine, 247
cyanogen, 564
nitrogen, 228
lime, 310
sodium, 300
Chlorine, 215
Chlorine, its affinity for metals, 282
its compounds, 219
nature of, 217, 233
bleaching powers of, 218
disinfecting powers of, 218
theories of constitution of, 216
Chlorindamit, 698
Chlorindine, 697
bichlorisatyde, 696
Chlorindopten, 697
Chlorisatine, 694
bichlorisatine, 693
Chlorisatyde, 696
Chlorites, 247
Chloroacetates, 626
Chlorobenzide, 594
Chlorocarbonic ether, 616
Chloronaphthalase, 733
Chloronaphthalese, 733
Chloronaphthalise, 733
Chloronitrous gas, 233
Chlorophane, 64
Chlorophyll, 687
Chlorosalicine, 604
Chlorosalicylimide, 603

Chlorurets, 218
Cholesterine, 677
Chondrine, 750
Chromates, 484
of chlorides, 490
Chromate of iron, 378
Chromium and its comp'ds, 378
sulphate of, 466
Chrome alum, 469
Chrome yellow, 490
Chrysammate of potassa, 702
Chrysolepate of potassa, 703
Chyle, 757
Chyme, 756
Cinchona bark, 706
bases of, 706
Cinchonine, 706
Cinnabar, 412
Cinnabar, factitious, 412
Cinnamon, oil of, 680
Cinnamule, 605
hydurets of, 605
Cinnameine, 606
Citrates, 649
Citric acid, 648
Classification of chemical substances, 5
Cleavage, 453
Cloves, oil of, 680
Coal-mines, fire-damp of, 259
wood or brown, 726
gases, 726
changes of, 727
nitrogen contained in, 727
Coagulation of the blood, *vide* Blood
Cobalt and its compounds, 345
Cyanides, 565
Cobalto-cyanide of potassium, 571
Cobalto-cyanides, 571
Codeine, 708
Cocculus Indicus, principle of, 711
Cochineal, 702
Cohesive attraction, 2, 120
influence of, over chemical action, 121
Cold, artificial methods of producing, 40, 48
Colouring matter,
non-azotized vegetable, 686
vide Blood
yellow, 686
red, 686
green, 686
Colours primitive, 61
Coke, 185
Columbin, 688
Columbium and its compounds, 395
Combination defined, 126
utility of, 131
laws of, 127, 128
Combining proportions explained, 128
table of, 134
Combining exemplifications of, 133
Combustion, 152
theories of, 153, 154
spontaneous, *vide* Phosphuretted hydrogen and Pyrophosphorus
Compound radical, 524
Composition of bodies, 132
how determined, 134
Conine, 705
Conductor, prime, 73
Conductors of heat, 9
Conduction of heat, 9
Cooling of bodies, 18
Copal, 685
Copper nickel, 348
Copper and its compounds, 354
test of, 356
alloys of, *vide* Alloys
pyrites, 358
glance, 358
sulphates of, 466
nitrate of, 474
arsenite of, 488
carbonate of, 497
tinning of, 434
acetates of, 623
black oxide of, 356
white muriate of, 357
sheathing, preservation of, 84
white, of the Chinese, 434
ore, blue, 497
Cork, *vide* Suberic acid
Corydaline, 713
Corrosive sublimate, 409
tests of, 410
Count Rumford's mode of ascertaining conducting power of articles of clothing, 10
Cream of lime, *vide* Milk of lime, 309
Creosote, 722
Crocus of antimony, 376
Cryophorus, 48
Crystallization, 446
systems of, 447
water of, 443
Crystallography, 446
octohedral system of, 449
square prismatic system of, 451
right prismatic system, 451
oblique, doubly oblique, and rhombohedral systems, 452
Crystals, simple form of, 447
compound form of, 448
angles, planes, and edges of, in, 447
structure of, 453
cleavage of, 453
Cubebine, 689
Cudbear, 689
Cyanates, 559
Cyanides, double, of metals, 567
Cyanogen, 271, 554
compounds of, 554
Cyanogen, decomposition of solution, 540
and carbonic oxide, 580
Cyanurates, 563
Cyanurets, metallic, (or Cyanides,) 565
double, 567
Cyanuret, red, of potassium and iron, 570
Cyclamine, 689
Cystic oxide, calculus, 759

D.

Daguerréotype, 63
Daturine, 710
Dead Sea, analysis of its water, 782
Decay of wood, 533
prevented by antiseptics, 720
Decomposition, simple, 115
double, 116
Decrepitation, 445
Definite proportions, doctrine of, *vide* Equivalents
Deflagration, 472
Deliquescence, 443
Delphine, 712
Density, 49
Dephlogisticated air, *vide* Oxygen
marine acid, *vide* Chlorine
Derbyshire spar, 310
Dew, formation of, 18
Dew-point, 51
Dextrine, 717
Diamond, 185
Diastase, 717
Differential thermometer, 26
Digestion, 756
respective action in, of gastric juice, hydrochloric acid, and oxygen, 756
Dioxides, 133
Disinfecting liquor, 218
Distilled waters, 780
Distillation by descent, 341
Drying oils, 674
Dutch gold, 434
Dyes, 686

E.

