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ELEMENTS

OF

CHEMISTRY

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RECENT DISCOVERIES AND DOCTRINES OF THE SCIENCE.

BY

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THIRD EDITION,

ENLARGED AND CAREFULLY REVISED.

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LONDON:
PRINTED BY THOMAS DAVISON, WHITEFRIARS.

TO

FREDERICK STROMEYER, M.D. F.R.S. L. & E.

PROFESSOR OF CHEMISTRY IN THE UNIVERSITY OF GÖTTINGEN,

ETC. ETC.

MY DEAR SIR,

THE feelings of respect and regard which prompted me to dedicate to you the former editions of this Treatise, continue unaltered. Increasing experience, indeed, has served but to enhance the value which I ever attached to the instruction received in your laboratory, and to the habits of accuracy in research inculcated by your precept, and enforced by your example. To you, therefore, permit me still to inscribe a work intended to promote the study of that Science, which you cultivate with so much zeal and success; and be assured that the opportunity of again publicly expressing gratitude for your kindness, and admiration of your distinguished analytical attainments, is a source of much pride and pleasure to your Friend and former Pupil,

EDWARD TURNER.

38, UPPER GOWER-STREET,
October 1, 1830.

PREFACE

TO

THE THIRD EDITION.

The remarks with which the second Edition of these Elements was prefaced, may with equal propriety be applied to the present. Every part of the Treatise has been carefully revised;—redundancies have been retrenched,—inaccuracies, as far as possible, corrected,—obscurities, it is hoped, removed,—and deficiencies supplied. It has been attempted, by the careful perusal of original essays, to give the latest and most correct information in every department of the Science. On the writings of Berzelius, especially on his *Lehrbuch der Chemie*, I have drawn more freely than in the former editions; partly from having become better acquainted with the work itself, and partly because my own experience, in enabling me more fully to appreciate the accuracy of its author, has induced me to attach a higher interest to his observations.

The most material change in the present edition will be found in the article on Galvanism, in the theory of which some modification has become necessary. An outline of the views of Berzelius on the *Haloid* and *Sulpho-salts* has also been introduced. Some changes have been made, of a nature not to require particular

mention, and too numerous to admit of it. The plan of the work remains precisely the same as it was explained in the original preface. The size of the volume has, indeed, been somewhat enlarged; but the additions, which were required by the state of the science, will render the work a safer and a more useful guide to the Student of Chemistry.

Upper Gower-street,
October 1, 1830.

PREFACE

TO

THE FIRST EDITION.

THE following pages comprehend a condensed view of the present state of Chemical Science. The chief purpose of the work is to make the Student intimately acquainted with the theory, at the same time that he is acquiring a knowledge of the facts of Chemistry; so that, by the establishment of fixed principles, the details may more easily be impressed on the memory, and excite an interest which they would not otherwise possess. Every one who is acquainted with modern Chemistry, will admit that the study of the Laws of Combination is fitted in a peculiar manner for promoting these objects; and hence I have treated at length of the Atomic Theory, and the subjects connected with it, at an early part of the volume.

To this arrangement, I am aware, it may be objected, that many of the facts adduced as illustrations must necessarily be unknown to the beginner. I do not anticipate, however, any serious inconvenience from this source; on the contrary, some experience in teaching the theoretical and practical details of the Science, gives me reason to think that the disadvantages of my plan will be very far outweighed by its advantages. I may observe, indeed, that this work is chiefly designed for persons who have either attended, or are

attending Lectures on Chemistry; and, to such readers, the objection to which I allude does not apply.

In the composition of this work, I have had recourse, as far as possible, to the original sources of information; but I have also derived much assistance from the Elements of Sir H. Davy, and Dr. Henry; from the Systems of M. Thenard and the late Dr. Murray; and from the System and First Principles of Dr. Thomson. I should also add, that the materials of the Small Treatise, published about eighteen months ago, on the laws of Combination and the Atomic Theory, are, with slight modifications, incorporated in the present Volume.

This Treatise, however, is not to be viewed in the light of a mere compilation. In the purely practical parts of the Work, for example, in describing processes, in giving the tests for demonstrating the presence of substances, and in explaining the rules for conducting Chemical Analysis, I have in general merely stated in writing what I am in the habit of practising in the Laboratory. It is likewise proper to mention, that in detailing the experimental results obtained by other Chemists, I have in many instances verified them by my own observation; and when treating of the obscure or disputed parts of the Science, I have taken pains to render the former clear, and to distinguish in the latter what is ascertained, from what is still undetermined.

EDINBURGH, *Feb.* 1, 1827.

CONTENTS.

		Page
INTRODUCTION,		1

PART I.

IMPONDERABLE SUBSTANCES.

SECT. I.	Caloric,	9
	Communication of Caloric,	11
	Radiation,	15
	On the Cooling of Bodies,	22
	Effects of Caloric,	23
	Expansion,	24
	Thermometer,	35
	Liquefaction,	54
	Vaporization,	61
	Ebullition,	63
	Evaporation,	68
	Constitution of Gases with respect to Caloric,	79
	Sources of Caloric,	80
SECT. II.	Light,	81
SECT. III.	Electricity,	89
SECT. IV.	Galvanism,	116

PART II.

INORGANIC CHEMISTRY.

PRELIMINARY REMARKS.		138
SECT. I.	Affinity,	144
	On the changes that accompany Chemical Action,	149
	On the Circumstances that modify and influence the operation of Affinity,	152
	On the Measure of Affinity,	162

		Page
SECT. II.	On the Proportions in which Bodies unite, and on the Laws of Combination,	163
	On the Atomic Theory of Mr. Dalton,	174
	On the Theory of Volumes,	180
	On the Theory of Berzelius,	187
SECT. III.	Oxygen,	193
	Theory of Combustion,	197
SECT. IV.	Hydrogen.—Water,	202
	Deutoxide of Hydrogen,	215
SECT. V.	Nitrogen,	217
	On the Atmosphere,	ib.
	Compounds of Nitrogen and Oxygen.—Protoxide,	229
	Deutoxide of Nitrogen,	232
	Hyponitrous Acid,	236
	Nitrous Acid,	237
	Nitric Acid,	240
SECT. VI.	Carbon,	247
	Carbonic Acid,	251
	Carbonic Oxide Gas,	255
SECT. VII.	Sulphur,	259
	Compounds of Sulphur and Oxygen.—Sulphurous Acid,	261
	Sulphuric Acid,	264
	Hyposulphurous Acid,	269
	Hyposulphuric Acid,	270
SECT. VIII.	Phosphorus,	272
	Compounds of Phosphorus and Oxygen.—Phosphoric Acid,	274
	Phosphorous Acid,	279
	Hypophosphorous Acid,	280
	Oxides of Phosphorus	281
SECT. IX.	Boron.—Boracic Acid,	282
SECT. X.	Selenium,	284
	Oxide of Selenium,	285
	Selenious and Selenic Acids,	286
SECT. XI.	Chlorine,	289
	Muriatic Acid,	294
	Compounds of Chlorine and Oxygen,	300
	Protoxide of Chlorine,	ib.
	Peroxide of Chlorine,	302
	Chloric Acid,	303
	Perchloric Acid.—Chloride of Nitrogen,	304
	Compounds of Chlorine and Carbon,	305
	Chloride of Sulphur,	308
	Chloride of Phosphorus,	ib.
	Chloro-carbonic Acid,	309
	Chloride of Boron,	310
	Nature of Chlorine,	311

		Page
Sect. XII.	Iodine,	314
	Hydriodic Acid,	317
	Iodic Acid,	320
	Iodous Acid,	322
	Chloriodic Acid.—Iodide of Nitrogen,	323
Sect. XIII.	Bromine,	325
	Hydrobromic Acid,	329
	Bromic Acid,	331
	Chloride and Iodide of Bromine,	332
	Bromuret of Sulphur and Phosphorus,	333
Sect. XIV.	Fluorine,	334
	Hydro-fluoric Acid,	335
	Fluo-boric Acid Gas,	339

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

Sect. I.	Hydrogen and Nitrogen.—Ammonia,	342
Sect. II.	Hydrogen with Carbon.—Light carburetted Hydrogen,	346
	Olefiant Gas,	350
	On the new Compounds of Hydrogen, discovered by Mr. Faraday,	355
	Naphtha from Coal Tar.—Naphthaline,	358
	On Coal and Oil Gas,	361
Sect. III.	Compounds of Hydrogen and Sulphur.—Sulphuretted Hydrogen,	364
Sect. IV.	Hydrogen and Selenium.—Hydro-selenic Acid,	368
Sect. V.	Hydrogen and Phosphorus.—Per-phosphuretted Hydrogen,	369
Sect. VI.	Nitrogen with Carbon.—Cyanogen,	375
	Cyanogen and Hydrogen.—Hydro-cyanic Acid,	376
	Cyanic Acid,	382
	Cyanous Acids.	383
	Cyanuret of Chlorine,	386
	Cyanuret of Iodine,	389
	Cyanuret of Bromine,	ib.
	Ferro-cyanic Acid,	390
	Sulpho-cyanic Acid,	393
Sect. VII.	Compounds of Sulphur with Carbon,	395
	with Phosphorus,	397
Sect. VIII.	Compounds of Selenium with Sulphur and Phosphorus,	398

METALS.

	GENERAL PROPERTIES OF METALS.	399
Sect. I.	Potassium and its Compounds with Oxygen, Chlorine, Sulphur, &c.	423

		Page
Sect. II.	Sodium and its Oxides, Chloride, &c.	430
Sect. III.	Lithium and its Oxide.—Lithia,	436
Sect. IV.	Barium and its Oxides, &c.	437
Sect. V.	Strontium, and its Oxide, Chloride, Sulphuret, &c.	441
Sect. VI.	Calcium and its Oxides, Chloride, &c.	443
	Chloride of Lime, or Bleaching Powder,	446
Sect. VII.	Magnesium and its Oxide.—Magnesia,	448
Sect. VIII.	Aluminium.—Alumina,	450
Sect. IX.	Glucinium, Yttrium, Thorium, Zirconium, and their Oxides,	456
Sect. X.	Silicium and Silica,	462
	Fluo-silicic Acid Gas,	467
Sect. XI.	Manganese and compounds with Oxygen, Chlorine, &c.	469
Sect. XII.	Iron, and its compounds with Oxygen, Chlorine, Sulphur, &c.	479
	Carburets of Iron.—Steel, Cast Iron, Graphite,	487
Sect. XIII.	Zinc and its compounds with Oxygen, Chlorine, and Sulphur,	489
	Cadmium and its Oxide,	492
Sect. XIV.	Tin and compounds with Oxygen, Chlorine, &c.	494
	Cobalt, Nickel,	497
Sect. XV.	Arsenic and compounds with Oxygen, Chlorine, &c.	503
	Tests for Arsenious Acid,	505
Sect. XVI.	Chromium and its compounds with Oxygen,	514
	Fluo-chromic Acid Gas,	518
	Chloro-chromic Acid Gas,	ib.
	Molybdenum and compounds with Oxygen,	519
	Tungsten and compounds with Oxygen,	520
	Columbium and compounds with Oxygen,	523
Sect. XVII.	Antimony, its Oxides, Chlorides and Sulphurets,	526
Sect. XVIII.	Uranium and its Oxides,	532
	Cerium and Oxides,	534
Sect. XIX.	Bismuth and its compounds with Oxygen, Chlorine, and Sulphur,	536
	Titanium and its compounds with Oxygen,	538
	Tellurium and its Oxide,	541
Sect. XX.	Copper and its compounds with Oxygen, Chlorine, &c.	542
Sect. XXI.	Lead and its Oxides, &c.	547
Sect. XXII.	Mercury and its Oxides,	552
	Chlorides.—Calomel and Corrosive Sublimate,	555
	Iodides, Cyanurets, and Sulphurets,	558
Sect. XXIII.	Silver, its Oxide, Chloride, &c.	560
Sect. XXIV.	Gold and its compounds with Oxygen, Chlorine, and Sulphur,	564
Sect. XXV.	Platinum and its compounds with Oxygen, &c.	569
Sect. XXVI.	Palladium, Rhodium, Osmium, and Iridium,	572
	Pluranium and Rhutenium,	580
Sect. XXVII.	On Metallic Combinations.—Alloys,	ib.

SALTS.

		Page
	GENERAL REMARKS ON SALTS.	587
SECT. I.	Sulphates,	607
	Sulphites,	617
	Hyposulphites and Hyposulphates,	618
SECT. II.	Nitrates,	ib.
	Nitrites,	624
	Chlorates,	625
	Iodates,	626
SECT. III.	Phosphates,	628
	Pyro-phosphates	632
	Phosphites and Hypophosphites,	633
	Arseniates,	ib.
	Arsenites,	634
SECT. IV.	Chromates,	635
	Borates,	637
	Fluo-borates,	638
SECT. V.	Carbonates,	ib.
SECT. VI.	Salts of the Hydracids,	646
	Muriates or Hydrochlorates,	647
	Hydriodates,	651
	Hydrofluates,	652
	Hydrosulphurets or Hydrosulphates,	655
	Hydrocyanates,	657
	Ferro-cyanates,	ib.
	Sulpho-cyanates,	662
SECT. VII.	Haloid Salts,	663
	Sulpho-salts,	664

PART III.

		Page
	ORGANIC CHEMISTRY.	668
	Vegetable Chemistry,	671
SECT. I.	Vegetable Acids,	674
	Acetic Acid and its Salts,	675
	Oxalic Acid and its Salts,	681
	Tartaric Acid and its Salts,	685
	Citric Acid and its Salts,	690
	Malic Acid and its Salts,	691
	Benzoic Acid and its Salts,	693
	Gallic Acid and Gallates,	694
	Succinic Acid and Succinates,	696
	Camphoric Acid,	697
	Saccholactic, Moroxylic, Sorbic, Boletic, Prussic, Igasuric, and Mellitic Acids,	698

		Page
	Suberic, Zymic, Meconic, and Pectic Acids, .	699
SECT. II.	Vegetable Alkalies, . . .	703
	Morphia—Narcotine, . . .	704
	Cinchonia and Quina, . . .	708
	Strychnia and Brucia, ...	711
	Veratria, Emetia, Picrotoxia, Solania, Delphia, &c.	713
SECT. III.	Substances which, in relation to Oxygen, contain an excess of Hydrogen, . . .	717
	Fixed Oils.—Eläine and Stearine, . .	ib.
	Volatile Oils, ...	719
	Camphor, ...	721
	Resins, ...	722
	Amber, Balsams, and Gum Resins, . .	724
	Caoutchouc.—Wax, . . .	725
	Alcohol, ...	727
	Ethers, ...	731
	Sulphuric, . . .	732
	Nitrous, ...	737
	Acetic, Muriatic, and Hydriodic, .	738
	Bituminous substances, . . .	739
	Naphtha and Petroleum, . . .	ib.
	Asphaltum, Mineral Pitch, Retinasphaltum, and Coal,	740
SECT. IV.	Substances, the Oxygen and Hydrogen of which are in exact proportion for forming water, . .	743
	Sugar, Molasses, Honey, and Manna, . .	ib.
	Starch—Amidine—Hordein, . .	747
	Gum—Mucilage, ...	750
	Lignin or Woody Fibre.—Pyroxylic and Pyro-acetic spirit, . . .	751
SECT. V.	Substances which, so far as is known, do not belong to either of the preceding Sections, . .	753
	Colouring Matter—Dyes, ...	ib.
	Tannin—Artificial Tannin, . . .	761
	Vegetable Albumen, . . .	764
	Gluten—Gliadine—and Zymome, . . .	765
	Yeast, ...	767
	Asparagin, Bassorin, Caffein, Cathartin, Fungin, Suberin, Ulmin, Lupulin, Inulin, Medullin, Pollenin, Piperine, Olivile, Sarcocoll, Extractive Matter, Bitter Principle, ...	768
SECT. VI.	On the spontaneous Changes of Vegetable Matter, .	773
	Saccharine Fermentation, . . .	774
	Vinous Fermentation, . . .	775
	Acetous Fermentation, . . .	778
	Putrefactive Fermentation, . . .	780
SECT. VII.	On the Chemical Phenomena of Germination and Vegetation, ...	783
	Germination, ...	ib.
	On the Growth of Plants, . . .	786
	On the Food of Plants, .	789

		Page
	ANIMAL CHEMISTRY,	792
SECT. I.	Substances which are neither acid nor oleaginous,	793
	Fibrin,	ib.
	Albumen,	795
	Gelatine,	798
	Urea,	799
	Sugar of Milk and Diabetes,	801
SECT. II.	Animal Acids,	802
	Uric Acid and its Salts,	ib.
	Purpuric Acid,	804
	Erythric and Rosacic Acids—Lateritious Sediment,	805
	Hippuric and Formic Acids,	806
	Lactic and Amniotic Acids,	807
SECT. III.	Oleaginous Substances,	808
	Animal Oils and Fats,	ib.
	Spermaceti,	812
	Adipocire, and Cholesterine,	813
	Ambergris,	815

ON THE MORE COMPLEX ANIMAL SUBSTANCES, AND SOME FUNCTIONS OF ANIMAL BODIES.

SECT. I.	On the Blood,	815
	Respiration,	823
	Animal Heat,	830
SECT. II.	On the secreted Fluids subservient to Digestion,	833
	Saliva,	ib.
	Pancreatic and Gastric Juices,	834
	Bile and Biliary Concretions,	836
SECT. III.	Chyle, Milk, Eggs,	840
SECT. IV.	On the Liquids of Serous and Mucous Surfaces, and Purulent Matter,	846
SECT. V.	On the Urine and Urinary Concretions,	850
SECT. VI.	On the solid Parts of Animals—Bones, Horn, Muscle, &c.	860
SECT. VII.	Putrefaction,	863

PART IV.

ANALYTICAL CHEMISTRY.

SECT. I.	Analysis of Mixed Gases,	865
SECT. II.	Analysis of Minerals,	869
SECT. III.	Analysis of Mineral Waters,	877
	Composition of Mineral Waters,	883

APPENDIX.

Table of Equivalents or Atomic Weights,	887
Table of the Force of Aqueous Vapour,	892
the Vapour of Alcohol, &c.	895
of the Strength of Sulphuric Acid,	896

Page

Table of the Strength of Nitric Acid, . . . 897
of the Strength of Alcohol, ... 898
of Specific Gravities indicated by Baumé's Hydrometer, . 898
Description of Plates, ... 899
Index, ... 901

The Plates to be inserted after the Description, page 900.

ERRATA.

At page 383, 33d line, and page 384, last line but one, for cyan*ic* read cyan*ous* acid.

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 motion, has no power either to move itself, or to arrest its own progress when an impulse is once communicated to it. This indifference to rest or motion has been expressed by the term *vis inertiæ*, as if it depended on some specific force resident in matter; but it may with greater propriety be regarded as a negative character, in consequence of which, matter is wholly given up to the operation of the various forces which are constantly acting upon it.

Matter is divisible to an extreme degree 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; yet the gold which covers the silver wire, used in making gold lace, is spread over a surface twelve times as great. (Nicholson's Introduction to Natural Philosophy, vol. i.) A grain of iron, dissolved in nitro-muriatic acid, and mixed with 3137 pints of water, will be diffused through the whole mass; and by means of the ferro-cyanate of potash, which strikes a uniform blue tint, some portion of iron may be detected in every part of the liquid. This experiment proves the grain of iron to have been divided into rather more than 24 millions of parts; and if the same quantity of iron were still further diluted, its diffusion through the whole liquid 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 by indirect means. In favour of the former view it was urged, that to whatever degree matter is divided, it may still be conceived, in possessing extension, to be divisible into two parts; and the minuteness to which matter may actually be reduced, gave additional weight to this argument. 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 are thought to be indivisible; and according to this belief have received the appellation of *atoms*. (From the privative α and τεμνω *I cut.*) The arguments adduced in favour of this opinion are derived from certain astronomical phenomena, from the laws of chemical union, and the relations which have been observed to exist between the composition and form of crystallized bodies. These subjects will be considered in their proper place; but I may observe here, in order to show the nature of the argu-

ment, that the supposed existence of atoms accounts for numerous facts, which do not admit of a satisfactory explanation on any other principle.

All bodies descend in straight lines towards the centre of the earth, 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.

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. The condition of bodies with respect to several of these properties seems dependent on the operation 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 in order that these particles should thus cohere, they must possess 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, 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 caloric, 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.

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 one another 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 proportion 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 parts; and those as simple or elementary, which contain but one kind of ponderable matter. The number of the latter amounts only to fifty-three; and of these all the bodies in the earth, as far as our knowledge extends, are composed. 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 demonstrate 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 the former method, 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 we first resolve a particle of water into its elements, and then reproduce it by causing them to unite—the evidence is in the highest degree conclusive.

I have followed, in the composition of this treatise, the same general arrangement which I adopt in my lectures. It is divided into four principal parts. The first 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 com-

binations, 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, the one comprehending the products of vegetable, the other of animal life.

The fourth part contains brief directions for the performance of *analysis*.

ELEMENTS

OF

CHEMISTRY.

PART I.

SECTION I.

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. To avoid any ambiguity that may arise from the use of the same expression in two such different senses, it has been proposed to employ the word *Caloric* to signify exclusively the principle or cause of the feeling of heat; and the use of this term has now become so general, that I have adopted it in the present treatise.

Caloric, on the supposition of its being material, is a subtile fluid, the particles of which repel one another, 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 caloric. It is present in all bodies, and cannot be wholly separated from them. For if we take any substance whatever, at any temperature, however low, and transfer it into an atmosphere, whose temperature is still lower, a thermometer will indicate that caloric is escaping from it. 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.

Caloric may be transferred from one body to another. Thus, if a cup of mercury at 60° be plunged into hot water, caloric 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 caloric, they will very soon acquire an equilibrium, so that a thermometer will stand at the same point in all of them. The varying sensations of heat and cold, which we experience, are owing to a like cause. On touching a hot body, caloric passes from it into the hand, and excites the feeling of warmth; when we touch a cold body, caloric is communicated to it from the hand, and thus arises the sensation of cold.

As the transportation of caloric is constantly going forward, it is important to determine by what means, and according to what laws, the equilibrium is established. When any substance is brought into contact with another, which differs from it in temperature—if, for example, a bar of cold iron be thrust among glowing embers, or a hot ball of the same metal be plunged into a basin of cold water—the excess of caloric in the hot body passes rapidly to the particles on the surface of the other; from them it is transferred to those situated more internally, and so forth, till the bar in the one case, and the ball in the other arrive at the same temperature as the embers or the water with which they are in contact. In such instances, caloric is said to pass by *communication*, or to be *communicated* from one body to another; and in its passage through any one of those bodies, it is said to be *conducted* by them.

But when a heated substance is placed under such circumstances as to preclude the possibility of its caloric being communicated—for instance, when a glass globe full of hot water is suspended in the vacuum of an air pump—the excess of its caloric still passes away, and in a very short time it will have acquired the temperature of the surrounding objects. It must then be capable of passing from one body to another

situated at a sensible distance; it is projected as it were from one to the other. In order that its passage should take place in this manner, it is not necessary that the body should be *in vacuo;* it passes, to all appearance, with equal facility through the air as through a vacuum.

It follows, therefore, that in establishing an equilibrium of temperature, caloric is distributed among the surrounding objects in two ways; partly through the means of intermediate bodies, or by *communication*, partly in consequence of an interchange established from a distance, or by *radiation*.

COMMUNICATION OF CALORIC.

Caloric passes through bodies with different degrees of velocity. Some substances oppose very little impediment to its passage, while it is transmitted slowly by others. Daily experience teaches, that though we 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 burnt; yet this may be done with perfect safety with a rod of glass or of wood. The caloric will speedily traverse the iron bar, so that, at the distance of a foot from the fire, it is impossible to support its heat; while we may hold a piece of red hot glass two or three inches from its extremity, or keep a piece of burning charcoal in the hand, though the part in combustion is only a few lines removed from the skin. The observation of these and similar facts, has led to the division of bodies into *conductors* and *non-conductors* of caloric. The former division, of course, includes those bodies, such as metals, which allow caloric 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.

Various methods have been adopted for determining the relative conducting power of different substances. The mode adopted by Ingenhouz*, who made experiments on this subject, is the following. He covered small rods of the same form, size, and length, but of different materials, with a layer of wax, plunged their extremities into heated oil, and noted to what

* Ingenhouz, Journal de Phys. 1789, p. 68.

distance the wax was melted on each during the same interval. The metals were found, by this method, to conduct caloric better than any other substances; and of the metals, silver is the best conductor; gold comes next; then tin and copper, which are nearly equal; then iron, platinum, and lead.

Some experiments have lately been made by M. 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
Platinum	981	Lead	179.6
Silver	973	Marble	23.6
Copper	898.2	Porcelain	12.2
Iron	374.3	Fine clay	11.4
Zinc	363		

The substances employed for these experiments were made into prisms of the same form and size. To one extremity a regular source of heat was applied, and the passage of caloric along the bar was estimated by small thermometers placed at regular distances, with their bulbs fixed in the substance of the prism. According to the table, the conducting power of platinum is superior even to that of silver, while Ingenhouz places it after copper. There must certainly be some mistake either in the experiments or calculations of M. Despretz, or in the report of them. From my own observation I agree with Ingenhouz in considering platinum as a much less perfect conductor than most of the metals in general use, and am satisfied from frequent experiment that it is much inferior to silver.

An ingenious plan was adopted by Count Rumford* 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 immersing it in boiling water, he transferred it into melting ice, and observed carefully the number of seconds which elapsed during the passage of the thermometer

* Rumford, Phil. Tr. 1792.

through 135 degrees. When there was air between the thermometer and cylinder, the cooling took place in 576 seconds; when the interstice was filled with fine lint, it took place in 1032″; with cotton wool in 1046″; with sheep's wool in 1118″; with raw silk in 1284″; with beaver's fur in 1296″; with eider down in 1305″; and with hare's fur in 1315″. The general practice of mankind is therefore fully justified by experiment. In winter we retain the animal heat as much as possible by covering the body with bad conductors, such as silk or woollen stuffs; and in summer, cotton or linen articles are employed with an opposite intention.

A variety of familiar phenomena arise from difference of conducting power. Thus if a piece of iron and glass be heated to the same degree, the sensation they communicate to the hand is very different; the iron will give the sensation of burning, while the glass feels but moderately warm. The quantity of caloric, which in a given time may be brought to the surface of the heated body, so as to pass into the skin, is much greater in the iron than in the glass, and therefore in the former case the sensation must be more acute. This proves that the sense of touch is a very fallacious test of heat and cold; and hence, on applying the hand to various contiguous objects, we are very apt to form wrong notions of their temperature. The carpet will feel nearly as warm as the hand; a book will feel cool, the table cold, the marble chimney-piece colder, and the candlestick colder still; yet, a thermometer applied to them will stand in all at exactly the same elevation. They are all colder than the hand; but those that carry away caloric most rapidly, excite the strongest sensation of cold.

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. Count Rumford found a considerable difference in the conducting power even of the same material, according to the state in which it was employed. His observations seem to warrant the conclusion, that in the same substance the conducting power increases with the compactness of structure.

Liquids may be said, in one sense of the word, to have the

power of communicating caloric with great rapidity, and yet they are very imperfect conductors. The transmission of caloric from particle to particle does in reality take place very slowly; but in consequence of the mobility of their particles upon each other, there are peculiar internal movements, which under certain circumstances may be occasioned in them by increase of temperature, and which do more than compensate for the imperfect conducting power with which they are really endowed.

When certain particles of a liquid are heated they expand, and thus become specifically lighter than those which have not yet received an increase of temperature; and consequently, according to a well-known law in physics, the colder and denser particles descend, while the warmer ones are pressed upwards. It therefore follows that if caloric enter at the bottom of a vessel containing any 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. Now 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. Hence, under certain circumstances, caloric is rapidly communicated through liquids.

But if, instead of heating the bottom of the jar, the caloric is made to enter by the upper surface, very different phenomena will be observed. The intestine movements cannot now be formed, because the heated particles have a tendency to remain constantly at the top; the caloric 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 he was mistaken; for the opposite opinion has been successfully supported by Dr. Hope, Dr. Thomson, and the late Dr. Murray, though they all admit that water, and liquids in general, mercury excepted, possess the power of conducting caloric in a very slight degree.

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 caloric, 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, these bodies allow a passage through them by radiation. Now the quantity of caloric 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 caloric being conveyed by means of a hot current; for all the heated particles have a uniform tendency to rise. Neither can it depend upon the conducting power of the air; since 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 caloric 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 transmission is called *Radiation* of Caloric, and the fluid so transmitted is called *Radiant*, or *Radiated Caloric*. It appears, therefore, that a heated body suspended in the air cools, or is brought down to an equilibrium with surrounding bodies, in three ways; first, by the conducting 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.

Caloric 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 circumference of a circle; 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 being arrested by the latter or in any way affecting its temperature. When

they fall upon the surface of a solid or liquid substance, they are either reflected from it, and thus receive a new direction, or they lose their radiant form altogether, and are absorbed. In the latter case, the temperature of the receiving substance is increased, in the former it is unchanged.

The absorption of radiant caloric may be proved by placing a thermometer before the fire, or any heated body, when the mercury will be seen to rise in the stem. It has been ascertained by accurate experiment, and may be demonstrated mathematically, that the intensity of effect diminishes according to the squares of the distance from the radiating point. 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 existence of a reflecting power may be shown in a familiar manner, by standing at the side of a fire in such a position that the caloric cannot reach the face directly, and then placing a large 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 the heated substance to the point of a plane surface from which it is reflected, and a second line from that point to the spot where it produces its effect, the angles which these lines form with a line perpendicular to the reflecting plane are equal to each other, or, in philosophical language, the angle of incidence is equal to the angle of reflection. It follows from the operation of 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 when these parallel rays impinge upon a second concave reflector, standing opposite to the former, they are made to converge, so as to meet in its focus, where a great degree of heat is developed. This fact, as applied to the sun's rays or red hot bodies, has been long known. But it is a modern discovery that caloric emanates in invisible rays, which are subject to the same laws of reflection as those that are accompanied by light.

This fact may be inferred from the experiments of the Flo-

rentine Academicians, and Lambert observed the reflection of non-luminous caloric; but the honour of establishing it in a decisive and unequivocal manner is due to Messrs. Saussure and Pictet* of Geneva, the latter of whom, at the suggestion of the former, first proved it of an iron ball heated so as not to be luminous even in the dark, and afterwards of a vessel of boiling water. For a knowledge of the laws of radiation in general, however, we are indebted to the researches of Professor Leslie, described in his Essay on Heat.

Mr. Leslie employed a hollow tin cube filled with hot water as the radiating substance. The rays proceeding from it were brought, by means of a concave mirror, into a focus, in which the bulb of a differential thermometer was placed. He found that certain substances radiate caloric much more rapidly than others, and that the nature of the surface of a heated body has a singular influence upon its radiation. By adapting thin plates of different metals to the sides of the tin cube, and turning them successively towards the mirror, he found a very variable effect produced upon the thermometer. A bright smooth polished metallic surface radiated caloric very imperfectly; but if the surface was in the least degree dull or rough, the radiating power was immediately augmented. By covering the tin surface with a thin layer of isinglass, paper, wax, or resin, its power of radiation increased surprisingly. Metallic substances were observed to be the worst possible radiators, particularly such as are susceptible of a high polish, as gold, silver, tin, and brass; but it is easy to make them radiate well by giving them the opposite properties, either by scratching their surface, or covering it with whiting, lamp-black, or any other convenient substance. It is commonly supposed that black surfaces radiate better than white ones, but I am not acquainted with any conclusive experiments in proof of this opinion.

Mr. Leslie next examined the power of different substances in reflecting caloric, and he soon arrived at the interesting conclusion, that those surfaces which radiate least reflect most powerfully. A polished plate of tin or brass is an excellent reflecting surface, but a bad radiating one; by removing the

* Pictet's Essai sur le Feu, p. 65. (1790.)

polish in any way, its reflecting power is diminished in the same proportion as its radiating power is increased. His experiments, indeed, justify the conclusion, that the faculty of radiation is inversely as that of reflection.

There are only two modes by which calorific rays, falling upon a solid opaque body, can dispose of themselves; they must either be reflected from it, or enter into its substance. In the latter case caloric is said to be absorbed. Now it is manifest, that those rays which are reflected cannot be absorbed; and those which are not reflected, must be absorbed. Hence it follows that the absorption of caloric in the same body is inversely as its reflection; and since the property of radiation is likewise inversely as that of reflection, the power of radiating and absorbing caloric must be proportional and equal.

In speaking of radiant caloric, it is necessary to distinguish calorific rays accompanied by light from those which are emitted by a non-luminous body, since their properties are not exactly similar. Thus the absorption of luminous caloric, whether proceeding from the sun or a common fire, is very much influenced by colour; it is most considerable in black and dark-coloured surfaces, while it is much less in white ones. The influence of colour, on the contrary, over the absorption of non-luminous caloric is exceedingly slight; it remains to be proved, indeed, whether any effect can fairly be attributed to this cause.

It may be asked, since radiant caloric passes without interruption though the air, whether it can pass in a similar manner through solid transparent media, such as glass or rock-crystal. The only point of view under which this subject can be considered at present, is with respect to radiant caloric emitted by a warm body that is not luminous. When a piece of clear glass is placed between such a body and a thermometer, the latter is not nearly so much affected as it would be were no screen interposed; and the glass itself becomes warm. These facts prove that at least the greater part of the calorific rays is intercepted by the glass. But the thermometer is affected to a certain degree; and the question is, by what means do the rays reach it? Professor Leslie contends that all the rays which fall upon the glass are absorbed by it, pass

through its substance by its conducting power, and are then radiated from the other side of the glass towards the thermometer, an opinion which Dr. Brewster has ably supported by an argument suggested by his optical researches. (Phil. Trans. for 1816, p. 106.) The experiments of Delaroche, on the contrary, (Biot, Traité de Physique, v. 4.) lead to the conclusion that glass does transmit some calorific rays, the number of which, in relation to the quantity absorbed, is greater as the intensity of the heat increases; and the general result obtained by that philosopher agrees with some experiments which Dr. Christison and myself performed in the year 1824 on the same subject.

The facts that have been determined concerning the laws of radiant caloric have given rise to two ingenious modes of accounting for the tendency of bodies to acquire an equilibrium of temperature. This takes place, according to M. Pictet, in consequence of the hot body giving calorific rays to the surrounding colder ones till an equilibrium is established, at which moment the radiation ceases. M. Prevost*, on the contrary, contends that radiation goes on at all times, and from all bodies, whether their temperature is the same or different from those that surround them. According to this view, the temperature of a body falls whenever it radiates more caloric than it absorbs; its temperature is stationary when the quantities emitted and received are equal; and it becomes warm when the absorption exceeds the radiation. A hot body, surrounded by others colder than itself, is an example of the first case; the second happens when all the substances which are near one another have the same temperature; and the third occurs when a cold body is brought into a warm room.

Though neither of these theories has been proved to be true, and both of them have the merit of accounting for the phenomena of radiation, the preference is commonly given to the latter. The theory of M. Prevost affords a more satisfactory explanation of the phenomena of radiant caloric than that of M. Pictet; but the chief argument in its favour is drawn from the close analogy between the laws of light and caloric.

* Recherches sur la Chaleur.

Luminous bodies certainly exchange rays with one another; —a less intense light sends rays to one of greater intensity; and the quantity of light emitted by either does not seem to be at all affected by the vicinity of the other. As, therefore, the radiation of light is not prevented by other luminous bodies, it is probable that the radiation of heat, the laws of which are so similar to those of light, is equally uninfluenced by the proximity of other radiating substances.

This ingenious theory applies equally well to the experiments with the conjugate mirrors, as to the phenomena of ordinary radiation. If a metallic ball in the focus of one mirror, and a thermometer in that of the other, are both of the same temperature as the surrounding objects, (say at 60° F.) the thermometer remains stationary. It does indeed receive rays from the ball; but its temperature is not affected by them, because it gives back an equal number in return. If the ball is above 60° the thermometer begins to rise, because it now receives a greater number of rays than it gives out. If, on the contrary, the ball is below 60°, then the thermometer, being the warmer of the two bodies, emits more rays than it receives, and its temperature falls.

The same mode of reasoning accounts very happily for an experiment originally performed by the Florentine Academicians, and since carefully repeated by M. Pictet, the result of which at first appeared quite anomalous. 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 withdrawn. 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 are made on the supposition that cold is merely a negative quality arising from the diminution of caloric. If, indeed, the result of M. Pictet's experiment could not be explained on the latter supposition, we should be obliged to adopt the former; but as we are not driven to that alternative, it is in nowise necessary to modify our views. The same mode of reasoning, hitherto employed, will account for this as

well as the preceding phenomena; for, in fact, as the thermometer gives more rays to the ice than it receives in return, it must necessarily become colder. It rises again when the ice is removed, because it then receives a number of calorific rays proceeding from the warmer surrounding objects, which were intercepted by the ice while it was in the focus. Whence it appears that the result of this experiment flows naturally out of the theory of Prevost.

A very elegant application of this theory was made by the late Dr. Wells to account for the formation of dew*. The most copious deposition 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 interesting and important phenomenon, the chief object is to discover the principle by which the reduction of temperature is effected. The explanation proposed by Dr. Wells, and now almost universally adopted, is founded on the theory of M. 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 is cloudy, the radiant caloric 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

* Wells on Dew.

dew, tend to confirm this explanation. It is found that dew is deposited sparingly or not at all in cloudy weather; that all circumstances which promote free radiation are favourable to the formation of dew; that good radiators of caloric, such as grass, wood, the leaves of plants, and filamentous substances in general, reduce their temperature, in favourable states of the weather, to an extent of ten, twelve, or even fifteen degrees below that of the circumambient air; and that 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.

ON THE COOLING OF BODIES.

It appears from the preceding remarks on the passage of caloric, that the cooling of bodies takes place by two very different methods. When a hot body is enveloped in solid substances, its caloric is withdrawn solely by means of communication, and the rapidity of cooling is dependent on the conducting power. The refrigeration is effected in a similar manner when the heated body is immersed in a liquid; but the rapidity of cooling 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 first attempt to fix the rate of cooling was by Newton. He conceived that a hot body exposed to a uniform cause of refrigeration, as by exposure to the air, loses at each instant a quantity of caloric which always bears the same proportion to its excess. Thus if a hot body is deprived of $\frac{1}{10}$th of its excess of caloric in one second, it should lose $\frac{1}{10}$th of the remaining $\frac{9}{10}$ths, or $\frac{9}{100}$ths in the next second, and in the third second it will lose $\frac{1}{10}$th of the remaining $\frac{81}{100}$ths, or $\frac{81}{1000}$ths, &c. In this way the following series of numbers may be obtained, expressing the proportion of the excess of caloric lost in equal intervals of time:

$\frac{1000}{10,000}$, $\frac{900}{10,000}$, $\frac{810}{10,000}$, $\frac{729}{10,000}$, $\frac{656}{10,000}$, $\frac{590{\cdot}5}{10,000}$, $\frac{531{\cdot}6}{10,000}$, &c.

and the excess remaining after each interval is,

$\frac{9000}{10,000}$, $\frac{8100}{10,000}$, $\frac{7290}{10,000}$, $\frac{6560}{10,000}$, $\frac{5905}{10,000}$, $\frac{5316}{10,000}$, &c.

It is obvious that the numerators of these fractions constitute a geometrical series, of which 1·111 is the ratio; for $5316 \times 1{\cdot}111 = 5905$, $5316 \times 1{\cdot}111^2 = 6559$, $5316 \times 1{\cdot}111^3 = 7286$, &c. Hence it was inferred by Newton, that while the times of cooling are in arithmetical progression, the refrigeration proceeds according to a geometrical progression.

This subject has been experimentally investigated with remarkable ingenuity and success by MM. Dulong and Petit. (An. de Ch. et Ph. vii. 225.) They have demonstrated that Newton's law of refrigeration may be adopted when the temperature is inconsiderable; but that when a body cools through an extensive range of temperature, as when the excess of caloric is great, the law is then found to be erroneous. They have examined with consummate skill the various circumstances by which the cooling of a hot body *in vacuo*, or when surrounded by an elastic fluid, is influenced; but their inquiry is too mathematical and abstruse for the purposes of an elementary treatise.

EFFECTS OF CALORIC.

The phenomena that may be ascribed to the agency of caloric, 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 would 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 torpid till it is again excited by the stimulus of caloric.

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 one another, producing expansion, so that the same quantity of matter is thus made to occupy a larger space; and the diminution of caloric has an opposite effect. Were the repulsion occasioned by this agent to cease entirely, the atoms of bodies would come into absolute contact.

The form of bodies is dependent on caloric. 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 caloric, all liquids, vapours, and doubtless even gases, would become permanently solid; and all motion on the surface of the earth would be arrested.

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

Caloric 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 the laws of caloric 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 caloric above enumerated, several will be discussed in other parts of the work. In this place it is proposed to treat only of the influence of caloric over the dimensions and form of bodies; and this subject will be conveniently studied under the three heads of expansion, liquefaction, and vaporization.

EXPANSION.

One of the most remarkable properties of caloric is the repulsion which exists among its particles; hence it happens, that when this principle enters into a body, its first effect is to remove the integrant molecules of the substance to a greater

distance from one another. The body therefore becomes less compact than before, occupies a greater space, or, in other words, expands. Now this effect of caloric is manifestly in opposition to cohesion—that force which tends to make the particles of matter approximate, and which must be overcome before any expansion can ensue. It may be expected, therefore, that a small addition of caloric will occasion a small expansion, and a greater addition of caloric a greater expansion; because in the latter case, the cohesion will be more overcome than in the former. It may be anticipated, also, that whenever caloric passes out of a body, the cohesion being then left to act freely, a contraction will necessarily follow; so that expansion is only a transient effect, occasioned solely by the accumulation of caloric. It follows, moreover, from this view, that caloric must produce the greatest expansion in those bodies, the cohesive power of which is least; and the inference is 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 is now obvious, that all bodies are expanded by heat, and that the expansion of the same body increases with the quantity of caloric which enters it. But this law does not apply, unless the form and chemical constitution of the body be preserved. For if a change in either of these respects 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.

In proof of 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. A familiar demonstration of the fact may be afforded by adapting a ring to an iron rod, the former being just large enough to permit the latter to pass through it while cold. The rod is next heated, and will then no longer pass through the ring. This dilatation from heat and consequent contraction in cooling take place with a force which appears to be irresistible.

The expansion of solids has engaged the attention of several experimenters, whose efforts have been chiefly directed towards ascertaining the exact quantity by which different substances are lengthened by a given increase of heat, and determining whether or not their expansion is equable at different temperatures. The Philosophical Transactions of London contain various dissertations on the subject by Ellicot, Smeaton, Troughton, and General Roy; and M. Biot, in his *Traité de Physique*, has given the results of experiments performed with great care by Lavoisier and Laplace. Their experiments establish the following points: 1. Different solids do not expand to the same degree from equal additions of caloric. 2. A body which has been heated from the temperature of freezing to that of boiling water, and again allowed to cool to 32° F., recovers precisely the same volume which it possessed at first. 3. The dilatation of the more permanent or infusible solids is very uniform within certain limits; their expansion, for example, from the freezing point of water to 122°, is equal to what takes place betwixt 122° and 212°. The subsequent researches of Dulong and Petit, (Annales de Ch. et de Ph. vol. 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 caloric. 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 therefore for all practical purposes may be disregarded.

The subjoined table includes the most interesting results of Lavoisier and Laplace. (Biot, vol. i. p. 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 .	$\frac{1}{534}$
Soft iron forged . . .	$\frac{1}{819}$

Names of Substances.	Elongation when heated from 32 to 212°.
Iron wire	$\frac{1}{812}$ of its length.
Untempered steel	$\frac{1}{947}$
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, it is easy to calculate its total increase in bulk, by trebling the number which expresses its increase in length. Thus if a tube of flint glass elongates by $\frac{1}{1248}$, when heated from the freezing to the boiling point of water, its cubic space will have increased by $\frac{3}{1248}$ or $\frac{1}{416}$ of its former capacity.

The expansion of glass, iron, copper, and platinum, has been particularly investigated by MM. Dulong and Petit. The following table contains the result of their observations on glass. (An. de Ch. et Ph. vii. 138.) It appears from the third column that at temperatures beyond 212° glass expands in a greater ratio than mercury.

Temperature by an air thermometer.	Mean absolute dilatation of glass for each degree.	Temperature by a thermometer made of glass.
Fahr.	Fahr.	Fahr.
From 32° to 212°	$\frac{1}{69660}$	212
—— 32 to 392	$\frac{1}{65340}$	415.8
—— 32 to 572	$\frac{1}{59220}$	667.2

The second, fourth, and sixth columns of the following table show the mean total expansion of iron, copper, and platinum, when heated from 32° to 212° and from 32° to 572°, for each degree. The third, fifth, and seventh columns indicate the degrees on a thermometer of iron, copper, and platinum, corresponding to a temperature of 572° on an air ther-

mometer. It is obvious that platinum is much more uniform in its expansion than either of the other metals.

Temp. by air thermometer.	Mean dil. of iron in volume for each degree.	Temp. by iron rod thermometer.	Mean dilat. of copper in volume for each degree.	Temp. by copper rod thermometer.	Mean dilat. of platinum in volume for each degree.	Temp. by platinum rod thermometer.
Fahr.	Fahr.	Fahr.	Fahr.	Fahr.	Fahr.	Fahr.
212°	$\frac{1}{30760}$	212°	$\frac{1}{34920}$	212°	$\frac{1}{67860}$	212°
572°	$\frac{1}{40678}$	702.5	$\frac{1}{31860}$	623.8	$\frac{1}{65340}$	592.9

The simplest method of proving the expansion of liquids is 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 is 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. From the frequency with which the latter 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 $\frac{1}{5412}$ of its volume; but the result obtained by Dulong and Petit, who

found it $\frac{1}{5550}$, 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 it occupied at the temperature of 32°. If the barometer, for instance, stands at 30 inches when the thermometer is at 32°, we may calculate what its elevation ought to be when the latter is at 60°, or at any other temperature*. The apparent expansion of mercury contained in glass is of course less than the absolute expansion. Between the limits of 32° and 212° F. 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. Dulong and Petit state that the mean total expansion of mercury from 32° to 572° F. for each degree is $\frac{1}{9540}$; and that the mean apparent expansion in glass from 32° to 572° F. for each degree is $\frac{1}{11372}$. The temperature in their experiments was estimated by an air thermometer, which they consider more uniform in its rate of expansion than one of mercury. The temperature of 572° F. on the air thermometer corresponds to 586° in the mercurial one.

All experimenters agree that liquids expand in an increasing ratio, or that equal increments of caloric 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

* The general formula is as follows: Let H be the height of the barometer when the thermometer is at 32° F.; H′ its elevation at any temperature above 32°, and let T express the number of degrees of Fahrenheit's thermometer above that point. Then $H' = H\left(1 + \frac{T}{9990}\right)$; hence $H'9990 = H(9990 + T)$; and $H' = H\,\frac{9990 + T}{9990}$; or if H is unknown, it may be calculated by the formula $H = \frac{H'9990}{9990 + T}$. For H and T in the first formula substitute their value, as stated in the text, and perform the calculation. $H' = 30\,\frac{9990 + 28}{9990} = 30.084$.

The rate of actual and not apparent expansion is employed in this calculation, because the length of the mercurial column, being determined by the atmospheric pressure, is not affected by the expansion or contraction of the tube.

in pure water as 4·7 to 15. Attempts have been made to discover a general law by which this progression is regulated, and Mr. Dalton conceives that the expansion observes the ratio of the square of the temperature estimated from the point of congelation, or of greatest density; but this opinion is merely hypothetical, and has been shown by Dulong and Petit to be inconsistent with the facts established by their experiments.

There is a peculiarity in the effect of caloric upon the bulk of some fluids; namely, that at a certain temperature an increase of heat causes them to contract, and its diminution makes them expand. This singular exception to the general effect of caloric is only observable in those liquids which acquire an increase of 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, as every one knows, swims upon the surface of water, and therefore must be lighter than it, which is a convincing proof that water, at the moment of freezing, must expand. The increase is estimated by Boyle at about $\frac{1}{9}$th of its volume. (Experiments on Cold.)

The most remarkable circumstance attending this expansion, is the prodigious force with which it is effected. Mr. Boyle filled a brass tube, three inches in diameter, with water, and confined it by means of a moveable plug; the expansion, when it froze, took place with such violence as to push out the plug, though preserved in its situation by a weight equal to 74 pounds. The Florentine Academicians burst a hollow brass globe, whose cavity was only an inch in diameter, by freezing the water with which it was filled; and it has been estimated that the expansive power necessary to produce such an effect was equal to a pressure of 27,720 pounds weight. Major Williams gave ample confirmation of the same fact by some experiments which he performed at Quebec in the years 1784 and 1785. (Philosophical Transactions of Ed. ii. 23.)

But it is not merely during the act of congelation that water expands; for it begins to dilate considerably before it actually freezes. Dr. Croune noticed this phenomenon so early as the year 1683, and it has since been observed by various philosophers. It may be rendered obvious to any one by the following experiment. Fill a flask, capable of holding three

or four ounces, with water at the temperature of 60° F. 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 will fall in the tube, marking contraction; but in a short time an opposite movement will be perceived, indicating that dilatation is taking place, while the water within the flask is at the same time yielding caloric to the freezing mixture in which it is immersed.