Earths, pure, 289
metallic bases of, 289
siliceous, 210
alkaline, 289
aluminous, 314
Earthy sulphates, mode of analyzing, 777
Earthy minerals, analysis of, containing silica, iron, alumina, manganese, lime and magnesia, 779

Ebullition, 42
Efflorescence, 444
influence of, over affinity, 122
Elaldehyde, 619
Elasticity, its effects on chemical affinity, 122
of vapours, 49
Electric attraction, 67
repulsion, 67
excitement, causes of, 71
intensity, 79
currents, 98
Electrics, positive, 110
negative, 110
Electrical battery, 74
accumulation, laws of, 79
machine, 71
unit jar, 78
Electricity, 67
elementary facts of, 67
conductor and non-conductors of, 68
vitreous or positive, 69
resinous or negative, 69
theories of, 69
induction of, 73
of atmospheric, 72
identical with lightning, 82
historical notice relating to, 81
velocity of, 81
light of, 81
condenser of, 74
Electro-chemical decomposition, theory of, 100
theory, 105
Electrodes, 101
Electro-dynamics, 96
Electro-magnetism, 96
Electrometer, balance, 78
quadrant, 77
gold leaf, 77
torsion, 77
Electrolyte, 101
Electro-negative and positive elements, 108
Electrophorus, 75
Electroscopes and electrometers, 77
Elements, 146, 147
Elementary substances, chemical equivalents of, 128
Emetine, 712
Empyreal air, *vide* Oxygen
Emulsine, 741
Epsom salts, 465
Equivalent, chemical, 128
scale of, 135
Eremacausis, 473, 533
Ergotine, 688
Erethryne, 689
Erythroleine, 690
Erythrolitmine, 690
Erythronium, 384
Essential oils, 678
non-oxygenated, 678
oxygenated, 679
containing sulphur, 681
Ethal, 646
Ether, 608
theory of the formation of, 608
constitution of, and its compounds, 607
acetic, 622
oxalic, 614
chloric, 611
hydriodic, 611
hydrochloric, 611
hydrobromic, 611
carbonic, 614
chlorocarbonic, 416
Etherine, 617
Etherole, 617
Ethionate of baryta, 617
Ethiop's mineral, 412
per se, 406
Ethule or Ethyle, 609
with oxygen, 608
with water, 609
and chlorine, 611
bromide of, 611
iodide of, 611
sulphuret of, 611
compounds of, sulphuret of, 611
bisulphuret of, 612
seleniuret of, 612
cyanide of, 612
sulphocyanide of, 612
oxide of, and oxalic acid, 614
double salts of oxalic acid, with oxide of 615
oxalate of, with ammonia, 615
bicarbosulphate of oxide of, 815
oxide of, and hydrated cyanic acid, 615
oxide of, and benzoic acid, 615
compounds of, of uncertain constitution, 616
salts of, 612
oxide of, and sulphuric acid, 613
double salts of the sulphate of oxide of, 613
oxide of, and phosphoric acid, 613
phosphate of oxide of ethule with metallic oxides, 613
oxide of, with nitric acid, 613
oxide of, with hyponitrous acid, 614
oxide of, with carbonic acid, 614
carbonate of oxide of, 614
sulphate of oxide of, 613
Eupione, 725
Evaporation, 46
circumstances influencing, 49
Evaporation, cause of, 50
limit to, 47
Leslie's method of freezing by, 48
Excrements, solid, 757
ashes of, 757
Expansion of solids, 20
force of, in solids irresistible, 20
of liquids, 21
of gases, 23
table of the expansion of different bodies, 21
increasing ratio of, in fluids, 22
of some fluids, by cold, 22
of some solids, 23
Extractive matter, 687
Eye, action of, on light, 58

F.

Factitious cinnabar, 412
Fat animal, its origin, 766
Feathers, 747
Fecula, 715
Ferment, 744
Fermentation, vinous, 637
viscous, 638
theory of, 537
Ferrid-cyanogen, 570
Ferro-cyanurets, 570
Ferro-cyanides, 568
Ferro-cyanide of potassium and iron, &c. 567
Fibre, woody, 720
Fibrine, 745
of the blood, 745
identity of vegetable and animal, 747
Filter, 770
Filtration, 770
Fire-damp of coal mines, 259
Fixed bodies, 41
Fixed air, 188
Fixed oils, 674
Flame, *vide* Combustion and Carburetted hydrogen
Flesh, 761
Flint, 211
Flowers of sulphur, 193
argentine of antimony, 373
Fluoborates, 252
Fluidity caused by heat, 37
heat of, 37
Fluosilicates, 254 *vide* Salts
Fluorides, metallic, 250
Fluorides, double, 516
oxy-, 519
Fluorine, 249
its attraction for metals, 283
theories, relating to, 251
Fluor-spar, 251
Fly powder, 364
Food of plants, 761
Formiates, 645
Formyle, 643
compounds of, 644
Fraxinine, 689

Freezing mixtures, 40
tables of, 40
Freezing in vacuo, Leslie's method, 48
Friction, heat produced by, 53
electricity excited by, 67
Frigorific mixtures with snow, table of, 40
Fulminates, 561
of copper and zinc, 562
Fulminating gold, 418
mercury, 561
Fulminating platinum, 423
silver, 561
Fumaramide, 657
Fuming liquor of Libavius, 352
of Boyle, 501
of arsenic, 370
Fusible metal, 299
Fusion, watery, 444
point of, 279

G.

Galena, 358
Gallates, 658
Gall-nuts, 659
Galvanic battery, 87
Galvanism, 82
how developed, 82
effects of, 92
chemical agency of, 100
electrical agency of, 92, 101
connection of, with magnetism, 97
theories of its production, 105
magnetic effects of, 93
chemical theory of, 105
Galvanometer, 83, 94
Gases, 41
constitution of, with respect to heat, 52
pressure required to liquefy, 52
table of refractive indices, 58
table of, exhibiting their distinctive properties, 775
become incandescent when strongly heated, 63
mode of finding the specific gravity of, 112
condensation of, 53
law of expansion of, 23
diffusion of, 171
formula for correcting the effects of heat on, 24
their bulk influenced by moisture, and the formula for correcting its effects, 50
qualitative analysis of, 775
Gases, absorption of, by charcoal, 186
mode of drying, 52
Gastric juice, 755
the action of, in digestion, 756
Gelatine, 750
sugar, 750
Gelatinous tissue, 750
Gentianine, 687
Germination, 761
Gibbsite, 317
Glance silver, 415
copper, 358
Glass, various kinds of, 212
of antimony, 376
of borax, 491
Glauberite, 467
Glauber salts, 463
Glaucopicrine, 710
Glucina, 318
test of, 319
Glucinium and its oxide, 318
Glue, 750
Gluten, 740
Glycerine, 648
Glycerule, 648
Gold and its compounds, 416
fulminating compound of, 418
ethereal solution of, 419
alloys of, 435
haloid salts of, 510
Golden sulphuret of antimony, 377
Gong, Chinese, 434
Goulard's extract, 623
Grain tin, 350
Graphite, 339
Gravel, urinary, 759
Gravitation, 2
Gravity, effect of, on chemical action, 125
modes of determining, 111
Green, Scheele's, 366, 488
mineral, 497
Brunswick, 513
Green vitriol, 465
Growth of plants, 762
Guaiacine, 689
Guano, 758
Gum, 718
tragacanth, 719
Gypsum, 464

H.

Haarkies, 345
Hæmatite, brown and red, 335
Hæmatosine, 761
Hæmatoxylin, 686
Hair, 747
Haloid salts, 509
Harmaline, 714
Hartshorn, spirit of, 254
Heat, 7
animal, how produced, 765
definition of, 7
Heat, nature of, 7
communication of, by contact, 8
conduction of, 9
conductors of, table of, 9
of fluidity, 38
slow conductors of, 10
conveyed by liquids, 10
effect of upon liquids, 10
effect of upon gases, 11
radiation of, 11
what surfaces best suited for radiation of, 12
radiation of, not affected by colours, 13
absorption of, 14
has different degrees of refrangibility, 17
polarization and double refraction of, 17
influence of upon vegetation, 19
dimensions and forms of bodies influenced by, 19
effect of, on chemical action, 19
quantity of, transmitted by different bodies, 15
relation of, to light, 66
emitted during combustion, 156
latent, 33, 38
free, 33
luminous, 65
non-luminous, 14
effects of, 19
expansion by, 20
expansion of solids, 20
expansion of liquids, 21
expansion of gases, 23
exception to the law of expansion by, 22
how conducted by liquids and gases, 10
specific, 31, 32
specific, table of, 34
laws of distribution by radiation, 12
capacities of bodies for, 32
sensible and insensible, 33
sources of, 53
radiated, 11
reflection of, 13
absorption of, 14
transmission of, 15
theory of, by Prevost and Pictet, 17
application of Prevost's theory to the formation of dew, by Dr. Wells, 18
Heavy spar, 464
Helenine, 683
Herbivora, bile of, 765
Homberg's pyrophorus, 468
Horn, 747
silver, 415
quicksilver, 406

Horn, lead, 362
Horny matter, membraneous and compact, 747
Humus, 721
Hydrargo-chlorides, 509
Hydracids, 439
Hydrates, nature of, 161
Hydriodates, 238
Hydro, how employed, 161
Hydrobenzamide, 595
Hydrocarburet, 258
Hydrochlorates, 499
Hydrogen, 156
preparation of, 156
properties of, 157, 163
compounds of, with sulphur, 263
compounds of, with phosphorus, 267
oxidation of, 157, 158
peroxide of, 163
arseniuretted, 370
carburetted, 258
and carbon, comp'ds of, 258
and carbon, new compounds of, 259
and nitrogen, 255
and potassium, 297
seleniuretted, 267
sulphuretted, 263
persulphuret of, 265
with metals, 289
phosphuretted, 268
perphosphuretted, 268
salts of, 501
aurochloride of, 510
phosphuretted, chlorides with, 515
platino-biniodide of, 516
Hydrogurets, or hydurets, of metals, 289
Hydrosalts, 498
Hydrosulphurets, 502
Hyduret of benzoyle, 591
Hyduret of cinnamyle, 605
Hygrometers, 50
Hyoscyamine, 710
Hyponitrite of oxide of ethyle, 614
Hyperoxymuriates, 226

I.