To the inference deduced from this experiment it was objected by some philosophers, that the ascent of the water in the tube did not arise from any expansion in the liquid itself, but from a contraction of the flask, by which its capacity was diminished. In fact, this cause does operate to a certain extent, but it is by no means 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 and a half and 40 degrees of Fahrenheit's thermometer; that is, boiling water obeys the usual law till it has cooled to the temperature of about 40°, after which the abstraction of caloric produces increase instead of diminution of volume. According to M. Hallström, whose experiments are the most recent, and appear to have been conducted with great care, the maximum density of water is 39°.39 F. (An. de Ch. et Ph. xxviii. 90.)

The cause of 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. No very satisfactory reason can be assigned for the expansion which takes place previous to congelation. It

* Philosophical Transactions of Edinburgh, v. 379.

is supposed, indeed, that the water begins to arrange itself in the order it will assume in the solid state before actually laying aside the liquid form; and this explanation is generally admitted, not so much because it has been proved to be true, but because no better one has been offered.

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.

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 caloric much more than solids or liquids. Now, chemists are in the habit of estimating the quantity of the gases employed in their experiments by measuring them; and since the volume occupied by any gas is so much influenced by temperature, it is essential to accuracy that a due correction be made for the variations arising from this cause; that they should know how much dilatation is produced by each degree of the thermometer, whether the rate of expansion is uniform at all temperatures, and whether that ratio is the same in all gases.

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; but at last the law of dilatation was detected by Dalton and Gay-Lussac nearly at the same time. Mr. Dalton's method of operating (Manchester Memoirs, vol. v.) was exceedingly simple. He filled with dry mercury a graduated tube, closed at one end and carefully dried; and then, plunging the open end of the tube into a mercurial trough, introduced a portion of dry air. After having marked the bulk and temperature of the air, he exposed it to a gradually increasing heat, the exact amount of which was regulated by a thermometer, and observed the dilatation occasioned by each increase of temperature. The apparatus of M. Gay-Lussac (An. de

Chimie, v. 43.) was the same in principle, but more complicated, in consequence of the precautions he took to avoid every possible source of fallacy.

It is proved by the researches of these philosophers, that all gases undergo equal expansions by the same addition of caloric, supposing them placed under the same circumstances; so that it is sufficient to ascertain the law of expansion observed by any one gas, in order to know the law for all. Now it appears from the experiments of Gay-Lussac, that 100 parts of air in being heated from 32° to 212° F. expand to 137·5 parts. The increase for 180 degrees is therefore 0·375 or $\frac{37{\cdot}5}{100}$th of its bulk; and by dividing this number by 180 it is found that a given quantity of dry air dilates to $\frac{1}{480}$th of the volume it occupied at 32°, for every degree of Fahrenheit's thermometer. The result of Dalton's experiments corresponds very nearly with the foregoing.

This point being established, it is easy to ascertain what volume any given quantity of gas should occupy at any given temperature. Suppose a certain portion of gas occupies 20 measures of a graduated tube at 32°, it may be desirable to determine what would be its bulk at 42° F. For every degree of heat it has increased by $\frac{1}{480}$th of its original volume, 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 $20 + 20 \times \frac{10}{480} = 20{\cdot}416$. It must not be forgotten that the volume which the gas occupies at 32° is a necessary element in all such calculations. Thus, having 20·416 measures of gas at 42° F. the corresponding bulk for 52° F. 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° F., which is 20 measures*. A

* Convenient formulæ for such calculations may be thus deduced: Let P′ be the volume of gas at any temperature above 32°, T the number of degrees above that point, and P its volume at 32°. Then, $P' = P\left(1 + \frac{T}{480}\right)$; hence $\frac{P'}{P} = 1 + \frac{T}{480}$; $P'\,480 = P\,(480 + T)$; and $P' = P\,\frac{(480 + T)}{480}$

Or if P is unknown, it may be calculated by the formula $P = \frac{P'\,480}{480 + T}$.

similar remark applies to the formula for estimating the effect of heat on the height of the barometer.

The rate of expansion of atmospheric air at temperatures exceeding 212° has been examined by MM. Dulong and Petit, and the following Table contains the result of their observations. (*An. de Ch. et Ph.* vii. 120.)

Temperature by the Mercurial Thermometer.		Corresponding volumes of a given volume of air.
Fahrenheit.	Centigrade.	
— 33	— 36..	0.8650
32	0..	1.0000
212	100..	1.3750
302	150..	1.5576
392	200..	1.7389
482	250..	1.9189
572	300..	2.0976
M. boils 680	360..	2.3125

Hydrogen gas was found to expand in the same proportion, so that all gases may be inferred to expand to the same extent, for equal increments of caloric, between — 33° F. and 680°; and the same law probably prevails at all temperatures.

It frequently happens, in the employment of Fahrenheit's thermometer, that when P′ for the above formula is known, it is not P itself which is wanted, but the volume of gas at some other temperature, as at 60° F. This value may be obtained without first calculating what P is. Let P′, for instance, be any known quantity of gas at a certain temperature; and let P″ be the quantity sought at some other temperature, the degrees of which above 32° may be expressed by T′. Now $P'' = \frac{(480+T')}{480} \times P$; but as P is unknown, let its value be substituted according to the above formula. Thus, $P'' = \left(\frac{480+T'}{480}\right) \times \left(\frac{P'\,480}{480+T}\right)$; which gives $P'' = \frac{480^2\,P' + 480\,T'\,P'}{480^2+480\,T} = \frac{P'\,480\,(480+T')}{480\,(480+T)} = \frac{P'(480+T')}{480+T.}$

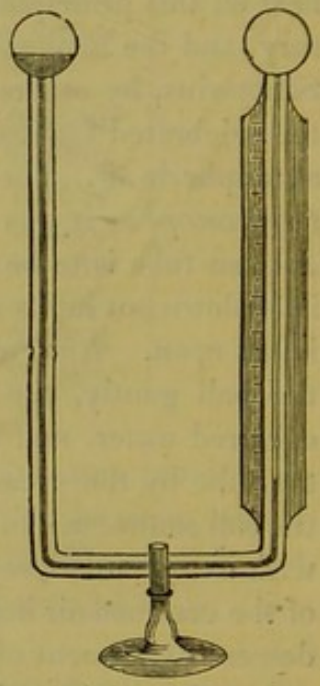
Suppose, for example, a portion of gas occupies 100 divisions of a graduated tube at 48° F., how many will it fill at 60° F? Here $P' = 100$; $T = 48-32$ or 16; $T' = 60-32$, or 28. The number sought, or the $P'' = \frac{100 \times 508}{496} = 102.42$.

ON THE THERMOMETER.

The influence of caloric 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. The construction of the thermometer itself, or *thermoscope* as it was sometimes called, is exceedingly simple. A glass tube is to be selected for the purpose, and one end of it is blown out into a spherical cavity, while its other extremity is left open. After expelling a small quantity of air by heating the ball gently, the open end of the tube is plunged into coloured water, and a portion of the liquid is forced up into the tube by the pressure of the atmosphere, as the air within the ball contracts. In this state it marks changes of temperature with extreme delicacy, the alternate expansion and contraction of the confined air being rendered visible by the corresponding descent and ascent of the coloured water in the stem; and in point of sensibility, indeed, it yields to no instrument. The material used in its construction, also, is peculiarly appropriate, because air, like all gases, expands uniformly by equal increments of caloric; but nevertheless, independently of these advantages, there are two forcible objections to the employment of this thermometer. For, in the first place, its dilatations and contractions are so great, that it will be inconvenient to measure them when the change of temperature is considerable; and, secondly, its movements are influenced by pressure as well as by caloric, 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 Professor 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 Professor 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 caloric than other liquids, while its dilatations between 32° and 212° are almost perfectly uniform. Strictly speaking, the same quantity of caloric 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.

The first object in constructing a thermometer is to select a tube with a very small bore, which is of the same diameter through its whole length; and then, by melting the glass, to blow a small ball at one end of it. The mercury is introduced by rarefying the air within the ball, and then dipping the open end of the tube into that liquid. As the air cools and contracts, the mercury is forced up, entering the bulb to supply the place of the air which had been expelled from it. Only a part of the air, however, is removed by this means; the remainder is driven out by the ebullition of the mercury.

Having thus contrived that the bulb and about one-third of the tube shall be full of mercury, the next step is to seal the open end hermetically. This is done by heating the bulb till the mercury rises very near the summit, and then suddenly darting a fine pointed flame from a blow-pipe across the opening, so as to fuse the glass and close the aperture before the mercury has had time to recede from it.

The construction of a thermometer is now so far complete that it affords a means of ascertaining the comparative temperature of bodies; but it is deficient in one essential point, namely, the observations made with different instruments cannot be compared together. To effect this object, the thermometer must be graduated, a process which consists of two parts. The first and most important, is to obtain two fixed points which shall be the same in every thermometer. The practice now generally followed for this purpose was introduced by Sir Isaac Newton, and is founded on the fact, that when a thermometer is plunged into ice that is dissolving,

or into water that is boiling, it constantly stands at the same elevations in all countries, provided there is a certain conformity of circumstances. The point of congelation is easily determined. The instrument is to be immersed in snow or pounded ice, which is liquefying in a moderately warm atmosphere, till the mercury becomes stationary. To fix the boiling point is a more delicate operation, since the temperature at which water boils is affected by various circumstances which will be more particularly mentioned hereafter. It is sufficient to state the general directions at present;—that the water be perfectly pure, free from any foreign particles, and not above an inch in depth,—the ebullition brisk, and conducted in a deep metallic vessel, so that the stem of the thermometer may be surrounded by an atmosphere of steam, and thus exposed to the same temperature as the bulb,—the vapour be allowed to escape freely,—and the barometer stand at 30 inches.

The second part of the process of graduation consists in dividing the interval between the freezing and boiling points of water, into any number of equal parts or degrees, which may be either marked on the tube itself, by means of a diamond, or first drawn upon a piece of paper, ivory, or metal, and afterwards attached to the thermometer. The exact number of degrees into which the space is divided, is not very material, though it would be more convenient did all thermometers correspond in this respect. Unfortunately this is not the case. In Britain we use Fahrenheit's scale, while the continental philosophers employ either the centigrade, or that of Reaumur. The centigrade is the most convenient in practice; its boiling point is 100, that of melting snow is the zero, or beginning of the scale, and the interval is divided into 100 equal parts. The interval in the scale of Reaumur is divided into 80 parts, and in that of Fahrenheit into 180; but the zero of Fahrenheit is placed 32 degrees below the temperature of melting snow, and on this account the point of ebullition is 212°.

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 arequal to five of the centigrade, and four of Reaumur's there

mometer. 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. Either of these may be reduced to Fahrenheit by reversing the process; the multiplier is nine in both cases, and the divisor four in the one and five in the other. But it must be remembered in these reductions, that the zero of Fahrenheit's thermometer is 32 degrees lower than that of the centigrade or Reaumur, and a due allowance must be made for this circumstance. An example will best show how this is done. To reduce 212° F. to the centigrade, first abstract 32, which leaves 180; and this number multiplied by $\frac{5}{9}$, gives the corresponding expression in the centigrade scale. Or to reduce 100° C. to Fahrenheit, multiply by $\frac{9}{5}$, and then add 32. 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.

Fahrenheit.	Centigrade.	Reaumur.
212	100·	80
200	93·33	74·66
190	87·77	70·22
180	82·22	65·77
170	76·66	61·33
160	71·11	56·88
150	65·55	52·33
140	60	48
130	55·55	43·55
120	48·88	39·11
110	43·33	34·66
100	37·77	30·22
90	32·22	25·77
80	26·66	21·33
70	21·11	16·88
60	15·55	12·44
50	10	8
40	4·44	3·55
32	0	0
20	— 6·66	— 5·33
10	—12·22	— 9·77
0	—17·77	—14·22

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 can be used for such purposes is alcohol. Our means of estimating high degrees of heat are as yet very unsatisfactory. Mercury is preferable to any other liquid; but even its indications cannot be altogether relied on. For, in the first place, its expansion for equal increments of caloric is greater at high than at low temperatures; and, secondly, glass expands at temperatures beyond 212° F. in a more rapid ratio than mercury, and consequently, from the proportionally greater capacity of the bulb, the apparent expansion of the metal is considerably less than its actual dilatation. Thus MM. Dulong and Petit observed, that when the air thermometer is at 572° F., the common mercurial thermometer stands at 586°; but when corrected for the error caused by the glass, it indicates a temperature of 597.5° F. No liquid can be employed for temperatures which exceed 680° F., since all of them are then either dissipated in vapour, or decomposed.

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 pyrometer invented by Mr. Wedgewood is best known. It is founded on the property which clay possesses of contracting, when strongly heated, without returning to its former dimensions as it cools. The earth alumina, whether precipitated from a solution by reagents, or found more or less pure in the earth as clay, is always in a state of chemical combination with water. On heating it to redness, part of the water is expelled; but some remains, which requires a very strong heat before it is dissipated; and in proportion as these last portions escape, the earth contracts. The contraction even continues after every trace of water has been removed, owing to partial vitrification taking place, which tends to bring the particles of the clay into nearer proximity. The intensity of the heat may, therefore, in some measure be estimated by the degree of contraction which it has occasioned.

The apparatus consists of a metallic groove, 24 inches long, the sides of which converge, being half an inch wide above, and three-tenths below. The clay, well washed, is made up into little cubes that fit the commencement of the groove, after having been heated to redness; and their subsequent contraction by heat is determined by allowing them to slide from the top of the groove downwards, till they arrive at a part of it through which they cannot pass. Mr. Wedgewood divides the whole length of the groove into 240 degrees, each of which he supposes equal to 130° F. The zero of his scale corresponds to the 1077th degree of Fahrenheit.

Wedgewood's pyrometer is rarely employed at present, 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 cube, 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.

Other pyrometers have been proposed, which act on the usual principle of dilatation. They consist of a metallic bar, the elongation of which from heat is rendered sensible by an index being attached to one end, while the other is fixed. The experiments of Lavoisier and Laplace on the expansion of solids were made with an apparatus of this kind, and Mr. Daniell has described a similar one in the 11th volume of the Quarterly Journal of Science. These instruments are in general too complicated for common use; and, moreover, scientific men have hitherto placed little confidence in them, in consequence of the irregularity with which solids expand at high temperatures.

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, 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 readily 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 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. This accident is prevented by putting some pure naphtha in the tube beyond the mercury, and its presence is likewise of use in preventing the oxidation of the mercury.—The above description applies to an improvement on Dr. Rutherford's thermometer, made by Mr. Adie of Edinburgh.

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 caloric any body contains. It does not follow, because the thermometer stands at the same elevation in any two bodies, that they contain equal quantities of caloric; nor is it right to infer that the warmer possesses more of this principle than the colder. The thermometer gives the same kind of information which may be discovered, though less accurately, by

the feelings; it recognises in bodies that state of caloric 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 caloric present in bodies.

Very 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 each at the same height, though their quantities of caloric 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 caloric;—if, for example, a pound of iron contains as much caloric as a pound of water or mercury. The foregoing remark shows that equality in temperature is not necessarily connected with equality in quantity of caloric; and the inference has been amply confirmed by experiment. If equal quantities of water are mixed together, one portion being at 100° F., and the other at 50°, the temperature of the mixture will be the arithmetical mean or 75°; that is, the 25 degrees lost by the warm water, have just sufficed 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 caloric; 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° F. be mixed with a pint of water at 40°, the mixture will have a temperature of 60°, so that the 40 degrees lost by the former have 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° 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 160° with a pound of water at 40°, a thermometer placed in the mixture will stand

at 45°; but if the mercury be at 40° and the water at 160° the mixture will have a temperature of 155°. If water at 100° be mixed with an equal weight of spermaceti oil at 40°, the mixture will be found at 80°; and when the oil is at 100° and the water at 40°, the temperature of the mixture will be only 60°.

It appears from the facts just stated, that the same quantity of caloric 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 water and spermaceti oil; and that the heat which gives 5 degrees to water will raise an equal weight of mercury by 115°, being the ratio of 1 to 23*. Hence if equal quantities of caloric 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, 11½, and 23; 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 23 times more caloric 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 Dr. Black. It is a law admitted to be universal, and may be thus expressed;—that similar quantities of different bodies require unequal quantities of caloric to heat them equally. This difference in bodies was expressed in the language of Dr. Black by the term *capacity* for caloric, a word apparently suggested by the idea that the heat present in any substance is contained in its pores, or the spaces left between its particles, and that the quantity of heat is regulated by the size of the pores. And indeed at first view there appear sufficient grounds for this opinion; for it is observed, that very compact bodies have the smallest capacities for caloric, and that the capacity of the same substance often increases as its density becomes less. But, as Dr. Black himself pointed out, if this were the real cause of the difference, the capacities of bodies for caloric should be inversely as their densities. Thus, since mercury is 13 times and a half denser than water, the capacity of the latter for caloric ought to be only 13 times and a half greater

* This proportion, which is given by Dr. Henry in the last edition of his Elements on the authority of Mr. Dalton, is I believe not far from the truth, and is certainly more correct than that of 1 to 28.

than the former, whereas it is 23 times as great. Oil occupies more space than an equal weight of water, and yet the capacity of the latter for caloric is double that of the former. The word capacity therefore is apt to excite a wrong notion, unless it is carefully borne in mind, that it is merely an expression of the fact without allusion to its cause; and to avoid the chance of error from this source, the term *specific caloric* has been proposed as a substitute for it, and is now very generally employed.

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 Dr. Black is the following: He conceived that caloric exists in bodies under two opposite conditions: in one it is supposed to be in a state of chemical combination, when it lays aside its prominent characters, and remains 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. For since caloric is regarded as a material substance, it would be altogether anomalous were it not influenced, like other kinds of matter, by chemical affinity; and if this be admitted, it ought certainly, in combining, to lose some of the properties by which it is distinguished in its free state. According to this view it is intelligible how two substances, from being in the same condition with respect to free caloric, may have the same temperature; and yet that their actual quantities of caloric may be very different, in consequence of one containing more of that principle in a combined or latent state than the other. 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 a hypothesis should not be unnecessarily associated with the phenomena to which it

owes its origin. Accordingly, the word *sensible* is better than *free* caloric, and *insensible* preferable to *combined* or *latent* caloric; for by such terms the fact is equally well expressed, and philosophical propriety strictly preserved.

It is of importance to know the specific caloric 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 caloric requisite for heating them by the same number of degrees. Thus the caloric required to heat equal quantities of water, spermaceti oil, and mercury by one degree, is in the ratio of 23, 11·5, and 1, and therefore their capacities for caloric are expressed by those numbers. Water is commonly one of the materials employed in such experiments, as it is customary to compare the capacity of other bodies with that of water.

This method was first suggested by Dr. Black, and was afterwards practised to a great extent by Drs. Crawford and Irvine*. But the same knowledge may be obtained by reversing the process,—by noting the relative quantities of caloric which bodies give out in cooling; for if water requires 23 times more caloric than mercury to raise its temperature by one or more degrees, it must also lose 23 times as much in cooling. The calorimeter, invented and employed by Lavoisier and Laplace, acts on this principle. The apparatus consists of a wire cage, suspended in the centre of a metallic vessel so much larger than itself, that an interval is left between them, which is filled with fragments of ice. The mode of estimating the quantity of caloric which is emitted by a hot body placed in the wire cage, depends upon the fact, that ice cannot be heated beyond 32° F.; since every particle of caloric which is then supplied is employed in liquefying it, without in the least affecting its temperature. If, therefore, a flask of boiling water is put into the cage, it will gradually cool, the ice will continue at 32°, and a portion of ice-cold water will be formed; and the same change will happen when heated mercury, oil, or any other substance is substituted for the hot water. The sole difference will consist in the quantity of ice liquefied, which will be proportional to the caloric

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

lost by those bodies while they cool; so that their capacity is determined merely by measuring the quantity of water produced by each of them. This is done by allowing the water, as it forms, to run out of the calorimeter by a tube fixed in the bottom of it, and carefully weighing the liquid which issues.

There is one obvious source of fallacy in this mode of operating, against which it is necessary to provide a remedy; namely, the ice not only receives caloric from the substance in the central cage, but must also receive it from the air of the apartment in which the experiment is conducted. This inconvenience is avoided by surrounding the whole apparatus by a larger metallic vessel of the same form as the smaller one, and of such a size that a certain space is left between them, which is to be filled with pounded ice or snow. No external heat can now penetrate to the inner vessel; because all the caloric derived from the apartment is absorbed by the outer one, and is employed, not in elevating its temperature, but in dissolving the pounded ice within it.

Notwithstanding this precaution, however, the accuracy of the calorimeter may fairly be questioned. For that the results obtained by it be correct, it is essential that all the water which is produced should flow out and be collected. But there is reason to suspect that some of the water is apt to freeze again before it has had time to escape; and if this be true, as *a priori* is very probable, then the information given by the calorimeter must be rejected as useless.

The determination of the specific heat of gaseous substances is a problem of importance, and has accordingly 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 only be viewed as approximations requiring to be corrected by future research. Dr. Crawford, to whom we are indebted for the first elaborate investigation of the subject, conducted his experiments in the following manner. He obtained two copper vessels made as light as possible, and exactly of the same form, size, and weight; exhausted one of them, and filled the other with the gas to be examined. They were next heated to the same extent by immersion in hot

water, and then plunged into equal quantities of cold water of the same temperature. Each flask heated the water; but while the exhausted flask communicated solely the heat of the copper, the other gave out an equal quantity of caloric from the metal of which it was made, together with that derived from the gas in its interior. The effect produced by the former deducted from that of the latter gave the heating power of the confined gas, the precise information wanted. By repeating the experiment with air and different gases, their comparative heating powers, or their specific heats, were ascertained. But correct as is the leading principle on which these experiments were founded, the results are now universally admitted to be very wide of the truth, and therefore it can answer no useful purpose to cite them. The fallacy is attributable to the circumstance of the heat derived from the containing vessel being so great compared to that emitted by the confined gas, that the effect ascribed to the latter is confounded with, and materially influenced by, the unavoidable errors of manipulation.

The same subject was investigated by Lavoisier and Laplace by means of their calorimeter. A current of gas was transmitted in a serpentine tube through boiling water in order to be heated, and was then made to circulate within the calorimeter in a similar tube surrounded with ice. Its temperature in entering and quitting the calorimeter was ascertained by thermometers, and the heat lost by each gas was estimated by the quantity of ice liquefied. Their experiments are of course liable to the objections already made to the use of ice; but a similar train of experiments, not exposed to this fallacy, was conducted in the year 1813 with extreme care by MM. Delaroche and Bérard. (An. de Chimie, LXXXV. and Annals of Phil., II.) They transmitted known quantities of gas, heated to 212° F., in an uniform current through the calorimeter; and, instead of ice, surrounded the serpentine tube with water, the temperature of which, as well as of the gas at its exit, was ascertained during the course of the process by delicate thermometers. By operating with a considerable quantity of gas, they avoided the error into which Crawford fell; and the experiments, though complicated and involving various sources of error, were conducted with such skill and caution that they inspired great

confidence, and are still admitted to be more accurate than any which have been made on this difficult subject. Their results are contained in the following table; the specific heat of the gases being referred to atmospheric air as unity in the two first columns, and to water in the third.

Names of Substances.	Under equal Volumes.	Under equal Weights.	
Atmospheric air	1·0000	1·0000	0·2669
Hydrogen gas	8·9033	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

Some experiments performed by MM. Clement and Desormes, and published in the year 1819 in the *Journal de Physique*, LXXXIX. 320, were confirmatory of the foregoing results; and Mr. Dalton, in the second volume of his *Chemical Philosophy*, page 282, states that he has repeated the experiment of Delaroche and Bérard on the specific heat of atmospheric air, and is convinced of their estimate being very near the truth. But the accuracy of their results has been questioned by others, and some of the objections are by no means deficient in force. One of these was stated by Mr. Haycraft in the Edinburgh Phil. Trans. for 1824, namely, that the gases were employed in a moist instead of a dry state; a circumstance which would doubtless in some measure modify the result: and others have been mentioned by MM. De la Rive and Marcet. (*An. de Ch. et Ph.* XXXV. 5. and XLI. 78.) For example, the precise temperature of the gases used in their experiments was not ascertained in an unexceptionable manner; because a thermometer surrounded by gaseous matter is affected, not only by contact with the gas itself, but likewise by the radiant heat emitted or absorbed by the containing vessel. It is also to be remarked that the heated gases, in passing through the calorimeter, diminished in volume in proportion as they cooled. Now it is found invariably that whenever the bulk of a gas is diminished, a certain portion of insensible heat

becomes sensible; so that in the experiments of Delaroche and Bérard the heating influence of the gases was a complex phenomenon, partly dependent on the caloric lost in cooling, and partly on that developed by the accompanying diminution in volume. This last source of heat ought to have been avoided, and in the experiments of Crawford it was so; for the heated gases with which he operated, being confined in a close vessel, underwent no change of volume while they cooled, though of course their elasticity was thereby diminished.

These considerations induced MM. De la Rive and Marcet to undertake this difficult inquiry. In their experiments the gases were confined in a thin globe of glass, and the temperature was estimated, not by a thermometer, but by the elastic force communicated by the heat, according to the law of Dalton and Gay-Lussac already mentioned. (P. 33.) The glass vessel was placed in the centre of a very thin copper globe, the inner surface of which was made to radiate freely by being blackened, and the air between it and the glass globe was withdrawn by an air-pump. The whole apparatus, being brought to the temperature of 68° F., was immersed during exactly five minutes in water kept steadily at 86°; and the heat imparted to the copper was radiated from its inner surface, and thus reached the glass globe in the centre. By always operating exactly in the same manner, it was conceived that the same volume of each gas would receive equal quantities of caloric in equal times; and that from the temperature thus communicated to each, its specific heat might be inferred. In two sets of experiments thus conducted, they found that each gas acquired the same elasticity, or was heated to the same degree: and thence they inferred that gases in general, for equal volumes and pressures, have the same capacity for caloric. They also operated with the same gas at different densities; and concluded that the specific heat of each gas, for equal volumes, diminishes slowly as its density decreases.

In the *An. de Ch. et Ph.* XLI. 113, M. Dulong has published some critical remarks on these experiments. He argues, in the first place, that the quantity of gas employed was so small, that any effect arising from a difference in specific heat could not be appreciated. He contends, further, that the temperature acquired by a gas in such experiments is not

influenced by its specific caloric only, but in part by the relative facility with which heat is transmitted through the gas. It has been already observed that heat is conducted by gaseous matter with extreme slowness, but is rapidly diffused through it in consequence of the mobility of its particles. Now gases differ considerably under this point of view. Hydrogen acquires the temperature of a hot body placed in it much more rapidly than carbonic acid; and therefore, were the same volume of these gases exposed for an equal short period to equal sources of caloric, the former would acquire a higher temperature simply from its conveying heat more readily. The validity of these strictures can scarcely, I apprehend, be denied. It may therefore be inferred from the foregoing observations, that the specific heats of the gases are not yet accurately known, and that the numbers stated by Delaroche and Bérard are probably the best approximations hitherto published.

The general facts hitherto determined concerning the specific heat of bodies may be arranged under the four 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 capacity for caloric.

2. The specific heat of a body varies with its form. A solid has a less capacity for caloric 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 only experiments in point are those of Crawford and Delaroche and Bérard. The former estimated the specific heat of vapour at 1.55, and the French philosophers at 0.847, compared to that of water as unity; nor is it possible to say which of these widely discordant results is nearer the truth, as neither can be relied on with confidence.

3. Of the specific heat of equal volumes of the same gas at different densities nothing certain has been established; for the experiments of MM. De la Rive and Marcet, above described, have led to no decisive conclusion. But all admit that the specific heat of equal weights of the same gas increases

as the density decreases. Thus, to maintain the temperature of 100 grains of atmospheric air at 60°, or any other temperature, more heat will be required when it occupies the room of 100 cubic inches than if it were contained in half that space; and still more heat will be requisite when its volume is augmented to 200 cubic inches. 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 caloric of any gas being 1, it is not 2, but between one and two, when its volume is doubled. This fact being established in the case of elastic fluids, it may reasonably be asked, whether the same law does not extend to liquids and solids? whether water, for instance, at 32°, possesses the same specific caloric as when dilated by a high temperature? Drs. Crawford and Irvine contended that it is permanent or nearly so, affirming that solids and liquids possess the same specific caloric at all temperatures, so long as they suffer no change of form or composition. Mr. Dalton, on the contrary (Chemical Philosophy, part I. p. 50), endeavours to show that the specific caloric of such bodies is greater in high than in low temperatures; and Petit and Dulong, in the essay already quoted, have proved it experimentally with respect to several of them. Thus the mean capacity of iron between

0° C and	.	100° Cent.	is	0.1098
0° C	.	200° C	.	0.1158
0° C	.	300° C	.	0.1218
0° C	.	350° C	.	0.1255

and the same is true of the substances contained in the following table.

	Mean Capacity between 0° and 100° C.	Mean Capacity between 0° and 300° C.
Mercury	0.0330	0.0350
Zinc	0.0927	0.1015
Antimony	0.0507	0.0549
Silver	0.0557	0.0611
Copper	0.0949	0.1013
Platinum	0.0335	0.0335
Glass	0.1770	0.1900

It is difficult to determine whether the increased specific caloric 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 capacity for caloric.

4. Change of capacity for caloric 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. Thus when air, confined within a flaccid bladder, is suddenly dilated by means of the air-pump, a thermometer placed in it will indicate the production of cold. On the contrary, when air is compressed, the corresponding diminution of its specific caloric gives rise to increase of temperature; nay, so much heat is evolved when the compression is sudden and forcible, that tinder may be kindled by it. The explanation of these facts is obvious. In the first case, a quantity of caloric becomes insensible, which was previously in a sensible state; in the second, caloric is evolved, which was previously latent.

From some experiments, the result of which is given in the 10th volume of the *An. de Ch. et Ph.*, MM. Dulong and Petit have inferred that the atoms of simple substances have the same capacity for caloric. The following table is taken from their essay. (Page 403.)

	Specific Caloric.	Relative Weights of Atoms.	Products of the Weight of each Atom by the corresponding Capacity.
Bismuth	0.0288	13.30.	0.3830
Lead	0.0293	12.95	0.3794
Gold	0.0298	12.43	0.3704
Platinum	0.0314	11.16	0.3740
Tin	0.0514	7.35	0.3779
Silver	0.0557	6.75	0.3759
Zinc	0.0927	4.03	0.3736
Tellurium	0.0912	4.03	0.3675
Copper	0.0949	3.957	0.3755
Nickel	0.1035	3.69	0.3819
Iron	0.1100	3.392	0.3731
Cobalt	0.1498	2.46	0.3685
Sulphur	0.1880	2.011	0.3780

In the new part of his Chemical Philosophy, page 293, Mr.

Dalton has made some strictures in reference to this table, tending to show that the opinion of Dulong and Petit cannot be correct, and that it stands in opposition to their own facts. Mr. Dalton argues that the product of the weight of an atom by the corresponding capacity for caloric, is not a constant quantity; because the capacity of the same substance varies with change of form, or even, according to their own experiments, with variation of temperature, without change of form. To the latter part of the criticism Dulong and Petit are certainly exposed; but they have anticipated the former by remarking, that the law is not affected by change of form, provided the substances compared are taken in the same state. Whether this position be correct or not, remains to be proved.

ON LIQUEFACTION.

All bodies, hitherto known, are either 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 separate from one another to an almost indefinite extent, unless restrained by external pressure, an aëriform substance will be produced.

Now the property of repulsion is manifestly owing to caloric; 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 general law. The converse ought also to be true; and, accordingly, several of the gases have already been condensed by means of pressure into liquids, 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 the discovery of Dr. Black, that a large quantity of caloric 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 caloric, all of which entered into the ice, and caused its liquefaction, but did not affect its temperature; and it follows, therefore, that a quantity of caloric becomes insensible during the melting of ice, sufficient to raise the temperature of an equal weight of water 140 degrees of Fahrenheit. 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° F. All the caloric which is added becomes insensible, till the liquefaction is complete.

The loss of sensible caloric which attends liquefaction seems essentially necessary to the change, and for that reason is frequently called the *caloric of fluidity*. The actual quantity of caloric 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 caloric of fluidity which is proper to it.

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

As so much heat disappears during liquefaction, it follows that caloric must be evolved when a liquid passes into a solid. This may easily be proved. The temperature of water in the act of freezing never falls below 32° F. though it be exposed to an atmosphere in which the thermometer is at zero. It is obvious that the water can preserve its temperature in a medium so much colder than itself, only by the caloric which it loses being instantly supplied; and it is no less clear that the only source of supply is the caloric of fluidity. Further, if pure recently boiled water be cooled very slowly, and kept very tranquil, its temperature may be lowered to 21° F. without any ice being formed; but the least motion causes it to congeal suddenly, and in doing so its temperature rises to 32° F.*

The explanation which Dr. Black gave of these phenomena constitutes what is called his *doctrine* of *latent heat*, which was partially explained on a former occasion. (Page 45.) He conceived that caloric 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 caloric of fluidity, heat is set free or becomes sensible, and the cohesion natural to the solid is restored. The same mode of reasoning was applied by Dr. Black to the conversion of liquids into vapours, a change during which a large quantity of caloric disappears.

A different explanation of these phenomena was proposed by Dr. Irvine. Observing that a solid has a less capacity for caloric than the same substance when in a liquid state, he argued that this circumstance alone accounts for caloric becoming insensible during liquefaction. For since the capacity of ice and water for caloric, 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, Dr. Irvine inferred that water must contain ten times more caloric than ice of the same temperature, and that as this difference must be supplied to the ice when it is converted into water, this change must necessarily be ac-

* Sir Ch. Blagden, in Philos. Trans. for 1788.

companied with the disappearance of caloric. Dr. Irvine applied the same argument to the liquefaction of all solids, and likewise to account for the caloric which is rendered insensible during the formation of vapour.

Two objections may properly be urged against the opinion of Dr. Irvine. In the first place, no adequate reason is assigned for the liquefaction. It accounts for the disappearance of caloric which accompanies liquefaction, but does not explain why the body becomes liquid; whereas the hypothesis of Dr. Black affords an explanation both of the change itself, and of the phenomena that attend it. But the second objection is still more conclusive. Dr. Irvine argued on the belief that a liquid has in every case a greater capacity for caloric than when in the solid state; 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 a greater specific caloric than solids, and that therefore Dr. Irvine's assumption is probably correct. In like manner he believed vapours to have a greater capacity for caloric than the liquids that yield them, and his opinion was supported by the experiments of Crawford on the specific caloric of water and watery vapour. But no reliance whatever can be placed on the researches of Dr. Crawford on this subject; not only because his result is so different from that obtained by Delaroche and Bérard, but because all his other experiments on the specific caloric of elastic fluids are decidedly erroneous. (Page 47.) Indeed from the fact of most gases having a less specific heat than liquids, it is probable that the capacity of elastic fluids in general for caloric is inferior to that of the liquids from which they are derived. The disappearance of caloric during vaporization is therefore not explicable on the views of Irvine; it is necessary to employ the theory of Dr. Black to account for that change, and therefore the same doctrine should be applied to the analogous phenomenon of liquefaction.

In speculating on the cause of the specific caloric of bodies at page 45, I had recourse to the doctrine of latent or combined caloric. Dr. Black restricted the use of this hypothesis to explain the phenomena of liquefaction and vaporization; but I apprehend it may be applied without impropriety to all cases

where caloric passes from a sensible to an insensible state. That this may happen when caloric enters a body, without change of form, is easily demonstrated. Thus, in order to raise an equal weight of water and mercury by the same number of degrees, it is necessary to add 23 times as much heat to the water as to the mercury; a fact which proves that a quantity of caloric becomes insensible to the thermometer when the temperature of water is raised by one degree, just as happens when ice is converted into water, or water into vapour. The phenomena are in this point of view identical; and, therefore, the same mode of reasoning by which one of them is explained, may be employed to account for the other.

The disappearance of sensible caloric in liquefaction is the basis of many artificial processes for producing cold. All of them are conducted on the principle of liquefying solid substances without the aid of heat. For the caloric of fluidity being then derived chiefly 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 caloric which disappears, and this again is dependent on the quantity of solid liquefied, and the rapidity of liquefaction.

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. The crystallized muriate of lime, proposed by Lowitz, is by far the most convenient in practice. This salt may be made by dissolving marble in muriatic acid. The solution should be concentrated 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, from Mr. Walker's paper in the Philosophical Transactions for 1801, contains the best proportions for producing intense cold.

FRIGORIFIC MIXTURES WITH SNOW*.

MIXTURES. Parts by Weight.	Thermometer sinks	Degree of Cold produced.
Muriate of Soda 1 Snow 2	From any Temperature to − 5°	
Muriate of Soda 2 Muriate of Ammonia 1 Snow 5	From any Temperature to − 12°	
Muriate of Soda 10 Muriate of Ammonia 5 Nitrate of Potash 5 Snow 24	From any Temperature to − 18°	
Muriate of Soda 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 Muriatic Acid 5 Snow 8	from + 32° to −27°	59
Concentrated Nitrous Acid 4 Snow 7	from + 32° to −30°	62
Muriate of Lime 5 Snow 4	from + 32° to −40°	72
Crystallized Muriate of Lime 3 Snow 2	from + 32° to −50°	82
Fused Potash 4 Snow 3	from + 32° to −51°	83

But freezing mixtures may be made by the rapid solution of salts, without the use of snow or ice; and the following table, taken from Walker's Essay in the Philosophical Transactions for 1795, includes the most important of them. The salts must be finely powdered and dry.

* 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.

MIXTURES. Parts by Weight.	Temperature falls	Degree of Cold produced.
Muriate of Ammonia . 5 Nitrate of Potash . 5 Water . . . 16	from + 50° to + 10°	40 degrees.
Muriate of Ammonia . 5 Nitrate of Potash . 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 Muriate of Ammonia . 4 Nitrate of Potash . 2 Diluted Nitrous Acid . 4	from + 50° to − 10°	60
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 Muriatic 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 may be thus produced; but it is found that when the difference between the mixture and the air becomes very great, caloric is so rapidly communicated from one to the other, as to limit the reduction to a certain point. The greatest cold produced by Mr. Walker did not exceed 100 degrees below the zero of Fahrenheit.

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

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

Though it is unlikely that we shall ever succeed in depriving any substance of all its caloric, it is presumed that bodies do contain a certain definite quantity of this principle, and various attempts have been made to calculate its amount. The mode of conducting such a calculation may be shown by the process of Dr. Irvine. That ingenious chemist proceeded on the assumption, that the actual quantity of caloric in bodies is proportioned to their capacity, and that the capacity remains the same at all temperatures, provided no change of form takes place. Thus, as the capacity of ice is to that of water as 9 to 10, it follows, according to the hypothesis, that the one contains 1-10th more caloric than the other, at the same temperature. Now Dr. Black ascertained that this tenth, which is the caloric of fluidity, is equal to 140 degrees; whence it was inferred that water at 32° contains 10 times 140 or 1400 degrees of caloric.

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 caloric in water vary from 900 to nearly 8000*. Besides, did even the estimates agree with each other, the principle of the calculation would still be unsatisfactory; for, in the first place, there is no proof that the quantity of heat in bodies is in the ratio of their capacities; and, secondly, the assumption that the capacity of a body for caloric is the same at all temperatures, so long as it does not experience a change of form, has been proved to be erroneous by the experiments of Dulong and Petit.

VAPORIZATION.

Aeriform substances are commonly divided into vapours and gases. The character of the former is, that they may be readily converted 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,

* Dalton's New System of Chemical Philosophy.

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.

Caloric appears to be the cause of vaporization, as well as of liquefaction, and it is a general opinion that a sufficiently intense heat would convert every liquid and solid into vapour. A considerable number of 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 are, in general, more easily vaporized than solids, as 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. According to the experiments of Gay-Lussac, water, at its point of greatest density, in passing into vapour, expands to 1696 times its volume, alcohol to 659 times, and ether to 443 times, each vapour being at a temperature of 212° F., 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 proportion of 1000 to 1604; or the density of air being 1000, that of watery vapour is 623. 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. As alcohol boils at a lower temperature than water, and ether than alcohol, it was conceived that the density of vapours might be in the direct ratio of the volatility of the liquids which produced them. But Gay-Lussac has shown that this law does not hold

generally; for the carburet of sulphur boils at a higher temperature than ether, and nevertheless it yields a heavier vapour.

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 the law does not hold unless the quantity of vapour continues the same. If the increase of temperature cause a fresh portion of vapour to rise, then the expansion will be greater than $\frac{1}{480}$th for each degree; because the heat not only dilates the vapour previously existing to the same extent as if it were a real gas, but augments its bulk by adding a fresh quantity of vapour. The contraction of a vapour on cooling will likewise deviate from the above law, whenever the cold converts any of it into a liquid; an effect which must happen, if the space had originally contained its maximum of vapour. Thus aqueous vapour at 32° supports a column of only 0·2 of an inch, while at 212° its elasticity is equal to a pressure of 30 inches of mercury. Hence the elastic force or expansion of watery vapour between 32° and 212°, supposing the space to be in a state of saturation, is as 1 to 150.

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. Thus, sulphuric ether boils at 96° F., alcohol at 173°, and pure water at 212°; while oil of turpentine must be raised to 316°, and mercury to 680°, before either exhibits marks of ebullition. 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 it. Thus,

Gay-Lussac observed that pure water boils precisely at 212° in a metallic vessel, and at 214° in one of glass. It is likewise affected by the presence of foreign particles. The same accurate experimenter found, that 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. But the circumstance which has the greatest influence over the boiling point of fluids 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 only time at which the pressure of the atmosphere is equal to a weight of 15 pounds on every square inch of surface, is when the barometer stands at 30 inches, and then only does water boil at 212° F. 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 rises above 30 inches, the temperature of ebullition will be proportionally increased. This is the reason why 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 atmospherical pressure is so exact, that it has been proposed as a method for determining the heights of mountains. An elevation of 530 feet makes a diminution of one degree of Fahrenheit. (Mr. Wollaston in Phil. Trans. for 1817.)

The influence of the atmosphere over the point of ebullition is best shown by removing its pressure altogether. The late Professor Robinson found that fluids boil *in vacuo* at a tem-

perature 140 degrees lower than in the open air. (Black's Lectures, p. 151.) Thus water boils *in vacuo* at 72°, alcohol at 33°, and ether at — 44° F. This proves that a liquid is not necessarily hot, because it boils. The heat of the hand is sufficient to make water boil *in vacuo*, as is exemplified by the common pulse-glass; and ether, under the same circumstances, will enter into ebullition, though its temperature is low enough for freezing mercury.

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.

In estimating the power of steam, it should be remembered that vapour, if separated from the liquid which produced it, does not possess a greater elasticity than an equal quantity of air. If, for example, the digester were full of steam at 212°, no water in the liquid state being present, it might be heated to any degree, even to redness, without danger of bursting. But if water be present, then each addition of caloric causes a fresh portion of steam to rise, which adds its own elastic force to that of the vapour previously existing; and in consequence an excessive pressure is soon exerted against the inside of the vessel. Professor Robison (Brewster's edition of his works, p. 25) found that the tension of steam is equal to two atmospheres at 244° F., and to three at 270° F. The results of Mr. Southern's experiments, given in the same volume, fix upon 250·3° as the temperature at which steam has the force of two atmospheres, on 293·4° for four, and 343·6° for eight atmospheres.

This subject has been lately 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. vii. 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	13	380·66
1½	233·96	14	386·94
2	250·52	15	392·86
2½	263·84	16	398·48
3	275·18	17	403·82
3½	285·08	18	408·92
4	293·72	19	413·96
4½	301·28	20	418·46
5	308·84	21	422·96
5½	314·24	22	427·28
6	320·36	23	431·42
6½	326·26	24	435·56
7	331·70	25	439·34
7½	336·86	30	457·16
8	341·96	35	472·73
9	350·78	40	486·59
10	358·88	45	491·14
11	367·34	50	510·60
12	374·00		

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 caloric, and its ready conversion into water by cold. The effect of both these properties is well shown by a little instrument devised by Dr. Wollaston. It consists of a cylindrical glass tube, six inches long, nearly an inch wide, and blown out into a spherical enlargement at one end. A piston is accurately fitted to the cylinder, so as to

move up and down the tube with freedom. When the piston is at the bottom of the tube, it is forced up by causing a portion of water, previously placed in the ball, to boil by means of a spirit-lamp. On dipping the ball into cold water, the steam which occupies the cylinder is suddenly condensed and the piston forced down by the pressure of the air above it. By the alternate application of heat and cold, the same movements are reproduced, and may be repeated for any length of time.

The moving power of the steam engine is the same as in this apparatus. The only essential difference between them is in the mode of condensing the steam. In the steam engine, the steam is condensed in a separate vessel called the *condenser*, where there is a regular supply of cold water for the purpose. By this contrivance, which constitutes the great improvement of Watt, the temperature of the cylinder never falls below 212°.

The formation of vapour is attended, like liquefaction, with loss of sensible caloric. 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 caloric which enters into the liquid is solely employed in converting a portion of it into vapour, without affecting the temperature of either in the slightest degree, provided the latter is permitted to escape with freedom. The caloric which then becomes latent, to use the language of Dr. Black, is again set free when the vapour is condensed into water. The exact quantity of caloric 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 Dr. Black and Mr. Watt, conducted on this principle, it appears that steam of 212°, in being condensed into water of 212°, gives out as much caloric 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.)

	Latent Heat.
Vapour of water at its boiling point	967°
Alcohol	442
Ether	302.379
Petroleum	177.87
Oil of turpentine	177.87
Nitric acid	531.99
Liquid ammonia	837.28
Vinegar	875

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

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 some dry cold days in winter, the evaporation is exceedingly rapid; whereas it goes on very tardily, if the atmosphere contains much vapour, even though the air be very warm.

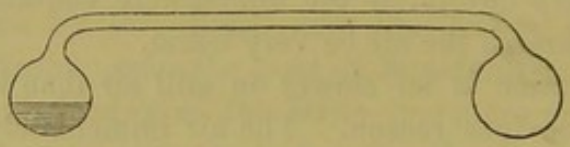
4. Evaporation is far slower in still air than in a current, and for an obvious reason. The air immediately in contact with the water soon becomes moist, and thus a check is put to evaporation. But if the air is removed from the surface of the water as soon as it has become charged with vapour, and its 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.

As a large quantity of caloric passes from a sensible to an insensible state during the formation of vapour, it follows that cold should be generated by evaporation. A very simple experiment will prove it. If a few drops of ether be allowed to fall upon the hand, a strong sensation of cold will be excited during its evaporation; 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 Mr. 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 †.

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 Mr. Dalton prove that caloric is the true and only cause of the formation of vapour. He finds that the actual quantity of vapour, which

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

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

can exist in any given space, is dependent solely upon the temperature. If, for instance, a little water be put into a dry glass flask, a quantity of vapour will be formed proportionate to the temperature. If a thermometer placed in it stands at 32°, the flask will contain a very small quantity of vapour. At 40°, more vapour will exist in it; at 50° it will contain still more; and at 60°, the quantity will be still further augmented. If, when the thermometer is at 60°, the temperature of the flask is suddenly reduced to 40°, then a certain portion of vapour will be converted into water; the quantity which retains the elastic form being precisely the same as when the temperature was originally at 40°.

It matters not, with regard to these changes, whether the flask is full of air, or altogether empty; for in either case, it will eventually contain the same quantity of vapour, when the thermometer is at the same height. The only effect of a difference in this respect, is in the rapidity of evaporation. The flask, if previously empty, acquires its full complement of vapour, or, in common language, becomes saturated with it, in an instant; whereas the presence of air affords a mechanical impediment to its passage from one part of the flask to another, and therefore an appreciable time elapses before the whole space is saturated.

Mr. Dalton 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. If, for example, in a vessel containing a liquid, the space occupied by its vapour should suddenly dilate, the vapour it contains will dilate also, and consequently suffer a diminution of elastic force; but its tension will be quickly restored, because the liquid yields an additional quantity of vapour, proportional to the increase of space. Again, if the space be diminished, the temperature remaining constant, the tension of the confined vapour will still continue unchanged; because a quantity of it will be condensed proportional to the diminution of space, so that, in fact, the remaining space contains the very same quantity of vapour as it did originally. The same law holds good, whether the vapour is pure, or mixed with air or any other gas.

The elasticity of watery vapour at temperatures below 212° F. was carefully examined by Mr. Dalton; (Manchester Memoirs, vol. v.) and his results, together with those since published by Dr. Ure, in the Philosophical Transactions for 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. But Mr. Dalton did not confine his researches to water; he extended them to the vapour of various liquids, such as ether, alcohol, ammonia, and solution of muriate of lime, and he inferred from them the following law:—That the force of vapour from all liquids is the same, at equal distances above or below the several temperatures at which they boil in the open air. Thus steam at 200° F. has the same elasticity as the vapour of ether at 85°, the boiling point of the former being 212°, and of the latter 97°. Biot and Amédé Berthollet (Biot, Traité de Ph. i. 282.) have found that this law applies exactly to many other liquids; but some experiments by Dr. Ure, on oil of turpentine and petroleum, would lead to the conclusion that it is not universal.