Ice, *vide* Water
Imperatorine, 689
Imponderables, 7
influence of, over chemical action, 125
Incandescence, 63
Indigo, 691
white, 692
blue and white, composition of, 692
action of sulphuric acid on, 693
products of oxidation of, 694
commercial, 691
Indine, 696
Induction, electric, 73
magneto-electric, 98
Inflammable air of marshes, 258
Ink, marking, 475
sympathetic, 347
Insolubility, influence of, on affinity, 121
Insulators, electrical, 68
Inulin, 717
Iodates, 479
Iodides, or iodurets, 236
Iodides, metallic, 282
double, 515
oxy-, 516
of cyanogen, 565
Iodine, 235
test for, 237
compounds of, 237
oxide of, 239
chlorides of, 241
bromide of, 248
attraction of, for metals, 282
Ipecacuanha, 712
Iridio-chlorides, 512
Iridium and its compounds, 427, 429
Iron and its compounds, 331
ores of, 331
cast, 332
rusting of, 333
pyrites, 339
malleable, 332
black oxide of, 333
red oxide of, 333
cyanide of, 566
ferrocyanide of, 569
ferrid-cyanide of, 570
pyrites, magnetic, 339
sulphates of, 465
alum, 469
meteoric, components of, 331, 347
chromate of, 378
carbonate of, 497
alloys of steel, 435
Iron and manganese, analytical mode of separating, 778
Isatine, 694
Isatyde, 696
Isethionates, 617
Isomeric bodies, 150
Isomorphism, 454
Ismorphous substances, table of, 456
Ivory black, 185

J.

Jalap, resins of, 685
Jervine, 713

K.

Kalium and Kali, 293
Kakodyle, 630
compounds of, 630
Kelp, 494
Kermes mineral, 377
Kinates, 661
King's yellow, 371
Kino, 659
Kinoyle, 728
Kupfernickel, 348

L.

Labarraque's soda liquid, 218
Lac, 685
Lactates, 639
Lactine, 636
Lactucine, 688
Lake, 702
Lamp, safety, 260
Lantanium, 399
Lapis causticus, 293
infernalis, 475
lazuli, 301
Lard, *vide* Fats
Latent heat, 33, 38
Laurel-water, 599
Laws of combination, 127, 128
Laws of combination in multiple proportions, 128
volumes, 138
of the distribution of radiant heat, 11
Lead and its compounds, 358
white, 360, 497
horn, 362
ceruse of, 497
nitrate of, 474
nitrite of, 475
phosphate of, 487
arseniate of, 488
carbonate of, 497
oxychloride of, 514
oxy-iodides of, 516
oxyfluoride of, 519
acetate of, 623
ferrocyanide of, 569
sulphocyanide of, 674
tests of, in wine, 361
alloys of, 433
Leather, 750
Lecanorine, 689
Legumine, 741
Lenses, achromatic, 61
of the eye, 59
Lepidolite, 302
Leucine, 748
Leukol, 729
Leyden jar, 74
Libavius, fuming liquor of, 352
Ligaments, 750
Light, theories of, 55
diffusion of, 55
ordinary ray of, 59
extraordinary ray of, 59
reflection of, 56
refraction of, 57
refraction, double of, 59
polarized, 60
decomposition of, 60
calorific rays of, 61
prismatic colours of, 60
chemical rays of, 63
magnetizing rays of, 63
terrestrial, 63

Light, sources of, 63
laws of its distribution, 56
velocity of, 56
laws of reflection of, 56
laws of refraction of, 57
table of refractive indices, 58
dispersion of the rays of, 61
calorific, rays of, 61
calorific rays of, 61
illuminating power of different rays of, 61
relation of, to heat, 66
coloured, emitted by different substances, 64
Lightning, 82
Lignine, 720
Lignone, 722
Lime, or quicklime, 308
fluate of, 251
water, milk of, and hydrate of, 309
slaked, 309
chloride of, 310
sulphate of, 464
sulphite of, 471
nitrate of, 474
phosphates of, 483
arseniate of, 488
carbonate of, 496
carbonates, double of, 498
oxalate of, 550
acetate of, 622
stone, 496
Lime and magnesia, analytic mode of separating, 776
Liquids become incandescent at high temperatures, 63
Liquefaction, 37
attended by disappearance of heat, 37
Liquids, expansion of, by heat, 21
conducting power of, 11
Liquor silicum, 211
Liriodendrine, 687
Litharge, 360
Lithates, *vide* Urates
Lithia, or Lithion, 302
sulphate of, 463
tests of, 302
Lithium and its compounds, 302
hydrosulphuret of, 503
carbosulphuret of, 504
arseniosulphuret of, 507
molybdosulphuret of, 508
hydrargo-chlorides of, 509
Litmus, 689
Liver of antimony, 376
Luna cornea, 415
Lunar caustic, 414
Lupuline, 688
Lymph, 759

M.