It is easy, on this principle, to account for the elastic force of the vapours of liquids, whose boiling point is very high, being inappreciable at moderate temperatures. Thus sulphuric acid boils at 620° F.; and therefore at 212°, that is 408 degrees below its point of ebullition, the elasticity of its vapour should be equal to that of aqueous vapour at — 196°, or 408 degrees below the boiling point of water. In like manner mercury, which boils at 680°, yields vapour whose elastic force at 212° may be estimated as equal to that of watery vapour at — 256°, or 468 degrees below the point at which water enters into ebullition. According to the same law, mercury requires a temperature of 500°, or 180 degrees below its boiling point, in order that its vapour should have the same tension as watery vapour at 32°. From these considerations it is inferred, that, though in a common barometer the space above the column may contain a little mercurial vapour, and consequently may not be an absolute vacuum, the influence of that vapour in depressing the column, even at considerable temperatures, is altogether inappreciable.

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 placed 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 Mr. Faraday, in his essay On the Existence of a Limit to Vaporization, published in the Philosophical Transactions for 1826. The argument employed by Mr. Faraday is founded on the principle by which the late Dr. Wollaston has accounted for the limited extent of the atmosphere. Since the volume of gaseous substances is dependent on the pressure to which they are subject, the air in the higher regions of the atmosphere must be much more rare than that in the lower, because the former sustains the pressure of a shorter atmospheric column than the latter; so that in ascending upwards from the earth, each successive stratum of air, being less compressed than the foregoing, is likewise more attenuated. Now it is found experimentally that the elasticity or tension of any gaseous matter diminishes in the same ratio as its volume increases; and, accordingly, whenever the tenuity of a portion of air, owing to its distance from the earth's surface or any other cause, is exceedingly great, its tension is exceedingly small. Reasoning on this principle, Dr. Wollaston conceives that at a certain altitude, probably at a distance of 40 or 50 miles from the surface of the earth, the rarefaction and consequent loss of elastic force is so extreme, that the mere gravity of the particles becomes equal to their elasticity, and thus puts a limit to their separation.

What Dr. Wollaston suggests of aërial particles, Mr. Faraday supposes to occur in all substances; and this supposition is perfectly legitimate, because gaseous matter in general is subject to the same law of expansion, and is likewise under the in-

fluence of gravity. He infers that every kind of matter ceases to assume the elastic form, whenever the gravitation of its particles is stronger than the elasticity of its vapour. The loss of tension necessary for effecting this object may be accomplished in two ways, either by extreme dilatation, or by cold. For substances of great volatility, such as air and most gases, the former is necessary; because the degree of cold which we can command at the earth's surface diminishes their tension in a degree quite insufficient to destroy their elasticity. But the volatility of innumerable bodies is so small, that their vapour at common temperatures approximates in rarity to the air at the limits of the atmosphere, and a small degree of cold may suffice for rendering its elasticity a force inferior to its opponent, gravity. In that case, the vapour would be entirely condensed. Mr. Faraday found that mercury, at a temperature varying from 60° to 80°, yields a small quantity of vapour; but in winter no trace of vapour could be detected. Hence it is inferred, that at the former temperature the elasticity of mercurial vapour is slightly superior to the gravity of its particles, and that in cold weather the latter power preponderates, and puts an entire check to the evaporation of mercury. The earths and metals, which are more fixed than mercury, have vapours of such feeble tension, that the highest natural temperature is unable to convert them into vapour. Another force, which co-operates with gravity in overcoming elasticity, is the attraction of aggregation, or the attraction exerted by a solid or liquid on the contiguous particles of the same substance in the gaseous form.—This argument affords very sufficient grounds for believing that the vapours of earthy and metallic substances are never present in the atmosphere.

The presence of vapour has a considerable influence over the bulk of gases; and as chemists often find it convenient to determine the quantity of gaseous substances by measure, it is important to estimate the effect thus produced, in order to make allowance for it. The mode by which a vapour acts is obvious. 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 tension 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 gives 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 tension of the dry air, equal to the atmospheric pressure; n' the bulk of the air when saturated with watery vapour, and f the tension of that vapour. (Biot's Traité de Phys. I. 303.)

It is a well-known law in pneumatics that the elasticity of a gas is inversely as its volume; so that, when the dry air increases in bulk from n to n', its elasticity diminishes in the ratio of n' to n. Hence its elasticity ceases to be $=p$, but is expressed by $\frac{pn}{n'}$; p is now $=\frac{pn}{n'}+f$; that is, the elasticity of the dilated 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° F., the barometer standing at 30 inches, how many measures would the air occupy if quite dry? $n'=100$; $p=30$; $f=0.524$, the tension of watery vapour at 60°, according to Mr. Dalton's table. Hence $n=\frac{100\times(30-0.524)}{30}=\frac{100\times 29.476}{30}=98.25$, which is the answer required.

The presence of watery vapour in the atmosphere is owing to evaporation. All the accumulations of water upon the surface of the earth are subjected by its means to a natural distillation; the impurities with which they are impregnated remain behind, while the pure vapour ascends into the air, gives rise to a multitude of meteorological phenomena, and

after a time descends again upon the earth. As evaporation goes on to a certain extent even at low temperatures, it is probable that the atmosphere is never absolutely free from vapour.

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.

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. Almost all bodies have the power of attracting moisture from the air, though in different proportions. A piece of glass or metal weighs sensibly less when carefully dried, than after exposure to a moist atmosphere; though neither of them is dilated, because the water cannot penetrate into their interior. Dilatation from the absorption of moisture appears to depend on a deposition of it within the texture of a body, the particles of which are moderately soft and yielding. The hygrometric property therefore belongs chiefly to organic substances, such as wood, the beard of corn, whalebone, hair, and animal membranes. 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 points out the opposite states of dryness and moisture by the rapidity of evaporation. Water does not evaporate at all when the atmosphere is completely saturated with moisture; and the freedom with which it goes on at other times, is in proportion to the dryness of the air. The hygrometric condition of the air may be determined, therefore, by observing the rapidity of evaporation.

The most convenient method of doing this, is by covering the bulb of a thermometer with a piece of silk or linen, moistening it with water, and exposing it to the air. The descent of the mercury, or the cold produced, will correspond to the quantity of vapour formed in a given time. Mr. Leslie's hygrometer is of this kind.

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. This is often seen when a glass of cold spring water is carried into a warm room in summer; and the phenomenon is witnessed during the formation of dew, the moisture appearing on those substances only which are colder than the air. The degree indicated by the thermometer when dew begins to be deposited, is called the *dew-point*. If the saturation is 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 M. le Roi, and since adopted by Mr. 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. This method, when carefully performed, is susceptible of great precision.

The hygrometer of Mr. Daniell, described in his Meteorological Essays, acts on the same principle. It consists of a cryophorus, as described at page 69, 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 Mr. Jones of London in the Philos. Trans. for 1826, and soon after in the Edin. Philos. Journal, No. xvii. p. 155, by Dr. Coldstream of Leith. 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 appears from some remarks of Mr. Daniell in the Quarterly Journal of Science, that this hygrometer was originally invented in Germany, so that Mr. Jones and Dr. Coldstream are second inventors. Mr. Daniell considers the instrument inaccurate, believing that, as the ether is applied to a part only of the bulb, the mercury within will be cooled unequally; that the portion corresponding to the covered part of the bulb will be colder than the mercury opposite to the exposed part, and consequently the dew-point will appear lower than it ought to be. This objection certainly applies when the muslin is rendered very moist with ether, and the temperature of the bulb rapidly reduced; but when the cooling is slowly effected, I believe the indications of this hygrometer to be at least as correct as those afforded by the very elegant, yet more costly and less portable, apparatus of Mr. Daniell. For facts confirmatory of this opinion the reader may consult an essay in the Edinburgh Journal of Science, No. xiii. p. 36, by Mr. Foggo, junior, of Leith.

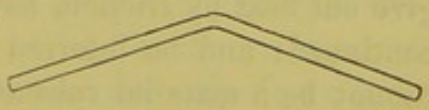
It is desirable on some occasions, not merely to know the hygrometric condition of air or gases, but also to deprive them entirely of their vapour. This may be done to a great

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 CALORIC.

The experiments of Mr. Faraday, on the liquefaction of gaseous substances, appear to justify the opinion that gases are merely 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. An intense degree of cold is produced at the same time, in consequence of caloric passing from a sensible to an insensible state.

The process for condensing gases (Philos. Trans. for 1823) consists in exposing them to the pressure of their own atmospheres. 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 Mr. Faraday.

Sulphurous acid gas	2 atmospheres at	45°F.
Sulphuretted hydrogen gas	17	50°F.
Carbonic acid gas	36	32°F.
Chlorine gas	4	60°F.
Nitrous oxide gas	50	45°F.
Cyanogen gas	3.6	45°F.
Ammoniacal gas	6.5	50°F.
Muriatic acid gas	40	50°F.

SOURCES OF CALORIC.

The sources of caloric may be reduced to six. 1. The sun. 2. Combustion. 3. Electricity. 4. The bodies of animals during life. 5. Chemical action. 6. Mechanical action. All these means of procuring a supply of caloric, except the last, will be more conveniently considered in other parts of the work.

The mechanical method of exciting caloric 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-tree of carriages has been burned from this cause, and the sides of ships are said to have taken fire by the rapid descent of the cable. Count Rumford has given an interesting account of the caloric 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 caloric cannot be a material substance, but is merely a property of matter. M. 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.

SECTION II.

LIGHT.

Light is similar to caloric in many of its properties. They are both emitted in the form of rays, traverse the air in straight lines, and are subject to the same laws of reflection. The intensity of each diminishes as the square of the distance from their source. They often accompany each other; and on some occasions seem to be actually converted into one another. It has been supposed, from this circumstance, that they are modifications of the same agent; and though most persons regard them as independent principles, yet they are certainly allied in a way which is at present quite inexplicable.

There are two kinds of light, natural and artificial; the former proceeding from the sun and stars, the latter from bodies which are strongly heated. The light derived from these sources is so different, that it is necessary to speak of them separately.

The solar rays come to us either directly, as in the case of sunshine, or indirectly, in consequence of being diffused through the atmosphere, constituting day-light. They pass freely through some solid and liquid bodies, hence called transparent, such as glass, rock-crystal, water, and many others, which, if clear and in moderately thin layers, intercept a portion of light that is quite inappreciable when compared with the quantity transmitted. Opaque bodies, on the contrary, intercept the rays entirely, absorbing some of them and reflecting others. In this respect, also, there is a close analogy between light and caloric; for every good reflector of the one reflects the other also.

Though transparent substances permit light to pass through them, they nevertheless exert considerable influence upon it in its passage. All the rays which fall obliquely are refracted, that is, are made to deviate from their original direction. It was this property of transparent media which enabled Sir Isaac Newton to discover the compound nature of solar light, and to resolve it into its constituent parts.

The substance commonly employed for this purpose is a triangular piece of glass called the *prism*. Its action depends upon the different refrangibility of the seven coloured rays which compose a colourless one. The violet ray suffers the greatest refraction, and the red the least: the other colours of the rainbow lie between them, disposed in regular succession according to the degree of deviation which they have individually experienced. The coloured figure so produced is called the *prismatic spectrum*, which is always bounded by the violet ray on one side, and by the red on the other.

The prismatic colours, according to the experiments of Sir W. Herschel, differ in their illuminating power. The orange possesses this property in a higher degree than the red; and the yellow rays illuminate objects still more perfectly. The maximum of illumination lies in the brightest yellow or palest green. The green itself is almost equally bright with the yellow; but from the full deep green, the illuminating power decreases very sensibly. That of the blue is nearly equal to that of the red; the indigo has much less than the blue; and the violet is very deficient. (Phil. Trans. 1800.)

The solar rays, both direct and diffused, possess the property of exciting heat as well as light. This effect takes place only when the rays are absorbed: for the temperature of transparent substances through which they pass, or of opaque ones by which they are reflected, is not affected by them. Hence it happens that the burning glass and concave reflector are themselves nearly or quite cool, at the very moment of producing intense heat by collecting the sun's rays into a focus. The extreme coldness that prevails in the higher strata of the air arises from the same cause. The rays pass on unabsorbed through the atmosphere; and its lower parts would also be excessively cold, did they not receive caloric by communication from the earth.

The absorption of light is much influenced by the nature of the surface on which it falls; and it is remarkable that those substances which absorb radiant non-luminous caloric most powerfully, are likewise the best absorbers of light. But there is one property of surfaces, namely, colour, which has a great influence over the absorption of light, but exceedingly little, if any, over that of pure radiant caloric. That dark-coloured

substances acquire in sunshine a higher temperature than light ones, may be inferred from the general preference given to the latter as articles of dress during summer; and this practice, founded on the experience of mankind, has been justified by direct experiment. Dr. Hooke, and subsequently Dr. Franklin, proved the fact by placing pieces of cloth of the same texture and size, but of different colours, upon snow, and allowing the sun's rays to fall upon them. The dark-coloured specimens always absorbed more caloric than the light ones, the snow beneath the former having melted to a greater extent than under the others; and it was remarked that the effect was nearly in proportion to the depth of shade. The late Sir H. Davy has more recently examined the subject, and arrived at the same conclusions.

The rays of the prismatic spectrum differ from one another in their heating power as well as in colour. Their difference in this respect was first noticed by Herschel, who was induced to direct his attention to the subject by the following circumstance. In viewing the sun by means of large telescopes through differently coloured darkening glasses, he sometimes felt a strong sensation of heat with very little light, and at other times he had a strong light with little heat,—differences which appeared to depend on the colour of the glasses which he used. This observation led to his celebrated researches on the heating power of the prismatic colours, which were published in the Philosophical Transactions for 1800.

The experiments were made by transmitting a solar beam through a prism, receiving the spectrum on a table, and placing the bulb of a very delicate thermometer successively in the different parts of it. While engaged in this inquiry, he observed not only that the red was the hottest ray, but that there was a point a little beyond the red, altogether out of the spectrum, where the thermometer stood higher than in the red itself. By repeating and varying the experiment, he discovered that the most intense heating power was always beyond the red ray, where there was no light at all; and that the heat progressively diminished in passing from the red to the violet, where it was least. 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 less degree from their original direction in passing through the prism.

All succeeding experiments confirm the statement of Sir W. Herschel, that the prismatic colours have very different heating powers; but they are at variance with respect to the spot at which the heat is at a maximum. Some assert with Sir W. Herschel that it is beyond the red ray; while others, and in particular Professor Leslie, contend that it is in the red itself. The observations of M. Seebeck in the Edinburgh Journal of Science, I. 358, appear decisive of the question. He found that the point of greatest heat was variable according to the kind of prism which was employed for refracting the rays. When he used a prism of fine flint glass, the greatest heat was constantly beyond the red. With a prism of crown glass, the greatest heat was in the red itself. When he employed a prism externally of glass, but containing water within, the maximum was neither in the red, nor beyond it, but in the yellow. It is difficult to account for these phenomena, except on the supposition that the different kinds of prisms differ in their power of refracting caloric. These experiments therefore confirm the opinion of Sir W. Herschel, that the sunbeam contains calorific rays, distinct from the luminous ones; and render it highly probable that the heating effect imputed to the latter, is solely owing to the presence of the former.

It has long been known that 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 the sunbeam. This effect was once attributed to the influence of the luminous rays; but it appears from the observations of Ritter and Wollaston, that it is owing to the presence of certain rays that excite neither heat nor light, and which, from their peculiar agency, are termed *chemical* rays. It is found that the greatest chemical action is exerted just beyond the violet ray of the prismatic spectrum; that the spot next in energy is occupied by the violet ray itself; and that the property gradually diminishes as we advance to the green, beyond which it seems wholly wanting. It hence follows that the chemical rays are still more refrangible than the luminous ones,

in consequence of which they are dispersed in part over the blue, indigo, and violet, but in the greatest quantity at a point which is even beyond the latter.

The more refrangible rays of light are said to possess the property of rendering steel or iron magnetic. The existence of this property was first asserted by Dr. Morichini of Rome. Other observers subsequently failed in obtaining the same results; but in the year 1826 the fact appeared to be decisively established by the learned and accomplished Mrs. Somerville, in an essay published in the Transactions of the Royal Society. In her experiments, sewing needles were rendered magnetic by exposure for two hours to the violet ray; and the magnetic virtue was communicated in still shorter time, when the violet rays were concentrated by means of a lens. The indigo rays were found to possess a magnetizing power almost to the same extent as the violet; and it was also observed, though in a less degree, in the blue and green rays. It is wanting in the yellow, orange, and red. Needles were likewise rendered magnetic by the sun's rays, transmitted through green and blue glass. These results have been verified by M. Zantedeschi of Pavia (Bibl. Univ. for May, 1829); but their accuracy is denied by M. M. Riess and Moser, who consider that the means employed by Mrs. Somerville for ascertaining the magnetic state of the needles were not sufficiently exact. They found the oscillation of needles to be wholly unaffected by exposure to the prismatic colours. (Brewster's Journal, II. 225. N. S.) This must still be regarded, therefore, as one of the disputed points in science.

The second kind of light is that which is emitted by substances when strongly heated. All bodies begin to emit light when caloric 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° F.; 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. Should the temperature still con-

tinue to increase, the character of the glow changes, and by degrees it becomes white, shining with increasing brilliancy as the intensity of 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.

All artificial lights are procured by the combustion or burning of inflammable matter. So large a quantity of caloric is evolved during the process, that the body is made incandescent in the moment of being consumed. Those substances are preferred for the purposes of illumination that yield gaseous products when strongly heated, which, by becoming luminous while they burn, constitute flame. The light derived from such sources differs from solar light in being accompanied by free radiant caloric similar to that emitted by a non-luminous heated body. The free radiant caloric may be separated by a screen of moderately thick glass; but the light so purified still heats any body that absorbs it, whence it would appear that it retains some calorific rays which, like those in the solar beam, accompany the luminous ones in their passage through solid transparent media*. Terrestrial light has been supposed to contain no chemical rays; but the experiments with lime strongly heated by the method of Mr. Drummond, have proved that artificial light of great intensity is productive of chemical changes similar to those occasioned by solar light. (Annals of Philosophy, xxvii. 451.)

Light is emitted by some substances at common temperatures, giving rise to an appearance which is called *phosphorescence*. This phenomenon seems owing in some instances to a direct absorption of light which is afterwards slowly emitted. A composition made by heating to redness a mixture of calcined oyster shells and sulphur, known by the name of *Canton's Phosphorus*, possesses this property in a very remarkable degree. It shines so strongly for a few minutes after exposure to light, that when removed to a dark room the hour on a watch may be distinctly seen by it. After some time it ceases

* Mr. Powel, in Phil. Trans. for 1825.

to be luminous, but regains the property when exposed during a short interval to light. No chemical change attends the phenomenon.

Another kind of phosphorescence is observable in some bodies when they are strongly heated. A piece of marble, 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 is sometimes of importance to measure the comparative intensities of light, and the instrument by which this is done is called a *photometer*. The only photometer which is employed for estimating the relative strength of the sun's light is that of Mr. Leslie. It consists of his differential thermometer, with one ball made of black glass. The clear ball transmits all the luminous rays that fall upon it, and therefore its temperature is not affected by them; they are all absorbed, on the contrary, by the black ball, and by heating and expanding the air within, cause 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 heat produced by the absorption of light. Mr. Leslie conceives that light when absorbed is converted into heat; but, according to the experiments already referred to, the effect must be attributed, not so much to the light itself, as to the absorption of the calorific rays by which it is accompanied.

Mr. Leslie recommends his photometer also for determining the relative intensities of artificial light, such as that emitted

by candles, oil, or gas. This application of it differs from the foregoing, because light proceeding from terrestrial sources contains caloric under two forms. One portion is analogous to that emitted by a hot body which is not luminous; the other is similar to that which accompanies solar light. It is presumed that the first form of caloric will not prove a source of error; that these rays are wholly intercepted by the outer case of glass; or that, should a few penetrate into the interior, they will be absorbed equally by both balls, and will therefore heat them to the same extent. It is probable that this reasoning is not wide of the truth; and, consequently, the photometer will give correct indications so far as regards the new element—non-luminous caloric. But it is not applicable to lights which differ in colour, because the relation between the heating and illuminating power of such lights is exceedingly variable. 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.

The second kind of photometer is on a totally different principle. It determines the comparative strength of lights by a comparison of their shadows. This instrument was invented by Count Rumford, and is described by him in his Essays. It is susceptible of great accuracy when employed with the requisite 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 mode of obtaining an approximative result, is by observing 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.

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

SECTION III.

ELECTRICITY.

When certain substances, such as amber, glass, sealing-wax, or sulphur, are rubbed, and then brought near small fragments of paper, cork, or other light bodies, the latter move rapidly towards the former, and adhere during a longer or shorter interval to their surface. If the body which is thus excited by friction is light and freely suspended, it will move towards the substances in its vicinity. After a while the excited body loses its influence; but it may be renewed for any number of times by friction. The movement observed in these instances is attributed to a peculiar kind of attraction, and the unknown cause of this attraction is called *Electricity*, from the Greek word ηλεκτρον, amber, because the electric property was first noticed in this substance.

The ancients were aware that amber and the *lyncurium*, (supposed to be our tourmalin,) may be rendered electric by friction, but it was not known that other bodies may be similarly excited until the commencement of the 17th century, when Dr. Gilbert of Colchester detected the same property in a variety of other substances. Of those which he has enumerated in his treatise *de Magnete*, the principal are the diamond, rock crystal, and several of the precious stones, glass, sulphur, mastic, sealing-wax, and resin; and in making this discovery he laid the foundation of the science of Electricity. A few additional facts were noticed during the course of the same century by Boyle, Otto de Guericke, and Dr. Wall, and in 1709 Mr. Hawkesbee published an account of many curious electrical experiments; but no material progress was made in this department of knowledge till between the years 1729 and 1733, when the discovery of new and important facts by Mr. Stephen Grey in this country, and M. Dufay in France, attracted general attention to the subject, and speedily acquired for it the regular form of a science *.

* For the historical details, see Priestley's History of Electricity.

The most important fact established by Mr. Grey was the fundamental one, that electricity passes freely along certain substances, and that its progress is more or less entirely arrested by others. M. Dufay, in repeating the experiments of Grey, observed that an electrified substance not only attracts light bodies, but causes them after contact to fly off from its surface as if by a principle of repulsion. This singular phenomenon, which is termed *electrical repulsion*, had been previously noticed by Otto de Guericke, but the merit of original observation seems also justly due to the French philosopher. Dufay likewise noticed that the electricity excited on glass is different from that of resin, and hence inferred the existence of two kinds of electricity, the *vitreous* and *resinous*, the former belonging to glass, and the latter to resin. He established an excellent mode of distinguishing them, by finding that substances possessed of the same kind of electricity always repel each other; and that attraction is as uniformly exerted between substances which are in opposite states of electrical excitement.

Another fact of consequence, relative to the excitement of electricity by friction, was discovered in 1759 by Mr. Symmer, (Philos. Trans. li. 340.) who found that when two bodies are rubbed together, both are excited, and that one always possesses vitreous and the other resinous electricity. This induced Symmer to modify the doctrine of the two electricities. Dufay conceived vitreous electricity to be peculiar to some substances and resinous electricity to others. Symmer, on the contrary, maintained, that bodies in their ordinary unexcited condition contain both kinds of electricity in a state of combination; and as they then neutralize or counteract each other's effects, no electrical phenomena are apparent; that friction produces excitement by separating the two principles; and that excitation continues until that kind of electricity, which has been withdrawn, is restored.

Dufay's doctrine of the two electricities, as modified by Symmer, is consistent with all the facts which subsequent observation has brought to light, and is adopted almost universally in France and other parts of the continent. It is found that all substances when electrified by friction, are thrown into opposite states of excitement; that electrical repulsion is never

observed but between bodies similarly electrified; and that electrical attraction is as uniformiy owing to the substances possessing different kinds of electricity. For these phenomena, however, Dr. Franklin proposed a different explanation, founded on the supposition of there being only one kind of electricity. According to this philosopher, when bodies contain their natural quantity of electricity, they do not manifest any electrical properties: but they are excited either by its increase or diminution. On rubbing a tube of glass with a woollen cloth, the electrical condition of both substances is disturbed; the former acquires more or is overcharged, the other less than its natural quantity or is undercharged. These opposite states he expressed by the terms *positive* and *negative*, the first corresponding to the vitreous, the second to the resinous electricity of Dufay. Electrical repulsion, according to Franklin, takes place between substances which contain either more or less than their natural quantity; and electrical attraction is only exerted between two bodies, one of which contains more than its natural quantity, and the other less. The excess of electricity has a strong tendency to pass from a positively to a negatively excited surface, so as to restore the equilibrium in both; and this always happens either by contact, or from such proximity that the electricity is able to pass from one to the other through the intervening stratum of air. The phenomena of electricity are explicable by both these theories; but as that of Dr. Franklin is commonly adopted in Britain, I shall employ it in preference in this treatise.

It has been objected to this hypothesis that it does not account satisfactorily for the repulsion observed between bodies negatively electrified. The separation of two positively electric bodies is easily accounted for by the repulsive power supposed to be exerted among the particles of the electricity accumulated upon them; while substances which are negative, or possess less than their natural quantity of electricity, cannot be influenced by such a power, and therefore, it is argued, ought not to diverge or separate. This mode of reasoning, however, is entirely hypothetical. There is no proof that the divergence observed in similarly electrified bodies is owing to actual repulsion; and the phenomenon may be explained equally well on the principle, that the two excited substances are attracted

in opposite directions, in consequence of the contiguous strata of air being rendered oppositely electrical by induction. In this way all the phenomena of electrical attraction and repulsion are referrible to the attractive power exerted between bodies in opposite states of excitement. The term repulsion, according to this view, is used merely to express the act of separation or divergence.

Nothing certain is known concerning the principle or cause of the phenomena of electricity. It may possibly be only a property of matter, called into action by particular circumstances; but the phenomena accord much better with the opinion, which is now almost universally received by philosophers, that it is a highly subtile elastic fluid, too light to affect the most delicate balances, capable of moving with extreme velocity, and present in all bodies. Its influence, in excited bodies, is diffused uniformly in every direction; and like light and other principles which are subject to this law, its power diminishes as the squares of the distance. It is one of the most energetic principles in nature. It is the cause of thunder and lightning; the phenomena of galvanism, and probably of magnetism, are produced by it; and the influence which it exerts over chemical changes is so great, that some philosophers regard it as the cause of chemical attraction. The particles of the electric fluid are supposed to be highly repulsive to each other, and to be powerfully attracted by other material substances. The tendency to pass from overcharged surfaces to those that are in a negative state, may be ascribed to one or other of these properties, or perhaps to their conjoint operation.

Electricity may be excited in all solid substances by friction. This assertion seems at first view contrary to fact. It is well known that a metallic substance, if held in the hand, may be rubbed for any length of time without exhibiting the least sign of electricity; an observation which led to the division of bodies into such as may be excited by friction, and into those that, under the same circumstances, give no sign of electrical excitement. The former were called *Electrics*, the latter *Non-electrics*. But the distinction is not founded in nature. A metallic substance does not indeed exhibit any trace of electricity when rubbed in the same way as a piece

of glass; but if, while it is rubbed with the dry fur of a cat, it is supported by a glass handle, it will then readily evince signs of electrical excitement.

The difficulty and apparent impossibility of exciting metallic bodies, receives an explanation from the fact observed by Grey, that the electric fluid passes with great facility along the surface of some substances, and with difficulty over that of others; and this discovery has led to the division of bodies into *conductors* and *non-conductors* of electricity. If an excited conductor, such as a metallic wire, be made to communicate at one of its extremities, with the earth the electricity will pass to it from the opposite end in an instant, even though it were several miles in length; so that when the equilibrium is disturbed, it will be at once restored along the whole wire, just as effectually as if every point of it communicated with the ground. But an excited stick of glass or resin is not affected in the same manner; for as electricity does not obtain a free passage along them, the equilibrium is restored in those parts only, which are actually touched. For this reason a non-conductor of electricity, though held in the hand, may be readily excited; but a good conducting body cannot be brought into that state, unless it be *insulated*, that is, cut off from communication with the earth by means of some non-conductor. This is generally effected either by supporting a body with a handle of glass, or by placing it on a stool made with glass feet.

To the class of conductors belong the metals, charcoal, plumbago, water, and most substances which contain water in its liquid state, such as animals and plants. The conductive power of these substances is different. Of the metals, according to the experiments of Mr. Harris, silver and copper are the best conductors of electricity; and then follow gold, zinc, platinum, iron, tin, and lead. (Philos. Trans. for 1827, Part I. 21.) To the list of non-conductors belong glass, resins, sulphur, the diamond, dried wood, precious stones, silk, hair, and wool. Atmospheric air is also a non-conductor. If it were not so, no substance could retain its electricity when surrounded by it. Aqueous vapour suspended in the air injures the non-conducting property of the latter, and hence electrical experiments do not succeed so well when the air is charged with

moisture as when it is dry. The presence of a little moisture communicates conducting properties to the most imperfect conductor; and hence it is impossible to excite glass by rubbing it with a moist substance.

A knowledge of the different conducting power of bodies is required for explaining some circumstances which appear contradictory to a preceding statement. It is above mentioned that when two bodies are excited by friction, they are rendered oppositely electric; but if a tube of glass is rubbed by a person communicating with the ground, the glass will become positively electrical, while the hand of the operator manifests no sign whatever of excitement. The cause of this is obvious. The operator is not electrified, because the earth restores the electric fluid as soon as it is withdrawn by the glass; but if he is insulated, the indications of negative electricity will immediately appear. Hence it is a rule to insulate a conductor, whenever it is wished to examine its electrical condition.

The experiments which have been made concerning the effects of friction, have demonstrated that the same substance is not always similarly electrified. Its electricity is influenced partly by the state of its surface, and partly by the nature of the body with which it is rubbed. Thus smooth glass is rendered positive by friction with woollen cloth; whereas if its surface is rough, it becomes negative from the same treatment. Smooth glass which is positive with woollen cloth, is rendered negatively electrical by being rubbed with a cat's fur. The following table from Cavallo's Complete Treatise on Electricity, shows the kind of excitement produced by the friction of various substances.

	Is rendered	By Friction with
The back of a cat	Positive	Every substance with which it has been hitherto tried.
Smooth glass . .	Positive	Every substance hitherto tried except the back of a cat.
Rough glass . .	Positive	Dry oiled silk, sulphur, and metals.
	Negative	Woollen cloth, quills, wood, paper, sealing-wax, white wax, the human hand.
Tourmalin . . .	Positive	Amber, a current of air.
	Negative	Diamond, the human hand.

	Is rendered	By Friction with
Hare's skin . .	Positive	Metals, silk, loadstone, leather, the hand, paper, baked wood.
	Negative	Other finer furs.
White silk . .	Positive	Black silk, metals, black cloth.
	Negative	Paper, hand, hair, weasel's skin.
Black silk . . .	Positive	Sealing-wax.
	Negative	The skin of the hare, weasel, and ferret, loadstone, brass, silver, iron, and the hand.
Sealing-wax . .	Positive	Metals.
	Negative	The skin of the hare, weasel, and ferret, the hand, leather, woollen cloth, paper.
Baked wood . .	Positive	Silk.
	Negative	Flannel.

Mr. Singer states that sealing-wax is not rendered positive by friction with all metals:—iron, steel, lead, and bismuth, as also plumbago, leave it negative. Mr. Cavallo's statement with respect to white silk and paper does not agree with my observation. The effect of white paper is variable; but in a number of trials I found that by coarse brown paper white silk was invariably rendered positive.

The foregoing remarks on the effects of friction will render intelligible the principle of the electrical machine. In the time of Grey a supply of electricity was obtained for experimental purposes by rubbing a glass tube with the dry hand. Glass globes made to revolve by machinery were afterwards substituted for the tube, the friction being at first produced with the hand, and subsequently by means of a fixed rubber. As now constructed, the electrical machine is formed either with a cylinder or plate of glass, which is pressed during its rotation by cushions stuffed with hair. The cushion is usually covered with an amalgam of tin and zinc, which, partly by increasing the friction, and partly by the oxidation of the metals, materially assists the action of the machine. The electricity developed on the glass is conducted away by an insulated bar of brass placed close to it, called the *prime conductor*, on which it is collected in considerable quantity. By this means the electricity spread over the whole surface of the prime con-

ductor may be carried off at the same instant, and thus act with far greater power than if accumulated on glass or any other imperfectly conducting substance.

The electricity which is so freely and unceasingly evolved during the action of a good electrical machine, is derived from the great reservoir of electricity, the earth. This is obvious from the fact, that if the whole apparatus is insulated, the evolution of electricity immediately ceases; but the supply is as instantly restored, when the requisite communication is made with the ground. In the state of complete insulation the glass and prime conductor are positive as usual, and the rubber is negatively excited; but as the electricity then developed is derived solely from the machine itself, its quantity is exceedingly small. When the machine is used, therefore, the rubber is made to communicate with the earth. As soon as friction is begun, the glass becomes positive, and the rubber negative; but as the latter communicates with the ground, it instantly recovers the electricity which it had lost, and thus continues to supply the glass with an uninterrupted current. If the rubber is insulated, and the prime conductor communicates with the ground, the electricity of the former and all conductors connected with it, is carried away into the earth, and they are negatively electrified.

Friction is not the only cause of electrical excitement. Bodies are sometimes excited by elevation of temperature, a property first noticed in certain crystallized minerals, such as tourmalin and boracite, which do not possess that symmetric arrangement of parts commonly existing in crystals. The electric equilibrium is disturbed in metallic rods or wires by one extremity having a different temperature from that of the other, as was first observed by Professor Seebeck, and since shown to be true of all metals by Professor Cumming. (Annals of Phil. V. 427. N. S.) The experiment is usually made by heating the point of junction of two metallic wires, which are soldered together; but M. Becquerel has proved that the contact of one metal with another is not essential. (An. de Ch. p. xli. 353.)

Another and apparently very fruitful source of electricity is chemical action. This was strongly denied by the late

Sir H. Davy in his Bakerian lecture for 1826; but the experiments of Becquerel, De la Rive, and Pouillet, afford in my opinion decisive proof that chemical union and decomposition are both attended with electrical excitement. (An. de Ch. et Ph. T. 35, 36, 37, 38, and 39.) M. Pouillet, in particular, has demonstrated that the gas arising from the surface of burning charcoal is positive, while the charcoal itself is negative; and he has proved that similar phenomena are produced by the combustion of hydrogen, alcohol, oil, and other inflammables of the same kind. In all these instances the combustible, in the act of burning, renders contiguous particles negative; while the oxygen imparts electricity to the products of combustion, which thereby become positive. The fact, with respect to charcoal, was originally noticed by Volta, La Place, and Lavoisier, but was subsequently denied by Saussure and Sir H. Davy. M. Pouillet has reconciled these conflicting statements by showing that the result depends on the mode in which the experiment is conducted. For if the carbonic acid be completely removed from the burning mass at the instant of its formation, both are found to be electrical; but if, on the contrary, the carbonic acid subsequently flows over the surface of the charcoal, the equilibrium will instantly be restored, and of course no sign whatever of excitement be perceptible.

The electric equilibrium is likewise disturbed by the contact of different substances, especially of metals; a fact first demonstrated by Volta, who founded on it a theory of Galvanism. The experiment is commonly made with well cleaned plates of zinc and copper, which are supported and insulated by handles of glass. On holding the zinc plate by its glass handle, laying it repeatedly on the copper, which at the time need not be insulated, and after each contact touching with it the instrument, shortly to be described, called the *Condenser*, a positive charge is gradually accumulated. On operating in the same way with the insulated plate of copper, it is found to communicate a negative charge. From such experiments it is inferred, that the contact of zinc and copper disturbs the electric equilibrium in both metals, the latter yielding some of its electricity to the former and becoming negative, while the zinc is thereby rendered positive. But the inference, though extremely probable, is not free from objection. In fact, so long as contact con-

tinues, there is no electric appearance whatever; and the metals are assumed to be differently electrified *at that time*, in consequence of the phenomena which they exhibit *after* their separation. There is, therefore, an obvious assumption. But, on the other hand, the absence of the indications of excitement is not conclusive against the received doctrine; because, consistently with the laws of electricity, the oppositely electrical state of the two metals, while they continue together, must counteract the effect to which either separately would give rise.

The excitement of electricity by contact has been denied by some philosophers, and of late this doctrine has been attacked by M. de la Rive of Geneva. (An. de Ch. et Ph. xxxix. 297.) He there contends that the phenomena ascribed to metallic contact are really due to slight oxidation produced by moisture and the oxygen of the air acting on the plate of zinc. He has adduced experiments to prove, that if the oxidation of the zinc be increased by acid fumes, the electric charge is proportionally augmented; and that the same effects arise when a very oxidable metal, such as potassium, is substituted for the zinc. He further states that when the experiment is made in a vessel of hydrogen or nitrogen, no electricity whatever is developed. This last observation however, the only decisive argument adduced, has since been corrected by Professor Pfaff of Kiel, in whose experiments the contact of zinc and copper affected the electrometer as much when made in a jar of hydrogen or nitrogen, as in atmospheric air. There is, therefore, no reason to doubt the fact as originally stated by Volta; although the quantity of electricity, excited by mere contact, appears to be very minute.

Change of form, such as liquefaction and the passage of liquids into the solid state, and the formation and condensation of vapour, is another reputed source of electricity. To processes of this nature, continually taking place in the atmosphere, the electricity of the clouds is generally ascribed. But the essays of M. Pouillet on the source of atmospheric electricity, tend to subvert the opinions hitherto received. He has proved the evaporation of water from a vessel of platinum to be unattended with electrical appearances; whereas if the process is accompanied with chemical decomposition, as in the evaporation of saline solutions, or if the vessel consists of

iron or other oxidable material, which is more or less chemically attacked by the evaporating water, then the development of electricity is very decisive. From experiments of this kind M. Pouillet concludes that the electricity, hitherto referred to changes of form, is entirely owing to the chemical action by which they are generally attended; and these phenomena, of which the evaporation of water from the ocean, from rivers, and the surface of the earth, affords an instance, as also the chemical changes that attend the growth and nutrition of plants, he regards as a fertile source of the electricity of the atmosphere. (An. de Ch. et Ph. xxxv. 401, and xxxvi. 5.)

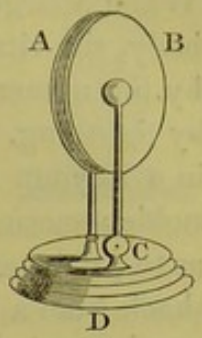
Another cause of excitement is proximity to an electrified body; and as the explanation of many electrical phenomena depends on a knowledge of this fact, it is of importance to understand it clearly. When a substance excited positively is brought near another in its natural state and insulated, the electric equilibrium of the latter is instantly disturbed; the parts nearest to the former become negative, and the distant parts positive. If the body is not insulated, its electricity passes into the earth, and it becomes negatively electrical. If, on the contrary, the exciting substance is negative, it causes the contiguous parts of a body in its vicinity to become positive. Hence it may be established as a law, that an electrified body tends to produce in contiguous substances an electric state opposite to its own. The electricity developed in this way is said to be *induced*, or to be excited by *induction*. The movement of light bodies towards an excited stick of sealing-wax, or glass tube, is accounted for on this principle. Thus, the vicinity of the negative sealing-wax renders the surrounding objects positive, and therefore a mutual attraction is exerted. When the inside of a glass bottle is rendered positive by contact with the prime conductor of the electrical machine, the outside, if in communication with the earth, parts with electricity and becomes negative. Both surfaces, therefore, are electrified and are in opposite states; and if a communication be established between them by means of a good conductor, the excess of electricity instantly passes along it, and both sides of the glass return to their natural condition. That the experiment may succeed in the most perfect manner, it is

necessary to cover the bottle externally and internally, except to within three or four inches of its summit, with tinfoil or some other good conductor, in order that every point of both sides of the glass may be brought into communication at the same moment. For without this precaution, the electric equilibrium of the two surfaces of the bottle, owing to the imperfect conducting power of glass, will be restored on those points only which are touched. The apparatus thus described is much employed by electricians, and has received the name of the Leyden phial, in consequence of its remarkable effects having been first exhibited at the University of Leyden. To render it more convenient for use, the aperture of the glass jar or phial is closed by some imperfect conductor, such as dry wood, through the centre of which passes a metallic rod that communicates with the tinfoil in the inside of the jar. The phial is electrified or *charged* by holding the outside in the hand, or placing it on the ground, while the metallic rod is made to receive sparks from the prime conductor of an electrical machine. If the jar is insulated, no charge will be received, or at least very slight indications of excitement will be manifested. By arranging a number of Leyden phials in a box lined with tinfoil, so that they may all communicate freely by their outer surfaces, and then bringing their inner surfaces into communication by wires, the whole series may be charged and discharged in the same manner as a single phial. This arrangement is known by the name of the *electrical battery.*

Some of the phenomena of lightning are explained on the principle of induced electricity. When, for instance, a negatively electrified cloud approaches the earth, all objects in its vicinity are positively excited; and when it comes within what is called the *striking distance*, that is, so near that the tendency of the electricity to pass from the positive to the negative body overcomes the resistance of the intermediate stratum of air, the equilibrium is restored with a report and flash of light, exactly as in the discharge of a Leyden phial. A similar effect is produced by an electrified cloud on other clouds within the sphere of its influence.

The principle of induced electricity was ingeniously applied by Volta in the construction of the Condenser. This appa-

ratus, shown in the annexed figure, 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 joint C, so that, though represented upright, it may be placed horizontally, and thus be withdrawn from the vicinity of the plate A, the support of which is made of glass. On communicating electricity to the insulated plate by contact with a positively excited body, the plate B, which for that purpose is placed close to A, is rendered negative by induction, its electricity passing along the stem into the earth; and, as happens in the Leyden jar, the excitement of B will be proportional to that of A. The negative charge of B tends to preserve the positive charge of A, which will consequently receive electricity from any positive 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 invented by Bennett.



The passage of electricity is frequently attended with the production of heat and light, effects which invariably ensue when it meets with an impediment to its progress, as in passing through an imperfect conductor. The most familiar illustration of this is afforded by its passage through the air, when it gives rise to a spark accompanied with a peculiar snapping noise, if in small quantity; or to the phenomena of thunder and lightning, when it takes place on a large scale. On the contrary, it passes along perfect conductors, such as the metals, without any perceptible warmth or light, provided the extent of their surface is in proportion to the quantity of electricity to be transmitted by them; but if the charge is too great in relation to the extent of the conducting surface, intense heat will be produced.

Electricity acts with surprising energy on the animal system. When a large quantity of the electric fluid passes through the body, the vital functions cease on the instant, as is exemplified by the numerous accidents on record of persons being killed by lightning. Even the small quantity of electricity contained in a Leyden phial gives a very powerful shock, exciting a sudden spasm of the muscles along which it passes, so violent as to produce a disagreeable or even painful sensation. The shock from a large electrical battery is much more severe, and smaller animals, such as rabbits and fowls, are destroyed by its action.

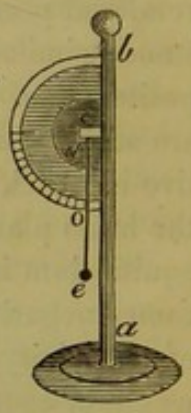
It is very important, in conducting electrical experiments, to possess an easy method of discovering when any substance is electrified, of ascertaining its *intensity* or the degree to which it is excited, and distinguishing the kind of excitement. The mode of effecting these objects is founded on electrical 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. A body is known to be excited by its power of attracting light substances; and a small ball made of the pith of elder, suspended on a silk thread, affords a convenient material for the experiment. Another mode of acquiring the same information is by means of two pith balls suspended from the same point by silk threads of equal length. When all the surrounding objects are unexcited, the pith balls remain in contact; but on the approach of any electrified body, the two balls are excited by induction, and, having the same electricity, diverge or retreat from each other. A more delicate contrivance, but of a similar kind, was invented by Mr. Bennett, and is known by the name of the *Gold Leaf Electrometer*. It consists essentially of a cylindrical glass bottle, with its aperture closed by a brass plate, from the centre of which two slips of gold leaf are suspended. The brass plate, with its slips of gold leaf, are thus insulated, and the latter prevented from being moved by currents of

air by the glass with which they are surrounded. The approach of any electrified body, even though feebly excited, to the brass plate, is immediately detected by the divergence of the leaves. In the annexed wood-cut this electrometer is exhibited with its leaves in a state of divergence.

A very simple method of distinguishing the kind of excitement is the following. If a piece of white silk be drawn a few times rapidly between the fingers, it will become negative; and if in this state it is suspended in the air, it will be attracted by a body positively excited, and repelled by one which is negative. When rubbed on black cloth the silk is rendered positive, and will then of course retreat from a substance similarly electrified, and be attracted by one in an opposite state. The indications of the gold leaf electrometer are still more delicate. If the leaves are diverging with positive electricity, the approach of a positively excited body to the brass plate increases the divergence; because the electric equilibrium is immediately disturbed, and while the plate becomes negative, the gold leaves acquire a still greater degree of electricity. The approach of a negatively excited body would of course be productive of a change precisely opposite, and the divergence, if produced by positive electricity, would be diminished, or even entirely destroyed. To prepare the electrometer for an observation, it is however necessary to communicate to it a known state of excitement. This may be done by touching the electrometer with an electrified body, such as an excited glass tube or stick of sealing-wax, when the whole metallic surface of the electrometer is electrified in the same manner as the substance by which it was touched. A more convenient method is to communicate electricity permanently by induction. Thus, on placing a negatively excited body, as for example a stick of sealing-wax after friction on woollen cloth, near the brass plate of the electrometer, the electric equilibrium of its whole metallic surface is disturbed; the brass plate becomes positive, and the slips of gold leaf diverge from being negative. On withdrawing the sealing-wax, the excess of electricity accumulated on the plate returns to the leaves, and the equilibrium is restored; but if, while

the sealing-wax is near the top of the instrument, the plate is touched with the finger, a portion of electricity is supplied to the gold leaves from the earth, and the divergence ceases more or less completely, while the excess of electricity is preserved on the plate by the vicinity of the sealing-wax. On removing *first* the finger, and *then* the sealing-wax, the brass is left with an excess of electricity, which extends over the whole metallic surface of the electrometer, and thus produces a divergence which continues for a considerable time if the glass be dry, and the atmosphere moderately free from moisture.

The electrometer most frequently used for estimating the intensity of electricity in ordinary experiments is that shown in the annexed wood-cut, invented by Mr. Henley, and known by the name of *quadrant electrometer*. It consists of a smooth round stem of wood *a b*, about seven inches long, to the upper part of which, and projecting from its side, is attached a semicircular piece of ivory. In the centre *c* of the semicircle is fixed a pin, from which is suspended, to serve as an index, a slender piece of wood or cane *d e*, four inches in length, and terminated by a small ball. When the apparatus is screwed on the prime conductor of the electrical machine, or placed on any electrified body, it indicates differences of electric intensity by the extent to which the index recedes from the stem; and in order to express the divergence in numbers, the lower half of the semicircle, which is traversed by the index, is divided into 90 equal parts called *degrees*. But this instrument, though convenient for experiments of illustration, is not suited to researches of delicacy, wherein the object is to examine the effects of substances feebly electrified, and ascertain their relative forces with accuracy. For such purposes the electrometer invented by Coulomb, commonly called the *electrical balance*, should be employed. It consists of a small needle of gum-lac or other non-conducting substance, suspended horizontally by a silk thread as spun by the silk-worm, or by a fine silver wire; 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 of a metallic conductor, 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, 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 the intensity of the excited body, and brings back the needle to its original position as soon as the electric equilibrium is restored.

In some of the preceding remarks a term has been employed which requires explanation. By electric *tension* or *intensity* is meant that state of a body which is estimated by an electrometer. When a body acts feebly on the electrometer its intensity is low, and it differs but little from its natural state; and on the contrary if it affects the electrometer powerfully, its electric tension is great. The higher the intensity of a body, the more is it removed from its natural state, and the greater its tendency to return to an equilibrium. *Intensity* is distinct from *quantity* of electricity. That intensity is not dependant on quantity alone, is proved by the fact that the tension of a charged Leyden phial may be equal to that of a large battery containing twenty times more electricity. The tension appears to depend on the quantity of electricity accumulated or deficient in a given space; so that the intensity of those substances is greatest, which have the greatest excess or deficiency of electricity in proportion to their surface.

This accounts for the freedom with which electricity is conducted away by pointed surfaces. For the electricity accumulated on a sharp point, though its quantity may be very small, is nevertheless large compared with the surface: the electric tension of the point is therefore very great; and hence if positive it gives off electricity to surrounding objects, and if negative receives it from them, with extreme velocity.

Electricity appears to diffuse itself over the surface of bodies;

and the quantity contained on the same substance, all other circumstances being the same, depends on the extent of surface, and is not connected with quantity of matter. Thus a solid sphere of brass cannot contain more electricity than a hollow sphere of the same diameter.

SECTION IV.

GALVANISM.

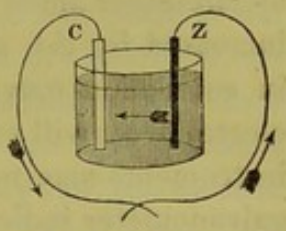
The science of Galvanism owes its name and origin to the experiments on animal irritability made by Galvani, Professor of Anatomy at Bologna, in the year 1790. In the course of the investigation he discovered the fact, that muscular contractions are excited in the leg of a frog recently killed, when 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 galvanic apparatus, which was described by him in the Philosophical Transactions for 1800, and which has pro-

perly 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.

The most simple kind of galvanic arrangement is made by placing a disc or plate of zinc and copper near each other in a vessel of water acidulated with sulphuric acid, and soldering on each a metallic wire, which wires may be made to touch one another at the will of the operator. The wires may even be dispensed with; for the object being to establish metallic communication between the plates by means of a conductor which is not covered by the liquid, it is sufficient to incline the upper part of the plates towards each other until they are in contact. The employment of wires, however, as shown in figure 1, is attended with many advantages in conducting galvanic experiments, and they are therefore always resorted to; but it must be remembered that they merely act as a convenient conducting material, without contributing essentially to the result.

Fig. 1.



The simple galvanic arrangement, or *circle* as it is often called, remains in activity as long as chemical action between the zinc and acid continues. The phenomena which may be observed in the apparatus vary according as the conducting wires do or do not communicate with each other. In the former case the *circuit,* or course along which the electric current passes, is said to be closed; and in the latter the circuit is broken or interrupted. Chemical action between the acid and zinc goes on in both cases; but the hydrogen evolved from water appears at the surface of the zinc only, if the circuit is broken, and arises from both metals when the circuit is closed. If in the interrupted state of the circuit the electric condition of the wires is examined, that attached to the copper plate will be found to be positive, and the wire connected with the zinc negative. If the wires are made to touch one another, their tension immediately ceases; because, as by the contact of oppositely electrified bodies in general, the equilibrium is thereby re-established. But since the condition which caused the excitement in the first instance remains the same, a continued development of electricity would be anticipated; and,

accordingly, the wires on the instant of separation are again oppositely electrified, and their tension as instantly disappears when the circuit is again closed. Hence it was inferred, that in the closed circuit a continuous current of electricity passes from the copper plate to the wire connected with it, is communicated by it to the other wire, and is then conducted to the zinc plate: the happy discovery of Oersted, by leading to the invention of the *Galvanometer*, which will be described in an after-part of this section, has supplied us with the means of discovering the presence of such a current, estimating its force, and even ascertaining its direction.

The electricity developed by a single pair of plates is of such low intensity, that the state of the opposite wires in the broken circuit can only be ascertained by means of a delicate electrometer aided by the condenser; but when the tension is increased by the united action of several different pairs, as in compound galvanic arrangements, the ordinary gold leaf electrometer will readily be affected. The employment of such instruments may now, however, be dispensed with; since the galvanometer indicates the positive and negative wire of any galvanic circle with ease and certainty, even when the intensity is too feeble to be appreciated by the most delicate electrometer.

As electricity accumulates on the wire attached to the copper plate, and is deficient on that connected with the zinc, it was supposed that in a galvanic circle electricity is excited on that part of the zinc plate which is covered with liquid, and that it is transmitted through the solution to the plate of copper. This supposition was supported by the phenomena observed by Volta to accompany the contact of these metals with each other; and the inference has been fully justified by a discovery of M. Ampère, who found that a galvanometer, placed above or below a galvanic circle, indicates the existence of an electric current passing through the solution in a direction opposed to that which is transmitted along the wires. The general conclusion therefore is, that in a simple closed galvanic circle there is a continued current of electricity, flowing, as shown by the arrows in figure 1, from the zinc to the solution, from the solution to the copper, and from the copper along the communicating wires back again to the zinc. Such at least is the

view of phenomena founded on the Franklinian doctrine; but according to the theory of the two electricities, there are two distinct currents, one of positive or vitreous electricity, which takes the direction above described, and the other of negative or resinous electricity which, starting from the copper, assumes a course exactly opposite.

These remarks will render intelligible several terms which will be employed in the course of this section. By the expression *positive wire* or *pole* of simple galvanic circles is always meant the wire connected with the copper plate, and by the *negative pole* or *wire* that attached to the plate of zinc. It is likewise usual to speak of the zinc plate being positive with respect to the copper plate, and of the latter being negative with respect to the former; and in all simple galvanic arrangements that element which corresponds to the zinc plate of the ordinary circle, and from which the current of electricity appears to set out, is said to be positive in relation to the other substance with which it is associated. Nor does this language appear inconsistent with the laws of electricity: for the electric fluid could scarcely be given off by the zinc, unless the surface so yielding it were positive; nor should it pass over to the copper, unless the surface of that metal were negative. It seems, indeed, that the zinc, *where covered with liquid*, becomes positive at the expense of the uncovered portion and its wire; while the wet surface of copper is rendered negative by yielding its own electricity, as well as that which it derives from the zinc, to the conducting wire to which it is attached.

Simple galvanic circles may be formed in various ways and of various materials; but the combinations 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 likewise found generally, if not universally, that the metal most attacked is positive with respect to the other, or bears to it the same relation as zinc to copper in the ordinary

circle. The late Sir H. Davy, in his Bakerian Lecture for 1826 (Phil. Trans.), has given the following list of the first kind of arrangements, the imperfect conductor being either the common acids, alkaline solutions, or solutions of the hydrosulphurets. The metal first mentioned is positive to all those standing after it in the series.

WITH COMMON ACIDS.

Potassium and its amalgams, barium and its amalgams, amalgam of zinc, zinc, amalgam of ammonium?, cadmium, tin, iron, bismuth, antimony?, lead, copper, silver, palladium, tellurium, gold, charcoal, platinum, iridium, rhodium.

WITH ALKALINE SOLUTIONS.

The alkaline metals and their amalgams, zinc, tin, lead, copper, iron, silver, palladium, gold, and platinum.

WITH SOLUTIONS OF HYDROSULPHURETS.

Zinc, tin, copper, iron, bismuth, silver, platinum, palladium, gold, charcoal.

The following table of Voltaic arrangements of the second kind is from Sir H. Davy's Elements of Chemical Philosophy.

Table of some electrical arrangements, consisting of one conductor, and two imperfect conductors.

Solution of Sulphur and Potash Potash Soda	Copper Silver Lead Tin Zinc Other Metals Charcoal	Nitric Acid Sulphuric Acid Muriatic Acid Any solutions containing Acid.

The most energetic of these combinations is that in which the metal is chemically attacked on one side by hydrosulphuret of potash, and on the other by an acid. The experiment may be made by pouring dilute nitric acid into a cup

of copper or silver, which stands in another vessel containing hydrosulphuret of potash. The following arrangements may also be employed. Let two pieces of thick flannel be moistened, one with dilute acid and the other with sulphuretted alkali, and then placed on opposite sides of a plate of copper, completing the circuit by touching each piece of flannel with a conducting wire: or, take two discs of copper, each with its appropriate wire, immerse one disc into a glass filled with dilute acid, and the other into a separate glass with alkaline solution, and connect the two vessels by a few threads of amianthus or cotton moistened with a solution of salt. A similar combination may be disposed in this order. Let one disc of copper be placed on a piece of glass or dry wood, on its upper surface lay in succession three pieces of flannel, the first moistened with dilute acid, the second with solution of salt, and the third with sulphuretted alkali, and then cover the last with the other disc of copper.

The use of metallic bodies is 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 of 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 galvanic circles just described, the only one used for ordinary purposes is that composed of a pair of zinc and copper plates excited by an acid solution. 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 wood-cut. (Fig. 3.) C is a cup made with two cylinders of sheet copper, of unequal size,

Fig. 2.

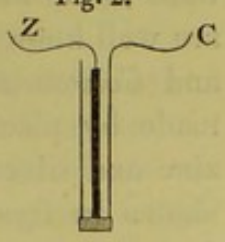
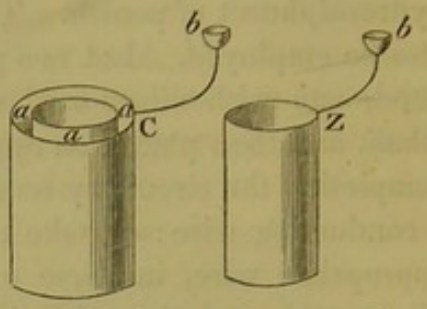


Fig. 3.



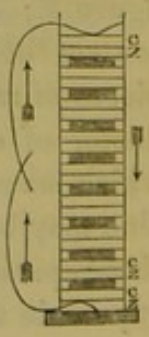
placed one within the other, and soldered together at bottom, so as to leave an intermediate space *a a a*, for containing the zinc-cylinder Z and the acid solution. The small copper cups *b b* are useful appendages; for by filling them with mercury, and inserting the ends of a wire, the galvanic circuit may be completed or broken with ease and expedition. This apparatus is very serviceable in experiments on electro-magnetism.

Another kind of circle may be formed by coiling a sheet of zinc and copper round each other, so that each surface may be opposed to one of copper, and separated from it by a small interval. The London Institution possesses an immense apparatus of this sort, made under the direction of Mr. 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. This contrivance was first resorted to by Dr. Hare of Philadelphia; but his apparatus, instead of being one large coil, consisted of eighty small coils, and is therefore a compound galvanic circle. From its remarkable power of igniting and deflagrating metals, Dr. Hare gave it the name of *Calorimotor* or *Deflagrator*. (An. of Phil. i. 329. N. S.)

COMPOUND GALVANIC CIRCLES.

This expression is applied to those galvanic arrangements which consist of a series of simple circles. The first combinations of the kind were described by Volta, and are well known under the names of Voltaic pile and *Couronne de Tasses*. The Voltaic pile is made by placing pairs of zinc and copper, or zinc and silver plates, one above the other, as shown in figure 4, 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

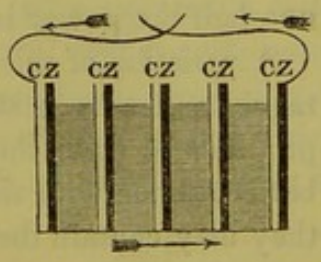
Fig. 4.



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 one pole of each pile with the opposite pole of the pile immediately following.

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 Mr. Cruickshank, consists of a trough of baked wood, about thirty inches long, in which are placed at equal distances fifty 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 wood-cut the mode in which the plates are arranged will easily be understood.

Fig. 5.



Other modes of combination are now in use, which facilitate the employment of the galvanic apparatus and increase its energy. Most of these may be regarded as modifications of the *Couronne de Tasses*. 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 the figure. (Fig. 6.) Instead of glasses, it is more convenient in practice to employ a trough of baked wood or glazed earthen-ware, 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 connexion between the zinc of one cell and the copper of the adjoining one being accomplished, as shown in figure 7, by a slip or wire of copper.

Fig. 6.

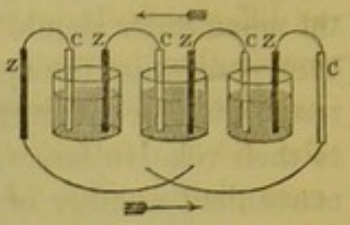
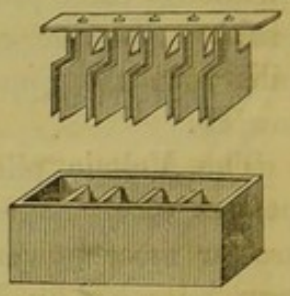


Fig. 7.



A material improvement in the foregoing apparatus was suggested by Dr. Wollaston, (Mr. Children's Essay in Phil. Trans. for 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.

A variation of this contrivance, which appears to me advantageous, has been suggested by Mr. Hart of Glasgow, who proposes to have the double copper plates of the preceding battery made with sides and bottoms, so that, as in figure 2, they may contain the exciting liquid. The plates are attached, as in figure 7, to a bar of wood, and supported above the ground by vertical wooden columns of the same material, by which they are insulated. The cells are filled by dipping the whole battery into a trough of the same form, full of the exciting liquid. (Brewster's Journal, IV. 19.)

The size and number of the plates may be varied at pleasure. The largest battery ever made is that of Mr. Children, described in the essay above referred to, the plates of which are six feet long, and two feet eight inches broad. The com-

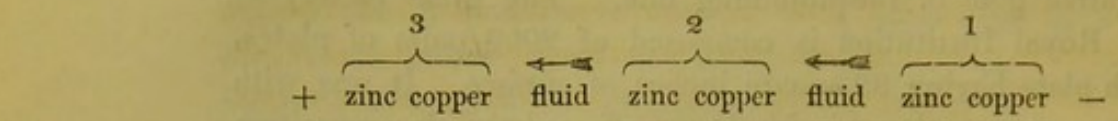
mon and most convenient size for the plates is four or six inches square; and when great power is required, a number of different batteries are united by establishing metallic communication between the positive pole of one battery and the negative pole of the adjoining one. The great battery of the Royal Institution is composed of 2000 pairs of plates, each plate having 32 square inches of surface. It was with this apparatus that Sir H. Davy effected the decomposition and determined the constitution of the alkalies, a discovery which has at once extended so much the bounds of chemical science, and conferred immortal honour on the name of the discoverer.

The electrical phenomena of compound galvanic arrangements are similar to those of the simple circle. The poles in the broken circuit are oppositely excited; and in the closed circuit an electric current passes through the apparatus and over the conductors as long as chemical action continues. The direction of the current appears at first view to be different from that of the simple circle; for the extremity which terminates with a copper plate is negative, the electricity passes from it through the battery itself towards the last zinc, which is positive, and thence along the conducting wires to the last copper-plate. (Figs. 4, 5, and 6.) It is hence customary, in reference to the compound circle, to speak of the zinc or positive pole as identical; whereas the wire connected with the zinc plate in the simple circle is negative. But the difference is rather apparent than real, and arises from the compound galvanic circle being terminated by two superfluous plates, which are not essential to the result. This will more fully appear in the course of the following remarks.

THEORIES OF GALVANISM.

Of the theories proposed to account for the development of electricity in galvanic combinations, three in particular have attracted 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 97.) 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 positive, and the corresponding copper plate to be negative; that the positive zinc in each pair except the last, being separated by an intervening stratum of liquid from the negative copper of the following pair, yields to it its excess of electricity; and that in this way each zinc 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 receives electricity from the first only, while the third pair draws a supply from the first and second. Hence electricity is most freely accumulated at one end of the battery, and is proportionally deficient at the opposite extremity. The intensity is therefore greatest in the extreme pairs, gradually diminishes in approaching the centre, and the central pair itself is neither positively nor negatively excited.

In batteries constructed according to the principle of the *Couronne de Tasses*, (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. But in single pairs, as in figures 1 and 2, where the wires are found to be excited without the plates having any metallic communication with each other, this explanation is inadmissible. It is then necessary, reasoning on the principles of Volta, to ascribe the electricity to contact between the metals and the exciting liquid; and a similar explanation must be applied to circles composed of one perfect and two imperfect conductors.

It may be objected to this view, that though contact, as nearly all admit, may disturb the electric equilibrium, the quantity of electricity thus developed is too small to account

for the astonishing phenomena of galvanism. But a far more powerful objection, which appears in fact unanswerable, is deduced from the chemical phenomena of galvanic circles, the study of which has given rise to the *chemical theory* of the pile. Volta attached little importance to the chemical changes, considering them as contributing nothing to the general result, and therefore leaving them entirely out of view in the formation 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 106) 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.

The late Dr. Wollaston, fully admitting electricity as the galvanic 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 Dr. Wollaston to conclude that the process begins with the oxidation of the zinc,—that the oxidation is the primary cause of the development of electricity; and he published several ingenious experiments in the Philosophical Transactions for 1801 in support of his opinion.

Recent researches, which have decisively established the important fact of electricity being freely developed by chemical action, (page 96) have added additional force to the arguments of Wollaston. The experiments of De la Rive in particular appear altogether irreconcileable with the theory of Volta. (An. de Ch. et Ph. xxxviii. 225.) This ingenious phi-

losopher contends that the direction of a galvanic 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 general result of his inquiries, he states, that of two metals composing a galvanic circle, that one, which is most energetically attacked, will be positive 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 towards the copper, as the zinc does in the common circle; 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 positive 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 positive. Even two plates of copper immersed in solutions of the same acid, or of common salt, of different strengths, will form a galvanic circle, the plate on which chemical action is most free giving a current of electricity towards the other. Nay, it is possible to construct a battery solely with zinc plates excited by the same acid of the same strength, provided one side of the plates is polished and the other rough; for the difference of polish causes the two surfaces of each plate to be unequally attacked by the acid, and an electric current is the result. These and similar facts of the same kind appear quite inconsistent with the views of Volta. They go far to establish the chemical theory of galvanism, and in my opinion entitle it to a preference over every other which has been suggested *.

But though the development of electricity in galvanic combinations is chiefly dependent on chemical action, which also determines the direction of the current, it does not follow that metallic contact is altogether inefficient. The quantity of electricity thus excited is, however, so small compared with what is evolved by chemical change, that the effect of the former is in general lost in the greater influence of the latter.

* The reader will find an able development of this theory in the article Galvanism, written for the Library of Useful Knowledge by Dr. Roget, to whose treatise I am indebted for several valuable suggestions.

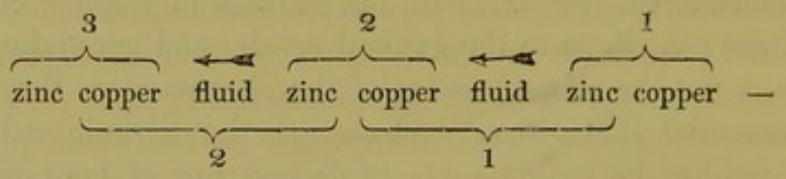
On some occasions, nevertheless, the agency of contact is conspicuous. The electric column of De Luc, formed by successive pairs of silver and zinc, or silver and Dutch gilt leaf, separated by pieces of paper, and contained in a glass tube, owes its action chiefly to metallic contact. This apparatus, which yields electricity in small quantity, but of considerable tension, will continue in activity for years. True it is that the more oxidable metal of the column is slowly corroded; but the chemical changes do not appear at all proportionate to the effects observed, and can scarcely I apprehend be admitted as the sole cause of their production.

The third theory of the pile is intermediate between the two others, and was proposed by the late Sir H. Davy. He inferred from numerous experiments, that there is no reason to question the fact originally stated by Volta, that the electric equilibrium is disturbed by the contact of different substances without any chemical action taking place between them. He acknowledged, however, with Dr. Wollaston, that the chemical changes contribute to the general result; and maintained that, though not the primary cause of the phenomenon, they are so far essential, that without such changes the galvanic excitement can neither be considerable in degree, nor of long duration. In his opinion the action is commenced by the contact of the metals, and kept up by the chemical phenomena.

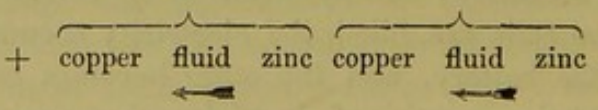
The mode in which Sir H. Davy conceived that the chemical changes act, is by restoring the electric equilibrium whenever it is disturbed. By the contact of the zinc and copper plates, the former is rendered positive throughout the whole series, and the latter negative; and by means of the conducting fluid with which the cells are filled, the electricity accumulates on one side of the battery, and the other becomes as strongly negative. But the quantity of electricity, thus excited, would not be sufficient, as is maintained, for causing energetic action. For this effect, the electric equilibrium of each pair of plates must be restored as soon as it is disturbed, in order that they may be able to furnish an additional supply of electricity. The chemical substances of the solution are supposed to effect that object in the following manner. The negative ingredients of the liquid, such as oxygen and the acids, pass over

to the zinc; while the hydrogen and the alkalies, which are positive, go to the copper; in consequence of which, both the metals are for the moment restored to their natural condition. But as the contact between them continues, the equilibrium is no sooner restored than it is again disturbed; and when, by a continuance of the chemical changes, the zinc and copper recover their natural state, electricity is again developed by a continuance of the same condition by which it was excited in the first instance. In this way Sir H. Davy explained why chemical action, though not essential to the first development of electricity, is necessary for enabling the Voltaic apparatus to act with energy.—It is obvious that the facts above adduced in opposition to the theory of Volta, apply also to that of Sir H. Davy.

The chemical theory of galvanism suggests a view of the essential elements of the pile, different from that taken by Volta. In the subjoined series, for instance,



Volta considered electro-motion to be caused by each of the three pairs of plates included in the upper brackets; whereas there are in fact only two simple circles, which are indicated by the lower brackets. The extreme plates are altogether superfluous, and on removing these the combination is reduced to the following simpler form:



In this arrangement the direction of the current is obviously the same as in the simple circle; and it only appears to be different in batteries of the usual construction, because the last efficient zinc plate is attached to a useless copper plate, and the last efficient copper is connected with a plate of zinc which is equally superfluous.

EFFECTS OF GALVANISM.

The more remarkable effects of galvanism may be conveniently considered under three heads: 1st, electrical effects; 2nd, its chemical agency; and 3d, its action on the magnet.

I. Under the first head are included all those effects of the battery which resemble the usual phenomena produced by the electrical machine. When a wire attached to the positive pole of a Voltaic battery is made to communicate with Bennett's Electrometer, the gold leaves diverge with positive electricity, and a wire from the negative side produces an effect precisely opposite. But in order that these phenomena should ensue, the two wires must not touch each other; for in that case an electric current would be established along the wires, and the tension cease. When wires connected with the opposite poles or sides of an active galvanic trough are brought near each other, a spark is seen to pass between them; and on establishing the communication by means of the hands previously moistened, a distinct shock is perceived. These effects are rendered more conspicuous by connecting one of the wires with the inner surface, and the other with the outside of a Leyden phial or battery, when successive charges will be received, by means of which all the ordinary electrical experiments may be exhibited. On connecting the opposite ends of a sufficiently powerful battery by means of fine metallic wires or slender pieces of charcoal, these conductors become intensely heated, the wires even of the most refractory metals are fused, and a vivid white light appears at the points of the charcoal, equal if not superior in intensity to that emitted during the burning of phosphorus in oxygen gas; and as this phenomenon takes place in an atmosphere void of oxygen, or even under the surface of water, it manifestly cannot be ascribed to combustion. If the communication be established by metallic leaves, the metals burn with vivid scintillations. Gold leaf burns with a white light tinged with blue, and yields a dark-brown oxide; and the light emitted by silver is exceedingly brilliant, and of an emerald green colour. Copper emits a bluish white light attended with red sparks, lead a beautiful purple light, and zinc a brilliant white light inclining to blue,

and fringed with red. (Singer.) The properties above enumerated naturally gave rise to the belief, that the agent or power excited by the Voltaic apparatus is identical with that which is called into activity by the electrical machine; and the arguments in favour of this opinion are quite satisfactory. For not only may all the common electrical experiments be performed by means of galvanism; but it has been shown by Dr. Wollaston, (Phil. Tr. for 1801) that the chemical effects of the galvanic battery may be produced by electricity.

The conditions required for producing the electrical effects of the Voltaic battery are different. Some phenomena are dependent altogether on the electric intensity of the apparatus; for others both quantity and intensity are essential; and for the production of other effects the passage of a large quantity of electricity is alone required. The electric tension of a battery depends chiefly on the number of the series, and comparatively little either on the size of the plates, or the fluid by which they are excited; whereas all these conditions have a material influence over the quantity of electricity. When it is wished to procure a high degree of tension, a great number of small plates should be employed, and the cells filled with water. On the contrary, when quantity of electricity is the chief object, great extent of surface is necessary; the individual plates should be of large size, and excited by an acid, which promotes the object, partly by producing brisk chemical action, and partly by conducting more perfectly than water or solutions of neutral salts.

Since the force of electrical attraction and repulsion arises from intensity independent of quantity of electric fluid, it is manifest that an electrometer is affected solely by the tension of a battery, and serves as a measure of its degree. For acting on the electrometer, therefore, a battery of numerous small plates is peculiarly suited; their size need not exceed an inch or two inches square. Mr. Singer, in his Treatise on Electricity and Galvanism, stated, that common river water is the best material for exciting a battery of this kind, and that the addition of saline or acid matter even diminishes the intensity. My own observations lead me to doubt the accuracy of this statement.

For producing sparks, charging an electrical battery, or

giving shocks, both tension and quantity of electricity are desirable; and the apparatus designed for such purposes should have a numerous series of plates about four inches square, and be excited with dilute acid. In burning metallic leaf, fusing wire, and igniting charcoal, a large quantity of electricity is the only requisite. The phenomena seem to arise from the electricity passing along these substances with difficulty; a circumstance which, as perfect conductors are used, can only happen when the quantity to be transmitted is out of proportion to the extent of surface over which it has to pass. It is therefore an object to excite as large a quantity of electricity in a given time as possible, and for this purpose a few large plates answer better than a great many small ones. A strong acid solution should also be used; for an energetic action, though of short duration, is more important than a moderate one of greater permanence. A mixture of fourteen or sixteen parts of water to one of nitrous acid is applicable; or for the sake of economy, a mixture of one part of nitrous to two parts of sulphuric acid may be substituted for pure nitrous acid. The large battery of Mr. 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 charge to a Leyden phial, and could not produce chemical decomposition.

II. The chemical agency of the Voltaic apparatus, to which chemists are indebted for their most powerful instrument of analysis, was discovered by Messrs. 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 poles 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 negative wire, and oxygen at the positive side. By collecting the gases in separate tubes as they escape, they are found to be quite pure, and in the exact proportion 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 negative pole; 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, earths, and the oxides of the common metals, were found at the negative pole; while oxygen, chlorine, and the acids, went over to the positive surface.

In performing some of these experiments, Sir H. 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, detailed in the Philosophical Transactions for 1807. In these experiments two agate cups, N and P, were employed, the first communicating with the negative, the second with the positive pole of the battery, and connected together by moistened amianthus. On putting a solution of sulphate of potash 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 negative cup, leaving free acid in the positive. 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 silver was substituted for the sulphate of potash, the amianthus leading to N was coated with a film of metal. A similar transfer may be 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 appears in P, and the alkali in N.

The galvanic action not only separates the elements of compound bodies, but suspends the operation of affinity so entirely, as to enable an acid to pass through an alkaline solution, or an alkali through water containing a free acid, without combination taking place between them. The three cups being arranged as in the last experiment, Sir H. Davy put a solution of sulphate of potash in N, pure water in P, and a weak solution of ammonia in the intermediate cup, so that no sulphuric acid could find its way to the distilled water in P without passing through the ammoniacal liquid in its passage. A battery composed of 150 pairs of 4-inch plates was set in action, and in five minutes free acid appeared at the positive pole. Muriatic and nitric acids were in like manner made to pass through strong alkaline solutions; and on reversing the experiment, alkalies were transmitted directly through acid liquids without entering into combination with them.

The analogy between the preceding phenomena and the attractions and repulsions exerted by ordinary electricity is too close to escape observation. If an acid or an alkali pass from one vessel to another in opposition to gravity and chemical affinity, it is clear that this singular phenomenon must arise from the substance so transferred being under the influence of a still stronger attraction; and the only power to which such an effect can in the present case be attributed, is electricity. Now, in all instances of common electrical attraction, the bodies attract one another in consequence of being in opposite states of excitement; and in like manner, the tendency of acids towards the zinc, and of alkalies towards the copper extremity of the Voltaic apparatus, can be explained, consistently with our present knowledge, only on the supposition that the former are negatively, and the latter positively electric, at the moment of being separated from one another.

To account for the elements of compounds being in such a state, a peculiar hypothesis was advanced by Sir H. Davy, which has received the appellation of the *electro-chemical theory*, and has been adopted by several philosophers, especially by Berzelius. This theory was first developed by its author in 1807 in his essay on *Some Chemical Agencies of Electricity*, and he gave an additional explanation of his views in the Bakerian Lecture for 1826. Some parts of the doctrine are unfortunately expressed in a manner somewhat obscure, and this circumstance has given rise to accidental misrepresentation; but a careful perusal of Sir H. Davy's essays induces me to hope, that the following is a correct statement of his opinions.

It was demonstrated by Volta that the mere contact of certain metals, as for example zinc and copper, causes the development of electricity; for after separation they are found, if insulated, to be oppositely electrified. It is inferred, and I conceive correctly, that the electric equilibrium is disturbed at the moment of contact, and that one metal becomes positively, and the other negatively electric; but so long as contact continues, no sign of electrical excitement is evinced, because the presence of two surfaces oppositely electrified to the same degree, counteracts or neutralizes the effect which either separately would produce. The development of electricity by contact is by no means confined to the metals. Sir H. Davy observed that a dry alkali or alkaline earth is excited positively by contact with a metal, and that dry acids after having touched a metal are negative; and he has further shown that acids and alkalies in their dry state excite each other, the former after contact being negative and the latter positive. A similar disturbance of the electric equilibrium is conceived to be produced by the contact of the ultimate particles or atoms of two bodies, as is developed in the same substances when in mass. The two particles are thus rendered oppositely electric, and if not prevented by cohesion to particles of their own kind or other causes, they remain permanently attached to each other by the force of electrical attraction, and thus give rise to a new compound. What chemists term chemical attraction or affinity is therefore, under this point of view, an electrical

force arising from particles of a different kind attracting each other, in consequence of being in opposite states of electrical excitement. The particles thus adhering or combined retain their electric state, as happens with two discs of zinc and copper while in contact, without exhibiting any signs of electrical excitement either at the moment of combination, or during its continuance. The very existence of the compound, indeed, depends on its elements retaining their state of excitement; and were they both brought into the same electric condition, or subjected to the influence of surfaces of greater intensity than that by which their union is maintained, decomposition would necessarily ensue. This is precisely the manner in which chemical decomposition is thought to be effected by the agency of galvanism. On immersing the extremities of wires connected with the opposite poles of a Voltaic battery into a cup of water, the wire attached to the zinc being positive will attract the oxygen; and if its intensity exceed that by which the elements of water are held together, the oxygen will be drawn towards it and the hydrogen repelled. The wire connected with the copper or negative side of the apparatus exerts an attraction for the hydrogen, and is repulsive to the oxygen; so that the same element which is repelled by one wire is attracted by the other. Other compounds will of course be liable to decomposition on the same principle.

It will appear on a little reflection, that the accuracy of this very ingenious doctrine has not yet been demonstrated. There is no proof that the ultimate particles of bodies do become electric by contact, or that they retain their opposite electricities when combined. Even were these points established, it would not necessarily follow that chemical affinity is identical with electrical attraction. Besides, it has not been fully proved, that the chemical agency of the Voltaic apparatus depends on electrical attraction and repulsion. The theory does not yet stand on so firm a basis as to induce chemists to abandon the nomenclature they have hitherto employed, and cease to regard affinity as a distinct species of attraction. But at the same time it must be admitted, that the electrochemical theory is founded, as all theoretical views ought to be, on extensive observation and numerous facts; that it sup-

plies chemists with a principle capable of accounting for the phenomena ascribed to affinity; and affords a consistent explanation of the chemical agencies of the Voltaic apparatus. Experience has shown that it is a safe guide in experimental research, and it has the unquestionable merit of having led to one of the most brilliant discoveries ever made in chemistry.

Regarding all compounds as constituted of oppositely electrical elements, Sir H. Davy conceived that none of them should resist decomposition, if exposed to a battery of sufficient intensity; and he accordingly subjected to galvanic action substances which till then had been regarded as simple, expecting that if they were compound, they would be resolved into their elements. The result exceeded expectation. The alkalies and earths were decomposed; a substance with the aspect and properties of a metal appeared at the negative pole, while oxygen gas was disengaged at the positive surface. (Phil. Trans. for 1808.)

The same views have been applied with considerable success on a very recent occasion. It has been long known that the copper sheathing of vessels oxidizes very readily in sea water, and consequently wastes with such rapidity as to require frequent renewal. Sir H. Davy observed that the copper derived its oxygen from atmospheric air dissolved in the water, and that the oxide of copper then took muriatic acid from the soda and magnesia, forming with it a submuriate of the oxide of copper. Now if the copper did not oxidize, it could not combine with muriatic acid; and according to Sir H. Davy, it only combines with oxygen, because by contact with that body it is rendered positively electrical. If, therefore, the copper could by any means be made negative, then the copper and oxygen would have no tendency to unite. The object then was to render copper permanently negative. Now this is done by bringing copper in contact with zinc or iron; for the former then becomes negative, and the latter positive.

Acting on this idea, it was found that the oxidation of the copper may be completely prevented. A piece of zinc as large as a pea, or the head of a small round nail, was found fully adequate to preserve forty or fifty 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 connexion 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. for 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 oxide and submuriate 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. It appears also that, in vessels whose sheathing is protected from corrosion, the negatively electric copper attracts the positively electric bodies, such as magnesia and lime, dissolved in sea-water; and that these earths then form a nidus for the adhesion of other matters. It is hoped that by duly adjusting the proportion of iron and copper, a certain degree of corrosion may be allowed to occur, sufficient to prevent the adhesion of foreign bodies, and yet materially to retard the waste of the copper; but the attempts to accomplish so desirable an object have not yet been altogether successful.

These principles may be usefully applied on other occasions. One obvious application of the kind, suggested by Mr. Pepys, is to preserve iron or steel instruments from rust by contact with a piece of zinc. The iron or steel is thereby ren-

dered negative; while the zinc, being positive, is oxidized with increased rapidity.

The electro-chemical theory furnishes a scientific principle, by which chemical substances may be arranged. According to the method suggested by this doctrine, bodies are divided into groups accordingly as their natural electric energies are the same or different. By the term *natural electric energy* is not meant that a substance, considered singly, naturally possesses one kind of excitement rather than another; but that by its nature it is disposed, from contact with other bodies, to assume one particular electrical state rather than the other. Thus oxygen is called a negative electric, because it is negatively excited by other bodies; whereas the natural electric energy of potassium is believed to be positive, because it acquires an excess of electricity by contact with other substances. The electric energies are ascertained by exposing compounds to the action of a galvanic battery, and observing the pole at which the elements appear. Those that collect around the positive pole are said to have a negative electric energy; and those are considered positive electrics which are attracted towards the negative pole. Of the elementary principles oxygen, chlorine, bromine, iodine, and fluorine, are regarded as negative electrics by Dr. Henry, who has adopted this principle of arrangement; and all the others compose his more numerous list of positive electrics.

Considerable difficulty arises in the arrangement of some substances, in consequence of their possessing one kind of electric energy in relation to some bodies, and an opposite energy with respect to others. Oxygen is negative in every combination, and potassium appears to be as uniformly positive; but sulphur, though positive with respect to oxygen, is negative in relation to the metals. Hydrogen is highly positive in regard to oxygen, chlorine, and other analogous principles; but with the metals its electric energy is negative.

The following columns, showing the electric energy of the different elementary substances in relation to each other, are taken from Berzelius's System of Chemistry. They are given by the author as an approximation to their true order, rather than as rigidly exact. All the bodies enumerated in the first

column are negative to those of the second. In the first column each substance is negative to those below it; and in the second, each element is positive with reference to those which occupy a lower place in the series.

1. Negative Electrics.	2. Positive Electrics.
Oxygen.	Potassium.
Sulphur.	Sodium.
Nitrogen.	Lithium.
Chlorine.	Barium.
Iodine.	Strontium.
Fluorine.	Calcium.
Phosphorus.	Magnesium.
Selenium.	Beryllium.
Arsenic.	Yttrium.
Chromium.	Aluminium.
Molybdenum.	Zirconium.
Tungsten.	Manganese.
Boron.	Zinc.
Carbon.	Cadmium.
Antimony.	Iron.
Tellurium.	Nickel.
Columbium.	Cobalt.
Titanium.	Cerium.
Silicon.	Lead.
Osmium.	Tin.
Hydrogen.	Bismuth.
	Uranium.
	Copper.
	Silver.
	Mercury.
	Palladium.
	Platinum.
	Rhodium.
	Iridium.
	Gold.

For exhibiting the chemical agency of galvanism, a combination of quantity and intensity is required. The larger of the two immense batteries constructed by Mr. Children had

scarcely any power in effecting chemical decomposition; and a series of numerous small plates charged with water, and capable of acting powerfully on the electrometer, decomposes water very feebly. The most appropriate apparatus for chemical purposes, is one made with a considerable number of plates of four or six inches square. An acid solution should be employed for exciting the battery, and its strength be such as to cause a moderate, long-continued action, rather than a violent one of short duration. Any of the stronger acids, such as the nitric, sulphuric, or muriatic, may be used with this intention; but the last, according to Mr. Singer, produces the most permanent effect, and is therefore preferable. The proportion should be one part of acid to about 14 or 20 parts of water; or if the series is extensive, the acid may be still further diluted with advantage. The chemical agency of a battery increases with the number of plates; but the exact rate of increase has not been satisfactorily determined.

In order that chemical decomposition should take place by means of galvanism, the compound subjected to its action must be made to connect the opposite poles of the battery. No effect is produced if a non-conductor is used, and hence potash is not decomposed by galvanism, unless slightly moistened; nor must the electric fluids pass through it with the same facility as along a metal, for the apparatus is then equally inert. The substance by which the opposite poles are connected, must be what is called an imperfect conductor, such as water, and saline and acid solutions. All such liquids may be considered perfect conductors in respect to common electricity; but to electrified surfaces of very low intensity, as in galvanic batteries even in their state of highest tension, they are imperfect conductors. Even water, when quite pure, transmits the electricity of a galvanic apparatus so imperfectly, that a very powerful battery occasions a slow disengagement of gas, when its opposite poles communicate through distilled water. Its conducting power is greatly improved by adding a little saline matter, such as sulphate of soda or potash; and the same battery which decomposed water feebly before the addition of the salt, will then cause a free disengagement of gas.

III. The power of lightning in destroying and reversing the poles of a magnet, and in communicating magnetic pro-

perties 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 or galvanic apparatus. Attempts were accordingly made to communicate the magnetic virtue by means of electricity or galvanism; but no results of importance were obtained till the winter of 1819, when Professor Oersted of Copenhagen made his famous discovery, which forms the basis of a new branch of science called *electro-magnetism*. (Annals of Philosophy, xvi. 273.)

The fact observed by Professor Oersted was, that an electric current, such as is supposed to pass from the positive to the negative pole of a Voltaic battery along a wire which connects them, 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.

The extent of the declination occasioned by a battery depends upon its power, and the distance of the connecting wire from the needle. If the apparatus be powerful, and the distance small, the declination will amount to an angle of 45°. But this deviation does not give an exact idea of the real effect which may be produced by galvanism; for the motion of the magnetic needle is counteracted by the magnetism of the earth. When the influence of this power is destroyed by means of another magnet, the needle will place 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. This is easily demonstrated by permitting a horizontally suspended magnet to assume the direction of north and south, and placing near it the conduct-

ing wire of a closed circuit, held vertically and at right angles to the needle, with the positive pole next the ground, so that the current may flow from below upwards. When the wire is exactly intermediate between the magnetic poles, no effect is observed; on moving the wire nearly midway towards the north pole, the needle will be attracted; and repulsion will ensue when the wire is moved close to the north pole itself. Similar effects occur on advancing the wire towards the south pole. Such are the phenomena if the current ascends on the west side of the needle; but they are reversed when the wire is placed vertically on the east side. Attractions and repulsions likewise take place in a dipping needle, when the current flows horizontally across it.

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 labourers in this field, MM. Ampère, Arago, and Biot of Paris, and Sir H. Davy and Mr. Faraday in this country, deserve to be particularly mentioned.

M. Ampère observed that the Voltaic apparatus itself acts on a magnetic needle placed upon or near it, in the same manner as the wire which unites its two extremities. But the declination was found to occur only when the opposite ends of the battery are in communication, and to cease entirely as soon as the circuit is interrupted,—a difference which was supposed to arise from the passage of an uninterrupted electric current through the apparatus, as along the connecting wire, taking place in the first case, and not in the second. M. Ampère therefore proposed the magnetic needle as an instrument for discovering the existence and direction of an electric current, (or currents according to the theory of the two electricities) as well as for pointing out the proper state and fitness of a galvanic apparatus for electro-magnetic experiments in general. When the needle is employed with this intention it is called a *galvanometer* or *galvanoscope*.

M. Ampère soon after discovered that a power of attraction and repulsion may be communicated by an electric current alone, without the use of a magnet. Two wires of copper, brass, or any other metal, placed parallel to each other, and

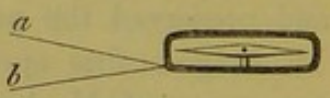
suspended so as to move freely, were connected with the opposite poles of a galvanic apparatus. If the electric current passed along both wires in the same direction, they attracted one another; if in an opposite direction, they repelled each other. The result of this experiment gave rise to the supposition that the magnetic property is actually communicated to the wires by the electric current; and this supposition was confirmed by M. Arago, who found that iron filings are attracted by a wire placed in the Voltaic circuit, and that they fall off when the communication between the poles is interrupted. This fact was also discovered about the same time by Sir H. Davy, whose experiments were minutely described, in the year 1821, in the Transactions of the Royal Society.

The communication of temporary magnetic properties to the common metals naturally led to an attempt to magnetize steel and iron permanently by the same agent. The experiment was made by M. Arago and Sir H. Davy about the same time, and both were successful. Sir H. Davy attached steel needles to the connecting wire; placing some parallel to it, and others transversely. The former merely acted as a part of the circuit; they did not possess poles, and lost their power of attracting iron filings as soon as the electric current ceased to circulate through them. But the latter acquired a north and south pole, and preserved the property after separation from the wire. M. Arago at first operated in a similar manner; but, at the suggestion of M. Ampère, he made the connecting wire into the form of a spiral or helix, and placed the needle to be magnetized in its centre. By this arrangement the maximum effect was obtained in a shorter time than by any other method. Sir H. Davy also rendered a needle magnetic by placing it across a wire, along which a charge from a common Leyden battery was transmitted. This series of experiments was completed by M. Ampère's discovery, that a connecting wire, suspended so as to have perfect freedom of motion, is influenced by the magnetic attraction of the earth.

For the next fact of importance, science is indebted to the researches of Mr. Faraday. He ascertained that the influence of the connecting wire on the direction of a magnet, is not owing to any attraction or repulsion exerted between them, but to a

tendency they have to revolve round each other. He contrived an apparatus, (Quarterly Journal, vol. xii.) by means of which either pole of a magnet was made to revolve round the wire as a fixed point; and then, by fixing the wire, and giving free motion to the magnet, both poles of the latter were made to revolve in succession round the former. He was also successful in causing the wire to revolve by the influence of the magnetism of the earth.

It is found that a magnetic needle 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 the galvanoscope of Schweigger, commonly called the *Multiplier*, is constructed. 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 the figure. 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 poles of the galvanic circle.—The multiplier of Schweigger, or some modification of it, is much employed in researches on galvanism.



The foregoing is a summary of the magnetic properties of the Voltaic apparatus, which form the basis of electro-magnetism, and were discovered soon after the original experiments of Oersted were made known to the public. Other facts of interest have since been observed, and some ingenious general views have been proposed to account for all the phenomena; but as a full discussion of electro-magnetism would lead into details too minute for an elementary treatise, I must refer the reader who wishes for more ample information to works written professedly on the subject. In addition to the essay of Oersted already referred to, the following may be mentioned as con-

venient for consultation. The Historical Sketch of Electro-magnetism in the Annals of Philosophy, N. S., Popular Sketch of Electro-magnetism by Mr. Watkins, the *Recueil d'Observations Electro-dynamiques* by M. Ampère, Professor Cumming's Manual of Electro-dynamics, and the second edition of Mr. Barlow's Essay on Magnetic Attractions.

PART II.

PRELIMINARY REMARKS.

In teaching a science, the details of which are numerous and complicated, it would be injudicious to follow the order of discovery, and proceed from the 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.

This necessity is in no case more sensibly felt than in the study of chemistry, and for this reason I shall commence the second part of the work by explaining the leading doctrines of the science. One inconvenience, indeed, does certainly arise from this method. It is often necessary, by way of illustration, to refer to facts of which the beginner is ignorant; and therefore 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. Specific gravity in particular is a point of great consequence; and as this expression will hereafter be used in almost every page, it will be proper, before proceeding further, to explain its meaning. Equal bulks of different substances, as a cubic inch of gold, silver, tin, and water, differ

more or less in weight: their densities are different; or in other words, they contain different quantities of ponderable matter in the same space. The tin will weigh eight times more than the water, the silver about ten times and a half, and the gold upwards of 19 times more than that fluid. The density of all solids and liquids may be determined in the same manner; and if they are compared with an equal bulk of water as a standard of comparison, a series of numbers will be obtained, which will show the comparative density or *specific gravity*, as it is called, of all of them.

The process for determining specific gravities is therefore sufficiently simple. It 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 weighs nine grains, and the same bulk of another body 20 grains, its specific gravity is determined by the formula, as 9 : 20 : : 1 (the specific gravity of water) to the fourth proportional 2.2222; so that the specific gravity 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 somewhat 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 that the difference corresponds exactly to the weight of the 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 specific gravity 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

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

weight of the displaced water is found by weighing the bottle again, after having wiped its outer surface with a dry cloth.

The determination of the specific gravity 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 experiments of Sir George Shuckburgh, 100 cubic inches of pure and dry atmospheric air, at the temperature of 60° F. and when the barometer stands at 30 inches, weigh precisely 30.5 grains. By a similar method the weight of any other gas may be determined, and its specific gravity be inferred accordingly. For instance, suppose 100 cubic inches of oxygen are found to weigh 33.888 grains, its specific gravity will be thus deduced; as 30.5 : 33.888 : : 1 (the sp. gr. of air) : 1.1111, the specific gravity 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 hygrometric condition. If it is saturated with moisture, the necessary correction may be made for that circumstance by the formula which will be found at page 75; 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 potash.

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 specific gravity of a gas, that the barometer must stand at thirty inches, by which means the operator is certain that each gas is subject to equal degrees of compression. An elevation of thirty inches is there-

fore 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 careful 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 a thirty inch column of mercury, will dilate to 200 measures, if the pressure be diminished by one half; and will be compressed to fifty measures, when the pressure is double, or equal to a mercurial column of sixty 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 portion of gas occupy the space of 100 measures at twenty-nine inches of the barometer, its bulk at thirty inches may be obtained by the following proportion; as

30 : 29 : : 100 : 96.66.

4. For a similar reason the temperature should always be the same. The standard or mean temperature is 60° F.; and if the gas be admitted into the weighing-flask when the thermometer is above or below that point, the formula of page 33 should be employed for making the necessary correction.

Chemistry is indebted for its nomenclature to the labours of four celebrated chemists, Lavoisier, Berthollet, Guyton-Morveau, and Fourcroy. The principles which guided them in its construction are exceedingly simple and ingenious. The known elementary substances and the more familiar compound ones were allowed to retain the appellation which general usage had assigned to them. The newly discovered elements were named from some striking property. Thus, as it was supposed that acidity was always owing to the presence of the vital air discovered by Priestley and Scheele, they gave it the name of *oxygen*, derived from two Greek words signifying generator of acid; and they called inflammable air *hydrogen*, from the circumstance of its entering into the composition of water.

Compounds, of which oxygen forms a part, were called *acids* or *oxides* according as they do or do not possess acidity. An oxide of iron or copper signifies a combination of those metals with oxygen, which has no acid properties. 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 signify acid compounds of sulphur and carbon with oxygen gas. If sulphur or any other body should form two acids, that which contains the least quantity of oxygen is made to terminate in *ous*, as sulphur*ous* acid. The termination in *uret* was intended to denote combinations of the simple non-metallic substances either with one another, with a metal, or with a metallic oxide. Sulph*uret* and carb*uret* of iron, for example, signify compounds of sulphur and carbon with iron. The different oxides or sulphurets of the same substance were distinguished from one another by some epithet, which was commonly derived from the colour of the compound, such as the black and red oxides of iron, the black and red sulphurets of mercury. Though this practice is still continued occasionally, it is now more customary to distinguish degrees of oxidation by the use of derivatives from the Greek. *Prot*oxide signifies the first degree of oxidation, *deut*oxide the second, and *trit*oxide the third. The term *per*oxide is often applied to the highest degree of oxidation. The sulphurets, carburets, &c. of the same substance are designated in a similar way. Compounds consisting of acids in combination with alkalies, earths, or metallic oxides, are termed *salts*, the names of which are so contrived as to indicate the substances contained in them. If the acidified substance contains a maximum of oxygen, the name of the salt terminates in *ate;* if a minimum, the termination in *ite* is employed. Thus, the sulph*ate*, phosph*ate*, and arseni*ate* of potash, are salts of sulphur*ic*, phosphor*ic*, and arsen*ic* acids; while the terms sulph*ite*, phosph*ite*, and arsen*ite* of potash, denote combinations of that alkali with the sulphur*ous*, phosphor*ous*, and arseni*ous* acids.

The advantage of a nomenclature which disposes the different parts of a science in so systematic an order, and gives such powerful assistance to the memory, is incalculable. The principle has been acknowledged in all countries where chemical science is cultivated, and its minutest details have been adopted in Britain. It must be admitted, indeed, that in some respects the nomenclature is defective. The erroneous idea of oxygen being the general acidifying principle, has exercised an

injurious influence over the whole structure. It would have been convenient also to have had a different name for hydrogen. But it is now too late to attempt a change; for the confusion attending such an innovation would more than counterbalance its advantages. The original nomenclature has therefore been preserved, and such additions have been made to it as the progress of the science rendered necessary. The most essential improvement was suggested by the discovery of the laws of chemical combination. The different salts formed of the same constituents were formerly divided into *neutral*, *super*, and *sub*-salts. They were called neutral, if the acid and alkali were in such proportion that one neutralized the other; super-salts, if the acid prevailed; and sub-salts, if the alkali was in excess. The name is now regulated by the atomic constitution of the salt. If it is a compound of an equivalent of the acid and the alkali, the generic name of the salt is employed without any other addition; but if two or more equivalents of the acid are attached to one of the base, or two or more equivalents of the base to one of the acid, a numeral is prefixed so as to indicate its composition. The two salts of sulphuric acid and potash are called sulphate and *bi*-sulphate; the first containing an equivalent of the acid and the alkali, and the second salt, two of the former to one of the latter. The three salts of oxalic acid and potash are termed the oxalate, *bin*oxalate, and *quadr*oxalate of potash; because one equivalent of the alkali is united with one equivalent of acid in the first, with two in the second, and with four in the third salt. As the numerals which denote the equivalents of the acid in a super-salt are derived from the Latin language, Dr. Thomson proposes to employ the Greek numerals, *dis*, *tris*, *tetrakis*, to signify the equivalents of alkali in a sub-salt.