Madder, purple, red, orange, &c., 686
Magnesia, 312
tests of, 312
sulphate of, 465
nitrate of, 474
phosphates of, 483
carbonate of, 496
oxalate of, 550
Magnesian limestone, 498
mode of analyzing, 776
Magnesite, 496
Magnesium, 312
and its compounds, 312
hydrosulphuret of, 504
arseniosulphuret of, 505
haloid salts of, 509
Magnet, horseshoe, 95
Magnetic iron pyrites, 339
Magnetism, electro, 93
Magneto-electric induction, 95
Malachite, 497
Manganese and its comp'ds, 323
sulphate of, 465
haloid salts of, 509
alum, 568
Manganesium, or Manganium, 323
Manna and Mannite, 639
Marble, 496
Manipulations in analytical processes, 770
Marble or carbonate of lime, mode of analyzing, 775
Margarine, 669
Margarone, 670
Massicot, 360
Mastic, 685
Matter, chemical properties of, 3
influence of quantity of, over affinity, 123
Meconates, 660
Meconine, 689
Melam, 577
Melamine, 577
Melampyrine, 689
Mellone, 575
Mellonide of potassium, 576
Menispermine, 714
Mercury and its compounds, 406
amalgams of, 433
fulminating compound of, 561
sulphates of, 467
nitrates of, 474
carbonates of, 498
oxychloride of, 514
cyanide of, 566
ferrocyanide of, 569
Mercaptan, 611
Mesitylene, 629
Mesityle, 629,
Mesityle, its compounds, 629
Metaldehyde, 619
Metallic combinations, 431
bases of the alkaline earths, 289
bases of the alkalies, 289
Metallic sulphocyanides, 574
Metals, 276
general properties of, 276
alloys of, 433
oxidation of, 280
alkaline or alkaligenous, 289
table of discovery of, 277
table of specific gravity of, 277
malleability of, 278
ductility of, 278
crystallization of, 279
tenacity of, 278
hardness of, 278
structure of, 277
native state of, 280
volatility of, 279
alloys of, 380
affinity of, 380
action of heat on, 379
action of electricity on, 276
fusibility of, table of, 279
reduction of, 281
compounds of, with chlorine, 282,
iodine, 282
Metals with bromine, 283
fluorine, 283
sulphur, 283
selenium, 285
cyanogen, 287
phosphorus, 288
carbon, 289
hydrogen, 289
nitrogen, 289
classification of, 289
Metaphosphates, 485
Meteoric stones, 231
Methule, 640
hydrate of oxide of, 640
salts of, 641
Milk, 745
sugar of, 636
cause of coagulation of, 535
Mindererus, spirit of, 622
Mineral chameleon, 328
green, 497
yellow, 514
Mineral waters, analysis of, 780
denominations of, 780
Minerals, needful to plants, are also indispensable to animals, 521
Minium, 361
Molecules, 137
Molybdates, 392
Molybdenum and its compounds, 390

Molybdo-sulphurets, 507
Mordant, 352
Morphia, or Morphine, 707
Pseudo-morphine, 708
Mucus, 747
Mulberry calculus, *vide* Calculus
Murexan, 589
Murexide, 588
Muriates, 499
Muscular tissue or fibre, 745
Mustard, oil of, 681
Myricine, 677

N.

Nails of animals, 747
Naphtha from coal tar, 737
Naphthalidam, 737
Naphthaline, 729
Naphalic acid, 736
Narceine, 708
Narcotine, 708
Natrium, 299
Natron, 300
Nervous matter, 755
contains phosphorus, 775
Neutral salts, characters of, 442
Neutralization, 119
Nickel and its compounds, 347
sulphates of, 466
Nicotine, 705
Nitrates, 471
table of, 472
Nitrate of soda, as a manure, 764
Nitre, 472
Nitric oxide gas, 175
Nitrites, 475
Nitrobenzide, 594
Nitrous ether, 614
Nitronaphthalase, 735
Nitronaphthalese, 736
Nitronaphthalise, 736
Nitrogen, 165
teriodide of, 242
sulphuret of, 275
Nitrogen gas,
properties of, 166
oxides of, 166
protoxide of, 174
binoxide of, 175
quadrochloride of, 228
compounds of, with carbon, 271
Nomenclature, 113
Nutrition of animals, 761

O.

Oil of vitriol, 195
of wine, 517
of mustard, bases of, 681
fixed, 674
Oils, drying, or siccative, 674
volatile, or essential, 678
Oil, vegetable, 678
Oil of turpentine, 678
of juniper, 679
Oils and fats occurring in nature, 674
Oils, sweet, principle of, 648
occurring in nature, 674
Olefiant gas, 261
Oleine, 672
Olive oil, 672
Olivile, 689
Olivine, 689
Opium, active principle of, 707
Orceine, 690
Orcine, 690
Organic chemistry, 521
substances, character of, 522
bases 703
Organic acids, 648
Orpiment, 371
Osmio-chlorides, 512
Osmium and its compounds, 428
test of, 429
Oxalates, 550
Oxalovinates, 615
Oxamethane, 615
Oxamethylane, 642
Oxamide, or Oxalamide, 550
Oxichloride of acetyle, 624
Oxidation, 152
Oxide of ammonium, 256
Oxide, carbonic, 190
Oxides, 113
nomenclature of, 113
Oxidium manganoso-manganicum, 327
Oxidum ferroso-ferricum, 335
Oxygen, 150
preparation of, 151
properties of, 152
necessary to respiration, 153
Oxyhydrogen blow-pipe, 158
Oxymuriate of potassa, 477
Oxiodine, 240
Oxychlorides, 512
Oxyfluorides, 519

P.

Palladio-chlorides, 511
Palmine, 674
Palladium and its comp'ds, 524
cyanide of, 566
Panary fermentation, *vide* Vinous
Pancreatic juice, 756
Papin's digester, 44
Paracyanogen, 272
Paraffine, 725
Paramenispermine, 714
Paranaphthaline, 737
Particles, integrant and component, 3
Patent yellow, 514
Pearlash, 493
Perchlorates, 477
Peruvine, 606
Petroleum, 737
Peucedanine, 689
Pewter, 434
Phillyrine, 689
Phloretine, 690
Phloridzeine, 690
Phloridzine, 690
Phlogiston, 156
Phosphates, 480
Phosphorescence, 64
Phosphorus, 201
iodides of, 242
bromides of, 248
combinations of, with oxygen, 203
with hydrogen, 267
chlorides of, 231
solar, 65
sulphuret of, 274
Baldwin's, 64
Canton's, 64
Homberg's, 64
Phosphuret of nitrogen, 273
Phosphurets, metallic, 288
Phosphuretted hydrogen gas, 288
salts of, 501
chlorides with, 515
Photography, 61
Photometer, 66
Picamar, 724
Picrolichenine, 687
Picrotoxine, 688
Pinchbeck, 434
Piperine, 714
Pitchblende, 397
Pittacal, 726
Plants, growth of, 702
derive ammonia and carbonic acid gas from the air, 762
digestion of, 762
food of, 764
Plaster of Paris, 464
Plasters, 677
Platino-chlorides, 511
Platinum and its compounds, 720
a powerful oxydizing agent, 421
spongy, 421, 423
fulminating powder of, 423
alloys of, 420
Plesiomorphism, 457
Plumbagin, 689
Plumbago, 339
Polychrome, 687
Populin, 687
Porphyroxine, 688
Potash, or pearlash, 493
Potash, or potassa, 293
cyanate of, 559
cyanurate of, 563
hydrate of, 293
solution of, 294
Potassa fusa, 293
tests of, 295
sulphates of, 462
sulphite of, 470
nitrate of, 472
nitrite of, 475