This method is in the true spirit of the original framers of our nomenclature. Chemists have already begun to apply the same principle to other compounds besides salts; and there can be no doubt that it will be applied universally whenever our knowledge shall be in a state to admit of its introduction.

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. Every thing 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 several circumstances; 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 commixture of two substances. Water and sulphuric acid, or water and alcohol, combine readily. On the contrary, water shows little disposition to unite with sulphuric 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 particles is a common occurrence. 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 of the kind. The phenomena however are often more complex. It frequently happens that the formation of a new compound is attended by the destruction of an existing one. The only condition necessary for this effect, is the presence of some third body which has a greater affinity for one of the elements of a compound than they have for each other. 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 muriatic acid. Combination and decomposition occur in each of these cases;—combination of sulphuric acid with ammonia, of water with alcohol, and of baryta with sulphuric acid;—decomposition of the compounds formed of oil and ammonia, of alcohol and camphor, and of muriatic 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,
Potash,
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 potash 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 attraction for sulphuric acid than lime, and yet that the latter, from the great influence of disturbing causes, may succeed in decomposing sulphate of ammonia.

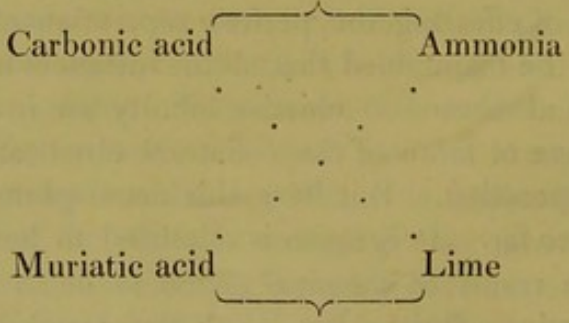
The justice of the foregoing remark will be made obvious by the following example.—When a stream of hydrogen gas is passed over oxide of iron heated to redness, the oxide is reduced to the metallic state, and water is generated. On the contrary, when watery vapour is brought into contact with red-hot 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.

To Berthollet is due the honour of pointing out the fallacy of Bergmann's opinion. He was the first to show 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; he 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 has surely gone too far. Bergmann is admitted to have erred in supposing the result of chemical action to be in every case owing to elective affinity; but Berthollet certainly 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 conceive, indisputable. Water has a much greater affinity for muriatic acid and ammoniacal gases than for carbonic acid and sulphuretted hydrogen, 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 sulphuretted hydrogen by iodine, is determined by the concurrence of any modifying circumstances.

Affinity is the cause of still more complicated changes than those which have been just 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 are most conveniently studied by aid of a diagram,—a method which was first employed, I believe, by Dr. Black, and has since been generally practised. Thus, in mixing together a solution of carbonate of ammonia and muriate 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 muriate of ammonia. According to the views of Bergmann the result is solely dependant on the comparative strength of affinities. If the affinity of carbonic acid for ammonia, and of muriatic acid for lime, exceed that of carbonic acid for lime, added to that of muriatic 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*. Mr. 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 muriate of lime by the mere force of a superior attraction, it is manifest that carbonate of lime ought never to decompose muriate 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 muriate 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 sulphuretted hydrogen 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. No ingenuity could guess, *a priori*, 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 Sir H. Davy proved them to be compound, and certainly they evince no sign whatever of containing oxygen gas and a metal. Numerous examples of a similar kind are afforded by the action of acids and alkalies on one another. Sulphuric acid and potash, 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. 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 specific gravity of the new body is greater than the mean of its components. Thus a mixture of 100 equal 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. Caloric 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 when 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 diminution in the capacity of the new compound for caloric; but intense heat sometimes accompanies chemical action under circumstances in which an explanation founded on a change of specific caloric is quite inadmissible. At present it is enough to have stated the fact; the theory of it 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, or liquids solid. Several familiar chemical phenomena, such as explosions, effervescence, and precipitations, are owing to these changes. The sudden evolution of a large quantity of gaseous matter occasions an explosion, as when gunpowder detonates. The slower disengagement of gas causes effervescence, as occurs when marble is put into muriatic 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. The colour of a compound is frequently quite different from that of the substances by which it is formed. There does not appear to be any uniform relation between the colour of a body and that of its elements, so that it is not possible to anticipate the colour of any particular compound by knowing the principles which enter into its composition. Iodine, whose vapour is of a violet hue, forms a beautiful red compound with mercury, and a yellow one with lead. The brown 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 often enables the chemist to distinguish bodies from one another when in solution.

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, and gravity. 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. For this reason 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 is useful 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. Caloric 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 it is easy to perceive that the cohesive power is still in operation: for a solid is commonly dissolved in greater quantity when its cohesion is diminished by caloric. 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 by caloric. 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 ascendancy 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 it certainly is applicable to many of the instances to be found in the tables of affinity. When, for example, muriatic 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, potash, 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, muriatic acid, and baryta, may give rise

either to sulphate of soda and muriate of baryta, or to sulphate of baryta and muriate 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 muriatic acid to combine with the soda. In like manner, muriate 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 potash and muriate of soda, no precipitate ensues; because the salts capable of being formed by double decomposition, sulphate of soda and muriate of potash, 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 muriatic acid, sulphuric acid, and baryta are mixed together in solution, the base may be conceived to be at first divided between the two acids, and muriate and sulphate of baryta to be generated. The latter being insoluble is instantly removed beyond the influence of the muriatic acid,

so that for an instant muriate 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 muriate 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 muriate of potash and sulphate of soda, four salts according to this view are generated, namely, the sulphates of soda and potash, and the muriates 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 potash, 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 potash is generated; and this process continues until the greater part of the sulphuric acid and potash 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 muriate of lime are mingled together in solution, double decomposition takes place, and 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, a mutual interchange of the constituents ensues. Carbonate of soda and muriate of lime 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 caloric 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 caloric 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, caloric favours affinity; as by diminishing the cohesion of a solid, or by converting a solid 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 substances from one another, which are already combined. There is one effect of caloric 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 body, the last will, in general, be completely driven off by the application of heat. The decomposition of muriate or any of the salts of ammonia, by the pure alkalies or alkaline earths, may be adduced as an example; and for the same reason, all the carbonates are decomposed by muriatic acid, and all the muriates by sulphuric acid. This explanation applies equally well to some cases of double decomposition. It explains, for instance, why the dry carbonate of lime will decompose muriate of ammonia by the aid of heat; for carbonate of ammonia is more volatile than the muriate, 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 muriate of ammonia and 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 muriate 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 potash may be effected by iron, though the affinity of this metal for oxygen seems much inferior to that of potassium for oxygen. If potash 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 potash.

QUANTITY OF MATTER.

The influence of quantity of matter over affinity is universally admitted. If one body A unites with another body 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 caloric; a higher temperature is required to decompose the deutoxide; 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 weakened to such a degree as to be un-

able to overcome the cohesion of the salt. The process then ceases, and a saturated solution is obtained.

Quantity of matter is employed advantageously in many chemical operations. If, for instance, a chemist is desirous of separating an acid from a metallic oxide by means of the superior affinity of potash for the former, he frequently uses rather more of the alkali than is sufficient for neutralizing the acid. He takes the precaution of employing an excess of 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 a 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 set out by supposing that the affinity of different acids for the same alkali, is 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 different, and ought to be held distinct. The relative weights

of muriatic and sulphuric acids required to neutralize an equal quantity of any alkali, or, in other words, their capacities of saturation, are as 37 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 same numbers. But in taking this estimate, we have to make three assumptions, all of which are disputable. There is no proof, in the first place, that muriatic acid has a greater affinity for an alkali, such as potash, 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 muriatic acid has the greater affinity, it does not follow that the attraction of those acids for potash is in the ratio of 37 to 40. And, thirdly, supposing this point settled, it is very improbable that the ratio of their affinity for one alkali will apply to all others; analogy would lead us to anticipate the reverse. Independently of these objections, M. Dulong has found that the principle of Berthollet is not in accord with the results of experiment.

But though this mode of determining the relative forces of affinity cannot be admitted, it is possible that quantity of matter may somehow or other compensate for a weaker affinity; and Berthollet attempted to prove it by experiment. (Researches into the Laws of Affinity.) On boiling sulphate of baryta with an equal weight of pure potash, the alkali is found to have deprived the baryta of a small portion of its acid; and on treating oxalate of lime with nitric acid, some nitrate of lime is generated. As these partial decompositions are contrary to the supposed order of elective affinity, it was conceived that they were produced by quantity of matter acting in opposition to force of attraction. But they by no means justify such a conclusion. In the decomposition of sulphate of baryta by potash, no care was taken to exclude the atmospheric air during the operation: the alkali must consequently have absorbed carbonic acid; and it is an established fact that carbonate of potash partially decomposes sulphate of baryta. A similar omission appears to have been made in the other ex-

periments where decomposition was attempted by pure potash or soda. In many instances the result may fairly be attributed to other causes. Acids and alkalies have often a tendency to unite in more than one proportion, and will readily form salts with excess of acid or of base when circumstances are favourable to their production. Thus on adding nitric acid to the insoluble phosphate of lime, the earth is divided between the two acids, and a nitrate and biphosphate of lime are generated. It is difficult, if not impossible, to effect the entire decomposition of nitrate of potash by a quantity of sulphuric acid just sufficient for neutralizing the alkali; for the sulphuric acid, instead of taking the whole of the potash, is apt to unite with part of it, and form the bisulphate. This tendency to the formation of an acid salt accounts for the fact quite satisfactorily; nor is there reason to infer the co-operation of any other cause. Another circumstance that influences the result of such experiments, and which Berthollet left entirely out of view, is the affinity of salts for one another. On the whole, therefore, we may infer that Berthollet has given no satisfactory case in which quantity of matter is proved to compensate for a weaker affinity. Saline substances, indeed, seem ill adapted to such researches. For it is impossible in many, if not in most cases, to decide upon the relative strength of the attraction of two acids for an alkali, or of two alkalies for an acid, a point, nevertheless, which is an important element in the inquiry; and even did we possess such knowledge, the influence of modifying circumstances is such, that it is difficult to appreciate the share they may have in producing a given effect.

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 from one another 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.

IMPONDERABLES.

The influence which caloric 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 principle, under the same circumstances, and subsequently by marking the comparative facility of decomposition when the compounds so formed are exposed to the same decomposing agent. Thus on exposing gold, lead, and iron, to air and moisture, the iron rusts with great rapidity, the lead is only tarnished, and the silver retains its lustre. It is hence inferred that iron has the greatest affinity for oxygen, lead next, and silver 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 only; and oxide of lead is decomposed by charcoal at a lower temperature than oxide of iron.

It is inferred from the action of caloric on the carbonate

of potash, baryta, lime, and oxide of lead, that potash 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 action on one another 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 of them 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, muriatic, and nitric acids, 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 in each

case they appear to unite perfectly with one another. A hundred grains of water, on the contrary, will dissolve any quantity of sea-salt which does not exceed forty grains. Its dissolving 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 the 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 minor importance; but they are exceedingly useful as instruments of research. They enable the chemist to present bodies to each other, under circumstances the most favourable possible 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 zinc and oxygen, or of chlorine and hydrogen. Others combine in two proportions. For example, two compounds are formed by copper and oxygen, or 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, excepting those which belong to the first division.

The combination of substances that unite in a few proportions only, is regulated by three remarkable laws. The first of these laws is, that the composition of bodies is fixed and invariable; that a compound substance, so long as it retains its characteristic properties, must always consist 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 two elements to unite in any other proportion, 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 78 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. Finding that the solubility of a salt and of a gas in water is limited, in the former by cohesion, and in the latter by elasticity, he conceived that the same forces would account for the unchangeable composition of certain compounds. He maintained, therefore, 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 78 of baryta, not because those substances are disposed to unite in that ratio

* By the expression 'parts' I always mean parts by weight.

rather than in another, but because the compound so constituted happens to have great cohesive power.

These opinions, which, if true, would shake the whole science of chemistry to its foundation, were founded on observation and experiment, supported by all the ingenuity of that highly gifted philosopher. They were ably and successfully combated by Proust, in several papers published in the *Journal de Physique*, 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. The controversy which ensued between these eminent chemists on that occasion, is remarkable for the moderation with which it is conducted on both sides, and has been properly quoted by Berzelius as a model for all future controversialists. How much soever opinion may have been divided upon this important question at that period, the dispute is now at an end. The infinite variety of new facts, similar to those observed by Proust, which have since been established, has proved beyond a doubt that the leading principle of Berthollet is quite 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 of a few definite compounds with each other.

The second law of combination is still more remarkable than the first. It has given plausibility to an ingenious hypothesis concerning the ultimate particles of matter, called the *atomic theory*. The law itself, however, contains nothing hypothetical, being the mere expression of a fact, first noticed by Mr. Dalton, and subsequently confirmed by many other chemists. Its nature will be at once understood by perusing the following table:—

Water is composed of	.	Hydrogen 1	.	Oxygen 8
Deutoxide of Hydrogen		Do. 1	.	Do. 16
Carbonic Oxide	. . .	Carbon 6	.	Do. 8
Carbonic Acid	. . .	Do. 6	.	Do. 16

Nitrous Oxide . . .	Nitrogen	14	Oxygen	8
Nitric Oxide	Do.	14	Do.	16
Hyponitrous Acid . .	Do.	14	Do.	24
Nitrous Acid	Do.	14	Do.	32
Nitric Acid	Do.	14	Do.	40

It will be perceived that in all these compounds, the numbers expressing the quantities of oxygen, which unite with a given weight of the same substance, bear a very simple ratio to one another. Deutoxide of hydrogen contains just twice as much oxygen as water. The oxygen in carbonic acid is double that of carbonic oxide. The oxygen in the compounds of nitrogen and oxygen is in the ratio of 1, 2, 3, 4, and 5. So obvious indeed is this law, that it is observed at once on comparing together the results of a few accurate analyses; and the only subject of surprise is, that it was not discovered before. It is by no means confined to the compounds of combustibles with oxygen. Thus, the ratio of the sulphur in the two sulphurets of mercury, and of chlorine in the two chlorides of mercury, is as 1 to 2. It extends also to the salts. Bicarbonate of potash, for example, contains twice as much carbonic acid as the carbonate; and the oxalic acid of the three oxalates of potash is in the ratio of 1, 2, and 4. We must regard it therefore as a law which regulates the union of bodies; and its enunciation may be stated in the following terms. When two substances, A and B, unite chemically in two or more proportions, the numbers representing the quantities of B combined with the same quantity of A are in the ratio of 1, 2, 3, 4, &c.; that is, they are multiples by some whole number of the smallest quantity of B with which A can unite. Thus, if A + B is the first compound, the others will be A + 2 B, or A + 3 B, or A with some similar multiple of B. This law is often called the *law of multiples*, or of combination in *multiple proportions*.

That the elements of compounds are often arranged according to the law of multiples, as thus expressed, is a fact which does not admit of the least question; but in the present state of chemical science, we are not prepared to maintain that it is universal. Instances are not unfrequently met with,

where a slight deviation from the law occurs. The three oxides of lead, for instance, are thus constituted:—

	Lead.	Oxygen.
Protoxide	104	8
Deutoxide	104	12
Peroxide	104	16

In these compounds the oxygen is as 1 : 1½ : 2; and the oxides of manganese afford a similar example. The oxides of iron are composed as follows:—

	Iron.	Oxygen.
Protoxide	28	8
Peroxide	28	12

in which the ratio of the oxygen is as 1 to 1½ or as 2 to 3. The oxygen in arsenious and arsenic acids, according to Berzelius, is as 3 to 5. These deviations from the law of multiples may perhaps be rather apparent than real. It is possible, for example, that deutoxide of lead may be a compound of the protoxide and peroxide with each other, and therefore that it ought not to be enumerated among the oxides of that metal. It is also possible that the anomaly is frequently owing to our ignorance of compounds which may hereafter be discovered. Thus the discovery of an oxide of lead consisting of 104 parts of metal to 4 parts of oxygen, would render this series of compounds conformable to the usual law of combination. But leaving these points to be decided by future observation, and taking facts as they are, we may state that bodies combine either strictly according to the law of multiple proportion as first stated, or according to the slight deviation from that law as illustrated in the preceding examples. In either case this law of combination is exceedingly simple.

The third law of combination is intimately connected with the preceding, and is not less remarkable. Its existence and nature will at once appear, on a comparison of the relative quantities of different bodies which combine together. Thus

8 parts of oxygen unite with 1 part of hydrogen, 16 of sulphur, 36 of chlorine, 40 of selenium, and 110 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 law already explained. Thus sulphuretted hydrogen is composed of 1 part of hydrogen and 16 of sulphur, and bisulphuretted hydrogen of 1 part of hydrogen to 32 of sulphur; 36 of chlorine unite with one of hydrogen, 16 of sulphur, and 110 of silver; and 40 parts of selenium with 1 of hydrogen, and 16 of sulphur.

It is manifest, from these examples, that bodies unite according to proportional numbers; and hence has arisen the use of certain terms, such as Proportion, Combining Proportion, Proportional, or Equivalent, to express them. Thus the combining proportions of the substances just alluded to are

Hydrogen	1
Oxygen	8
Sulphur	16
Chlorine	36
Selenium	40
Silver	110

The most common kind of combination is one proportion of one body either with one or with two proportions of another. Combinations of 1 to 3, or 1 to 4, are very uncommon, unless the more simple compounds likewise exist. Ammonia, however, is a singular instance of the reverse. It is composed of 14 parts of nitrogen, and 3 of hydrogen. Now 14 being the precise quantity of nitrogen that unites with 8 of oxygen, is considered as one proportion of nitrogen, and this quantity is combined in ammonia with three proportionals of hydrogen. No compound of nitrogen and hydrogen in any other proportion has as yet been discovered. In some cases it appears that bodies unite in the ratio of 2 equivalents of one body to 3 or 5 equivalents of the other. There is good reason to believe that hyposulphuric acid is constituted in this manner; and Berzelius is of opinion that this kind of arrangement is by no means unfrequent.

But this law does not apply to elementary substances only, since compound bodies have their combining proportions, which may likewise be expressed in numbers. Thus, since water is composed of one proportion or eight parts of oxygen, and one proportion or 1 of hydrogen, its combining proportion or equivalent is 9. The proportion of sulphuric acid is 40, because it is a compound of one proportion or 16 of sulphur, and three proportions or 24 of oxygen; and in like manner, the combining proportion of muriatic acid is 37, because it is a compound of one proportion or 36 of chlorine and one proportion or 1 of hydrogen. The equivalent number of potassium is 40, and as that quantity combines with 8 of oxygen to form potash, the combining proportion of potash is 48. Now when these compounds unite, one proportion of the one combines with one, two, three, or more proportions of the other, precisely as the simple substances do. Hydrate of potash, for example, is constituted of 48 parts of potash and 9 of water, and its combining proportion is consequently 48 + 9 or 57. Sulphate of potash is composed of 40 sulphuric acid + 48 potash; and muriate of the same alkali of 37 muriatic acid + 48 potash. The combining proportion of the former salt is therefore 88, and of the latter 85.

The composition of the salts affords a very neat illustration of this subject; and to exemplify it still further, I subjoin a list of the proportional numbers of a few acids and alkaline bases.

Hydrofluoric Acid	18.86	Lithia	18
Phosphoric Acid	35.71	Magnesia	20
Muriatic Acid	37	Lime	28
Sulphuric Acid	40	Soda	32
Nitric Acid	54	Potash	48
Arsenic Acid	57.68	Strontia	52
Selenic Acid	64	Baryta	78

It will be seen at a glance, that the neutralizing power of the different alkalies is very different; for the proportion of each base expresses the precise quantity required to neutralize a proportion of each of the acids. Thus 18 of lithia, 32 of soda, and 78 of baryta, combine with 18.86 of hydrofluoric

acid, forming the neutral hydrofluates of lithia, soda, and baryta. The same fact is obvious with respect to the acids; for 35.71 of phosphoric, 40 of sulphuric, and 57.68 of arsenic acid unite with 28 of lime, forming a neutral phosphate, sulphate, and arseniate of lime.

These circumstances afford a ready explanation of a curious fact, first noticed by the Saxon chemist Wenzel; viz., that when two neutral salts mutually decompose each other, the resulting compounds are likewise neutral. The cause of this fact is now obvious. If 72 parts of dry sulphate of soda are mixed with 132 of nitrate of baryta, the 78 parts of baryta unite with 40 of sulphuric acid, and the 54 parts of nitric acid of the nitrate combine with the 32 of soda, 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 .	32	78 Baryta.
	72	132

It matters not whether more or less than 72 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.

The utility of being acquainted with these important laws is almost too manifest to require mention. Through their aid, and by remembering the proportional numbers of a few elementary substances, the composition of an extensive range of compound bodies may be calculated with facility. By knowing that 6 is the combining proportion 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. Forty is the equivalent of potassium; and potash being its protoxide, is composed of 40 potassium + 8 of oxygen. From these few data, we know at once the composition of carbonate and bicarbonate of potash. The former is composed of 22 carbonic acid + 48 potash; the latter of 44 carbonic acid + 48

potash. This knowledge is retained with very little effort of the memory; and the assistance derived from the method will be manifest on comparing it with the common practice of stating the composition in 100 parts.

Carbonic Oxide.		Carbonic Acid.
Carbon	42.86	27.27
Oxygen	57.14	72.73

Carbonate of Potash.		Bicarbonate of Potash.
Carbonic acid	31.43	47.83
Potash	68.57	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 in 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 is found to contain one proportion of the combustible with 7.99 of oxygen, it is fair to infer that 8, or one proportion 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 earths

are known to be composed of one proportion of each constituent, and the oxides to contain one proportion of oxygen. If it be found, therefore, by analysis, that neutral sulphate of lithia is composed of 40 parts of sulphuric acid and 18 of lithia, it may be inferred, since 40 is one proportion of the acid, that 18 is the equivalent for lithia; and that this oxide is formed of 8 parts of oxygen and 10 of lithium.

The method of determining the proportional 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. No two bodies are better adapted for this purpose than oxygen and hydrogen, and that compound is selected which contains the smallest quantity of oxygen. Water is such a substance, and it is therefore regarded as a compound of one proportion of oxygen with one proportion of hydrogen. But analysis proves that it is composed of 8 parts of the former to 1 of the latter, and therefore the equivalent of oxygen is eight times heavier than that of hydrogen.

Some compounds are next examined, which contain the smallest proportion of oxygen or hydrogen in combination with some other substance. Carbonic oxide with respect to carbon, and sulphuretted hydrogen with respect to sulphur, answer this description perfectly. The former consists of 8 parts of oxygen and 6 of carbon; the latter of 1 part of hydrogen and 16 of sulphur. The proportional number of carbon is consequently 6, and that of sulphur 16. The proportions of all other bodies may be determined in a similar manner.

Since the proportional numbers 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, we may make the combining proportion of hydrogen 10 if we please; 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 effectually do away with the advantage above ascribed to the use of the

proportional numbers; and it is the object of every one to employ such as are simple, that their relation may be perceived by mere inspection. The opinions of different chemists concerning the simplicity of numbers being somewhat at variance, we possess several series of them. Dr. Thomson, for example, makes oxygen 1, so that hydrogen is eight times less than unity, or 0.125, carbon 0.75, and sulphur 2. Dr. 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, have selected hydrogen as their unit; and therefore the equivalent of oxygen is 8. One of these series may easily be reduced to either of the others by an obvious and simple calculation, and it is not very material to which of them the preference is given; but I have myself adopted the last, because, as it rarely contains fractional parts, it appears best adapted to the purpose of teaching.

ON THE ATOMIC THEORY OF MR. DALTON.

The brief sketch which has been given of the laws of combination will, I trust, serve to set the importance of this department of chemical science in its true light. It is founded, as will have been seen, 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.

It is not uncommon, for persons commencing the study of chemistry, to entertain a vague notion that this department of the science comprehends something uncertain and hypothetical in its nature, and to be thus led to form an erroneous idea of its importance. This misapprehension may easily be traced to its source. It was impossible to reflect on the regularity and constancy with which bodies obey the laws of combination, 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 Mr. 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 Dr. Wollaston and Sir H. Davy, recommended and practised an opposite course, both subjects have been but too commonly comprised under the name of *atomic theory;* and 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 understood, 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 atoms which are of such a nature as not to admit of division. 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 the general attention to this controversy, by affording a far stronger argument in favour of the atomic constitution of bodies than was ever advanced before, and one which I conceive is almost irresistible. We have only in fact to assume with Mr. Dalton, that all bodies are composed of ultimate atoms, the weight of which is different in different kinds of matter, and we explain at once the foregoing laws of chemical union. Nor do the phenomena 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 one atom of hydrogen and one atom of oxygen, deutoxide of hydrogen will consist of one atom of hydrogen and two atoms of oxygen. If carbonic oxide is formed of one atom of carbon and one atom of oxygen, carbonic acid will consist of one atom of carbon and two atoms of oxygen. If in the compounds of nitrogen and oxygen enumerated at page 167, the first or protoxide is constituted of one atom of nitrogen and one atom of oxygen, the four others will be regarded as compounds of one 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 two or more atoms of one substance may not combine with 2, 3, 4, 5, or more atoms of another. Such combinations will account for the complicated proportion noticed in some 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 one equivalent of oxygen and one equivalent of hydrogen, it is said to consist of one atom of each element. In like manner sulphate of potash is said to be formed of one atom of sulphuric acid and one atom of potash, 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 eight parts of oxygen and one of hydrogen, it follows, on the supposition of water consisting of one atom of each element, that an atom of oxygen must be eight times heavier than an atom of hydrogen. If carbonic oxide is formed of an atom of carbon and an atom of oxygen,

the relative weight of their atoms is as 6 to 8; and in short the relative weights of all other bodies are expressed by the numbers which denote their combining proportions.

Though the phenomena of chemical combination leave little doubt of the atomic constitution of matter, other powerful arguments may now be adduced in favour of this theory. Dr. Wollaston, in his Essay on the Finite Extent of the Atmosphere, (Philos. Trans. for 1822,) has supported this doctrine on a new and independent principle, the particulars of which will be stated in the section on nitrogen. Another argument, of much greater force, is deducible from the peculiar connexion noticed by Professor Mitscherlich between the form and composition of certain substances, a subject which will be discussed under the head of crystallization.

But in adopting the notion that matter is composed of ultimate individual particles, I am by no means satisfied of the propriety of expressing the facts of the science in language founded on this theory; because, though the elements of bodies be arranged atomically, we have no certain method of ascertaining, in the present state of chemistry, how many atoms are contained in any compound. This difficulty is particularly felt with respect to those series of compounds in which half a proportion occurs; for as the idea of half an atom is inconsistent with the atomic theory, such an arrangement of the atoms must be imagined, as shall avoid the occurrence of a fraction. The mode of accomplishing this object may be exemplified in reference to the oxides of lead and iron, the constituents of which were mentioned on a former occasion. (Page 168.) The oxides of lead may either be regarded as composed, the protoxide of one atom of lead and one atom of oxygen, the deutoxide of two atoms of lead and three atoms of oxygen, and the peroxide of one atom of lead and two atoms of oxygen; or they may be viewed as compounds, the protoxide of one atom of lead and two atoms of oxygen, the deutoxide of one atom of lead and three atoms of oxygen, and the peroxide of one atom of lead and four atoms of oxygen. In like manner the oxides of iron are either composed, the protoxide of one atom of iron and one atom of oxygen, and the peroxide of two atoms of iron and three atoms of oxygen; or the protoxide of one atom of iron and two atoms of oxygen, and the peroxide

of one atom of iron and three atoms of oxygen. The uncertainty attending these atomic speculations cannot be more forcibly evinced than by the fact, that Berzelius two or three years ago regarded all the stronger bases, such as the alkalies, alkaline earths, and the protoxides of several of the common metals, as composed of one atom of metal and two atoms of oxygen; but that he has subsequently abandoned this view, and now believes the very same substances to contain one atom of metal and one atom of oxygen. Such sudden changes cannot take place without producing material confusion; and they tend to show that the science is not yet so far advanced as to admit of the atomic constitution of bodies being settled on permanent principles. Until the period when this desirable object may be accomplished, it is to be hoped that chemists will persevere in the practice, which is now universal in Britain and adopted by several distinguished philosophers on the continent, of stating the combining proportions of bodies as nearly as possible in the way supplied by analysis, instead of doubling some numbers and halving others to make them conformable to some favourite hypothesis of the moment.

Mr. Dalton supposes that the atoms of bodies are 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.

⊙ Hydrogen
◑ Nitrogen.
○ Oxygen.
● Carbon.

BINARY COMPOUNDS.

○ ⊙ Water.
○ ● Carbonic oxide.

TERNARY COMPOUNDS.

○ ⊙ ○ Deutoxide of hydrogen.
○ ● ○ Carbonic acid.
&c. &c. &c.

All substances, containing only two atoms, he called binary compounds, those composed of three atoms ternary compounds, of four, 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.

It is but justice to the memory of the late Mr. Higgins of Dublin, 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 two 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 Mr. Higgins do not appear to have had the slightest connexion with the subsequent views of Mr. Dalton. Indeed, from facts which have come to my knowledge relating to the history of Mr. Dalton's discovery, I am satisfied that this philosopher had not seen the work of Mr. Higgins till after he had given an account of his own doctrine. The observations of Mr. Higgins, therefore, though highly creditable to his sagacity, do not affect Mr. 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 Mr. Higgins himself attached no particular interest to them. Mr. Dalton's chief merit lies in the discovery of the Laws of Combination, a discovery which is solely and indisputably his; but in which he would have been anticipated by Mr. Higgins, had that chemist perceived the importance of his own opinions.

ON THE THEORY OF VOLUMES.

Soon after the publication of the New System of Chemical Philosophy in 1808, in which work Mr. Dalton explained his views of the atomic constitution of bodies, a paper appeared in the second volume of the *Mémoires d'Arcueil*, by M. Gay-Lussac, on the "Combination of Gaseous Substances with one another." He there proved that gases unite together by volume in very simple and definite proportions. In the combined researches of himself and M. Humboldt, those gentlemen found that water is composed precisely of 100 measures of oxygen and 200 measures of hydrogen; and M. Gay-Lussac, being struck by this peculiarly simple proportion, was induced to examine the combinations of other gases with the view of ascertaining if any thing similar occurred in other instances.

The first compounds which he examined were those of ammoniacal gas with muriatic, carbonic, and fluoboric acid gases. 100 volumes of the alkali were found to combine with precisely 100 volumes of muriatic acid gas, and they could be made to unite in no other ratio. With both the other acids, on the contrary, two distinct combinations were possible. These are

100	Fluoboric acid gas, with	100	ammoniacal gas.
100	do.	200	do.
100	Carbonic acid gas	100	do.
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 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 M. 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 the true gases merely, but to vapours likewise. For example, sulphuretted hydrogen, sulphurous acid, and hydriodic acid gases are composed of

100 vol.	hydrogen	and 100	vol.	vapour of sulphur.
100	oxygen	100	. .	sulphur.
100	hydrogen	100	. .	iodine.

There are very good grounds to suppose, also, that solid bodies which are fixed in the fire would, if in the form of vapour, be subject to the same law. By a method which will shortly be explained, it may be calculated that the specific gravity of the vapour of carbon is 0·4166, atmospheric air being unity. Now, if we assume that carbonic acid is formed of 100 volumes of oxygen, and 100 volumes of the vapour of carbon, condensed into the space of 100 volumes, the specific gravity of carbonic acid will be 1·1111 (the sp. gr. of oxygen) + 0·4166 = 1·5277, which is the precise number determined by experiment. Again, it follows from our assumption, that carbonic acid is composed by weight of

Oxygen	1·1111	. 16 or 2 proportionals.
Carbon	0·4166	. 6 or 1 proportional.

and this deduction is confirmed by analysis.

If we assume that carbonic oxide is composed of 50 volumes of oxygen and 100 volumes of the vapour of carbon, condensed into the space of 100 volumes, then its specific gravity will be 0·5555 (half the sp. gr. of oxygen) + 0·4166 = 0·9721; and its composition will be

Oxygen	0·5555	. 8 or 1 proportional.
Carbon	0·4166	. 6 or 1 proportional.

both of which results have been determined by other methods.

The compounds of carbon and hydrogen are equally illus-

trative of the same point. If light carburetted hydrogen is formed of 200 volumes of hydrogen and 100 volumes of the vapour of carbon, condensed into 100 volumes, its specific gravity should be 0.1388 (twice the sp. gr. of hydrogen) +0.4166=05554; and its composition by weight will be

Hydrogen	.	0.1388	. 2 or 2 P.
Carbon . .		0.4166	. 6 or 1 P.

If olefiant gas is composed of 200 volumes of hydrogen and 200 volumes of the vapour of carbon, its specific gravity will be 0.1388+0.8332=9720; and its composition by weight must be

Hydrogen	.	0.1388	. 2 or 2 P.
Carbon	.	0.8332	. 12 or 2 P.

Both of these results have been ascertained by analysis.

Another remarkable fact established by M. Gay-Lussac in the same paper is, that the diminution of bulk which gases frequently suffer in combining, is also in a very simple ratio. Thus, the 4 volumes of which ammonia is constituted, (3 volumes of hydrogen and 1 of nitrogen) contract to one-half or two volumes when they unite. There is a contraction to two-thirds in the formation of nitrous oxide gas. The same applies to the combination of gases and vapours. There is contraction to a half in the formation of sulphuretted hydrogen; and to a third in that of sulphurous acid. The instances just quoted relative to the vapour of carbon confirm the same remark. There is a contraction to two-thirds in carbonic oxide; to a half in carbonic acid; to a third in light carburetted hydrogen; and to a fourth in olefiant gas.

The rapid progress which chemistry has made within the last few years is in great measure attributable to the ardour with which pneumatic chemistry has been cultivated. That very department, which at first sight appears so obscure and difficult, has afforded a greater number of leading facts than any other; and the law of Gay-Lussac, by giving an additional degree of precision to such researches, as well as from its own

intrinsic value, is one of the brightest discoveries that adorn the annals of the science. The practice of estimating the quantity in weight of any gas, by measuring its bulk or volume, of itself susceptible of much accuracy, is rendered still more precise and satisfactory by the operation of this law. It will not perhaps be superfluous, therefore, to exemplify the method of reasoning employed in these investigations by a few examples; which will serve, moreover, as a useful specimen to the beginner of the nature of chemical proof.

One essential element in every inquiry of this kind, which is indeed the keystone of the whole, is a knowledge of the specific gravity of the gases. But it is exceedingly difficult to determine the specific gravity of gases with perfect accuracy; for not only do slight alterations of temperature and pressure during the experiment affect the result, but the presence of a little watery vapour, atmospheric air, or other impurity, may cause material error, especially when the gas to be weighed is either very light or very heavy. The specific gravity of important gases has, accordingly, been stated differently by different chemists, and there is none in regard to which more discordant statements have been made than that of hydrogen gas. Fortunately we possess the power of correcting the results, and of testing their accuracy, by other means which are less liable to error. The specific gravity of oxygen, hydrogen, and nitrogen gases, air being 1, may be thus estimated:

Oxygen . .	1.1111
Hydrogen . .	0.0694
Nitrogen . .	0.9722

It has been proved by analysis that 200 volumes of ammoniacal gas are composed of 300 volumes of hydrogen and 100 volumes of nitrogen, a fact from which the specific gravity of that alkali may be calculated.

$$\text{Thus, } 0.9722 + (0.0694 \times 3) = 1.1804$$

$\frac{1.1804}{4} = 0.2951$, the specific gravity which ammoniacal gas should have, if its constituent gases suffered no contraction; but as they contract to one-half, the real specific gravity is

double what it otherwise would be, that is 0.5902. Now, if by weighing a certain quantity of ammoniacal gas, the same number is procured for its specific gravity, there is a very strong presumption that the elements of the calculation are correct.

Nitric oxide is composed of 100 volumes of nitrogen and 100 volumes of oxygen, united without any contraction; and forming, consequently, 200 volumes of the compound. Its specific gravity must, therefore, be the mean of its components, or $\frac{1.1111 + 0.9722}{2} = 1.0416$. The correspondence of this number with that found by weighing the gas itself, affords powerful testimony that the density of oxygen and nitrogen gases has been correctly determined. It is obvious, indeed, that the calculated results, as being free from the unavoidable errors of manipulation, must be the more accurate, provided the elements of the calculation may be trusted.

Dr. Henry has proved by careful analysis that 100 volumes of light carburetted hydrogen gas, a compound of carbon and hydrogen, require 200 volumes of oxygen for complete combustion; that water and carbonic acid are the sole products; and that the latter amounts precisely to 100 volumes. From these data, the proportions of its constituents and its specific gravity may be determined. For 100 volumes of carbonic acid contain 100 volumes of the vapour of carbon, which must have been present in the carburetted hydrogen, and 100 volumes of oxygen. One half of the oxygen originally employed is thus accounted for; and the remainder must have combined with hydrogen. But 100 volumes of oxygen require 200 volumes of hydrogen for combination, all of which must likewise have been contained in the carburetted hydrogen. Hence it is inferred, that 100 volumes of light carburetted hydrogen are composed of 100 volumes of the vapour of carbon and 200 volumes of hydrogen. Its specific gravity must therefore be 0.5554; that is, 0.4166 (the sp. gr. of carbon vapour) + 0.1388 or twice the sp. gr. of hydrogen gas.

Having ascertained that light carburetted hydrogen gas is composed of two measures of hydrogen and one of the vapour of carbon, it is easy to calculate the proportion of its constituents by weight. For this purpose we need only multiply the

bulk of the gases by their respective specific gravities. Thus $200 \times 0.0694 = 13.88$, and $100 \times 0.4166 = 41.66$. Hence light carburetted hydrogen is composed by weight of

Carbon . .	41.66 .	6
Hydrogen . .	13.88 .	2

The theory of volumes has very considerable resemblance to the laws of combination by weight developed by Mr. Dalton; for the multiple proportions are as apparent in the former as in the latter. But there is one remarkable difference between them. The weight of either element of a compound has no apparent dependence on that of the other. Thus 6 parts of carbon and 8 of oxygen constitute carbonic oxide, and 8 parts of oxygen and 14 of nitrogen are contained in nitrous oxide; but 8 is not a multiple by any whole number of 6, nor 14 of 8. On the other hand, the elements of a compound are always united by volume in the ratio of 1 to 1, 1 to 2, 1 to 3, and so on. This simple ratio is peculiarly interesting, because it appears to indicate a close correspondence in the size of the atoms of gaseous bodies. It naturally suggests the idea that this peculiarity may arise from the atoms of elementary principles possessing the same magnitude. On this supposition, equal measures of such substances in the gaseous form, at the same temperature and pressure, would probably contain an equal number of atoms; and the specific gravity of these gases would depend on the relative weight of their atoms. The same numbers which indicate the specific gravity of elementary principles in the gaseous state, would then express the relative weights of their atoms; so that the latter would be ascertained by means of the former, or the atomic weight of a solid or liquid represent the specific gravity of its vapour. The proportional numbers adopted by Sir H. Davy in his Elements of Chemical Philosophy, and the atomic weights employed by Berzelius in his System of Chemistry, were selected in accordance with this view. Thus water being formed of 2 measures of hydrogen and 1 measure of oxygen, is believed by Berzelius to consist of 2 atoms of the former and 1 atom of the latter; and for a similar reason, he regards protoxide of nitrogen as a compound of 2 atoms of nitrogen and 1 atom of oxygen. The

atoms and volumes of the four elementary gases, oxygen, chlorine, hydrogen, and nitrogen, are thus made to coincide with each other. This method, though perhaps preferable to any other, has not hitherto been generally followed. Most chemists consider water, protoxide of chlorine, and protoxide of nitrogen, as containing one atom of each of their elements; and consequently, as these compounds consist of 1 measure of oxygen united with 2 measures of the other constituent, the atom of hydrogen, chlorine, and nitrogen is supposed to occupy twice as much space as an atom of oxygen. An atom of oxygen is therefore represented by half a volume, and an atom of the other three gases by a whole volume.

Dr. Prout, in an ingenious Essay "On the Relation between the Specific Gravities of Bodies in their Gaseous State and the Weights of their Atoms," published in the 6th volume of the Annals of Philosophy, (Old Series, p. 321,) considers it probable that the same relation, which is thought to exist between the atoms and volumes of the four elementary gases, may hold equally of the vapours of the other elements. Thus in representing the atom of oxygen by half a volume, he believes the atoms of the other elementary principles, such as iodine, carbon, and sulphur, correspond to a whole volume of their vapour. From this he has deduced a mode of calculating the specific gravity of any vapour from the atomic weight of the body which yields it. The rule consists in multiplying 0.5555, or half the specific gravity of oxygen gas, by the atomic weight of any element, and dividing the product by the atomic weight of oxygen; the quotient is the specific gravity of the vapour. For example, the specific gravity of the vapour of carbon is thus found: As

$$8 : 6 : : 0.5555 : 0.4166$$

in which 8 is the atomic weight of oxygen, 6 that of carbon, and 0.4166 the specific gravity of the vapour of carbon. The same relation which exists between the atomic weight of oxygen and half its specific gravity, subsists between the atomic weight of any other element, and the specific gravity of its vapour. Though the accuracy of Dr. Prout's views has not yet been established by experiment, his formula may often be employed with advantage.

In the essay above quoted, Dr. Prout has advanced several instances, in which the equivalents or atomic weights of bodies appear to be multiples by a whole number of the atomic weight of hydrogen gas; and he threw out a conjecture that the same relation may perhaps exist in other cases. This subject has since been experimentally investigated by Dr. Thomson, who has declared after a most elaborate inquiry, the fruits of which are contained in his "First Principles of Chemistry," that the law is of universal application; that the atomic weights of all the simple substances which he has examined, are not only multiples by a whole number of the atomic weight of hydrogen, but with a few exceptions of two atoms of hydrogen. But in opposition to this statement, Berzelius insists that the law is inconsistent with the results of his analyses, and that the experiments of Dr. Thomson are inaccurate. My own observations have satisfied me, that some of the fundamental experiments of Dr. Thomson are faulty; and I cannot hesitate in concluding that the question is just as far from being decided as ever.

ON THE THEORY OF BERZELIUS.

It is well known that the celebrated Professor of Stockholm has for many years devoted himself to the study of the laws of definite proportions, and that he has been led to form a peculiar hypothesis, by way of generalizing the facts which his industry had collected. To give a detailed account of his system does not fall within the plan of this work; but considering the extraordinary number of facts with which this indefatigable chemist has enriched the science, and especially this department, I think it proper to give a short account of his doctrines, offering at the same time a few comments upon them.

Berzelius mentions in the historical introduction to his treatise on the "Theory of definite Proportions," that he commenced his researches on the subject in the year 1807; and that they originated in the study of the works of Richter. From Richter's explanation of the fact, that when two neutral salts decompose one another, the resulting compounds are likewise neutral, he perceived that one good analysis of a few salts would furnish the means of calculating the composition

of all others. He accordingly entered upon an inquiry, which was at first limited in its object; but as he proceeded, his views enlarged, and advancing from one step to another, he at length set about determining the laws of combination in general. In perusing his account of the investigation, we are at a loss whether most to admire the number of exact analyses which he performed, the variety of new facts he determined, his acuteness in detecting sources of error, his ingenuity in devising new analytical processes, or the persevering industry which he displayed in every part of the inquiry. But it is at the same time impossible to suppress regret, that, instead of forming a complex system of his own, he did not adopt the more simple views of Mr. Dalton. This he might have done with very great propriety; since the fundamental laws which he discovered are, with very little exception, either identical with those previously pointed out by the British philosopher, or the direct result of their operation.

Berzelius assumes, with Mr. Dalton, the existence of ultimate indivisible atoms, to the combination of which with one another the laws of chemical proportion are owing.

The first law of Berzelius is the following. "One atom of one element unites with 1, 2, 3, or more atoms of another element." This coincides with the law of Mr. Dalton, and requires no comment, further than that it has been amply confirmed by the labours of Berzelius. The second is, that "two atoms of one element combine with three and five atoms of another." These are the two laws which regulate the union of simple or elementary atoms.

The combination of compound atoms with each other obeys another law, and is confined within still narrower limits. "Two compounds which contain the same electro-negative body, always combine in such a manner that the electro-negative element of the one is a multiple by a whole number of the same element of the other." Thus, for instance, if two oxidized bodies unite, the oxygen of one is a multiple by a whole number of the oxygen in the other. Of this various examples may be given. Hydrate of potash is composed of

Potash 48, the oxygen of which is 8.
Water 9, do. 8.

In like manner, if two acids or two oxides combine, the same will be observed.

In the earthy minerals, which often contain several oxides, the same law is found to prevail with great uniformity.

The composition of the salts is likewise under its influence. Carbonate of potash, for example, is composed of

Carbonic acid	22,	the oxygen of which is	16.
Potash .	48,	do.	8.

and sulphate of potash of

Sulphuric acid	40,	the oxygen of which is	24.
Potash .	48,	do.	8.

Berzelius has remarked, that the nitrates, phosphates, and arseniates, may in some instances prove exceptions to the law. There is also a similar relation, in salts which contain water of crystallization, between the oxygen of the base of the salt and that of the water. For instance, crystallized sulphate of soda is composed of

Sulphuric acid	40.		
Soda .	32,	the oxygen of which is	8.
Water .	90,	do.	80.

Double salts are also influenced by the same law. In tartrate of potash and soda, for example, the oxygen of the potash is exactly equal to the oxygen in the soda; and the oxygen in the tartaric acid, which neutralizes the potash, is equal to that of the soda.

But this is not all that Berzelius has remarked with respect to the constitution of the salts. He observes that in each series of salts, the same relation always exists between the oxygen of the acid and that of the base. In all the neutral sulphates this ratio is as one to three, as may be seen in the sulphates of soda and potash. In the carbonates, the oxygen of the acid is double, and in the bicarbonates quadruple the oxygen of the base.

The existence of these remarkable laws was discovered by

Berzelius at a very early period of his researches; and he mentions, that as subsequent observation, during the course of several years, has not afforded a single exception to them, he now regards them as universal. He accordingly places unlimited confidence in their accuracy, and is in the habit of calculating the composition of bodies on this principle.

It will of course be interesting to inquire into the cause of these phenomena; to ascertain if there is any property peculiar to oxygen, or other negative electrics, which may give rise to them. Berzelius himself says that "the cause is involved in such deep obscurity, that it is impossible at the present moment to give a probable guess at it." I have the misfortune to differ entirely from Berzelius on this question. So far from being obscure, it is perfectly intelligible, and is precisely what may be anticipated from the present state of chemical knowledge. Most of the salts called neutral sulphates are composed of one proportion or one atom of sulphuric acid, and one proportion of some protoxide. This is the case with all the alkaline and earthy sulphates, and with several of the common metals, such as lead, zinc, and iron. Now, one proportion of sulphuric acid is composed of

Sulphur 16 or 1 proportion,
Oxygen 24 or 3 proportions;

and every protoxide of

Metal — or 1 proportion,
Oxygen 8 or 1 proportion.

Hence a number of laws may be deduced which must hold in every sulphate of a protoxide.

1. The oxygen of the acid is a multiple of that of the base.

2. The acid contains three times as much oxygen as the base.

3. The sulphur of the acid is just double the oxygen of the base.

4. The acid itself is five times as much as the oxygen of the base.

Metallic sulphurets are frequently composed of one propor-

tion of each element; and should oxidation ensue, so that the sulphur is converted into sulphuric acid, and the metal into a protoxide, they will be in the exact proportion for forming a neutral sulphate. Berzelius has proved by analysis that this happens frequently, and he is disposed to convert it into a general law.

Again, the carbonates are composed of one proportion of carbonic acid, and one proportion of some protoxide. But one proportion of carbonic acid is composed of

Carbon 6, or 1 proportion,
Oxygen 16, or 2 proportions;

and every protoxide of

Metal — or 1 proportion,
Oxygen 8, or 1 proportion:

It is inferred, therefore, that in all the carbonates, the oxygen of the acid is exactly double that of the base; and the same mode of reasoning is applicable to the various genera of salts. These few examples will suffice to show, that the phenomena which seemed so obscure to Berzelius, are rendered quite obvious by the Daltonian method. We perceive, moreover, that no constant ratio can exist between the quantity of oxide and that of the acid or oxygen of the acid; and the reason is, because the atomic weights of the metals in general are different. But this view of the subject answers another useful purpose; it enables us to see whether the law of Berzelius is or is not universal. This subject has been ably discussed in his "First Principles" by Dr. Thomson, who has adduced several instances where, from the constitution of the combining substances, the law of Berzelius does not and cannot apply.