Potassa fusa, chlorate, oxymuriate, or hyperoxymuriate of, 476
iodates of, 479
phosphates of, 482
Potash, or potassa
arseniates of, 487
arsenite of, 489
chromates of, 489
carbonates of, 493
oxalates of, 550
acetate of, 622
citrate of, 649
tartrates of, 656
tartrate of, and soda, 652
triple prussiate of, 567
Potassium and its comp'ds, 291
cyanide of, 565
ferro-cyanide of, 568
ferrid-cyanide of, 570
cobalto-cyanide of, 571
sulpho-cyanide of, 574
mellonide of, 576
sulphur-salts of, 503
haloid-salts of, 510
hydrosulphuret of, 503
sulphocyanuret of, 574
carbo-sulphuret of, 504
arsenio-sulphurets of, 505
molybdo-sulphuret of, 507
Precipitate, red, 407
Pressure, influence of, on the bulk of gases, 167
Prism, 60
Prismatic or solar spectrum, 60
Proportions, definite, 126
combining, 127
Proportions in which bodies unite, 126
Proteine and its modifications, 748
Protide, 748
Prussian, or Berlin blue, 569
Prussiates, *vide* Hydrocyanates
Prussiate, triple, 567
Pulvis antimonialis, 375
Purple powder of Cassius, 419
Putrefaction, 539
Putrefactive fermentation, 538
Pyrites, iron, 339
copper, 358
Pyrogallic acid, 658
Pyrometer of Daniell, 28
Wedgewood, 30
Pyrophorus of Homberg, 468
Pyrophosphates, 484
Pyroxilic spirit, 722

Q.

Qualitative analysis, directions for performing, 772
Quantitative analysis, directions for performing, 775
Quantity, its influence on affinity, 123
Quassine, 688
Quicklime, 308
Quicksilver, 406
horn, 408
Quills, *vide* Feathers
Quina, or Quinine, 706
Quinoline, 706

R.

Radiation, *vide* Heat
Radicals, organic, 524, 542
Rays of heat, angles of incidence and reflection of, 13
luminous, 15
Realgar, 371
Red lead, 361
antimony, 376
precipitate, 407
dyes, 686
oxide of manganese, 324
oxide of copper, 356
Reduction of metals, 281
Resin of copper, 357
Resin of aldehyde, 619
Resins, 684
Respiration, 765
Rhodizonate of potassa, 552
Rhodio-chlorides, 512
Rhodium and its comp'ds, 426
Rochelle salt, 652
Rouge, 687

S.

Sabadilline, 711
Saccharine fermentation, 716
Saccharum Saturni, 623
Sacchulmine, 637
Safety-lamp, Sir H. Davy's, 260
improvement of, by Messrs. Upton and Roberts, 261
Sal-ammoniac, 500
Salicine, 601
Salicyle, 601
Salicylamide, 602
Salicylites, 601
Salifiable base, 437
Saliva, 766
Salt, common, 300
of Alembroth, 509
neutral, 119
of Seignette or Rochelles salt, 652
-petre, 472
Salts, general remarks on, 436
nomenclature of, 113
classification of, 437, 442
affinity of, for water, 443
crystallization of, 446
double and triple, 459
Salts, deliquescent, 443
aqueous fusion of, 444
efflorescence of, 444
water of crystallization of, 444
decrepitation of, 445
plesiomorphism of, 457
isomorphous, 454
oxy-, 458
sulphates, 460
table of, 461
double, 467
table of, 460
sulphites, 470
nitrates, 471
table of, 472
cyanates, 559
nitrites, 475
chlorates, 476
perchlorates, 477
hypochlorites, 478
iodates, 479
bromates, 480
chlorites, 477
phosphates, 480
table of, 481
pyrophosphates, 484
metaphosphates, 485
table of, 485
arseniates, 486
table of, 487
arsenites, 488
chromates, 489
chlorides, 218
borates, 491
carbonates, 492
table of, 492
double, 498
hydro-salts, 498
ammoniacal, 499
table of, 499
of phosphuretted hydrogen, 501
sulphur-salts, 502
hydro-sulphurets, 502
table of 503
sulpho-cyanurets, 574
carbo-sulphurets, 504
table of, 504
arsenio-sulphurets, 505
table of, 506
molybdo-sulphurets, 507
table of, 508
antimonio-sulphurets, 508
tungsto-sulphurets, 508
haloid-salts, 509
hydrargo-chlorides, 509
table of, 509
auro-chlorides, 510
table of, 510
platino-chlorides, 510
table of, 511
palladio-chlorides, 511
rhodio-chlorides, 512
iridio-chlorides, 512
osmio-chlorides, 512
oxy-chlorides, 512
chlorides with ammonia, 514