An attempt has been made within these few years to determine the atomic constitution of minerals, an inquiry in which Berzelius has highly distinguished himself. The composition of minerals must of course be influenced by the usual laws of combination, though there are sometimes obstacles in the way of discovering it. In the compounds made artificially, chemists possess the power of having each constituent perfectly

pure; but, unfortunately, we cannot always command the same condition with respect to natural productions. The materials of which a mineral is composed, once formed part of some heterogeneous fluid or semifluid mass; and in assuming the solid form they are very likely to have enclosed within them some substance which is not, chemically considered, an essential ingredient of the mineral. The result of chemical analysis, accordingly, does not always give us a view of the actual constitution of a mineral species; some substances are often detected which are foreign to it, and the chemist must exercise his judgment in determining what is and what is not essential. Now nothing is so well calculated to direct him as a knowledge of the laws of combination; but as a great discretionary power is in his hands, it is important that his mode of investigation should be the simplest possible, and that his rules should be founded on well-established principles, which involve nothing hypothetical. It is but very lately that due care has been bestowed in selecting sufficiently pure specimens for examination, or in performing the analyses themselves with the precision necessary for determining the chemical constitution of minerals. It were much to be wished, that the first essays in this difficult field should be confined as much as possible to such minerals as contain but few substances, and which occur in distinct transparent crystals.

We are indebted to Berzelius for this mode of studying the composition of minerals; and certainly if skill in analytical investigation could encourage any one to make the attempt, none could undertake it with greater chance of success than the indefatigable Professor of Stockholm. In the analytic part of the inquiry, the province in which this celebrated chemist shines pre-eminent, his labours have been greatly conducive to the interests of science; but it is to be regretted that his facts, themselves simple and unchangeable, are too often complicated by calculations founded on theoretical views which are liable to change. These views it is foreign to the purpose of this work to develope; but the reader will find an able account of them, and of the symbols which Berzelius has devised for expressing the atomic constitution of minerals, in the ninth volume of the Annals of Philosophy, N. S., by Mr. Children.

SECTION III.

OXYGEN.

Oxygen gas was discovered by Priestley in 1774, and by Scheele a year or two after, without previous knowledge of Priestley's discovery. Several appellations have been given to it. Priestley named it *Dephlogisticated air;* it was called *Empyreal air* by Scheele, and *Vital air* by Condorcet. The name it now bears, derived from the Greek words οξὺς *acid* and γεννάω I *generate*, was proposed by Lavoisier, from the supposition that it is the sole cause of acidity.

Oxygen gas may be obtained from several sources. The peroxide of manganese, lead, and mercury, nitre, and chlorate of potash, yield it in large quantity when they are exposed to a red heat. The substances commonly employed for the purpose are peroxide of manganese and chlorate of potash. 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 earthen-ware; or by putting it, in the state of 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	28 or 1 prop.	+ 8	= 36
Deutoxide	28	+ 12	= 40
Peroxide	28	+ 16	= 44

On applying a red heat to the last, it parts with half a proportion of oxygen, and is converted into the deutoxide. Every 44 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. The action of sulphuric acid is different. The peroxide loses a whole proportion of oxygen, and is converted into the protoxide, which

unites with the acid, forming a sulphate of the protoxide of manganese. Every 44 grains of peroxide must consequently yield 8 grains of oxygen and 36 of protoxide, which by uniting with one proportion (40) of the acid, forms 76 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 muriatic or nitric acid; but when oxygen of great purity is required, it is better to obtain it from chlorate of potash. 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 theory of the decomposition is as follows. Chlorate of potash is composed of

Chloric acid	76 or 1 proportion.
Potash	48 or 1 proportion.
	124

These compounds are thus constituted:—

Chlorine .	36 or 1 prop.	Potassium	40 or 1 prop.
Oxygen .	40 or 5 prop.	Oxygen	8 or 1 prop.
Chloric acid	76 or 1 prop.	Potash	48 or 1 prop.

The chlorine and potassium are both separated form oxygen, and then unite together. So that 124 grains of the salt are resolved into 76 grains of chloride of potassium, and 48 grains, or 141 cubic inches, of pure oxygen.

Oxygen gas is colourless, has neither taste nor smell, is not chemically affected by the imponderables, refracts light very feebly, and is a non-conductor of electricity. It is the most

perfect negative electric that we possess, always appearing at the positive pole when any compound which contains it is exposed to the action of galvanism. It emits light, as well as heat, when suddenly and forcibly compressed. When not united with other ponderable matter, it is always in the form of gas; but even in this its purest state it is probably combined, as is most likely true of all elementary principles, with heat, light, and electricity.

Oxygen gas is heavier than atmospheric air. Chemists differ as to its precise weight; but according to the experiments of Dr. Thomson, whose estimate is generally adopted in Britain, 100 cubic inches of oxygen, when the thermometer is at 60° F, and the barometer stands at 30 inches, weigh 33·888 grains. Its specific gravity is hence regarded as 1·1111.

Oxygen gas is very sparingly absorbed by water, 100 cubic inches of that liquid dissolving only three or four of the gas. It has neither acid nor alkaline properties; for it does not change the colour of blue flowers, nor does it 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 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 want 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 is exemplified by the rusting of iron when exposed to a moist atmosphere. 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 properly secured by a cork, the light will in a 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 gas. 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. The 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 suffers only diminution of volume, 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. It has also in-

creased 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 requisite care, it is constantly found that the combustible matter weighs more after than before combustion; and that 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. It may therefore be anticipated that oxygen is consumed 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 is necessary to respiration, in a state of purity it is deleterious. When an animal, as a rabbit for example, is supplied with an atmosphere of 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, which continue to increase till death supervenes.

ON THE 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 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 Dr. Black's Theory of latent caloric. Heat is always evolved, whenever 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 caloric 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 less quantity of combined caloric, or has a less specific caloric, 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 caloric 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 caloric than its elements did before combination, it is obvious that heat will, in that case, be disengaged. But if this is the sole cause of the phenomenon, it follows that a rise of temperature ought always to be preceded by a corresponding diminution of capacity for caloric, and that 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, (Annales de Chim. et de Phys. vol. x.) that the degree of heat developed during combination, bears no relation to the specific caloric of the combining substances; and that in the majority of cases, the evolution of heat is not attended by any diminution in the capacity of the compound. It is a well known fact, that increase of temperature frequently attends chemical action, though the products contain much more insensible caloric than the substances from which they are 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 caloric.

These circumstances leave no doubt that the evolution of caloric 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 capacity 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; and he believes 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 phial.—But such an opinion can only be held by those who adopt the electro-chemical theory; and even admitting the accuracy of this doctrine, the reasoning founded on it by Berzelius appears to me inadmissible. For, according to the theory, the two elements of a compound retain their peculiar state of excitement. This condition is essential to the continuance of the union, and therefore the act of combination is not analogous to the discharge of a Leyden phial. The equilibrium is restored in one case, but not in the other.

The caloric 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 Mr. 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.

Mr. Dalton further states that generally the combustible gases give out heat nearly in proportion to the oxygen which they consume.

In the thirty-seventh volume of the An. de Ch. et Ph. page 180, M. Despretz has given a notice of some experiments on the heat developed in combustion. 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 caloric 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 Mr. Dalton.

SECTION IV.

HYDROGEN.

This gas was formerly termed *inflammable* air, from its combustibility, and *phlogiston* from the supposition that it was the matter of heat; but the name *hydrogen*, derived from ὑδωρ *water*, has now become general. Its nature and leading properties were first pointed out in the year 1766 by Mr. Cavendish. (Philos. Trans. LVI. 144.)

Hydrogen gas may be easily procured 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 most 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 sulphuretted hydrogen, and probably with the same im-

* The mode of collecting gases, together with the apparatus employed for that purpose, will be described in the fourth part of this work.

purities, though in a less degree, which 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 potash. To obtain hydrogen of great purity, distilled zinc should be employed.

Hydrogen is a colourless gas, and has neither odour nor taste when perfectly pure. It is a powerful refractor of light. Like oxygen, it cannot be resolved into more simple parts, and, like that gas, has hitherto resisted all attempts to compress it into a liquid. It is the lightest body in nature, and is consequently the best material for filling balloons. From its extreme lightness it is difficult to ascertain its precise density by weighing, because the presence of minute quantities of common air or watery vapour occasions considerable error. From the composition of water hydrogen gas is inferred to be sixteen times lighter than oxygen; and the weight of 100 cubic inches at 60°, and thirty inches of the barometer, should therefore be $\frac{33{\cdot}888}{16}$, or 2·118 grains. Its specific gravity is consequently 0·0694, as stated some years ago by Dr. Prout.

Hydrogen does not change the blue colour of vegetables. It is sparingly absorbed by water, 100 cubic inches of that liquid dissolving about one and a half of the gas. It cannot support respiration; for an animal soon perishes when confined in it. 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, the light disappears on the instant.

Hydrogen gas is inflammable in an eminent degree, though, like other combustibles, it requires the aid of a supporter for enabling its combustion to take place. This is exemplified by the experiment above alluded to, in which the gas is kindled by the flame of the candle, but burns 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 quan-

tity of atmospheric 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 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, explodes from all the causes above enumerated. M. 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. I find that 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 *.

* 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. lxxxii.; Sir H. Davy's work on Flame;

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 caloric 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. Mr. Dalton fixes the quantity 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 blowpipe, was contrived by Mr. Newman, and employed by the late Professor Clarke in his experiments on the fusion of refractory 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

Dr. Henry's Essay in the Philosophical Transactions for 1824; and a paper by myself in the Edinburgh Philosophical Journal for the same year.

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. But this apparatus is rarely necessary in chemical researches. A very intense heat, quite sufficient for most purposes, 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.

Water is the sole product of the combustion of hydrogen gas. For this important fact we are indebted to Mr. Cavendish. 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.

It will soon appear that a knowledge of the exact proportions in which oxygen and hydrogen gases unite to form water, is a necessary element in many chemical reasonings. Its composition by volume was demonstrated very satisfactorily by Messrs. Nicholson and Carlisle, in their researches on the chemical agency of galvanism. On resolving water into its elements by this agent, 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 Eudio-

metry, 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 de Ph. vol. xv.) that 100 parts of pure water consist of 88.9 of oxygen and 11.1 of hydrogen. Now,

$$11.1 : 88.9 :: 1 : 8.009$$

which is so near the proportion of 1 to 8 as to justify the adoption of that ratio. Hence, the constitution of water by weight and measure, may be thus stated:

	By Weight.	By Volume.
Oxygen	8	1
Hydrogen	1	2

These are the data from which it was inferred that oxygen gas is just 16 times heavier than hydrogen. The atomic weights of oxygen and hydrogen are deduced from the same analysis. As no compound of these substances is known which has a less proportion of oxygen than water, it is supposed to contain one atom of each of its constituents. This view of the atomic constitution of water appears to be justified by the strong affinity which its elements evince for each other, as well as from the proportions with which they respectively combine with other bodies. Consequently, re-

garding the atom of hydrogen as unity, 8 will be the relative weight of an atom of oxygen.

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. 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
Iron . . .	28
Protoxide of iron (28 iron + 8 oxygen)	36
Sulphate of the protoxide of iron (40 + 36)	76

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 grains of sulphuric acid, yielding 76 of sulphate of the protoxide of iron. A similar calculation may be employed when zinc is used, merely by substituting the atomic weight of zinc (34) 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 appearance of 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, only 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.

Water is a transparent colourless liquid, which has neither smell nor taste. It is a powerful refractor of light, conducts heat very slowly, and is an imperfect conductor of electricity. The experiments of Oersted and Culladon and Sturm have proved that water is compressible by great pressure; and according to the latter observers, its absolute diminution for each atmosphere is 51.3 millionths of its volume. (An. de Ch. et Ph. xxxvi. 140.) The relations of water, with respect to caloric, are highly important; but they have already been discussed in the first part of the work. The specific gravity of water is 1, the density of all solid and liquid bodies being referred to it as a term of comparison. One cubic inch, at 62° F. and 30 inches of the barometer, weighs 252.458 grains; so that it is 831 times heavier than atmospheric air.

Water is one of the most powerful chemical agents which we possess. Its agency is owing partly to the extensive range of its own affinity, and partly to the nature of its elements. The effect of the last circumstance has already appeared in the process for procuring hydrogen gas; and indeed there are few complex chemical changes 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 *hy-*

drates. Thus, concentrated sulphuric acid is a compound of one equivalent of the real dry acid and one equivalent of water; and its proper name is *hydrous sulphuric acid*, or *hydrate of sulphuric acid.* The adjunct *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.

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 in oxygen gas than atmospheric air. According to the experiments of 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 of that gas. All water which has once fallen on the ground becomes impregnated with more or less earthy or saline matters, and it 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 Dr. Henry's Chemistry, shows the absorbability of different gases by water, deprived of all its air by ebullition.

100 cubic inches of such water, at the mean temperature and pressure, 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 Mr. Dalton and Dr. Henry for nitrous oxide, according to

the experiments of Sir H. Davy, is considerably beyond the truth.

DEUTOXIDE OF HYDROGEN.

The deutoxide or peroxide of hydrogen, was discovered by M. Thenard in the year 1818. Before describing the mode of preparing this compound, it must be observed that there are two oxides of barium; and that when the peroxide of that metal is put into water containing free muriatic acid, oxygen gas is set at liberty, and the peroxide is converted into protoxide of barium or baryta, which combines with the acid. 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 M. Thenard*; the general directions are the following:— To six or seven ounces of water add so much pure concentrated muriatic 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 deutoxide of barium 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; in order that the muriatic acid, which had been combined with that earth, may be completely separated from it. Another portion of deutoxide of barium, amounting to 185 grains, is then put into the liquid; the free muriatic acid instantly acts upon it, and as soon as it is dissolved, the baryta is again converted into 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 muriatic acid which has served to decompose

* In the An. de Chim. et de Phys. vol. viii. ix. and x.; Annals of Philosophy, vol. xiii. and xiv.; and M. Thenard's Traité de Chimie.

the peroxide of barium during the whole process, is now removed by the cautious addition of sulphate of silver, and the sulphuric acid afterwards separated by solid baryta.

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 specific gravity 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.

Peroxide of hydrogen, of specific gravity 1.452, is a colourless transparent liquid without odour. It whitens the surface of the skin when applied to it, causes a prickling sensation, and even destroys its texture if the application is long continued. It acts in a similar manner on the tongue; in addition to which it thickens the saliva, and tastes like certain metallic solutions. Brought into contact with litmus and turmeric paper, it gradually destroys their colour and makes them white. It is slowly volatilized *in vacuo*, a fact which shows that its vapour is much less elastic than that ofwater. It preserves its liquid form at all degrees of cold to which it has hitherto been exposed. At the temperature of 59° F. it is decomposed, being converted into water and oxygen gas. For this reason it ought to be preserved in glass tubes surrounded with ice.

The most remarkable property of peroxide of hydrogen 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° F., and the sudden application of a higher temperature, as of 212° F., 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 the peroxide of hydrogen, 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.

Peroxide of hydrogen is decomposed at common temperatures by many of the metallic oxides. That some protoxides should have this effect, would be anticipated in consequence of their tendency to pass into a higher state of oxidation. The protoxide of iron, manganese, tin, cobalt, and others, act on this principle, and are really converted into peroxides. The peroxide 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, and I am not aware that any satisfactory explanation of it has been given, that some oxides decompose peroxide of hydrogen without passing into a higher degree of oxidation. The peroxide of silver, 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 caloric 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 muriatic, 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 potash, 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 and sulphurous acids, and sulphuretted hydrogen. 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. According to two careful analyses, conducted on this principle, 864 parts of the peroxide are composed of 466 of water, and 398 of oxygen gas. The 466 of water contain 414 of oxygen, whence it may be inferred that peroxide of hydrogen contains twice as much oxygen as water. A small deficiency of oxygen in this experiment was to be expected, owing to the difficulty of obtaining peroxide of

hydrogen perfectly free from water. The peroxide consists, therefore, of

Hydrogen	1	or	1 proportion.
Oxygen	16	or	2 proportions.

SECTION V.

NITROGEN.

The existence of nitrogen gas, as distinct from every other gaseous substance, appears to have been first noticed in the year 1772 by the late Dr. Rutherford of Edinburgh. Lavoisier discovered in 1775 that it is a constituent part of the atmosphere; and the same discovery was made soon after, or about the same time, by Scheele. Lavoisier called it *Azote* from *a privative*, and ζωὴ life, because it is unable to support the respiration of animals; but as it possesses this negative property in common with most other gases, the more appropriate term *nitrogen* has been since applied to it, from the circumstance of its being an essential ingredient of nitric acid.

Nitrogen is most conveniently prepared 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, phosphoric 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 potash. Several other substances may be employed for withdrawing oxygen from atmospheric air. A solution of proto-sulphate of iron, charged with deutoxide of nitrogen, absorbs the oxygen in the space of a few minutes. A stick of phosphorus produces the same effect in 24 hours, if exposed to a temperature of 60° F. A solution of sulphuret of potash or lime 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. Nitrogen gas may likewise be obtained by exposing a mixture of fresh muscle and nitric acid of specific gravity 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.

Pure nitrogen is a colourless gas, wholly devoid of smell and taste. It does not change the blue colour of vegetables, and 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. Water, when deprived of air by ebullition, takes up about one and a half per cent of it. Its specific gravity is 0.9722 *; and therefore 100 cubic inches at the mean temperature and pressure, will weigh 29.652 grains.

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 Sir H. 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 the only method of forming it is by the action of galvanism on a salt of ammonia, in

* This number is calculated on the assumption that air consists of one measure of oxygen and four of nitrogen, and that 1.1111 is the specific gravity of oxygen gas. See Thomson's First Principles, vol. i. p. 99.

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 levity, 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. Sir H. Davy accounts 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 Sir H. Davy's attempt to decompose that gas by aid of potassium, intensely heated by a galvanic current, attended with better success. Berzelius has defended the idea that nitrogen is a compound body on other principles; but as his arguments, though very ingenious, are merely speculative, they cannot be admitted as decisive of the question.

ON THE ATMOSPHERE.

The earth is every where 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 specific gravity is unity, being the standard with which the density of all gaseous sub-

stances is compared. It is 831 times lighter than water, and nearly 11.260 times lighter than mercury. The knowledge of its exact weight is an essential element in many physical and chemical researches. According to the experiments of Sir G. Shuckburgh Evelyn, 100 cubic inches of pure and dry atmospheric air, at 60° F. and 30 inches Bar., weigh exactly 30.5 grains; and this estimate, since supported by Mr. Rice, (An. of Ph. xiii. 339.) has of late years been adopted generally by British philosophers. But it is probably short of the truth. The observations of Dr. Henry and Mr. Dalton induce them to consider 31 grains as more accurate; and the elaborate, but as yet unfinished, inquiry of Dr. Prout has led him to the same conclusion. The estimate of 30.5, which is still adopted in this work, is therefore only retained provisionally, until all doubts on this important subject shall be finally removed.

The pressure of the atmosphere was first noticed early in the seventeenth 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 one inch square and 30 inches long has the same weight (nearly 15 pounds) as a column of water of the same size and 34 feet long, and as a column of air of the same size 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 11.260 inches or 938 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. (Daniell's Meteorological Essays, 2d 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. It has been found experimentally that 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 M. 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. (Edinb. Journal of Science, IV. 224.) It has, indeed, been recently stated by M. Despretz that the easily condensible gases vary from this law, diminishing under increase of pressure much more rapidly than atmospheric air; but the detail of his experiments has not, I believe, been published. (An. de Ch. et Ph. xxxiv. 335 and 443.) 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 va-

rious 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 Dr. 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 the late Dr. Wollaston in an Essay on the Finite Extent of the Atmosphere, published in the Philosophical Transactions for 1822. On the supposition that the atmosphere is unlimited, it would 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 Dr. Wollaston inferred from astronomical observations made by himself and Captain 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? Dr. 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. It is further argued, that this mode of reasoning is inapplicable unless the air be supposed to consist of ultimate atoms. Then only can each particle be separated from contiguous ones, to a degree sufficient for producing

that diminution of elasticity required by the argument; for if the material substance of air is divisible without limit, each particle will in itself contain an infinite number of other particles, the tension of which, in consequence of their proximity, should lead to their mutual separation. The production of fresh portions of air would on this principle be endless.

In order to account for the limited nature of the atmosphere, according to this principle, the air is inferred to consist of atoms; and if the inference be granted, it is fair to presume that matter in general has a similar constitution. The tendency of Dr. Wollaston's reasoning, therefore, is to demonstrate the truth of the atomic theory. But even admitting astronomical observations as conclusive against the existence of a solar atmosphere, and as proving by inference the extent of ours to be limited, it scarcely follows, I apprehend, that much weight can be attached to the argument. The tension or elasticity of gaseous matter is lessened by two causes, diminution of pressure, and reduction of temperature. The former alone was taken into account by Dr. Wollaston; but as the tendency of the latter to deprive gases of their elastic form is now fully established, it appears to me that the extreme cold which is admitted to prevail in the higher regions of the air, may of itself be a condition sufficient to put a limit to the extent of the atmosphere. Some very ingenious remarks have been made on this subject by Mr. Graham. (Philos. Mag. and Annals, i. 107.)

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. The air receives its caloric 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 specific caloric 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 300 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 potash, 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 twenty-seven measures of oxygen and seventy-three of nitrogen. The analysis of Scheele gave a somewhat higher proportion of oxygen. Priestley found that the quantity of

oxygen varies from twenty to twenty-five per cent; and Cavendish estimated it only at twenty. 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 Mr. Cavendish. The results of Scheele and Priestley are clearly referrible to this cause. It is now known that the processes they employed cannot be relied on, unless certain precautions are taken of which those chemists were ignorant. Recently boiled water absorbs nitrogen; and, consequently, if sulphuret of potash 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 alkaline sulphuret in cold unboiled water. The deutoxide 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 very 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 twenty or twenty-one volumes of oxygen, and eighty or seventy-nine of nitrogen. Dr. Thomson, whose analysis is the most recent, fixes the quantity of oxygen at twenty per cent; and the reasons he has assigned for regarding this estimate as more accurate than the other, appear satisfactory. The oxygen was determined (First Principles of Chemistry, vol. i. p. 97,) by 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. 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. Theodore 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. 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.)

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 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 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. It appears, on the contrary, that the composition of the 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 miasmata 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 in the simple ratio of one to four, which agrees perfectly with the law of combination by volume; and by weight they are as eight to twenty-eight, which corresponds to one proportion of oxygen and two 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 twenty per cent of oxygen. When oxygen and nitrogen gases are mixed together in the ratio of one to four, the mixture occupies precisely five 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. Chemists are divided on this subject between two opinions. It is conceived, according to one view, that the affinity of oxygen and nitrogen for one another, though insufficient to cause their combination when mixed together at ordinary temperatures, may 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 the late Dr. Murray. This doctrine, however, is not satisfactory. It is, indeed, quite 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:—Mr. Dalton took two cylindrical vessels, one of which was filled with carbonic acid, the other with hydrogen gas; the latter was placed perpendicularly over the other, and a communication was esta-

blished between them. In the course of a few hours hydrogen was detected in the lower vessel, and carbonic acid 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, with any shadow of reason, be ascribed to the action of affinity. It is well known that carbonic acid cannot be made to unite either with hydrogen, oxygen, or nitrogen; and, therefore, it is quite 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 Mr. 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. It follows, from this supposition, that one gas acts as a vacuum with respect to another; and, therefore, if a vessel full of carbonic acid be made to communicate with another of hydrogen, the particles of each gas 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 considerable support from some experiments, recently described in the Quarterly Journal of Science, N. S. VI. 74. by Mr. Graham of Glasgow. He

finds that the tendency of gases to be diffused varies with their density. When a gas is contained in a bottle which communicates with the air or any gaseous substance by means of a narrow tube, the rapidity of diffusion will depend on its density, being rapid if the gas is light, and less so if heavy. In fact, the diffusiveness of gases is inversely as some function, probably the square root, of their densities. This subject is still under investigation; but the explanation manifestly depends rather on the mechanical constitution of gases, than on any chemical principle.

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 by 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 and Davy, 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.

COMPOUNDS OF OXYGEN AND NITROGEN.

Chemists are acquainted with five compounds of nitrogen and oxygen, the composition of which, as deduced from the

researches of Gay-Lussac, Dr. Henry, and Sir H. Davy, is as follows:

	By Volume.		By Weight.	
	Nitrogen.	Oxygen.	Nitrogen.	Oxygen.
Nitrous oxide	100	50	14	8
Nitric oxide	100	100	14	16
Hyponitrous acid	100	150	14	24
Nitrous acid	100	200	14	32
Nitric acid	100	250	14	40

The first of these as containing the smallest quantity of oxygen, is regarded as a compound of one proportion, or according to the atomic theory of one atom, of each element. The atomic weight of nitrogen, that of oxygen being 8, will therefore be 14. The other four compounds must consequently be composed of one atom of nitrogen, united in the second with two, in the third with three, in the fourth with four, and in the fifth with five, atoms of oxygen.

PROTOXIDE OF NITROGEN.

This gas was discovered by Priestley, who gave it the name of *dephlogisticated nitrous air*. Sir H. Davy called it *nitrous oxide*. According to the principles of chemical nomenclature its proper appellation is *protoxide of nitrogen*. 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. The nitric oxide loses one half of its oxygen, and is converted into the protoxide. But the most convenient method of procuring it is by means of nitrate of ammonia. When this salt is exposed to a temperature of 400° or 500° F. it liquefies, bubbles of gas begin to rise from it, and in a short time brisk effervescence ensues, which continues till all the salt disappears. The nitrate of ammonia should be contained in a glass retort, and the heat be applied by means of a lamp, placed at such a distance below it as to maintain a moderately rapid evolution of gas.

The sole products of this operation, when carefully conducted, are water and protoxide of nitrogen. The theory of the process admits of an easy explanation.

Nitrate of ammonia is composed of

Nitric acid	54 parts, or one proportion.
Ammonia	17 parts, or one proportion.
	71

These compounds are thus constituted:—

Nitrogen	14 or 1 prop.	Nitrogen	14 or 1 prop.
Oxygen	40 or 5 prop.	Hydrogen	3 or 3 prop.
Nitric Acid	54 or 1 prop.	Ammonia	17 or 1 prop.

By the action of heat these elements arrange themselves in a new order. The hydrogen 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. The decomposition of 71 grains of the salt will therefore yield

Water . .	27 or 3 pr.	Oxygen	24 or 3 pr.
		Hydrogen	3 or 3 pr.
Protoxide of Nitrogen	44 or 2 pr.	Oxygen	16 or 2 pr.
		Nitrogen	28 or 2 pr.
	71		

Protoxide of nitrogen is a colourless gas, which does not affect the blue vegetable colours, even when mixed with atmospheric air. Recently boiled water, which has cooled without exposure to the air, absorbs nearly its own bulk of it at 60° F., and gives it out again unchanged by boiling. The solution, like the gas itself, has a faint agreeable odour and sweet taste. The action of water upon it affords a ready means of testing its purity; removing it readily from all other gases, such as oxygen and nitrogen, which are sparingly absorbed by that liquid. For the same reason it cannot be preserved over cold water; but should be collected either over hot water or mercury.

Protoxide of nitrogen 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 it is immersed while the combustion is lively, the size of the flame is increased considerably. 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. The protoxide of nitrogen suffers decomposition when a succession of electric sparks is passed through it. 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.

Sir H. Davy discovered that protoxide of nitrogen may be taken into the lungs with safety, and that it supports respiration for a few minutes. He breathed nine 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 unusual disposition to muscular exertion. These feelings however soon subside; and the person returns to his usual state without experiencing the languor 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, headach, and other disagreeable symptoms. (Researches on the Nitrous Oxide.)

The protoxide of nitrogen was analyzed by Sir H. Davy by means of hydrogen gas. He mixed 39 measures of the former with 40 measures of hydrogen, and fired the mixture by the electric spark. Water was formed; and the residual gas, which amounted to 41 measures, had the properties of pure nitrogen. As 40 measures of hydrogen require 20 of oxygen for combustion, it follows that 39 volumes of the protoxide of nitrogen

contain 41 of nitrogen and 20 of oxygen. But since no exception has hitherto been found to Gay-Lussac's law of gaseous combination, it may be inferred that protoxide of nitrogen contains its own bulk of nitrogen and half its volume of oxygen. The analysis of this compound by Dr. Henry, (Annals of Phil. viii. 299, N. S.) performed by means of carbonic oxide gas, has proved beyond a doubt that this is the exact proportion. Now,

100 cubic inches of nitrogen weigh 29.652 grains,
and 50 do. oxygen 16.944.

These numbers added together amount to 46.596;
which must be the weight of 100 cubic inches of the protoxide; and its specific gravity is therefore 1.5277. Its composition by weight is determined by the same data, being 16.944 of oxygen to 29.652 of nitrogen, or as 8 to 14. Its atomic weight or equivalent is, of course, 8 + 14 or 22.

DEUTOXIDE OF NITROGEN.

This compound is best obtained by the action of nitric acid, of specific gravity 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 peroxide of copper. The chemical changes that occur are the following.—One portion of nitric acid suffers decomposition: part of its oxygen unites with the copper and converts it into peroxide; while another part is retained by the nitrogen of the nitric acid, forming deutoxide of nitrogen. The peroxide of copper attaches itself to some undecomposed nitric acid, and forms the blue nitrate of copper. 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 gas derived from this source was discovered by Dr. Hales. It was first carefully studied by Priestley, who called it *nitrous air*. The terms *nitrous gas*, and *nitric oxide*, are

frequently applied to it; but *deutoxide of nitrogen*, as indicative of its nature, is the most suitable appellation.

Deutoxide of nitrogen is a colourless gas. When mixed with atmospheric air, or any gaseous mixture that contains oxygen in an uncombined state, dense, suffocating, acid vapours, of a red or orange colour, are produced, called *nitrous acid vapours;* which are copiously absorbed by water, and communicate acidity to it. This character serves to distinguish the deutoxide from every other substance, and affords a convenient test of the presence of free oxygen. Though it gives rise to an acid by combining with oxygen, deutoxide of nitrogen itself does not redden the blue colour of vegetables; but for this experiment, the gas must be previously well washed with water to separate all traces of nitrous acid. Water absorbs the deutoxide sparingly;—100 measures of that liquid, cold and recently boiled, take up about 11 of the gas.

Very few inflammable substances burn in deutoxide of nitrogen. Burning sulphur and a lighted candle are instantly extinguished by it. Charcoal and phosphorus, however, if in a state of vivid combustion at the moment of being immersed in it, burn with increased brilliancy. The product of the combustion is carbonic acid in the former case, and phosphoric 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 are the products.

Deutoxide of nitrogen is quite irrespirable, exciting strong spasm of the glottis, as soon as an attempt is made to inhale it. The experiment, however, is a dangerous one; for if the gas did reach the lungs, it would there mix with atmospheric air, and be converted into nitrous acid vapours, which are highly irritating and corrosive.

Deutoxide of nitrogen is partially resolved into its elements by being passed through red-hot tubes. 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 iron filings, and alkaline sulphurets. Sir H. Davy ascertained its composition by the combustion of charcoal. (Elements of Chemical Philosophy, p. 200.)

Two volumes of the deutoxide 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, in his essay in the *Memoires d'Arcueil*, proved that this proportion is rigidly exact. He decomposed 100 measures of the gas, by heating potassium in it; 50 measures of pure nitrogen were left, and the loss of weight corresponded to 50 measures of oxygen. The same fact has been lately proved by Dr. Henry in the paper already referred to. From these data, its composition by weight, and its specific gravity, may be determined by a simple calculation:—

50 cubic inches of oxygen	weigh	16.944 grains.
50 . .	nitrogen	14.826.
		31.770

Hence 100 cubic inches of deutoxide of nitrogen, at the mean temperature and pressure, weigh 31.77 grains; and its specific gravity is therefore 1.0416. This is nearly the mean density of the deutoxide, as determined directly by Davy, Thomson, and Bérard, which confirms the accuracy of the data on which the calculation is founded. The elements of the deutoxide are obviously in the ratio, by weight, of 14 of nitrogen to 16 of oxygen; that is, one proportion of the former to two of the latter. An equivalent of the compound is therefore $14 + 16 = 30$.

From the invariable formation of red coloured acid vapours, whenever deutoxide 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 deutoxide of nitrogen in Eudiometry. But in this opinion he was mistaken. The discordant results that were obtained by his method, soon excited suspicion of its 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 Mr. Dalton, that for 100 measures of oxygen, 400 of the deutoxide may be absorbed as a maximum, and 133 as a minimum; and that between these extremes, the quantity of the deutoxide corresponding to 100 of oxygen, is exceedingly variable. It does not follow from this, that oxygen and deutoxide 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 deutoxide 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 deutoxide, or the deutoxide to the oxygen.

Notwithstanding these many sources of error, Dalton and Gay-Lussac maintain that deutoxide of nitrogen may nevertheless be employed in eudiometry; and they have described the precautions which are required to ensure accuracy. Mr. Dalton has given his process in the 10th volume of the Annals of Philosophy, page 38; and further directions have been published by Dr. Henry in his Elements. The method of Gay-Lussac, to which my own observation would lead me to give the preference, may be found in the 2d volume, page 247, of the *Memoires d'Arcueil.* Instead of employing a narrow tube, such as is commonly used for measuring gases, Gay-Lussac advises that 100 measures of air should be introduced into a very wide tube or jar, and that an equal volume of deutoxide of nitrogen should then be added. 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. The diminution almost always, according to Gay-Lussac, amounts to 84 measures, one-fourth of which is oxygen. Gay-Lussac has applied this process to the analysis of various mixed gases, in which the oxygen was sometimes in a greater, at others in a less proportion than in the atmosphere, and the indications were always correct. When the proportion of oxygen is great, a proportionally large quantity of the deutoxide must of course be employed, in order that an excess of it may be present.

There is another mode of absorbing oxygen by means of deutoxide of nitrogen. If a current of the deutoxide 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.

Sir H. Davy ascertained that deutoxide of nitrogen is dissolved, without decomposition, by a cold solution of protosulphate of iron; and that when the solution is heated, the greater part of the gas is disengaged, and the remainder decomposed. The decomposition is determined chiefly by the affinity of protoxide of iron for oxygen gas. The protoxide of iron decomposes a portion of water and deutoxide of nitrogen at the same time, and unites with the oxygen of both; while the hydrogen of the water and nitrogen of the deutoxide combine together, and generate ammonia. Nitric acid is formed when the solution is exposed to the air or oxygen gas, but not otherwise.

It is singular that both deutoxide 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.

HYPONITROUS ACID.

On adding deutoxide of nitrogen in excess to oxygen gas,

confined in a glass tube over mercury, Gay-Lussac observed that the absorption is always uniform, provided a strong solution of pure potash is put into the tube before mixing the two gases. He found that 100 measures of oxygen gas combined under these circumstances with 400 of the deutoxide, forming an acid which unites with the potash. The compound so formed is hyponitrous acid, the composition of which may be easily inferred from the proportions just mentioned. For as deutoxide of nitrogen contains half its volume of oxygen gas, the new acid must be composed of 200 measures of nitrogen and 300 of oxygen, or of 100 and 150. It contains, therefore, three times more oxygen than protoxide of nitrogen; so that, by weight, it is formed of

Nitrogen	14	1 proportion,
Oxygen	24	3 proportions;

and its proportional number is 38.

Another method of forming hyponitrous acid is by keeping deutoxide of nitrogen for three months in a glass tube over mercury, in contact with a concentrated solution of pure potash. The deutoxide is resolved into hyponitrous acid, which unites with the potash, and into protoxide of nitrogen which remains in the tube.

Hyponitrous acid has not hitherto been obtained in a free state. When an acid is added to hyponitrite of potash, hyponitrous acid, instead of being dissolved by the water of the solution, suffers decomposition, and is converted, according to Gay-Lussac, into nitrous acid and deutoxide of nitrogen.

NITROUS ACID.

To form pure nitrous acid by the mixture of oxygen gas with deutoxide of nitrogen, the operation should not be conducted over water or mercury. The presence of the former determines the production of nitric acid; the latter is oxidized by the nitrous acid, and therefore decomposes it. Sir H. Davy made this compound by mixing two measures of deutoxide of nitrogen and one of oxygen, free from moisture, in a dry glass

vessel, previously exhausted by the air-pump. (Elements, p. 261.) Nitrous acid vapours were produced, and a contraction ensued, amounting to about one-half the volume of the mixed gases. The experiments of Gay-Lussac (An. de Ch. et de Ph. I.) were similar in principle. He agrees with Sir H. Davy as to the proportion of the two gases, but is of opinion that they condense, in uniting, to 1-3d of their original volume. The conclusions of those chemists respecting the composition of nitrous acid have been confirmed by the researches of Dulong. (An. de Ch. et de Ph. II.) It is composed therefore of

	By Volume.	By Weight.
Nitrogen	100	14 or 1 equivalent,
Oxygen	200	32 or 4 equivalents;

and its combining proportion is $32 + 14 = 46$.

Nitrous acid vapour is characterized by its orange red colour. 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 may exist in the liquid as well as in the gaseous form. The liquid acid is most conveniently prepared by exposing crystallized nitrate of lead, carefully dried, to a low red heat. The nitric acid of the salt is by this means resolved into nitrous acid and oxygen; and if the products are received in vessels kept moderately cool, the greater part of the former is condensed into a liquid. This substance was first obtained by Gay-Lussac, who regarded it as hyponitrous acid, and described it as such in the essay above referred to; but M. Dulong has proved, by a careful analysis, that it is in reality anhydrous nitrous acid. Dulong procured it by mixing deutoxide of nitrogen and oxygen gases in the ratio of 2 to 1, and exposing the nitrous acid vapours to a low temperature.

The liquid anhydrous acid has the following properties.— It is powerfully corrosive, has a strong acid taste and pungent odour, and is of a yellowish orange colour. Its density is 1.451.

It preserves the liquid form at the ordinary temperature and pressure, and boils at 82° F. Exposed to the atmosphere, it evaporates with great rapidity, forming the common nitrous acid vapours, which, when once mixed with air or other gases, require intense cold for condensation.

The action of water on anhydrous nitrous acid is very remarkable. On mixing it with a large quantity of water, it is instantly resolved into nitric acid and deutoxide of nitrogen; the former unites with the water, making a colourless solution, while the greater part of the latter escapes in the form of gas. When nitrous acid is added to a very small quantity of water, none of the deutoxide is disengaged; and a green coloured liquid is produced. If, instead of employing a very large or a very small proportion of water, the anhydrous acid be dropped into a moderate quantity of that fluid, the disengagement of deutoxide of nitrogen, at first considerable, becomes less and less at each addition of the acid, till at last the evolution of gas ceases altogether. The colour of the solution varies considerably during the experiment. From being quite colourless, the liquid acquires a greenish blue tinge, thence passes into green of various depths of shade, and at length becomes of a yellowish orange,—the colour of nitrous acid itself.

These changes are of a complicated nature, and may be accounted for in different ways. The following explanation appears to me most consistent with the phenomena, though I by no means insist on its accuracy. It is founded on the supposition, or rather, as I conceive, upon the fact, that nitrous and hyponitrous acids cannot exist alone in water, but are always decomposed by that fluid in consequence of its affinity for nitric acid. When a drop of nitrous acid is added to a very small quantity of water, it is resolved into nitric and hyponitrous acids, the latter being protected from decomposition by the former having combined with the water. The hyponitrous acid is therefore mixed with the solution of nitric acid, or is perhaps chemically united with it. On adding a second portion of nitrous acid, that acid is protected from decomposition by the same circumstance which preserves the hyponitrous; and, consequently, it remains in a state of mixture or combination with the two other acids. If the anhydrous nitrous acid be mixed with a large quantity of water, it is

converted into nitric acid and deutoxide of nitrogen; and every successive addition experiences a similar change, till the water has become sufficiently charged with nitric acid to enable the hyponitrous to exist in it. The subsequent additions of nitrous acid will then be converted into nitric and hyponitrous acids, until the affinity of the water for nitric acid is so far satisfied that it can no longer decompose nitrous acid.

The changes which are produced in anhydrous nitrous acid by adding successive portions of water, may be anticipated from the preceding remarks. It is resolved into nitric and hyponitrous acids, and into nitric acid and deutoxide of nitrogen; and when the dilution is considerable, the greater part, if not the whole, of the hyponitrous acid will likewise be decomposed. The colour of the fluid at different periods of the process is attributed to the quantity of nitrous acid which is dissolved, and to the degree of its dilution. It is difficult however to perceive how an orange coloured liquid should give different shades of green and blue merely by being diluted. May not the blue be caused by hyponitrous acid, the different shades of green by mixtures of hyponitrous and nitrous acids, and the yellow and orange by the preponderance of the latter? Some observations of M. Dulong seem to justify this idea; and it is supported by the action of deutoxide of nitrogen on nitric acid.

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. Nitrous acid is of course decomposed at the same time; pure nitrogen and protoxide of nitrogen are sometimes evolved, but most commonly it is converted into the deutoxide. When transmitted through red-hot porcelain tubes, it suffers decomposition, and a mixture of oxygen and nitrogen gases is obtained.

NITRIC ACID.

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 potash, or what is better, by putting a solution of pure potash instead of water into the tube at the beginning of the experiment, a salt is obtained which possesses all the properties of nitrate of potash. This experiment was performed in 1785 by Mr. Cavendish, who inferred from it that nitric acid is composed of oxygen and nitrogen. 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 deutoxide 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. This result agrees with the proportion which Sir H. Davy has deduced from his observations; and it is confirmed by an analysis of nitrate of baryta recently made by Dr. Henry. Nitric acid is therefore composed of

	By Volume.		By Weight.		
Nitrogen .	100	:	14	:	1 equivalent
Oxygen .	250	:	40	:	5 equivalents;

and its combining proportion or equivalent is 54.

Nitric acid cannot exist in an insulated state. Deutoxide 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 concentrated sulphuric acid; and common nitre, as the cheapest of the nitrates, is always employed for the purpose. This salt, previously well dried, is put into a glass retort, and a quantity of the strongest

sulphuric acid 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 sulphuric acid; and the Edinburgh and Dublin Colleges employ three parts of nitre to two of the acid. The proportion of the London College is so calculated, that the potash of the nitre shall be entirely converted into a bisulphate; for one proportion of nitre (54 nitric acid + 48 potash) is 102, and 98 corresponds to two proportions of concentrated sulphuric acid. To comprehend the nature of this process, it is necessary to observe, that the strong sulphuric acid of commerce consists of one equivalent of dry acid and one of water, and that the strongest nitric acid contains nearly one equivalent of dry or real acid and two equivalents of water. Unless supplied with this proportion of water, the nitric acid is resolved, at the moment of quitting the potash, into oxygen and nitrous acid. Now in the process of the London College, the water in the oil of vitriol is precisely sufficient for uniting with the nitric acid, and therefore the latter passes over almost entirely as such into the receiver. 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 potash. 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, very strong and fuming, and of a greater specific gravity, though proportionally less in quantity, than that obtained by the foregoing process. The specific gravity 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, Dr. 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 one equivalent 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 almost every case 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 muriatic 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 muriate of baryta and nitrate of silver to separate portions of nitric acid, diluted with three or four parts of distilled water. If muriate of baryta cause a cloudiness or precipitate, sulphuric acid must be present; if a similar effect be produced by nitrate of silver, the presence of muriatic acid may be inferred. Nitric acid is

purified from sulphuric acid by redistilling it from a small quantity of nitrate of potash, with the alkali of which the sulphuric acid unites, and remains in the retort. To separate muriatic acid, it is necessary to drop a solution of nitrate of silver into the nitric acid as long as a precipitate is formed, and draw off the pure acid by distillation.

Nitric acid possesses acid properties in an eminent degree. A few drops of it diluted with a considerable quantity of water form an acid solution, which reddens litmus paper permanently. It unites with and neutralizes alkaline substances, forming with them salts which are called *nitrates*. In its purest and most concentrated state it is colourless, and has a specific gravity of 1.50 or 1.510. It still contains a considerable quantity of water, from which it cannot be separated without decomposition, or by uniting with some other body. An acid of density 1.50 contains 25 per cent of water, according to the experiments of Mr. Phillips; and 20.3 per cent according to those of Dr. 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 specific gravity is diminished. A rise of temperature is occasioned by mixing it with a certain quantity of water. Dr. Ure found that when 58 measures of nitric acid, of specific gravity 1.5, are suddenly mixed with 42 of water, the temperature rises from 60 to 140° F; 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 59.)

Nitric acid boils at 248° F, and may be distilled without suffering material change. An acid of less specific gravity 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.

Nitric acid may be frozen by cold. The temperature at which congelation takes place, varies with the strength of the

* See his Table in the Appendix, showing the strength of diluted acid of different densities.

acid. The strongest acid freezes at about 50 degrees below zero. When diluted with half its weight of water, it becomes solid at $-1\frac{1}{2}^{0}$ F. By the addition of a little more water its freezing point is lowered to -45^{0} F.

Nitric acid acts powerfully on substances which are disposed to unite with oxygen; and hence it is 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 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 deutoxide of nitrogen. This gas is sometimes given off nearly quite pure; but in general some nitrous acid, protoxide of nitrogen, or pure nitrogen is disengaged at the same time. 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 deutoxide 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 upon the quantity of deutoxide of nitrogen which has been employed. The first portion communicates a pale straw colour, which gradually deepens as the absorption of the deutoxide continues, till the nitric acid has acquired a deep orange hue, together with all the characters of strong fuming nitrous acid. But the solution still continues to absorb the deutoxide; and in doing so, its colour passes through different shades of olive and green, till it becomes greenish blue. By applying heat to the blue liquid, deutoxide of nitrogen is evolved; and in proportion as it escapes, the colour of the solution changes to green, olive, orange, and yellow, at length becoming pale as at first. Nitrous acid vapours are likewise disengaged as well as the deutoxide. These phenomena are very favourable to the view that the conversion of the orange colour into olive, green, and blue, is owing to the formation of hyponitrous acid.

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, and by its forming with potash a neutral salt, which crystallizes in prisms, and has all the properties of nitre. Gold leaf is a still more delicate test. When muriatic 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 muriatic acid on the salts of chloric and bromic 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. A new test of the presence of nitric acid has recently been proposed by Dr. Liebig. The liquid to be examined must be mixed with a sufficient quantity of a solution of indigo in sulphuric acid for acquiring a distinct blue colour, a few drops of sulphuric acid be then added, and the mixture boiled. If a nitrate is present, the liquid will be bleached, or, if the quantity is very small, rendered yellow. By this process nitric acid may be detected, though diluted with 400 times its weight of water; or by adding a little muriate of soda to the liquid before applying heat, 1-500th part of nitric acid may be discovered. (Quarterly Journal of Science for July 1827, p. 204.)

SECTION VI.

CARBON.

When wood is heated to a certain degree in the open air, it takes fire, and burns with the formation of water and carbonic acid gas till the whole of it is consumed. A small portion of ashes, consisting of the alkaline and earthy matters which had formed a part of the wood, is the sole residue. But if the wood be heated to redness in close vessels, so that atmospheric air cannot have free access to it, a large quantity of gaseous and other volatile matters is expelled, and a black, hard, porous substance is left, called *charcoal.*

Charcoal may be procured from other sources. When the volatile matters are driven off from coal, as in the process for making coal gas, a peculiar kind of charcoal, called *coke*, remains in the retort. Most animal and vegetable substances yield it when ignited in close vessels. Thus, a very pure charcoal may be procured from starch or sugar; and from the oil of turpentine or spirit of wine, by passing their vapour through tubes heated to redness. When bones are made red-hot in a covered crucible, a black mass remains, which consists of charcoal mixed with the earthy matters of the bone. It is called *ivory black* or *animal charcoal.*

Charcoal is hard and brittle, conducts heat very slowly, but is a good conductor of electricity. Its density is stated much too low in chemical works:—according to Mr. Leslie, its specific gravity is rather greater than that of the diamond. It is 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.

Charcoal 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 box-wood absorbs, during the space of 24 or 36 hours, of

Ammoniacal gas . .	90 times its volume.
Muriatic acid . .	85
Sulphurous acid . .	65
Sulphuretted hydrogen .	55
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 relation 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.

Messrs. 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 rendered sweet and eatable by this means, and foul water may 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.

The pure inflammable principle, which is the characteristic ingredient of all kinds of charcoal, is called *carbon*. In coke it is in a very impure form. Wood-charcoal contains about

1-50th of its weight of alkaline and earthy salts, which constitute the ashes when this species of charcoal is burned. In plumbago, the carbon is combined with a small portion of metallic iron. Charcoal derived from spirit of wine is almost quite pure; and the diamond is carbon in a state of absolute purity.

The diamond is the hardest substance in nature. Its texture is crystalline in a high degree, and its cleavage very perfect. Its primary form is the octohedron. It has a specific gravity of 3.520. Acids and alkalies do not act upon it; and it bears the most intense heat in close vessels without fusing or undergoing any perceptible change. Heated to 14° W, 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 of the Florentine academicians in 1694, and subsequently confirmed by several philosophers. 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 Sir H. 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 dependant on a difference of aggregation*. This conclusion was confirmed by the experiments of Allen and Pepys†, and Sir H. Davy‡, who compared the product of the combustion of the diamond with that derived from different kinds of charcoal. The latter chemist did indeed

* Philos. Trans. for 1797. † Ibid. 1807. ‡ Ibid. 1814.

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 exceedingly 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.

CARBONIC ACID.

Carbonic acid was discovered by Dr. Black in 1757, and described by him in his inaugural dissertation *de Magnesia Alba*, 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 late Mr. 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.

Carbonic acid is most conveniently prepared for the purposes of experiment by the action of muriatic acid, diluted with two or three times its weight of water, on fragments of marble. The muriatic acid unites with the lime, forming muriate of lime, and carbonic acid gas escapes with effervescence.