Salts, chlorides with phosphuretted hydrogen, 515
double iodides, 545
oxy-iodides, 516
double bromides, 516
double fluorides, 516
boro-fluorides, 517
silico-fluorides, 518
titano-fluorides, 518
oxy-fluorides, 519
double cyanurets, 567
ferro-cyanurets, 568
cobalto-cyanurets, 511
oxalates, 550
acetates, 622
lactates, 639
of saccharic acid, 635
mucates, 637
pyromucates, 636
formiates, 645
meconates, 660
citraconates, 651
tartralates, 653
margarates, 669
stearates, 670
oleates, 672
sebates, 673
elaidates, 673
hydrocyanates, 558
molybdates, 392
vegetable bases, salts of, 703
antimonies, 375
antimoniates, 575
mellitates, 553
fulminates, 561
cyanurates, 563
cyanides, 565
ferrocyanides, 563
ferridcyanides, 570
cobalto-cyanides, 571
metallo-sulphocyanides, 574
of melamine, 577
of ammeline, 577
urates, 581
alloxanates, 584
thionurates, 585
formobenzoates, 592
hippurates, 593
hyposulphobenzoates, 593
benzilates, 596
cinnamates, 606
oxalovinates, 615
isethionates, 617
methionate of baryta, 617
of oxide of methule, 641
of amule, 647
kinates, 661
malates, 656
citrates, 649
tartrates, 651
benzoates, 591
tannates, 657
gallates, 658
succinates, 672
camphorates, 665
Santonine, 687
Saponine, 688
Scale of Equivalents, 135
Scheele's green, 488
Scillitine, 688
Sea water, analysis of, 782
Sebates, 673
Seignette, salt of, 652
Selenite, 464
Selenium, 212
its oxide, 113
sulphuret of, 275
Seleniurets, metallic, 275
of phosphorus, 275
Senegine, 689
Serum, 759
Silica, or siliceous earth, 211
Silica, alumina, and iron, mode of analyzing compounds of, 777
Silicates, 211
Silicated alkali, 211
Siliceous waters, analysis of, 782
Silicium, and its compounds, 210
Silico-fluorides, 518
Silicon, 210
terchloride of, 232
terbromide of, 249
Silicum liquor, 211
Silver and its compounds, 412
cyanurate of, 563
cyanide of, 566
fulminating compounds of, 415
glance, 415
alloys of 435
amalgamation of, 412
sulphate of, 467
nitrate of, 475
phosphates of, 484
dipyrophosphate of, 485
arseniates of, 488
granulated, 415
horn, 415
Sinnamine, 706
Sinapoline, 706
Slacked lime, 308
Slag formed in the reduction of iron, 332
Smalt, 346
Smilacine, 689
Soap, 677
Soda, or Natrium, 299
tests of, 299
chloride of, 300
sulphates of, 463
sulphite of, 470
nitrate of, 472
nitrite of, 475
perchlorate of, 477
phosphates of, 481
pyrophosphates of, 484
metaphosphates of, 485
arseniates of, 487
arsenites of, 488
borate of, 491
carbonate of, 494
acetate of, 622
citrates of, 649
Soda, tartrate of, and potassa, 652
Sodium, or Natrium, and its compounds, 299
chloride of, 300
hydrosulphuret of, 503
Solanine, 711
Solar rays, *vide* Light
Solders, 434
Solids, expansion of, by heat, 20
liquefaction of, 37
conducting power of, 9
specific heat of, 34
Solution, 115
Spaniolitmine, 690
Spar, fluor, 251
Specific gravity, 49
mode of determining, 111
Specific heat, 32
of gases, 34
Speiss, 347
Spelter, 341
Spermaceti, 677
Spirea ulmaria, volatile oil of, 601
Spirit, proof, 611
of wine, 610
Spirit of hartshorn, 257
Stannates, 352
Staphysine, 712
Starch, 715
Steam, temperature of, 44
elasticity of, 45
elastic force of at different temperatures, 44
latent heat of, 45
Stearates, 670
Stearine, 670
Steel, 340
Stramonine, 711
Stream tin, *vide* Tin
Stibium, 372
Strontia, or Strontites,
tests of, 307
sulphate of, 464
sulphite of, 470
nitrate of, 473
nitrite of 475
carbonate of, 496
Strontianite, 596
Strontium and its compounds, 306
hydrosulphuret of, 503
carbo-sulphurets of, 504
haloid-salts of, 509
Strychnia, 712
Styracine, 685
Styrol, 679
Suet, *vide* Fat
Sugar, 632
of lead, 623
of starch, 633
of grapes, 633
of milk, 636
of diabetes, 633
compounds of, with bases, 633
action of acids, 637
preparation of, from starch, 633

Sugar, from woody fibre, 633
mushroom, 637
action of heat on, 635
Sugar-candy, 632
Sulphates, 460
double, 467
Sulphésatyde, 696
Sulphites, 470
Sulphobenzide, 594
Sulphocyanurets, 574
Sulphur, 192
its oxides, 194
flowers of, 193
hydrate of, 193
chlorides of, 230
bromide of, 248
compounds of, with carbon, 273
iodide of, 243
its attraction for metals, 283
salts, 438, 502
bases, 438, 402
acids, 438, 502
Sulpho-cyanogen, 573
Sulphovinic acid, 613
Sulphonaphthaline and sulphonaphthalide, 735
Sulphurets, metallic, 283
Sulphuret of phosphorus, 274
Sulphuretted hydrogen, 263
Sulphuretted sulphites, 199
Sulphuric ether, 608
Sulphurous and saline waters, 781
Supporters of combustion, 154
Symbols, 146
Synaptase, 599
Synthesis defined, 5

T.