Carbonic acid, as thus procured, is a colourless, inodorous, elastic fluid, which possesses all the physical characters of the gases in an eminent degree, and requires a pressure of thirty-six atmospheres to condense it into a liquid. According to the experiments of Dr. Thomson, (First Principles, vol. i. p. 143.) 100 cubic inches of it, at 60° F, and when the barometer stands at thirty inches, weigh 46.597 grains; and therefore its specific gravity is 1.5277.

Carbonic acid 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 acid.

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, 597.) 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.

Carbonic acid 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.

Carbonic acid is absorbed by water. This may be easily demonstrated by agitating the gas with that liquid, or by leaving a jar full of it inverted over water. In the first case the gas disappears in the course of a minute; and in the latter it is gradually absorbed. Recently boiled water dissolves its own volume of carbonic acid at the common temperature and pressure; 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 of carbonic acid 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 champaign, is owing to the escape of carbonic acid gas. Water, which is 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.

A knowledge of the exact composition of carbonic acid gas is of very great importance. The researches of Allen and Pepys, and Sir H. Davy, have proved incontestably that oxygen gas, in combining with carbon, so as to form carbonic acid, suffers no change of volume; or, in other words, that carbonic acid contains its own volume of oxygen. It hence follows that 100 cubic inches, or 46.597 grains of carbonic

acid, consist of 100 cubic inches, or 33.888 grains of oxygen, united with 12.709 grains (46.597 — 33.888) of carbon.

Now, 12.709 : 33.888 : : 6 : 16;

and since, as will soon appear, 6 is the combining proportion of carbon, carbonic acid is composed of

Carbon	6	1 proportional.
Oxygen	16	2 proportionals.

By a rule, which is given at page 186, it may be calculated that carbon, if supposed to exist in the form of vapour, would have a specific gravity of 0.4166; from which it follows, that 100 cubic inches of the vapour of carbon, at 60° F, and when the barometer stands at 30 inches, would weigh 12.709 grains. Consequently, 100 cubic inches of carbonic acid gas are composed of

Oxygen gas	100 Cubic inches.
Vapour of Carbon	100 Do.

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 accumu-

lations happily never take place, except when there is some local origin for the carbonic acid; 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 potash, soda, and lithia. For the same reason, all the carbonates, without exception, are decomposed by the muriatic and all the stronger acids; carbonic acid is displaced, and escapes in the form of gas.

CARBONIC OXIDE GAS.

When two parts of well-dried chalk and one of pure iron filings are mixed together, and exposed in a gun-barrel to a red heat, a large quantity of aeriform matter is evolved, which may be collected over water. On examination, it is found to

contain two compounds of carbon and oxygen, one of which is carbonic acid, and the other *carbonic oxide*. By washing the mixed gases with lime water, the carbonic acid is absorbed, and carbonic oxide gas is left in a state of purity.

A very elegant mode of preparing carbonic oxide has been suggested by M. Dumas. (Edinburgh Journal of Science, VI. 350.) The process consists in mixing bin-oxalate of potash with five or six times its weight of concentrated sulphuric acid, and heating the mixture in a retort or other convenient glass vessel. 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 means of lime water or solution of potash, 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 potash and water of the bin-oxalate, and the oxalic acid being thus set free, is instantly decomposed. Oxalic acid may be substituted in this process for bin-oxalate of potash.

Priestley discovered this gas by igniting chalk in a gun-barrel, and afterwards obtained it in greater quantity from chalk and iron filings. He supposed it to be a mixture of hydrogen and carbonic acid gases. Its real nature was pointed out by Mr. Cruickshank *, and about the same time by Clément and Désormes †.

Carbonic oxide gas is colourless and insipid. It does not affect the blue colour of vegetables in any way; nor does it combine, like carbonic acid, with lime or any of the pure alkalies. It is very sparingly dissolved by water. Lime water does not absorb it, nor is its transparency affected by it.

Carbonic oxide is inflammable. When a lighted taper is plunged into a jar full of that gas, 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.

* Nicholson's Journal, 4to Ed. vol. v. † Annales de Chimie, vol. xxxix.

Carbonic oxide gas cannot support respiration. It acts injuriously on the system; for if diluted with air, and taken into the lungs, it very soon occasions headach 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 they are mixed together in the proportion 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, which was ascertained by Berthollet, and has been amply confirmed by subsequent observation, the exact composition of carbonic oxide gas may be easily deduced. For carbonic acid contains its own bulk of oxygen; and since 100 measures of carbonic oxide with 50 of oxygen form 100 measures of carbonic acid, it follows that 100 of carbonic oxide are composed of 50 of oxygen united with precisely the same quantity of carbon as is contained in 100 measures of carbonic acid. Consequently, the composition of carbonic acid being

	By Volume.		By Weight.
Vapour of carbon	100	Carbon	6
	or		
Oxygen gas	100	Oxygen	16
	100 carbonic acid gas.		22 carbonic acid;

that of carbonic oxide must be

	By Volume.		By Weight.
Vapour of carbon	100	Carbon	6
	or		
Oxygen gas	50	Oxygen	8
	100 carbonic oxide gas.		14 carbonic oxide.

	Grains.
Also, since 50 cubic inches of oxygen gas weigh	16.944
and 100 of the vapour of carbon	12.709
100 cubic inches of carbonic oxide gas must weigh	29.653

Its specific gravity is therefore 0.9721; and to be satisfied of the accuracy of the data on which these calculations are founded, it is sufficient to state, that its density, as determined by Dr. Thomson, is 0.9700, and 0.9727 according to the observation of Berzelius and Dulong.

No compound of carbon and oxygen is known which contains a less quantity of oxygen than carbonic oxide. For this reason it is regarded as a combination of one proportion of carbon = 6 and one of oxygen = 8; and carbonic acid of one proportion of carbon = 6 and two of oxygen = 16. The combining proportion of carbonic oxide is therefore 14, and that of carbonic acid 22.

The first process mentioned for generating carbonic oxide will now be intelligible. The principle of the method 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, potash, 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 converted into 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. It may also be formed by transmitting a current of carbonic acid gas over ignited charcoal. 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.

Dr. 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 Dr. 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.

SECTION VII.

SULPHUR.

Sulphur 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 an oblique rhombic octohedron. It exists much more abundantly in combination with several metals, such as silver, copper, antimony, lead, and iron. It is procured in large quantity by exposing iron pyrites to a red heat in close vessels.

Sulphur is a brittle solid, of a greenish yellow colour, emits a peculiar odour when rubbed, and has little taste. It is a non-conductor of electricity, and is excited negatively by friction. Its specific gravity is 1.99. Its point of fusion is 216° F ; between 230° 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 becomes liquid again, 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. (Dumas.)

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° F. 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.

Sulphur is insoluble in water, but unites with it under favourable circumstances, forming the white *hydrate of sulphur*, termed *Lac Sulphuris*. 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. Sulphur 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. Sir H. Davy detected its presence by exposing sulphur to the strong heat of a powerful galvanic battery, when some sulphuretted hydrogen gas was disengaged. The hydrogen, from its minute quantity, can only be regarded in the light of an accidental impurity, and as in nowise essential to the nature of sulphur.

When sulphur is heated in the open air to 300° F. 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.

COMPOUNDS OF SULPHUR AND OXYGEN.

Chemists are at present acquainted with four compounds of sulphur and oxygen, all of which have acid properties. Their composition is shown by the following table.

	Sulphur.	Oxygen.	S.	Ox.
Hyposulphurous acid	32	8	2	1
Sulphurous acid .	16	16	1	2
Sulphuric acid .	16	24	1	3
Hyposulphuric acid	32	40	2	5

SULPHUROUS ACID GAS.

Pure sulphurous acid, at the common temperature and pressure, is a colourless transparent gas, which was first obtained in a separate state by Priestley. It is the sole product when sulphur is burned in air or dry oxygen gas, and is the cause of the peculiar odour emitted by that substance during its combustion. It may also be prepared by depriving sulphuric acid of one proportion of its oxygen. This may be done in several ways. If chips of wood, straw, cork, oil, or other vegetable matters, be heated in strong sulphuric acid, the carbon and hydrogen of those substances deprive the acid of part of its oxygen, and convert it into sulphurous acid. Nearly all the metals, with the aid of heat, have a similar effect. One portion of sulphuric acid yields oxygen to the metal, and is thereby converted into sulphurous acid; while the metallic oxide, at the moment of its formation, unites with some of the undecomposed sulphuric acid. The best method of obtaining pure sulphurous acid gas, is by putting two parts of mercury and three of sulphuric acid into a glass retort, the beak of which is received under mercury, and heating the mixture by an Argand lamp. Effervescence soon takes place,

a large quantity of pure sulphurous acid is disengaged, and sulphate of the oxide of mercury remains in the retort.

Sulphurous acid gas is distinguished from all other gaseous fluids by its suffocating pungent odour. All burning bodies, when immersed in it, are extinguished without setting fire to the gas itself. It is fatal to all animals which are placed in it. A violent spasm of the glottis takes place, by which the entrance of the gas into the lungs is prevented; and even when diluted with air, it excites cough, and causes a peculiar uneasiness about the chest.

Recently boiled water dissolves about 33 times its volume of sulphurous acid at 60° F. and 30 inches of the barometer, forming a solution which has the peculiar odour of that compound, and from which the gas may be expelled by ebullition, without change.

Sulphurous acid has considerable bleaching properties. It reddens litmus paper, and then slowly bleaches it. Most vegetable colouring matters, such as those of the rose and violet, are speedily removed, without being first reddened. It is remarkable that the colouring principle is not destroyed; for it may be restored either by a stronger acid or by an alkali.

Sir H. Davy inferred from his experiments on the combustion of sulphur in dry oxygen gas, (Elements, p. 273,) that the volume of the oxygen is not altered during the process, a fact which is now admitted by most chemists; so that 100 cubic inches of sulphurous acid contain 100 cubic inches of oxygen. According to Dr. Thomson, (Annals of Philosophy, xvi. 256,) sulphurous acid gas is just twice as heavy as oxygen; and the experiments of Davy and of Thenard correspond very closely with his result. It follows, therefore, that sulphurous acid consists of equal weights of sulphur and oxygen; and consequently that 100 cubic inches weigh 67.776 grains, and contain 33.888 grains of sulphur. This proportion is also established by the researches of Berzelius. (An. de Ch. et de Ph. vol. v.)

By the formula, page 186, it may be calculated that the specific gravity of the vapour of sulphur is the same as that of oxygen gas, or 1.1111; and hence 100 cubic inches of that vapour must weigh 33.888 grains. From this it is ma-

nifest, that 100 cubic inches of sulphurous acid gas are composed of

Vapour of sulphur	.	100 cubic inches.
Oxygen . . .		100 do.

The specific gravity of sulphurous acid gas is of course double that of oxygen, or 2.2222.

It is inferred from the compounds of sulphur with oxygen, hydrogen, and many other substances, that 16 is the number which expresses the combining proportion of that substance. Hence sulphurous acid is composed of 16 or 1 proportion of sulphur, and 16 or 2 proportions of oxygen. Its atomic weight is therefore 32.

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. The facility with which this change ensues is such, that a solution of sulphurous acid in water cannot be preserved, except atmospheric air be carefully excluded. Many of the chemical properties of sulphurous acid are owing to its affinity for oxygen. When mixed with peroxide of iron in solution, it deprives that compound of part of its oxygen, and converts it into the protoxide. 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.

Of all the gases, sulphurous acid is most readily liquefied by compression. According to Mr. Faraday, it is condensed by a force equal to the pressure of two atmospheres. M. Bussy (Annals of Phil. viii. 307, N. S.) has obtained it in a liquid form under the usual atmospheric pressure, by passing it through tubes surrounded by a freezing mixture of snow and salt. The anhydrous liquid acid has a density of 1.45, and it boils at 14° F. From the rapidity of its evaporation at common temperatures, it may be used advantageously for producing an intense degree of cold. M. Bussy succeeded in freezing mercury, and liquefying several of the gases, by the cold produced during its evaporation. De la Rive states it to be a non-conductor of electricity. He adds also, that when exposed to cold in the moist state, a crystalline solid hydrate is formed, which contains 20 per cent of water, and probably consists of one equivalent of the acid to 14 of water.

Sulphurous acid combines with metallic oxides, and forms salts which are called *sulphites*.

SULPHURIC ACID.

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 protosulphate of iron (green vitriol) by heat. This salt contains seven proportionals of water of crystallization; and when strongly dried by the fire, it crumbles down into a white powder, which, according to Dr. Thomson, contains one proportional 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 specific gravity is stated at 1.896 and 1.90. According to Dr. Thomson it consists of 80 parts or 2 equivalents of anhydrous acid, and 9 parts or 1 equivalent 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 shown by the experiments of Thomson, Ure, and Bussy, to be pure anhydrous sulphuric acid. It is tough and elastic; liquefies at 66° F. 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. 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 potash. 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 potash 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, I apprehend, into deutoxide 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 Desormes, (An. de Ch. lix.) and Sir H. 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, a white crystalline compound is immediately produced. The French chemists believed it to consist of sulphuric acid, deutoxide of nitrogen, and water; and they ascribed the conversion of sulphurous into sulphuric acid to the oxygen supplied by nitrous acid during its change into deutoxide of nitrogen. This opinion was supported by the fact, that when the crystalline compound is put into water, a solution of sulphuric acid is obtained, and deutoxide of nitrogen is disengaged with effervescence. Davy regarded the solid as consisting of sulphurous acid, water, and nitrous acid; and supposed the transfer of oxygen from the latter to the former not to take place, until the compound was brought in contact with water. It is doubtful if either of these doctrines is altogether correct. The more probable theory is, that the crystalline matter contains sulphuric and hyponitrous acids; and that when put into water, the latter is resolved into deutoxide of nitrogen, which escapes as gas, and into nitric acid which remains in solution together with sulphuric acid. This opinion is founded, partly on the tendency of sulphuric acid to unite with nitrous and hyponitrous acids, but chiefly on the analysis by Dr. Henry of a crystalline substance, similar to that above alluded to, which was generated in the leaden chamber of a manufacturer of sulphuric acid. (An. Phil. xxvii. 367.)

While it is admitted, therefore, that this subject requires the aid of further inquiry, the most probable account of the phenomena which take place within the leaden chambers is the following. When moist nitrous and sulphurous acids are intermixed, the former communicates oxygen to the latter, and a crystalline compound of water, hyponitrous acid, and sulphuric acid, in proportions not yet determined, is generated. This substance, falling into the water at the bottom of the leaden chamber, is there instantly resolved, as above mentioned, into sulphuric and nitric acids, and deutoxide of nitrogen. The gas which is thus set free, in mixing with atmo-

spheric air, is again converted into nitrous acid, and thus gives rise to a second portion of the crystalline solid, which undergoes the same change as the first. When the water, by these successive combinations and decompositions, is sufficiently charged with acid, it is drawn off, and concentrated by evaporation. During this process the nitric acid, formed in the leaden chamber, is expelled. 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.

Sulphuric acid, as thus prepared, is never quite pure. It contains some sulphate of potash and lead, the former derived from the nitre employed in making it, and the latter from the leaden chamber. To separate these impurities, the acid should be distilled from a glass or platinum retort. The former may be used with safety by putting into it some fragments of platinum leaf, which cause the acid to boil freely on the application of heat, without danger of breaking the vessel.

Pure sulphuric acid, as obtained by the second process, is a dense, colourless, oily fluid, which boils at 620° F, and has a specific gravity, in its most concentrated form, of 1.847 or a little higher, never exceeding 1.850. It is one of the strongest acids with which chemists are acquainted. When undiluted it 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.

Sulphuric acid in a very concentrated state 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.

Sulphuric acid has a very great affinity for water, and unites with it in every proportion. 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 Dr. Ure, to 300° F. By its attraction for water it causes the sudden liquefaction of snow; and if mixed with it in due proportion, (p. 59), 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. The action of sulphuric acid in destroying the texture of the skin, in forming ethers, and in decomposing animal and vegetable substances in general, seems dependant on its affinity for water.

It is frequently important to know the quantity of real acid contained in liquid sulphuric acid of different strengths. When great accuracy is requisite, this information should always be ascertained by neutralizing a specimen of the acid with an alkali. For this purpose, 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 54 parts of carbonate of soda, required to produce this effect, correspond to 40 parts of real sulphuric acid. But if minute precision is not desired, the strength of the acid may be estimated by its specific gravity, according to the table of Dr. Ure inserted in the Appendix.

Sulphuric acid of commerce freezes at —15° F. Diluted with water so as to have a specific gravity of 1.78 it congeals even above 32°, and remains in the solid state, according to Mr. Keir, till the temperature rises to 45°. When mixed with rather more than its weight of water, its freezing point is lowered to —36° F.

When sulphuric acid is passed through a small porcelain tube heated to redness, it is entirely decomposed; and Gay-Lussac found that it is resolved into two measures of sul-

phurous acid and one of oxygen. Hence it follows that real sulphuric acid is composed of

	By Weight.		By Volume.
Sulphur	16	1 p. or vapour of sulphur	100
Oxygen	24	3 p. oxygen gas	150;

and its atomic weight is 40. Berzelius ascertained its composition by converting a known weight of sulphur into sulphuric acid; and his result confirms the conclusion of Gay-Lussac.

Chemists possess an unerring test of the presence of sulphuric acid. If a solution of muriate of baryta is added to a liquid containing sulphuric acid, it causes a white precipitate, sulphate of baryta, which is characterised 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.

Hyposulphurous Acid.—This acid 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 hydrosulphuret of lime or strontia. 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, sulphurous acid is deprived of one half of its oxygen by the hydrogen of the sulphuretted hydrogen, while the other half of its oxygen unites both with the sulphur of the sulphurous acid and sulphuretted hydrogen, to form hyposulphurous acid. If the hydrosulphuret of lime employed contains bisulphuretted hydrogen, as is the case when lime and sulphur are boiled together, the action of sulphurous acid is accompanied by precipitation of sulphur. Mr. Herschel states that hyposulphurous 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 in the 85th volume of the *Annales de Chimie*, under the name of *Sulphuretted Sulphites*. Dr. 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. The subsequent researches of Mr. Herschel (Edinburgh Philos. Journal, i. 8 and 396) seemed to give such direct analytic proof of the correctness of this opinion, that it was universally adopted; but it appears from a recent essay by Dr. Thomson, that this view of its composition is nevertheless erroneous, and that the acid consists of 32 parts or two equivalents of sulphur, and 8 parts or one equivalent of oxygen. Its combining proportion is therefore 40. (On the Compounds of Chromium, Philos. Trans. for 1827.)

Hyposulphurous acid cannot exist permanently in a free state. On decomposing a hyposulphite by any stronger acid, such as the sulphuric or muriatic, the hyposulphurous acid, at the moment of quitting the base, resolves itself into sulphurous acid and sulphur. Mr. 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 nitrate of silver and mercury black, as sulphuret of the metals; and salts of lead and baryta are thrown down as white insoluble hyposulphites of those bases. That of baryta is soluble without decomposition in water acidulated with muriatic 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.

Dr. Thomson, in the essay above quoted, mentions that an acid exists composed of one equivalent of sulphur and one of oxygen; but he has given no description of it.

Hyposulphuric Acid.—This acid was discovered in 1819 by Welter and Gay-Lussac, who published their description of it in the 10th vol. of the *An. de Ch. et de Physique*. It is formed by transmitting a current of sulphurous acid gas through water containing peroxide of manganese in fine powder. The manganese yields oxygen to the sulphurous acid, converting one part of it into sulphuric, and another

part into hyposulphuric acid, both of which unite with the protoxide of manganese. To the liquid, after filtration, a solution of pure baryta is added in slight excess, which precipitates the protoxide of manganese, and forms an insoluble sulphate of baryta with the sulphuric, and a soluble hyposulphate with the hyposulphuric acid. The hyposulphate of baryta is then decomposed by a quantity of sulphuric acid exactly sufficient for precipitating the baryta, and the hyposulphuric acid is left in solution.

This compound reddens litmus paper, has a sour taste, and forms neutral salts with the alkalies. It has no odour, by which circumstance it is distinguished from sulphurous acid. It cannot be confounded with sulphuric acid; for it forms soluble salts with baryta, strontia, lime, and oxide of lead, whereas the compounds which sulphuric acid forms with those bases are all insoluble. Hyposulphuric acid 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° F. this salt suffers complete decomposition; sulphurous acid gas is disengaged, and neutral sulphate of baryta is obtained. It was thus ascertained that seventy-two grains of hyposulphuric acid yield thirty-two grains of sulphurous, and forty 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 two equivalents of sulphur and five of oxygen. Whether regarded as a definite compound of sulphurous and sulphuric acids, or of sulphur and oxygen, it consists of 32 parts of sulphur and 40 of oxygen, and therefore 72 is its combining proportion.

SECTION VIII.

PHOSPHORUS.

Phosphorus was discovered about the year 1669 by Brandt, an alchemist of Hamburgh. It was originally prepared from urine; but Scheele afterwards described a method of obtaining it from bones. The object of both processes is to bring phosphoric acid in contact with charcoal at a strong red heat. The charcoal takes oxygen from the phosphoric acid; carbonic acid is disengaged, and phosphorus set free. When urine is employed, the phosphoric acid contained in it should be separated by acetate of lead. Phosphate of lead subsides, which, if heated to redness with one-fourth of its weight of powdered charcoal, yields phosphorus readily. If bones are used, they should first be ignited in an open fire till they become quite white, so as to destroy all the animal matter they contain, and oxidize the carbon proceeding from its decomposition. The calcined bones, of which phosphate of lime constitutes nearly four-fifths, should be reduced to fine powder, and digested for a day or two with half their weight of concentrated sulphuric acid, so much water being added to the mixture as to give it the consistence of thin paste. The phosphate of lime is decomposed by the sulphuric acid, and two new salts are generated,—the sparingly soluble neutral sulphate, and a soluble super-phosphate of lime. On the addition of boiling water the super-phosphate is dissolved, and may be separated by filtration from the sulphate of lime. The solution is then evaporated to the consistence of syrup, mixed with one-fourth of its weight of charcoal in powder, and heated in an earthen retort well luted with clay. The beak of the retort is put into water, in which the phosphorus, as it passes over in the form of vapour, is collected. When first obtained, it is frequently of a reddish-brown colour, owing to the presence of phosphuret of carbon, which is generally formed during the process. It may be purified by being put into hot water, and pressed while liquid through chamois leather; or the purification may be rendered still more complete by a second distillation.

Pure phosphorus is transparent and almost colourless. It is so soft that it may be cut with a knife, and the cut surface has a waxy lustre. At the temperature of 108° F. it fuses, and at 550° is converted into vapour. It is soluble by the aid of heat in naphtha, in mixed and volatile oils, and in chloride, carburet, and phosphuret of sulphur. On its cooling from solution in the latter, Professor 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 octahedral form, and as large as a cherry-stone.

Phosphorus 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° F, 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 is 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° F. 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°
166	. .	and 1	ditto	of vapour of turpentine	186°

Phosphorus 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 air is promoted by the presence of muriatic 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.

COMPOUNDS OF PHOSPHORUS AND OXYGEN.—PHOSPHORIC ACID.

Recent observations appear to justify the conclusion, that under the term *phosphoric acid* chemists have hitherto included two distinct acids, the *phosphoric* and *pyro-phosphoric*. These compounds afford an instance of a fact very lately noticed, and of great interest in reference to the atomic theory; viz., that two substances may consist of the same ingredients, in the same proportion, and nevertheless differ essentially in their chemical properties. Such, at least, is an obvious deduction from the experiments which have been published on the subject. But the inquiries have not yet been carried sufficiently far to admit of the mutual relations of these acids being stated with accuracy; and therefore it will be the safest course, at present, to describe phosphoric acid in the usual manner, and afterwards to enumerate the facts known respecting pyrophosphoric acid.

Phosphoric acid is commonly prepared either by the oxidation of phosphorus, or by the action of sulphuric acid on calcined bones. One method of oxidizing phosphorus is by its combustion in air or oxygen gas, when phosphoric acid appears in the form of a copious white vapour, which soon collects into distinct particles, and falls to the bottom of the vessel like flakes of snow. In this state it is the anhydrous phosphoric acid of chemists, and is a white, bulky, rather tenacious solid; but in the open air its appearance soon changes, in consequence of its attracting moisture rapidly from the atmosphere, and forming with it a dense acid solution. The conversion of all the phosphorus, into phosphoric acid, rarely, if ever, ensues in this process; for, on the spot where the burning phosphorus lay, a small quantity of red matter is always found, which is supposed to be an oxide. When the supply of oxygen is insufficient for completing the combustion, the residue is a mixture of this oxide and unburned phosphorus.

The oxidation of phosphorus may also be effected by means of strong nitric acid, which communicates oxygen to the phosphorus, and emits a large quantity of deutoxide of nitrogen. The unpractised operator should be cautious in performing this experiment, as the disengagement of gas is sometimes so rapid as to endanger the apparatus.

The process is best conducted by adding fragments of phosphorus to concentrated nitric acid contained in a platinum capsule. 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, super-phosphate 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 the neutral 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.

Solid phosphoric acid unites with water in every proportion, and forms, if concentrated, a dense oily liquid. On heating the solution in a platinum vessel, the greater part of the water is driven off; the residue fuses at a low red heat, and concretes on cooling into a brittle glass, called *glacial phosphoric acid.* This substance is a hydrate, which cannot be decomposed by fire; for on exposing it to a strong red heat, with the view of expelling the water, the compound itself is volatilized, and in open vessels sublimes with considerable rapidity. It is erroneously said to be fixed at intense degrees of heat, this character applying to the acid only in its impure state, as when combined with earthy or alkaline substances. The composition of glacial phosphoric acid is not yet established; for while M. Dulong reports it to contain 17.08 per cent of water, M. Rose found only 9.44 per cent. (Poggendorff's Annalen, VIII. 201.) The analysis of Rose, though not rigidly exact, is probably not far from the truth. The acid after being fused in glass vessels is anhydrous.

Phosphoric acid is intensely sour to the taste, reddens litmus paper strongly, and neutralizes alkalies. It is therefore a powerful acid; but it does not destroy the texture of the skin like sulphuric and nitric acids. It may be distinguished from all other acids by the following circumstances:—that it neither suffers precipitation, nor change of colour, when a stream of sulphuretted hydrogen gas is passed through its solution; and that when carefully neutralized by pure carbonate of potash or soda, it is precipitated white by acetate of lead, and yellow by nitrate of silver. The former precipitate, phosphate of lead, dissolves completely on the addition of nitric or phosphoric acid; the latter, phosphate of silver, is dissolved by both these acids and by ammonia.

The composition of phosphoric acid has been investigated

by Sir H. Davy, Dr. Thomson, Berzelius, Dulong, and Rose. The subject is one of much difficulty, and the results of the two former chemists differ widely from those of the latter. The direct method, of burning a known weight of phosphorus in oxygen gas, is objectionable, on account of the difficulty by this process of converting all the phosphorus into phosphoric acid. Dr. Thomson and others have endeavoured to infer its constitution by means of the analysis of phosphuretted hydrogen; but the composition and purity of the gas employed in these researches were not known with sufficient certainty to inspire confidence in the results which were obtained. Berzelius converted a known weight of phosphorus into phosphoric acid by digestion in a neutral solution of muriate of gold or sulphate of silver, the oxygen required for that change being derived from the metallic oxide, and its quantity estimated by the amount of metal reduced. Dr. Thomson infers, from experiments made by Sir H. Davy and himself, that 28 is the combining proportion of phosphoric acid; and that it consists of 12 parts, or what he considers one equivalent, of phosphorus, and 16 parts or two equivalents of oxygen. According to the researches of Berzelius, as well as of M. Dulong, the oxygen contained in phosphorous and phosphoric acids is in the ratio of 1.5 to 2.5, or 3 to 5; and the former states phosphoric acid to be composed of 56 parts of oxygen and 44 of phosphorus. Now, judging from these data, and from the composition of the phosphates analyzed by Berzelius and Mitscherlich, we may regard 35.71 as the equivalent of phosphoric acid, and the acid itself as a compound of 15.71 parts or one equivalent of phosphorus, and 20 parts or two equivalents and a half of oxygen. Berzelius believes that it consists of two atoms of phosphorus and five atoms of oxygen, and therefore doubles the preceding numbers. The estimate of Berzelius appears to me most deserving of confidence, and I have accordingly adopted it; but that of Dr. Thomson is commonly employed in this country.

Pyrophosphoric acid.—It is above remarked, as a distinctive character of phosphoric acid, that it forms a yellow salt with oxide of silver; but if crystallized phosphate of soda be dried gently on a sand-bath and then heated to redness, it afterwards yields a white instead of a yellow precipitate with

nitrate of silver, and is found to have undergone an entire change in its properties. It appears, nevertheless, that in the ratio of its ingredients no alteration is occasioned, the only visible effect of heat being confined to the expulsion of water: nothing is absorbed from the atmosphere; and nothing, except water, is expelled. These remarkable facts were brought under the notice of chemists in the year 1827 by Mr. Clarke of Glasgow, who applied to the new acid the appropriate appellation of *pyrophosphoric*. (Brewster's Journal, VII. 298.) Heat has a similar effect on phosphate of potash, and probably on most other phosphates.

This interesting subject has lately occupied the attention of Gay-Lussac and Stromeyer. The fact observed by Dr. Engelhardt, that albumen is precipitated by a solution of recently ignited phosphoric acid, and that after keeping the solution for a few days this property entirely disappears, is found by Gay-Lussac to be allied to the observation of Mr. Clarke. Common phosphoric acid is, in fact, converted by a red heat into the pyrophosphoric, as is inferred from its yielding a white precipitate with oxide of silver; but when its solution is kept for a few days, it is gradually reconverted into phosphoric acid, as is proved by its then forming with silver a yellow precipitate. In the former state it renders turbid a moderately dilute solution of albumen, and in the latter it does not disturb its transparency; so that albumen, as well as the colour of the salt of silver, affords a good character for distinguishing the two acids from each other. (An. de Ch. et Ph. XLI. 331.)

The observation of Gay-Lussac shows, that the substance above described under the name of *glacial phosphoric acid* is really hydrated pyrophosphoric acid; and Stromeyer finds that the white solid, procured by the combustion of phosphorus, is pyrophosphoric acid in the dry state. Hence it appears that solid phosphoric acid is wholly unknown. The conversion of pyrophosphoric into phosphoric acid, which takes place gradually at common temperatures, is rapidly effected by boiling the solution; and even the salts of pyrophosphoric acid, which may be long preserved in the liquid form without change, are quickly converted into phosphates when heated with various acids, such as the nitric, muriatic, sulphuric,

acetic, or phosphoric. But the acid, which by its presence determines the change, does not itself undergo the least decomposition. (Brewster's Journal, N. S., III.)

Phosphoric acid seems a stronger acid than the pyrophosphoric. Thus, if phosphate of soda is boiled with pyrophosphate of silver, phosphate of silver is quickly generated; but pyrophosphate of soda cannot decompose any of the insoluble phosphates. The neutralizing power of phosphoric acid is likewise greater. Stromeyer states, for example, that 118 parts of oxide of silver combine with 38.52 parts of pyrophosphoric acid, and with only 23.4 of the phosphoric; a remarkable difference which amply accounts for the uncertainty which has long prevailed concerning the equivalent of phosphoric acid, and throws great doubt on the estimates above given on the authority of Berzelius and Thomson. The foregoing facts fully prove these acids to be essentially distinct; while, as already observed, it appears equally certain that in point of composition they differ neither in the nature nor the proportion of their elements, but solely in the manner in which they are arranged.

Phosphorous Acid.—When phosphorus is burned in air highly rarefied, imperfect oxidation ensues, and phosphoric and phosphorous acids are both generated, the latter being obtained in the form of a white volatile powder. In this state it is anhydrous. Heated in the open air, it takes fire, and forms phosphoric acid; but if exposed to heat in close vessels, it is resolved into phosphoric acid and phosphorus. 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 the 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, of course, converts it into phosphoric acid.

Phosphorous acid may be procured more conveniently by subliming phosphorus through powdered corrosive sublimate, (a compound of chlorine and 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 muriatic 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 muriatic acid; and the residue, which is hydrate of phosphorous acid, becomes a crystalline solid on cooling. When this hydrate is heated in close vessels, the elements of the water and acid react on each other, forming phosphoric acid and a gaseous compound of hydrogen and phosphorus. The nature of this gas will be more particularly noticed in the section on phosphuretted hydrogen.

Phosphorous acid 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. M. Dulong thinks that a distinct acid is generated in this case, which he calls *phosphatic acid;* but the opinion of Sir H. Davy, that it is merely a mixture of phosphoric and phosphorous acids, is in my opinion perfectly correct.

The composition of phosphorous, like that of phosphoric acid, is not yet satisfactorily ascertained. According to Sir H. Davy and Dr. Thomson the oxygen in the two acids is in the ratio of 1 to 2, while it is stated by Dulong and Berzelius to be as 3 to 5.

Hypophosphorous Acid.—This acid was discovered in 1816 by M. Dulong*, and is produced by the action of water on phosphuret of baryta. Mutual decomposition ensues; and the elements of water uniting with different portions of phosphorus, give rise to the formation of three compounds—phosphuretted hydrogen, phosphoric acid, and hypophosphorous acid. 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. On evaporating the solution, a viscid liquid remains, highly acid and even crystallizable, which is

* Mém. d'Arcueil, vol. iii.; or An. de Ch. et de Physique, vol. ii.

a *hydrate of hypophosphorous acid.* When exposed to heat in close vessels, it undergoes the same kind of change as hydrated phosphorous acid.

Hypophosphorous acid 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 potash, soda, and ammonia, dissolve in every proportion in rectified alcohol; and hypophosphite of potash 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 baryta.

M. Dulong determined the proportion of its elements by converting it into phosphoric acid by means of chlorine. He infers from his analysis that it contains 27.25 per cent of oxygen. According to Sir H. Davy, it has exactly one half less oxygen than phosphorous acid; but as the composition of this acid is not known with certainty, no inference can be safely deduced from this statement. Professor Henry Rose finds that it contains 20.31 per cent of oxygen, being the ratio of 31.42 parts or two proportionals of phosphorus, to eight parts or one proportional of oxygen. (Poggendorff's Annalen, IX. 367.) This result is probably more accurate than that of M. Dulong.

Oxides of phosphorus.—Chemists have not yet succeeded in proving the existence of any oxide of phosphorus. When phosphorus is kept under water for some time, a white film is formed upon its surface, which some regard as an oxide of phosphorus. The red-coloured matter which remains after the combustion of phosphorus, is also supposed to be an oxide. The nature of these substances has not, however, been determined in a satisfactory manner. The formation of the white film is materially promoted by the agency of light; and Mr. Phillips has observed this change to be attended with decomposition of water, and production, in small quantity, of phos-

phuretted hydrogen and one of the acids of phosphorus. (An. of Phil. xxi. 470.)

SECTION IX.

BORON.

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 an alkaline borofluate by means of potassium. (Annals of Philosophy, xxvi. 128.)

Boron 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 an intense heat in close vessels, without fusing or undergoing any other change, except a slight increase of density. Its specific gravity 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° F., it suddenly takes fire, oxygen gas disappears, and boracic acid is generated. It experiences a similar change when heated in nitric acid, or with any substance that yields oxygen with facility.

Boracic acid. This is the only known compound of boron and oxygen. As a natural product it is found in the hot springs of Lipari, and in those of Sasso in the Florentine territory. It is a constituent of several minerals, among which the datolite and boracite may in particular be mentioned. It occurs much more abundantly under the form of borax, 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,

* Recherches Physico-Chimiques, vol. i.

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; and 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.

Boracic acid in this state is a hydrate. Its precise degree of solubility in water has not been determined with accuracy; but it is much more soluble in hot than in cold water. 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 specific gravity 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. Mr. Faraday has noticed that it renders turmeric paper brown like the alkalies. From the weakness of its acid properties, all the borates, when in solution, are decomposed by the stronger acids.

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 specific 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 as a flux.

The most obvious mode of determining the composition of boracic acid is to burn a known quantity of boron, and ascertain its increase of weight when the combustion ceases. This

method, however, though apparently simple, is very difficult of execution; for the boracic acid fuses at the moment of being generated, and by glazing the surface of the unconsumed boron, protects it from oxidation. Hence it was that the experiments performed by Gay-Lussac and Thenard on this subject, led to results widely different from those which Sir H. Davy obtained by a similar process. Dr. Thomson, from data furnished partly by himself, and partly by Sir H. Davy, infers that the atomic weight of boron is 8, and that boracic acid is composed of

Boron	. .	8, or one equivalent.
Oxygen	. .	16, or two equivalents.

Consequently, the equivalent of boracic acid is 24.

Crystallized boracic acid, according to the same chemist, is composed of

Boracic acid	.	24, or one equivalent.
Water	. .	18, or two equivalents.

and therefore its equivalent is 42.

Sulphuret of Boron.—This compound may be formed, according to Berzelius, by igniting boron strongly in the vapour of sulphur; and the combination is accompanied with the phenomena of combustion. The product is a white opaque mass, which is converted by the action of water into sulphuretted hydrogen and boracic acid; and the liquid becomes milky at the same time from a deposition of sulphur. (Annals of Philosophy, xxvi. 129.)

SECTION X.

SELENIUM.

Selenium has hitherto been found in very small quantity. It occurs for the most part in combination with sulphur in some kinds 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 mountains, combined, according to Stromeyer and

Rose, with several metals, such as lead, cobalt, silver, mercury, and copper. It was discovered in 1818, by Berzelius, 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 horse-radish, which induced him to submit it to a careful examination, and thus led to the discovery of selenium*.

Selenium, 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 is of a deep red colour when reduced to powder. Its specific gravity 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 caloric 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 blow-pipe flame, it tinges the flame with a light blue colour, and exhales so strong an odour of decayed horse-radish, 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.

Oxide of Selenium.—This compound is formed in greatest abundance by heating selenium in a limited quantity of atmo-

* An. de Ch. et de Phys. vol. ix.; or Annals of Philosophy, vol. xiii.

spheric 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. Its composition has not been determined, but it probably contains an atom of each of its elements.

Selenious Acid.—This acid is most conveniently prepared by digesting selenium in nitric or nitro-muriatic 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 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. Sulphuretted hydrogen also decomposes it; and an orange-yellow precipitate subsides, which is a sulphuret of selenium.

The atomic weight of selenium, deduced chiefly from the experiments of Berzelius, is 40; and selenious acid, according to the analysis of the same chemist, consists of 40 parts or one equivalent of selenium, and 16 parts or two equivalents of oxygen.

Selenic acid.—The preceding compound, discovered by Berzelius, was till lately the only known acid of selenium, and has hitherto 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 Professor Mitscherlich, and its properties have been examined and described by the Professor himself. (Edin. Journal of Science, VIII. 294.)

This acid is prepared by fusing nitrate of potash 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 muriatic 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° F. 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 and sal-ammoniac; when mutual decomposition ensues, the soda unites with muriatic acid, the hydrogen of the ammonia combines with the oxygen of the selenic acid, and selenium and nitrogen are set free. The selenium thus obtained 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 lead. The seleniate of lead, which is as insoluble as the sulphate, after being well washed, is exposed to a current of sulphuretted hydrogen gas, which precipitates all the lead as a sulphuret, but does not decompose the selenic acid. The excess of sulphuretted hydrogen 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 muriate of baryta after being boiled with muriatic acid. Any nitric acid which may be present is expelled by concentrating the solution by means of heat.

Selenic acid is a colourless liquid, which may be heated to 536° F. 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 specific gravity 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 576°, 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 contained.

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 sulphuretted hydrogen, and hence this gas may be employed for decomposing seleniate of lead or copper. With muriatic acid the change is peculiar; for on boiling the mixture mutual decomposition ensues, water and selenious acid are formed, and chlorine 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 muriatic acid before sulphurous acid is added.

Selenic acid, in its affinity for alkaline bases, is little inferior to sulphuric acid; so much so, indeed, that seleniate of baryta cannot be completely decomposed by sulphuric acid. It is therefore an acid of great power. From the analysis of this acid and of the seleniates of potash and soda, by Professor Mitscherlich, it is established that the oxygen combined in selenious and selenic acids with the same quantity of selenium, is in the ratio of 2 to 3, as is the case with sulphurous and sulphuric acids. Hence selenic acid is a compound of 40 parts or one equivalent of selenium, and 24 parts or three equivalents of oxygen; and its equivalent is 64.

Professor 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 XI.

CHLORINE.

The discovery of chlorine was made in the year 1770 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 oxymuriatic acid might be regarded as a simple body, though they gave the preference to the doctrine advanced by Berthollet. Sir H. Davy engaged in the inquiry about the same time; and after having exposed oxymuriatic 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 almost universally received by chemists, and accordingly is adopted in this work. The grounds of preference will hereafter be briefly stated.

Chlorine gas is obtained by the action of muriatic acid on peroxide of manganese. The most convenient method of preparing it is by mixing concentrated muriatic 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 in inverted glass bottles filled with warm water; and when the water is wholly displaced by the gas, the bottles should be closed with a well-ground glass stopper. As some muriatic acid gas commonly passes over with it, the chlorine should not be considered quite pure, till after being transmitted through water.

Before explaining the theory of this process, it may be premised that muriatic acid consists of 36 parts or one equivalent of chlorine, and 1 part or one equivalent of hydrogen. Peroxide of manganese, as already mentioned, (page 193) is composed of 28 parts or one equivalent of manganese, and 16 or two equivalents of oxygen. When these compounds react on each other, one equivalent of each is decomposed. The peroxide of manganese gives one equivalent of oxygen to the hydrogen of the muriatic acid, in consequence of which one equivalent of water is generated, and one equivalent of chlorine disengaged; while the protoxide of manganese unites with an equivalent of undecomposed muriatic acid, and forms an equivalent of muriate of the protoxide of manganese. Consequently, for every 44 grains of peroxide of manganese, 74 (37 × 2) grains of real muriatic acid disappear; and 36 parts of chlorine, 9 of water, and 73 of protomuriate of manganese, are the products of the decomposition. The affinities which

determine these changes are the attraction of oxygen for hydrogen, and of protoxide of manganese for muriatic acid.

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, muriatic acid is disengaged, which reacts as in the former case upon the peroxide of manganese; so that, instead of adding muriatic acid directly to the manganese, the materials for forming it are employed. In this process, however, the protoxide of manganese unites with sulphuric instead of muriatic acid, and the residue is sulphate of manganese and sulphate of soda.

Chlorine (from $\chi\lambda\omega\rho\circ\varsigma$, 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, a character which it possesses in common with oxygen gas. According to Sir H. Davy, 100 cubic inches of it at 60° F., and when the barometer stands at 30 inches, weigh between 76 and 77 grains. Dr. Thomson states its weight at 76.25 grains, and his result agrees very nearly with that of Gay-Lussac and Thenard. Adopting this estimate, its specific gravity is 2.5. 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.

In consequence of the extensive range of affinity possessed by chlorine, it is important that its combining proportion should be determined with precision. The number stated by Berzelius is 35.43, and according to Dr. Thomson 36 is its equivalent. The estimate of Dr. Thomson is usually employed in Britain, and therefore, for want of better grounds of choice, I have adopted it in this work; but the subject is exactly one of those, of which a careful examination is much to be wished.

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° F. yellow crystals are formed, which consist of water and chlorine in definite proportions. They are composed, according to Mr. Faraday, of 36 parts or one equivalent of chlorine, and 90 or ten equivalents of water.

Chlorine 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. Sir H. 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 muriatic acid, and oxygen gas is set at liberty. This change takes place quickly in sunshine, more slowly in diffused day-light, and not at all when light is wholly excluded. Hence the necessity of keeping moist chlorine gas, or its solution, in a dark place, if it is wished to preserve it for any time.

Chlorine unites with some substances with evolution of heat and light, and is hence termed a supporter of combustion. If a lighted taper be plunged 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 chlorine 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; and most compound substances, of which hydrogen is an element, are deprived of that principle, and therefore decomposed

in like manner. 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. Hence it happens that chlorine is, indirectly, one of the most powerful oxidizing 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 negative, and chlorine to the positive pole of the battery. This establishes a close analogy between oxygen and chlorine, both of them being supporters of combustion, and both negative electrics.

Chlorine, though formerly called an acid, 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.

The mutual action of chlorine and the pure alkalies leads to complicated changes. If chlorine gas is passed into a solution of potash till all alkaline reaction ceases, a liquid is obtained which has the odour of a solution of chlorine in water. But on applying heat, the chlorine disappears entirely, and the solution is found to contain two neutral salts, chlorate and muriate of potash. The production of the two acids is owing to decomposition of water, the elements of which unite with separate portions of chlorine and form chloric and muriatic acids. The affinities which give rise to this change are the attraction of chlorine for hydrogen, of chlorine for oxygen, and of the two resulting acids for the alkali.

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. Sir H. 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 muriatic acid is always generated when chlo-

rine 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 deutoxide of hydrogen and chromic acid, 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; and it probably acts in a similar way on contagious effluvia. A peculiar compound of chlorine and soda, the nature of which will be considered in the section on Sodium, has been lately introduced for this purpose by M. Labarraque.

Chlorine is in general easily recognised by its colour and odour. Chemically it may be detected by its bleaching property, added to the circumstance that a solution of nitrate 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 by nitrate of silver; for the oxygen of the oxide of silver unites with a portion of chlorine, and converts it into chloric acid.

The 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.

COMPOUND OF CHLORINE AND HYDROGEN.—MURIATIC ACID GAS*.

Muriatic or hydrochloric acid gas was discovered in 1772 by Priestley. It may be conveniently prepared by putting an ounce of strong muriatic acid into a glass flask, and heating

* I have here deviated slightly from my arrangement. I have done so, because it will facilitate the study of the compounds of chlorine with the simple non-metallic bodies, to describe them in the same section. Iodine and Bromine, for a like reason, will be treated in a similar manner.

it by means of a lamp till the liquid boils. Pure muriatic acid 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 muriatic acid gas is disengaged. In the former process, muriatic acid, previously dissolved in water, is simply expelled from the solution by increased temperature. The explanation of the latter process is more complicated. Sea-salt was formerly supposed to be a compound of muriatic acid and soda; and, on this supposition, the soda was believed merely to quit the muriatic and unite with sulphuric acid. But according to the experiments of Gay-Lussac and Thenard and Sir H. Davy, sea-salt in its dry state consists not of muriatic acid and soda, but of chlorine and sodium, the metallic base of soda. The proportion of its constituents are

Chlorine	36	.	1 proportional.
Sodium	24	.	1 proportional.

When sulphuric acid is added to it, one proportion of water is resolved into its elements: its hydrogen unites with chlorine, forming muriatic acid, which escapes in the form of gas; while soda is generated by the combination of its oxygen with sodium, which combines with the sulphuric acid, and forms sulphate of soda. The water contained in liquid sulphuric acid is therefore essential to the success of the operation. The affinities which determine the change are the attraction of chlorine for hydrogen, of sodium for oxygen, and of soda for sulphuric acid.

Muriatic 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 muriatic 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 or electricity, sudden inflammation of the whole mixture, accompanied with explosion; and, according to Mr. Brande, the vivid light emitted by charcoal intensely heated by galvanic electricity acts in a similar manner.

The experiments of Davy and Gay-Lussac and Thenard concur in proving that hydrogen and chlorine unite in equal volumes, and that the muriatic 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 muriatic acid is easily inferred. For, as

		Grains.
50 cubic inches of	Chlorine weigh .	38.125
and 50	Hydrogen . .	1.059
100 c. i. of Muriatic acid gas must weigh		39.184

Its specific gravity, therefore, is 1.2847. By weight it consists of

Chlorine .	38.125 .	36
Hydrogen .	1.059 .	1

Since chlorine and hydrogen unite in one proportion only, most chemists regard muriatic acid as a compound of one equivalent of each of its elements; a conclusion which appears to be justified by the proportions in which chlorine and hydrogen unite with other bodies. Hence, 36 is one equivalent of chlorine, and 37 the equivalent of muriatic acid.

Muriatic acid is a colourless gas, of a pungent odour, and acid taste. Under a pressure of 40 atmospheres, and at the temperature of 50° F. it is liquid. 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, and the gas itself does not take fire on the approach of flame.

Muriatic acid gas is not chemically changed by mere heat. It is readily decomposed by galvanism, hydrogen appearing at the negative, and chlorine at the positive 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 muriatic acid gases is electrified, the oxygen unites with the hydrogen of the muriatic acid to form water, and chlorine is set at liberty. For this and the preceding fact we are indebted to the researches of Dr. Henry.

One of the most striking properties of muriatic acid gas is its powerful attraction for water. A dense white cloud appears whenever muriatic acid escapes into the air, owing to combination which ensues between the acid and watery vapour. When a piece of ice is put into a jar full of the gas confined over mercury, the ice 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 muriatic 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.