Tallow, 670
Tanghinine, 689
Tannates, 657
Tannin, or Tannic acid, 657
Tantalum, 395
Tantalite, 395
Tartar, 652
Tartarized iron, 652
Tartar, cream of, 652
soluble, 652
emetic, 652
Tartralates, 654
Tartrates, 652
Taurine, 753
Telerythrine, 690
Telescope, construction of, 58
Telluretted hydrogen, 405
Tellurium and its comp'ds, 403
Temperature, 31
at which bodies become luminous, 63
equilibrium of, 7
Tenacity of metals, 278
Test-liquids, their application and their mode of action, 770
example of, 770
Test tube, 770
Tests for detecting the presence of certain bases and the mode of application, 773
effects produced by, on the several substances to which they are applied, 773
Thebaine, 708
Thermometer, or thermoscope, 25
Thermometer, Centigrade and Fahrenheit's, table for the conversion of the degrees of one into the other, 829
Fahrenheit's, 27
Reaumur's, 27
Centigrade, 27
air, 25
differential, 26
formula for converting the expression of one into another, 27
graduation of, 27
Theobromine, 715
Thiosinnamine, 706
Thorina, 321
its tests, 321
Thorium and its compounds, 320
Tin and its compounds, 350
alloys of, 434
oxychlorides of, 513
permuriate of, 352
Tincal, 401
Titanium and its compounds, 402
Titanofluorides, 519
Tombac, 434
Transfer, galvanic, 100
Trona, 495
Trough, galvanic, 87
Tungstates, 394
Tungsten and its comp'ds, 393
Tungsto-sulphurets, 508
Turkey red, 686
Turpentine, oil of, 678
Turpeth mineral, 467
Type, metal for, 434

U.

Ultramarine, 301
Upas poison, 688
Uramile, 586
Uranium and its compounds, 397
Urates, 580
Urea, 560
nitrate of, 560
Urethane, 616
Urethylane, 642
Uric acid, 580
Urine of man, 757
analysis of, 757
of herbivora, 757
of carnivora, 757
of serpents, 757
Urine, importance of, as a manure, 758
Urinary concretions or calculi, 758

V.

Vacuum, boiling in, 44
evaporation in, 49
Vanadium and its compounds, 384
Vaporization, 41
cause of, 48
Vapour, elastic force of aqueous, at different temperatures, table of, 826
dilatation of, 42
density of, 42
elasticity of, or tension of, 45
latent heat of, 45
presence of, in gases, 48
table of elastic force of, 44
variable quantity in the atmosphere, 50
Vapours of alcohol, ether, oil of turpentine, and petroleum, or naphtha, elastic force of at different temperatures, table of, 828
Varvicite, 327
Vegetable alkalies, 703
Vegetables, changes that occur during the life, growth, and nutrition of, 762
first produce albumen, fibrine, and caseine, 762
Vegetable tissues, mineral substances essential to, 762
Veratrine, 711
Verdigris, 623
Verditter, 497
Vermilion, 412
Vienna green, 623
Vinegar, 621
theory of making, 620
qualities of, 621
from wood, 621
Vinous fermentation, 637
Vision, *vide* Eye, action of
Vital air, *vide* Oxygen
Vitriol, oil of, 195
blue, 466
green, 465
white, 466
Volatile alkali, 255
bodies, 41
Volta-electric induction, 97
-electrometer, 98
Volta's pile, 82
Voltaic circles, laws of the action of, 90
simple, 83
one described by Davy, 85
compound, 87
that of Volta, 87

Volumes, theory of, 138
Volumes, combining, 138
table of, 139

W.

Water, composition of, 159
Water, rain and snow, rich in oxygen, 779
spring, well, and river, 779
hardness of, the cause of, and how removed, 780
properties of, 161
expansion of, in freezing, 23
boiling and freezing points of, 27
of crystallization, 144
Waters, mineral, 779
analysis of, 779
acidulous, 780
alkaline, 780
chalybeate, 780
sulphureous, 781
saline, 781
siliceous, 782
Waters, of the sea, 782
of the Dead Sea and River Jordan, 782
Watery fusion, 444
Wax, 677
Welding, 332
White lead, 360, 497
White copper, 357
White precipitate, 544
White vitriol, 466
Wine, oil of, 617
Witherite, 496
Wood, products of the distillation of, 721
Wood coal, or brown coal, 721
Woody fibre, 720
decay of, 720

X.

Xanthic oxide calculus, 759
Xylites, 722

Y.

Yeast, 744
Yellow, mineral or patent, 514
king's, 371
Yellow, chrome, 490
Yellow dyes, 686
Yttria, 319
Yttrium, 319
Yttro-tantalite, 395

Z.

Zaffre, 345
Zanthopicrine, 688
Zinc and its compounds, 341
tests of the presence of, 342
blende, 341, 343
brown and blue blaze of, 341
butter of, 342
alloys of, 434, 435
amalgam of, 433
sulphate of, 466
acetate of, 623
Zinc-cyanuret, 566
Zinetum, 341
Zirconium and its comp'ds, 321

THE END.