A concentrated solution of muriatic acid gas in water has long been known under the names of *spirit of salt*, and of *marine* or *muriatic acid*. It is made by transmitting a current of gas into water as long as any of it is absorbed. Considerable increase of temperature takes place during the absorption, and therefore the apparatus should be kept cool by ice. Sir H. Davy states (Elements, p. 252.) that water at the temperature of 40° F. absorbs 480 times its volume of the gas, and that the solution has a density of 1.2109. Dr. Thomson finds that one cubic inch of water at 69° F. absorbs 418 cubic inches of gas, and occupies the space of 1.34 cubic inch. The solution has a density of 1.1958, and one cubic inch of it contains 311.04 cubic inches of muriatic 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 grains of marble correspond to 37 of real acid. The following table from Dr. 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.
1	6	40.650	1.203
1	7	37.000	1.179
1	8	33.945	1.162
1	9	31.346	1.149
1	10	29.134	1.139
1	11	27.206	1.1285
1	12	25.517	1.1197
1	13	24.026	1.1127
1	14	22.700	1.1060
1	15	21.512	1.1008
1	16	20.442	1.0960
1	17	19.474	1.0902
1	18	18.590	1.0860
1	19	17.790	1.0820
1	20	17.051	1.0780

All the Pharmacopœias give directions for forming muriatic acid. The process recommended 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 already been explained. The residue is a mixture of sulphate and bi-sulphate of soda. The specific gravity of muriatic acid obtained by this process is 1.170.

Muriatic acid of commerce has a yellow colour, and is always impure. Its usual impurities are nitric acid, sulphuric acid, and oxide of iron. The presence of nitric acid may be inferred if the muriatic acid has the property of dissolving gold leaf. Iron may be detected by ferrocyanate of potash, and

sulphuric acid by muriate of baryta, the suspected muriatic 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 muriate of iron and sulphuric acid which pass over, and the muriatic acid gas is condensed in the second.

Pure concentrated muriatic acid is a colourless liquid, which emits white vapours when exposed to the air, is intensely sour, reddens litmus paper strongly, and unites with 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° F., or a little higher, giving off pure muriatic acid gas in large quantity.

Muriatic 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, and selenic acids act on the same principle. The action of nitric acid is illustrative of the same circumstance. A mixture of nitric and muriatic acids, in the proportion 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 muriatic and nitrous acids, which is incapable of dissolving gold. The explanation of these facts is, that nitric and muriatic acids decompose one another, giving rise to the production of water and nitrous acid, and the separation of chlorine: while muriatic and nitrous acids may be heated together without mutual decomposition. It is hence inferred that the power of nitro-muriatic acid in dissolving gold is owing to the chlorine which is liberated. (Sir H. Davy in the Quarterly Journal, vol. i.)

Muriatic acid is distinguished by its odour, volatility, and

strong acid properties. With nitrate 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 muriatic acid, and the chlorine in consequence is entirely precipitated. Notwithstanding that nitrate of silver yields the same precipitate with chlorine and muriatic acid, there is no difficulty in distinguishing between them; for the bleaching property of the former is a sure ground of distinction.

COMPOUNDS OF CHLORINE AND OXYGEN.

Chlorine unites with oxygen in four different proportions. 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, consequently, 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. Notwithstanding this, their union is always regulated by the law of definite proportions, as appears from the following tabular view of the constitution of the compounds to which they give rise *.

	Chlorine.		Oxygen.
Protoxide of Chlorine	36	.	8
Peroxide of Chlorine	36	.	32
Chloric acid	36	.	40
Perchloric acid	36	.	56

Berzelius contends for the existence of a fifth compound, intermediate between peroxide of chlorine and chloric acid, and for which he has proposed the name of *chlorous acid*; but his arguments in favour of this opinion, which will be more particularly specified in my general remarks on the metals, cannot, I apprehend, be admitted as decisive.

Protoxide of Chlorine.—This gas was discovered in 1811 by Sir H. Davy, and was described by him in the Philosophical Transactions for that year under the name of *Euchlorine*. It is made by the action of muriatic acid on chlorate of potash; and its production is explicable by the fact, that muriatic and

* Note by Gay-Lussac in the 9th volume of the An. de Ch. et de Physique.

chloric acids mutually decompose each other. When muriatic acid and chlorate of potash are mixed together, part of the muriatic acid unites with the potash of the salt, and thus sets chloric acid free, which instantly reacts on the free muriatic acid. The result of the reaction depends on the relative quantity of the substances. If chlorate of potash is mixed with excess of concentrated muriatic acid, the chloric acid undergoes complete decomposition. For each equivalent of chloric, five equivalents of muriatic acid are decomposed: the five equivalents of oxygen, contained in the former, unite with the hydrogen of the latter, producing five equivalents of water; while the chlorine of both acids is disengaged. If, on the contrary, chlorate of potash is in excess, and the muriatic acid diluted, the chloric acid is deprived of part of its oxygen only; and the products are water, protoxide of chlorine, and chlorine, the two latter escaping in the gaseous form. From the relative proportion in which these gases are evolved, it is probable that for each equivalent of chloric, three of muriatic acid must be decomposed; and that by the reaction of their elements, they yield three equivalents of water, two of pure chlorine, and two of the protoxide of chlorine.

The best proportion of the ingredients for forming this compound is two parts of chlorate of potash, one of strong muriatic acid, and one of water; and the reaction of the materials should be promoted by heat sufficient to produce moderate effervescence. The gases should be collected over mercury, which combines with the chlorine, and leaves the protoxide of chlorine in a pure state.

Protoxide of chlorine has a yellowish green colour similar to that of chlorine, but considerably more brilliant, which induced Sir H. Davy to give it the name of *euchlorine*. Its odour is like that of burned sugar. Water dissolves eight or ten times its volume of the gas, and acquires a colour approaching to orange. It bleaches vegetable substances, but gives the blue colours a tint of red before destroying them. It does not unite with alkalies, and therefore is not an acid.

Protoxide of chlorine is explosive in a high degree. The heat of the hand, or the pressure occasioned in transferring it from one vessel to another, sometimes causes an explosion. This effect is also occasioned by phosphorus, which bursts into flame at the moment of immersion. All burning bodies, by

their heat, occasion an explosion, and then burn vividly in the decomposed gas. With hydrogen it forms a mixture which explodes by flame or the electric spark, with production of water and muriatic acid. The best proportion is fifty measures of protoxide of chlorine to eighty of hydrogen.

Protoxide of chlorine is easily analyzed by heating a known quantity of it in a strong tube over mercury. An explosion takes place; and 50 measures of the gas expand to 60 measures, of which 20 are oxygen, and 40 chlorine. The specific gravity of a gas so constituted must be 2.444; and it consists of 36 parts of chlorine and 8 of oxygen. Its atomic weight is consequently 44.

Peroxide of Chlorine.—This compound was discovered in 1815 by Sir H. Davy (Phil. Trans. for 1815), and soon after by Count Stadion of Vienna. It is formed by the action of sulphuric acid on chlorate of potash. 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 still richer colour than protoxide of chlorine is disengaged, which has an aromatic odour without any smell of chlorine, is absorbed rapidly by water, to which it communicates its tint, and has no sensible action on mercury. This gas is peroxide of chlorine.

The chemical changes which take place in the process are explained in the following manner. The sulphuric acid decomposes some of the chlorate of potash, 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 chlorate of potash, and converts it into perchloric acid. The whole products are bisulphate and perchlorate of potash, and peroxide of chlorine. It is most probable, from the data contained in the preceding table, that every three equivalents of chloric acid yield one equivalent of perchloric acid and two equivalents of peroxide of chlorine.

Peroxide of chlorine does not unite with alkalies. It destroys most vegetable blue colours without previously reddening them.

Phosphorus takes fire when introduced into it, and occasions an explosion. It explodes violently when heated to a temperature of 212° F., emits a strong light, and undergoes a greater expansion than protoxide of chlorine. According to Sir H. 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 36 parts or one equivalent of chlorine, united with 32 or four equivalents of oxygen; and its specific gravity must be 2.361. Count Stadion considers the chlorine to be united with three instead of four equivalents of oxygen.

Chloric acid.—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.

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. It gives no precipitate in solution of nitrate of silver, and hence cannot be mistaken for muriatic acid. Its solution may be concentrated by gentle heat till it acquires an oily consistence without decomposition; but at a higher temperature, part of the acid is volatilized without change, while another portion is converted into chlorine and oxygen. It 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 sulphuretted hydrogen, water is generated, while sulphur and chlorine are set free. The power of muriatic acid in effecting its decomposition has already been explained.

Chloric acid is readily known by forming a salt with potash, 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 potash, 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.)

Perchloric acid.—The saline matter which remains in the retort after forming peroxide of chlorine, is a mixture of perchlorate and bisulphate of potash; 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 properties of perchloric acid have hitherto been little examined. Count Stadion *, its discoverer, found it to be a compound of one equivalent or 36 parts of chlorine, and 56 or seven equivalents of oxygen; and his analysis has been confirmed by Gay-Lussac †.

CHLORIDE OF NITROGEN.

The mutual affinity of chlorine and nitrogen is very slight: they do not combine at all if presented to each other in their gaseous form; and when combined, they are easily separated. Chloride of nitrogen is formed by the action of chlorine on some salt of ammonia. Its formation is owing to the decomposition of ammonia (a compound of hydrogen and nitrogen) by chlorine. The hydrogen of the ammonia unites with chlorine, and forms muriatic acid; while the nitrogen of the ammonia, being presented in its nascent state to chlorine dissolved in the solution, enters into combination with it.

A convenient method of preparing chloride of nitrogen is the following. An ounce of muriate of ammonia is dissolved in twelve or sixteen ounces of hot water; and when the solution has cooled to the temperature of 90° F., 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 twenty minutes or half an hour, minute 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 chloride of nitrogen,

* Annales de Ch. et de Physique, vol. viii. † Ibid. vol. ix.

as they descend, should be collected in a small saucer of lead, placed for that purpose under the mouth of the bottle.

Chloride of nitrogen, discovered in 1811 by M. Dulong, (An. de Chimie, vol. lxxxvi.) is one of the most explosive compounds yet known, having been the cause of serious accidents both to its discoverer and to Sir H. Davy*. 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 at 160° F.; 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.

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 144 parts or four equivalents of chlorine, and 14 parts or one equivalent of nitrogen.

COMPOUNDS OF CHLORINE AND CARBON.—PERCHLORIDE OF CARBON.

For the knowledge of the compounds of chlorine and carbon, chemists are indebted to the ingenuity of 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, muriatic acid is set free, and the carbon, at the moment of separation, unites with the chlorine‡.

* Philosophical Transactions, 1813.

† Nicholson's Journal, vol. xxxiv.

‡ The reader will find the details of this process in the Philosophical Transactions for 1821, or in the second volume, N. S., of the Annals of Philosophy.

Perchloride of carbon, as this compound is named by Mr. Faraday, 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 specific gravity is exactly double that of water. It fuses at 320° F., 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.

Perchloride of carbon 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 muriatic, nitric, or sulphuric acids, even with the aid of heat; charcoal is separated, and muriatic 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.

From the proportions of chlorine and olefiant gas employed in forming perchloride of carbon, and from its analysis, made by passing it over peroxide of copper at the temperature of ignition, Mr. Faraday infers that this compound consists of 108 parts or 3 equivalents of chlorine, and 12 parts or 2 equivalents of carbon.

Protochloride of carbon.—When the vapour of perchloride of carbon is passed through a red-hot glass or porcelain tube, containing fragments of rock crystal to increase the extent of heated surface, partial decomposition takes place; chlorine gas escapes, and a fluid passes over which Mr. Faraday calls the *protochloride of carbon.*

Protochloride of carbon is a limpid colourless fluid, which does not congeal at zero of Fahrenheit, and at 160° or 170° F. 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. Its specific gravity is 1.5526. In its che-

mical relations it is very analogous to perchloride of carbon. Mr. Faraday analyzed it by transmitting its vapour over ignited peroxide of copper; and he infers from the products of its decomposition—carbonic acid and chloride of copper—that it is composed of 36 parts or one equivalent of chlorine, and 6 parts or one equivalent of carbon.

A third compound of chlorine and carbon is described in volume xvii. of the Annals of Philosophy. It 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° F. 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 muriatic acid gas.

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. From these facts, the greater part of which were ascertained by Messrs. Phillips and Faraday, it follows that the substance brought from Sweden by M. Julin is a compound of chlorine and carbon; and the same able chemists conclude, from their analysis, that its elements are united in the ratio of one equivalent of chlorine to two equivalents of carbon. (An. of Phil. xviii. 150.)

CHLORIDE OF SULPHUR.

Chloride of Sulphur was discovered in the year 1804 by Dr. 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. Direct combination takes place, and the product is obtained under the form of a liquid which appears red by reflected, and yellowish-green by transmitted light. Its density is 1.6. It is volatile below 200° F., 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, the water becomes cloudy from deposition of sulphur, and a solution is obtained, in which muriatic, sulphurous, and sulphuric acids may be detected. Similar phenomena ensue when it is mixed with alcohol or ether.

According to Sir H. Davy, chloride of sulphur is composed of thirty parts of sulphur, and 68.4 of chlorine; a proportion which leaves little doubt of its being a compound of 36 or one equivalent of chlorine, and 16 or one equivalent of sulphur. (Elements, p. 280.)

COMPOUNDS OF CHLORINE AND PHOSPHORUS.

There are two definite compounds of chlorine and phosphorus, the nature of which was first satisfactorily explained by Sir H. 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° F. 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

* Nicholson's Journal, vol. vi. † Memoires d'Arcueil, vol. i.

each other; and the sole products are muriatic and phosphoric acids. Now in order that these products should be formed, consistently with the constitution of phosphoric acid, as stated at page 273, the perchloride must consist of 15.71 parts or one equivalent of phosphorus, and 90 parts or two equivalents and a half of chlorine. One equivalent of the chloride and two and a half of water will then mutually decompose each other without any element being in excess, and yield one equivalent of phosphoric, and two and a half equivalents of muriatic acid. This proportion is not far from the truth; for, according to Sir H. Davy, one grain of phosphorus is united in the perchloride with six of chlorine.

Protochloride 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 specific gravity 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 muriatic and phosphorous acids is obtained. It hence appears to consist of 15.71 parts, or one proportional, of phosphorus, and 54 parts or one proportional and a half of chlorine.

When sulphuretted hydrogen gas is transmitted through a vessel containing perchloride of phosphorus, muriatic acid is disengaged, and a liquid produced which Serullas states to be a compound of three equivalents of chlorine, one of phosphorus, and one of sulphur. (An. de Ch. et Ph. XLII. 25.)

CHLOROCARBONIC ACID GAS.

This compound was discovered in 1812 by Dr. John Davy, who described it in the Philosophical Transactions for that year, under the name of *phosgene gas**. It is made by exposing a mixture of equal measures of dry chlorine and carbonic oxide gases to sunshine, when rapid but silent combination ensues, and they contract to one half their volume. Diffused

* From φως light and γινναω I produce.

day-light also effects their union slowly; but they do not combine at all when the mixture is wholly excluded from light.

Chlorocarbonic acid gas is colourless, 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 muriatic acids. When tin is heated in chlorocarbonic acid 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 105.9 grains; namely, 76.25 of chlorine added to 29.65 of carbonic oxide. Its specific gravity is therefore 3.4721; and it consists of 36 parts or one equivalent of chlorine, and 14 parts or one equivalent of carbonic oxide.

CHLORIDE OF BORON.

Sir H. 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 the production of muriatic and boracic acids. The watery vapour of the atmo-

sphere occasions a similar change, so that when the gas is mixed with air containing hygrometric moisture, a dense white cloud is produced. The specific gravity 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 muriatic acid. It unites with ammoniacal gas, forming a fluid volatile substance, the nature of which is unknown.—(Annals of Phil. xxvi. 129.)

M. 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. M. Despretz also appears to have invented a similar process.—(Philos. Magazine and Annals, i. 469.)

The composition of the chloride of boron may be inferred from its action on water. If the constitution of boracic acid, as estimated by Dr. Thomson, is correct, page 283, the chloride of boron should consist of 72 parts or two equivalents of chlorine, and 8 parts or one equivalent of boron; for one equivalent of such a compound, with two of water, will yield one of boracic and two equivalents of muriatic acid.

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. Muriatic acid, by the same rule, is considered to be a compound of chlorine and hydrogen. For when it is 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, muriatic acid gas is the product. Chemists have no other kind of proof of the composition of water, of potash, or of any other compound.

Very different is the evidence in support of the theory of Berthollet. According to that view, muriatic 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, muriatic 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 muriatic 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 is attracted 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 muriatic 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 muriatic 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 muriatic acid gas, and thus to establish the old theory to the subversion of the new. Into this discussion, however, I shall not enter here, as it would lead into details too minute for an elementary treatise. I may only observe, in referring the reader to the original papers on the subject*, that Dr. Murray did not succeed in establishing his point; and that his arguments, though exceedingly plausible and ingenious, were fully answered by Sir Humphrey and Dr. John Davy. I must also state, that the history of the only experiment which strictly bears upon the question,—that, namely, in which muriatic acid and ammoniacal gases were mixed together,—amounts very nearly to a demonstration of the absence of combined water in muriatic acid gas. The traces of humidity, which were observed, may easily be accounted for by the difficulty of rendering gases absolutely dry, which have themselves a strong affinity for moisture; whereas the absence of so large a quantity of water, as ought, according to Dr. Murray's argument, to be present in muriatic acid gas, does not admit of a satisfactory explanation, except by supposing that gas to be anhydrous.

SECTION XII.

IODINE.

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, investigating

* In Nicholson's Journal, vols. xxxi. xxxii. and xxxiv. Edinburgh Philos. Trans. vol. viii. and Philos. Trans. for 1818.

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. Clement, who recognised 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 Sir H. Davy, each of whom proved that it is a simple non-metallic substance, exceedingly analogous to chlorine *.

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 specific gravity, according to Gay-Lussac, is 4.948; but Dr. Thomson found it only 3.0844. At 225° F. 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 specific gravity, as calculated by the formula of page 186, being 8.6102; or 8.716 as directly observed by M. Dumas. Hence 100 cubic inches, at the standard temperature and pressure, must weigh 262.612 grains. Dr. Thomson infers, partly from the experiments of Gay-Lussac, and partly from his own researches, that the atomic weight of iodine is 124; but according to the experiments of Berzelius its equivalent is 126.26.

Iodine is a non-conductor of electricity, and, like oxygen and chlorine, is a negative electric. It has a very acrid taste, and its odour is almost exactly similar to that of chlorine, when much diluted with air. It acts energetically on the animal system as an irritant poison, but is employed medicinally in very small doses with advantage.

* 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.

Iodine 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 favourable circumstances may, like chlorine, be made to unite with oxygen. A solution of the pure alkalies acts upon it in the same manner as upon chlorine, giving rise to decomposition of water, and the formation of iodic and hydriodic acids.

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 MM. 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 recognised with certainty by its deep blue colour. This test, according to Professor Stromeyer, is so delicate, that a liquid containing 1—450,000 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 unite with starch. Secondly, the solution should be quite cold at the time of adding the starch; for boiling water decomposes the blue compound, and consequently removes its colour.

IODINE AND HYDROGEN—HYDRIODIC ACID GAS.

When a mixture of hydrogen and the vapour of iodine is transmitted through a red-hot porcelain tube, direct combination takes place between them, and a colourless gas, possessed of acid properties, is the product. To this substance the term *Hydriodic acid gas* is applied.

This gas may be obtained quite pure by the action of water on iodide of phosphorus. Any convenient quantity of the ioduret 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 acid, the latter of which passes over in the form of a colourless gas. The preparation of the ioduret 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, and about twelve inches long, displacing the air by a current of dry carbonic acid gas, and then adding the iodine by degrees. The action should be promoted towards the close by a gentle heat. The materials should be well dried with bibulous paper, and the phosphuret 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 M. 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.

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 muriatic acid gas. It combines with alkalies, forming salts which are called *hydriodates*. Like muriatic acid gas it cannot be collected over water; for that liquid dissolves it in large quantity.

Hydriodic acid 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; muriatic 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 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. This result induced him to suspect that the composition of hydriodic must be analogous to that of muriatic acid gas; that, as 100 measures of the latter contain 50 of hydrogen and 50 of chlorine, 100 measures of the former consist of 50 of hydrogen and 50 of the vapour of iodine. If this view be correct, then the composition of hydriodic acid gas, by weight, may be determined by calculation. For since

		Grains.
50	cubic inches of the vapour of iodine weigh	131.306
50	. . hydrogen gas .	1.059
100	of hydriodic acid gas must weigh	132.365;

and its specific gravity will be 4.3398. Now Gay-Lussac ascertained, by weighing hydriodic acid gas, that its density is 4.443,—a number which corresponds so closely with the preceding, as to leave no doubt that the principle of the calculation is correct. There is good reason to believe, indeed, that the calculated result, if not rigidly exact, is very near the truth; for Gay-Lussac states, that the number determined by him directly is too high. (An. de Chimie, vol. xci. p. 16.)

Hydriodic acid is regarded as a compound of one equivalent of each element,—an opinion supported both by the proportions in which iodine combines with other substances, and by the

analogy of muriatic acid. The constitution of hydriodic acid may therefore be thus stated:

	By Volume.	By Weight.
Iodine	50	124 or one proportional.
Hydrogen	50	1 or one proportional;
	100	125

and its combining proportion is 125.

When hydriodic acid 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 density of 1.7. It may be prepared also by transmitting a current of sulphuretted hydrogen gas through water in which iodine in fine powder is suspended. The iodine, from having a greater affinity than sulphur for hydrogen, decomposes the sulphuretted hydrogen; 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 sulphuretted hydrogen, and subsequently filtered to separate free sulphur.

The solution of hydriodic acid is readily decomposed. Thus, 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 acids 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 muriatic 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.

Hydriodic acid is frequently met with in nature in combina-

tion with potash or soda. Under this form it occurs in many salt and other mineral springs, both in England and on the continent. 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 Dr. Fyfe (Edinburgh 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 the hydriodic acid, which they contain, from the sea. Vauquelin has found it also in the mineral kingdom, in combination with silver. (Annales de Chimie et de Physique, vol. xxix.)

All 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, 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 hydriodic acid, combined with soda or potash. By adding a sufficient quantity of sulphuric acid, the hydriodic acid is separated from the alkali, 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 some peroxide of manganese to the mixture. The oxygen of the manganese decomposes the hydriodic acid, and protosulphate of manganese is formed. (Dr. Ure's Paper in the 50th volume of the Philosophical Magazine.) Another method, proposed by M. Soubeiran, is by adding to the ley from kelp a solution made with one part of sulphate of copper and two and a quarter of protosulphate of iron, both in crystals, as long as a white precipitate appears. The proto-iodide 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.

IODINE AND OXYGEN.—IODIC ACID.

Iodic acid was discovered about the same time by Gay-

Lussac and Sir H. Davy; but the latter first succeeded in obtaining it in a state of perfect purity. When iodine is brought into contact with protoxide of chlorine, immediate action ensues; the chlorine of the protoxide unites with one portion of iodine, and its 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. (Philos. 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. (An. de Ch. et Ph. xliii. 216.)

This compound, which was termed *oxiodine* by Sir H. Davy, is *anhydrous iodic acid.* It is a white semitransparent solid, which has a strong astringent sour taste, but no odour. Its density 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.

Iodic acid deliquesces in a moist atmosphere, and is very soluble in water. The liquid acid thus formed reddens vegetable blue colours, and afterwards destroys them. 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 was said by Davy to unite with several acids, such as the sulphuric, nitric, phosphoric, and boracic acids, and to form crystallizable compounds with the three former; but Serullas denies the existence of such compounds. It is decomposed by sulphurous, phosphorous, and hydriodic acids,

and by sulphuretted hydrogen. Iodine in each case is set at liberty, and may be detected as usual by starch. Muriatic and iodic acids decompose each other, water and chloriodic acid being generated.

Sir H. Davy analyzed iodic acid by determining the quantity of oxygen which it evolves when decomposed by heat. Gay-Lussac effected the same object by heating iodate of potash, when pure oxygen was given off, and iodide of potassium remained. From the result of these analyses, it appears that iodic acid is a compound of 124 parts or one equivalent of iodine, and 40 parts or five equivalents of oxygen. The sum of these numbers, or 164, is therefore the combining proportion of the acid.

Iodous acid.—This name was applied to a compound prepared in 1824 by Professor Sementini of Naples by the action of iodine on chlorate of potash. (Quarterly Journal of Science, XVII. 381.) Equal weights of the materials well triturated together were exposed to heat in a retort, when a yellow volatile liquid of the consistence of oil, the supposed iodous acid, passed over into the receiver. But it appears from the subsequent experiments of Wöhler, that this matter does not consist of iodine and oxygen, but of iodine and chlorine. Its formation is owing to part of the chloric acid being decomposed. Its elements unite with separate portions of iodine, and generate two compounds;—iodic acid, which remains in the retort combined with potash, and chloride of iodine, similar to that described by Gay-Lussac, which is sublimed. (Edin. Journ. of Science, No. XII. 352.) From some other experiments, however, M. Sementini has almost proved the existence both of iodous acid and an oxide of iodine. He states that on bringing together the vapour of iodine and oxygen gas considerably heated, the violet tint of the former disappears, and a yellow matter of the consistence of solid oil is generated. This he regards as oxide of iodine; and if the supply of oxygen is 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, at the same time, the new compounds have not been examined analytically, nor has the

chemical constitution of the substances hitherto prepared by M. Sementini been determined with that accuracy which is required for inspiring confidence in his results. (Quarterly Journal of Science, N. S. I. 478.)

Mitscherlich has observed, that on dissolving iodine in a rather dilute solution of soda, until the solution began to acquire a red tint, permanent crystals were obtained by spontaneous evaporation. They had the form of a six-sided prism, and dissolved in cold water without change; but by the action of water moderately heated, or by alcohol, they were converted into iodate of soda and ioduret of sodium. On the addition of an acid, iodine and iodic acid were set at liberty. From these facts the crystals were inferred to be iodite of soda. (An. de Ch. et Ph. xxx. 84.)

CHLORIODIC ACID.

Chlorine is absorbed at common temperatures by dry iodine with evolution of caloric, and a solid compound of iodine and chlorine results, which was discovered both by Sir H. 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, is very sour to the taste, and reddens vegetable blue colours, but afterwards destroys them. From its acid properties Sir H. 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 muriatic and iodic acids, which he supposes to be generated by decomposition of water. The opinion of Sir H. Davy appears to me more probable; for we know that free muriatic and iodic acids mutually decompose each other, and therefore could hardly be generated by the action of water on the compound of iodine and chlorine. A fact greatly in favour of this opinion has been added by Serullas; namely, that chloride of iodine is precipitated from its solution by gradually adding a large quantity of sulphuric acid, and at the same time preventing a rise of temperature by the application of

cold. He also found that on mixing solutions of iodic and muriatic acid, and then adding sulphuric acid as before, chloriodic acid was precipitated. But this compound does not unite with alkaline substances. On mixing it, for example, with baryta, muriate and iodate of baryta are obtained. From this it may be inferred, that water and chloriodic acid decompose each other when an alkali is present.

The composition of chloriodic acid is not known with precision.

Iodide 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 iodine, and thus cause the formation of hydriodic acid and iodide of nitrogen. The latter subsides in the form of a dark powder, which is characterised, like chloride 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 proportional 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, iodide 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.

Serullas has also remarked that water and iodide 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.)

Iodide of Phosphorus.—Iodine and phosphorus combine readily in the cold, evolving so much caloric as to kindle the phosphorus, if the experiment is made in the open air; but in close vessels no light appears. The combination takes place in several proportions, which have not been determined. Its most interesting property is that of decomposing water, with formation of hydriodic and phosphoric acids.

Iodide of Sulphur.—This compound is formed by heating gently a mixture of iodine and sulphur. The product has a dark colour and radiated appearance, like antimony. Its elements are easily disunited by heat.

Periodide of Carbon.—When a solution of pure potash in alcohol is mixed with an alcoholic solution of iodine, a portion of alcohol is decomposed; and its hydrogen and carbon, uniting separately with iodine, give rise to periodide of carbon and hydriodic acid. The latter combines with the potash, and remains in solution. The former has a yellow colour like sulphur, and forms scaly crystals of a pearly lustre; its taste is very sweet, and it has a strong aromatic odour resembling saffron. It was discovered by Serullas, and described by him as a hydro-carburet of iodine; but its real nature was pointed out by Mitscherlich. (An. de Ch. et Ph. xxxvii. 86.)

The protiodide is formed by distilling a mixture of the preceding compound with corrosive sublimate. It is a liquid of a sweet taste, and has a penetrating ethereal odour.

SECTION XIII.

BROMINE.

This peculiarly interesting substance was discovered about two years ago by M. Balard of Montpellier, and the first description of its properties appeared in the *Annales de Chimie et de Physique* for August, 1826. The name originally applied to it was *muride;* but it has been since changed to *brome*, a word derived from the Greek *βρωμος, graveolentia*, signifying a strong or rank odour. This appellation may be conveniently changed in English into that of *bromine.*

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 hydrobromic acid combined, in the opinion of M. Balard, with magnesia. Its relative quantity, however, is very minute; and even the uncrystallizable residue called *bittern*, left after muriate of soda 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. Dr. 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. M. Balard found that it exists in marine plants growing on the shores of the Mediterranean, and he has procured it in appreciable quantity from the ashes of the 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.

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 specific gravity is about 3. Its volatility is considerable; for at common temperatures it emits red coloured vapours, which are very similar in appearance of those of nitrous acid; and at 116.5° F. it enters into ebullition. By a temperature between zero and —4° F. it is congealed, and in that state is brittle. The density of its vapour, as calculated by Berzelius, is 5.3933.

Bromine 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. Bromine 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, M. 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 muriatic and hydriodic acid gases, whence it has received the name of *hydro-bromic* 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 disengagement of 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, but it has a strong attraction for metals. By the action of alkalies it is resolved into hydro-bromic and bromic acids, suffering the same kind of change as chlorine or iodine when similarly treated.

Bromine is usually extracted from bittern, and its mode of preparation is founded on the property which chlorine possesses of decomposing hydro-bromic 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 M. Balard for procuring this substance, as well as for detecting the presence of hydro-bromic 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 potash, its colour entirely disappears, owing to the formation of hydro-bromate and bromate of potash; and the former salt is obtained in cubic crystals by evaporation. The bromine may then be set free by means of chlorine, and separated by heat. M. Balard has subsequently improved the mode of preparation so much, that it is now produced in considerable quantity, and sold in Paris as an article of commerce.

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 M. Balard at first suspected 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 M. 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 positive and iodine at the negative 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.

The combining proportion of bromine, according to the composition of bromuret of silver, as determined by Berzelius, is 78.26.

Bromine, like chlorine, 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°. (Lowig.)

HYDRO-BROMIC ACID GAS.

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 without 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, sulphuretted hydrogen, or phosphuretted hydrogen gases, decomposition ensues, and hydro-bromic 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 hydro-bromic acid gas, which should be collected either in dry glass bottles, or over mercury.

Hydro-bromic acid gas is colourless, 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 muriatic acid gas. 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 muriatic 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.

Hydro-bromic acid gas is very soluble in water. The aqueous solution may be made by treating bromine with sulphuretted hydrogen dissolved in water, or still better, by

transmitting a current of hydro-bromic acid gas through 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 hydro-bromic 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-hydro-bromic acid is analogous to *aqua regia*, and possesses the property of dissolving gold.

The elements of sulphuric and hydro-bromic acids react on each other in a slight degree; and hence, on decomposing hydro-bromate of potash by sulphuric acid, the hydro-bromic is generally mixed with a little sulphurous acid gas.

Metallic oxides, as might be expected, do not act in a uniform manner on hydro-bromic acid. The alkalies, earths, oxides of iron, and peroxide of copper and mercury, form compounds which may be regarded as hydro-bromates; whereas oxide of silver and protoxide of lead give rise to double decomposition, in consequence of which water and a metallic bromuret result.

The composition of hydro-bromic acid gas is easily inferred from the two following facts. 1. On decomposing hydro-bromic 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 hydro-bromic acid occupies the very same space as the gas which is decomposed. It is hence apparent that hydro-bromic is analogous to hydriodic and muriatic acid gases; or, in other words, that 100 measures of hydro-bromic acid gas contain fifty measures of the vapour of bromine, and fifty of hydrogen. By weight it may be regarded as a compound of one proportional of each element.

Since bromine decomposes hydriodic, and chlorine hydro-bromic acid, it is obvious that 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 hydro-bromic acid are termed *hydro-bromates*. Like the free acid, they are decomposed, and the presence of bromine is detected, by means of chlorine. On mixing a soluble hydro-bromate with nitrate of lead, silver, and of protoxide of 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.

BROMIC ACID.

The only compound yet known of bromine and oxygen is that formed by the action of pure potash on bromine, when by decomposition of water, and the union of its elements with separate portions of bromine, bromic and hydro-bromic acids are generated. Of the bromate and hydro-bromate of potash thus produced, the former is much less soluble in water than the latter, and by means of this difference in solubility the two salts are easily separated. The bromate of the other alkalies and alkaline earths may be prepared in a similar manner.

The bromates are analogous to the chlorates and iodates. Thus bromate of potash is converted by heat into bromuret 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 acid and sulphuretted hydrogen, in the same manner as the acid of the iodates. The bromates likewise suffer decomposition from the action of hydro-bromic and muriatic acids.

Bromate of potash is said not to precipitate the salts of lead, but to occasion a white precipitate with nitrate of silver, and a yellowish-white with proto-nitrate of mercury; characters which, if true, serve as a good test to distinguish bromate from iodate and chlorate of potash.

Bromic 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 acquires 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.

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 potash, bromic acid is obviously similar in constitution to iodic, chloric, and nitric acids; that is, it consists of one proportion of bromine united with five of oxygen.

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 the oxides of chlorine, and it enables metals to burn as in an atmosphere of chlorine, doubtless giving rise to the formation of metallic chlorides and bromurets.

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 muriatic and bromic acids.

Bromuret of Iodine.—These substances act readily on each

other, and appear capable of uniting in two proportions. The proto-bromuret 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 hydro-bromic and iodic acids.—The existence of two bromurets of iodine can scarcely be regarded as satisfactorily established.

Bromuret 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 bromuret of sulphur; but at a boiling temperature the action is so violent that a slight detonation occurs, and three compounds, hydro-bromic and sulphuric acids and sulphuretted hydrogen, 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. Bromuret of sulphur is likewise decomposed by chlorine, which unites with sulphur, and displaces bromine.

Bromuret 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 latter is regarded by M. Balard as a proto-bromuret, and the former as a deuto-bromuret of phosphorus.

The proto-bromuret 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 caloric, hydro-bromic 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 deuto-bromuret is yellow in its solid state; but with gentle heat it becomes a red-coloured liquid, which by increase of temperature is converted into 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 bromurets and phosphurets. It emits dense penetrating fumes on exposure to the air, and with water gives rise to the production of hydro-bromic and phosphoric acids.

Chlorine has a greater affinity for phosphorus than bromine, and decomposes both the bromurets with evolution of the vapour of bromine. These compounds are not decomposed by iodine; but on the contrary bromine decomposes iodide of phosphorus.

Bromuret of Carbon.—This compound is formed by the action of bromine on half its weight of periodide of carbon, when bromuret of carbon and a sub-bromuret of iodine are formed, the latter of which is removed by a solution of caustic potash. At common temperatures it is liquid; but crystallizes at 32° F. Its taste is sweet, and it has a penetrating ethereal odour. It resembles protoxide of carbon in many respects; but is distinguished from it by the vapour which it emits on exposure to heat. (Serullas, in the An. de Ch. et Ph. xxxix. 225.)

SECTION XIV.

FLUORINE.

The substance to which this name is applied has not hitherto been obtained in an insulated form, and therefore the properties which are peculiar to it in that state are entirely unknown. 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. With hydrogen it constitutes a peculiar and very powerful acid, the *hydro-fluoric*, the history of which will occupy the greater part of this section.

HYDRO-FLUORIC ACID.

This acid was first procured in its pure state in the year 1810 by MM. 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*, 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 hydro-fluoric acid is found in the receiver, and the retort contains dry sulphate of lime. The chemical changes are similar to those which occur in the decomposition of chloride of sodium by sulphuric acid, as explained at page 298. Fluor-spar consists of fluorine and calcium, and when acted on by oil of vitriol, the water of that acid is resolved into its elements; the hydrogen uniting with fluorine generates hydro-fluoric acid, and the lime, formed by the union of the oxygen of water and calcium, combines with sulphuric acid. If the oil of vitriol is of sufficient strength, all its water is decomposed, and the resulting hydro-fluoric acid is anhydrous.

Hydro-fluoric acid, at the temperature of 32° F., is 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 specific gravity 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 accom-

panied with a hissing noise, as when red-hot iron is quenched by immersion in water.

The vapour of hydro-fluoric acid 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 the preparation of pure hydro-fluoric acid.

This acid when concentrated acts energetically on glass. The transparency of the glass is instantly destroyed, caloric 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 hydro-fluoric 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, hydro-fluoric 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.

Hydro-fluoric acid has all the usual characters of a powerful acid. It has a strong sour taste, reddens litmus paper, and with alkaline substances forms salts, which are termed *hydro-fluates*. All these salts are decomposed by strong sulphuric acid with the aid of heat, and the hydro-fluoric acid while escaping may be detected by its action on glass.

Hydro-fluoric acid acts violently on some of the metals, 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-muriatic acid. Thus it dissolves silicium, zirconium, and columbium, with evolution of hydrogen gas; and when mixed with nitric acid, it proves a solvent for silicium which has been condensed by heat, and

for titanium. Nitro-hydro-fluoric acid, however, is incapable of dissolving gold and platinum. Several oxidized bodies, which are not attacked by sulphuric, nitric, or muriatic acid, are readily dissolved by hydro-fluoric 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.)

Chemists are not agreed as to the precise combining proportion of fluorine. According to the experiments of Dr. Thomson, 18 is the true atomic weight of this substance; but as Berzelius has far more practical knowledge of the compounds of fluorine than other chemists, his result is probably nearer the truth. He found that 100 parts of pure fluoride of calcium, prepared with the greatest care, yielded with sulphuric acid 175 parts of sulphate of lime. According to these numbers, fluoride of calcium consists of 20 parts or one proportion of calcium, and 18.86 parts or one proportion of fluorine, giving 38.86 as an equivalent of the compound; and as the constitution of hydro-fluoric is analogous to that of muriatic and hydriodic acids, it is composed of 18.86 parts of fluorine and 1 part of hydrogen.

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 hydro-fluoric 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 hydro-fluoric acid is, according to this hypothesis, hydrated fluoric acid; and when acted on by potassium, this metal is oxidized at the expense of the water, and potash thus generated unites with fluoric acid, forming, not fluoride of potassium, but fluate of potash. The combining proportion of fluoric acid, as inferred from the analysis of Berzelius, is 10.86; for 38.86 parts or one equivalent of fluor-spar is supposed to contain 28 parts of lime (20 calcium and 8 oxygen), thus leaving 10.86 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 Sir H. Davy. It was found that pure hydro-fluoric 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 hydro-fluoric 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. Sir H. Davy explained these phenomena by supposing that hydro-fluoric 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 Sir H. 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 very recently received strong additional support from the experiments of M. Kuhlman. (Quarterly Journal of Science for July 1827, p. 205.) 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 hydro-fluoric acid was produced. M. Kuhlman also transmitted dry muriatic acid gas over fluor-spar at a red heat, when hydro-fluoric 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 hydro-fluoric 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.

FLUO-BORIC ACID GAS.

The chief difficulty in determining the nature of hydro-fluoric 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 of *fluo-boric acid gas*. A similar train of reasoning led Sir H. Davy about the same time to the same discovery; though the French chemists had the advantage in priority of publication. Fluo-boric acid gas may be prepared more conveniently by mixing one part of vitrified boracic acid, and two of fluor-spar, with twelve parts of strong sulphuric acid, and heating the mixture gently in a glass retort. (Dr. John Davy, Philos. Trans. for 1812.) When thus prepared, however, it contains fluo-silicic acid, according to Berzelius, in considerable quantity; and Dr. Thomson detected in it traces of sulphuric acid. The gas may likewise be formed by the action of hydro-fluoric acid on a solution of boracic acid.

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 fluo-boric 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. Fluo-boric 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 portion, yielding borate of lime and fluo-boric acid gas.

Fluo-boric acid gas is colourless, has a penetrating pungent odour, and extinguishes flame on the instant. Its specific gravity, according to Dr. Thomson, is 2.3622. It reddens litmus paper as powerfully as sulphuric acid, and forms salts with alkalies which are called *fluo-borates*. It has a singularly great affinity for water. When it is mixed with air or any gas which contains watery vapour, a dense white cloud appears, which is a combination of water and fluo-boric acid gas. From this circumstance it affords an exceedingly delicate test of the presence of moisture in gases. Fluo-boric acid gas is rapidly absorbed by water. According to Dr. John Davy, water absorbs 700 times its volume. Caloric is evolved during the absorption, and the water acquires an increase of volume. The saturated 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 fluo-boric 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 fluo-boric acid and water mutually decompose each other, with formation of boracic and hydro-fluoric acids. The latter unites, according to Berzelius, with undecomposed fluo-boric acid, forming what he has called *boro-hydrofluoric acid*. On concentrating the liquid by evaporation, the boracic and hydro-fluoric acids decompose each other, and the original compound is re-produced.

Fluo-boric acid gas does not act on glass, but attacks animal and vegetable matters with energy, converting them like sul-

phuric acid into a carbonaceous substance. This action is most probably owing to its affinity for water.

When potassium is heated in fluo-boric acid gas, the metal takes fire, and a chocolate-coloured solid, wholly devoid of metallic lustre, is formed. This substance is a mixture of fluoride of potassium and boron, from which the former is dissolved by water, and the boron is left in a solid state.

The composition of fluo-boric 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 proportion of each, it will be thus constituted,

Fluo-boric acid gas	2.3622	68.04	one proportional,
Ammoniacal gas	0.5902	17	one proportional;

so that the combining proportion of the acid may be assumed in round numbers to be 68. Now supposing this acid to be formed of three proportionals of fluorine and one of boron, its equivalent will be 64.58, a number which approximates to the preceding. But this view is quite hypothetical. Dr. Thomson considers 34 as the equivalent of fluo-boric acid gas, and believes it to consist of one proportion of fluorine and two of boron. His opinion, however, is very improbable; for the formation of the gas from a mixture of boracic acid and fluor-spar, according to this supposition, appears quite inexplicable. These remarks will serve to show that the data for forming an opinion on this subject are uncertain.

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

SECTION I.

HYDROGEN AND NITROGEN—AMMONIACAL GAS.

Spirit of hartshorn has been long known to chemists; the existence of ammonia as a gas was first noticed by Dr. Priestley, and was described by him in his works under the name of *alkaline air*. It is sometimes called the *volatile alkali;* but the terms *ammonia* and *ammoniacal gas* are now more commonly employed.

The most convenient method of preparing ammoniacal gas for the purposes of experiment is by applying a gentle heat to the concentrated solution of ammonia, contained in a glass vessel. It soon enters into ebullition, and a large quantity of pure ammonia is disengaged.

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. Ammonia, 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. (Dr. Henry in the Philos. Trans. for 1809.)

Ammoniacal gas at the temperature of 50° F. and under a

pressure equal to 6.5 atmospheres, becomes a transparent colourless liquid. It is also liquefied, according to Guyton-Morveau, under the common pressure, by a cold of 70 degrees below zero of Fahrenheit; but there is no doubt that the liquid which he obtained was a solution of ammonia in water.

Ammonia 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 re-appears 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 potash or lime, the union of which with the acid of the salt causing 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 muriatic, the compound itself sublimes unchanged by heat; but if it is in combination with an acid, such as the phosphoric, which is fixed at a low red heat, the ammonia alone is expelled.

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 ammonia through porcelain tubes heated to redness. The late 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. Dr. 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	3.177
and 50 of nitrogen . . .	14.826
100 cubic inches of ammonia must weigh	18.003;

and it is composed by weight of

Hydrogen	3.177	3	or 3 proportionals,
Nitrogen	14.826	14	or 1 proportional.

Its equivalent, therefore, is 17.

The specific gravity of ammonia, according to this calculation, is 0.5902, a number which agrees closely with those ascertained directly by Sir H. Davy and Dr. Thomson.

Ammoniacal gas has a powerful affinity for water, and for this reason must always be collected over mercury. 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. Sir H. Davy, in his Elements, stated that water at 50° F., and when the barometer stands at 29.8 inches, absorbs 670 times its volume of ammonia; and that the solution has a specific gravity of 0.875. According to Dr. 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. Caloric is evolved during its absorption; and a considerable expansion, independently of the increased temperature, occurs at the same time.

The concentrated solution of ammonia, commonly though incorrectly termed *liquid ammonia*, is made by transmitting a current of the gas, as long as it continues to be absorbed, into distilled water, which is kept cool by means of ice or moist cloths. The gas may be prepared from any salt of ammonia by the action of any pure alkali or alkaline earth; but muriate of ammonia and lime, from economical considerations, are always employed. The proportions to which I give the preference are equal parts of muriate of ammonia and well-burned quicklime, considerable excess of lime being taken, in order to decompose the muriate 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 muriate 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 tempera-

ture gradually increased as long as free evolution of gas continues. The ammonia should be conducted by means of a safety tube of Welter into a quantity of distilled water equal to the weight of the salt employed. The residue consists of muriate of lime, or strictly chloride of calcium, and lime.

The concentrated solution of ammonia, as thus prepared, is a clear colourless liquid, of specific gravity 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° F. 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 Sir H. Davy's Elements of Chemical Philosophy, shows the quantity of real ammonia contained in 100 parts of solutions of different densities, at 59° F. and when the barometer stands at 30 inches. The specific gravity 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		32.5	9435		14.53
8875		29.25	9476		13.46
9000	contain	26.00	9513	contain	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, muriate of ammonia, when a glass rod moistened with muriatic acid is brought near it.

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 gas; but the researches of Mr. Faraday have enriched the science by the discovery of two new substances of a similar nature, and the same able chemist has demonstrated the existence of others, though he has hitherto been unable to obtain them in an insulated form. According to Dr. Thomson, naphtha and naphthaline are likewise pure carburets of hydrogen.

LIGHT CARBURETTED HYDROGEN.

This gas is sometimes called *heavy inflammable air*, the *inflammable air of marshes*, *hydro-carburet*, and *protocarburet of hydrogen*. Dr. Thomson proposed the term of *bi-hydroguret of carbon*; but it is more generally known by the name of *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 potash, and 1-15th or 1-20th of nitrogen. This is the only convenient method of obtaining it.

Light carburetted hydrogen is tasteless and nearly inodorous, and it does not change the colour of litmus or turmeric paper. Water, according to Dr. Henry, absorbs about 1-60th of its volume. It extinguishes all burning bodies, and is of course 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.

Mr. Dalton first ascertained the real nature of light carburetted hydrogen, and it has since been particularly examined by Dr. Thomson, Sir H. Davy, and Dr. 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. From this it may be inferred (page 184), that 100 cubic inches of light carburetted hydrogen contain 100 cubic inches of the vapour of carbon and 200 cubic inches of hydrogen gas; and that it is composed by weight of 6 parts or one equivalent of carbon, and 2 parts or two equivalents of hydrogen. Consequently, 8 is its equivalent.

From the same data it follows that 100 cubic inches of light carburetted hydrogen, at 60° F., and when the barometer stands at 30 inches, must weigh 16.939 grains; and its specific gravity is therefore 0.5554. This calculated result is almost identical with the specific gravity of the gas as determined directly by Dr. Henry and Dr. Thomson.

Light carburetted hydrogen is not decomposed by electricity, or by being passed through red-hot tubes, unless the temperature is very great. It may be inferred from the experiments of Berthollet, and from the phenomena that attend the formation of oil gas at high temperatures, that light carburetted hydrogen is resolved into its elements, at least in part, when the heat is very intense. It follows from the nature of the gas, that for each volume so decomposed, two volumes of hydrogen must be set free.

Chlorine and light carburetted hydrogen do not act on each other at common temperatures, when quite dry, even if they are exposed to the direct solar rays. If the gases are 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 product depends upon the proportion of the gases. If four measures of chlorine and one of light carburetted hydrogen are present, carbonic and muriatic acid gases will be produced. For during this action, 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,—which forms muriatic 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. (Dr. Henry.) If a mixture of chlorine and light carburetted hydrogen is electrified or exposed to a red heat, muriatic acid is formed, and charcoal deposited.

It was first ascertained by Dr. Henry (Nicholson's Journal, vol. xix.), and his conclusions have been fully confirmed by the subsequent researches of Sir H. 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 a dreadful explosion ensues. These accidents, which were formerly so frequent and so fatal, are now comparatively rare, owing to the employment of the safety lamp; and I conceive it to be demonstrable, on the view that light carburetted hydrogen is the sole constituent of fire-damp, that accidents of the kind cannot occur at all, provided the gauze lamp is in a due state of repair, and employed with the requisite precautions. For this invention we are indebted to Sir H. Davy; and we must in justice remember that it is not, like many discoveries, the offspring of chance, but the fruit of elaborate experiment and close induction; an invention which originated solely with that philosopher, and which may be regarded as one of the happiest efforts of his genius. (Essay on Flame.)

Sir H. 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 three or four times its volume of air, it does not explode at all. It detonates feebly when mixed with five or six times its bulk of air, and powerfully when one to seven or one to

eight 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 which is 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 Sir H. Davy 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* (see the plate), 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 cannot communicate to 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 Sir H. Davy has shown that the temperature necessary for pro-

ducing 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 caloric 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 caloric, 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.

OLEFIANT GAS.

This gas was 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 sometimes called *bi-carburetted* or *per-carburetted hydrogen* and *hydroguret* of *carbon;* but as none of these terms convey a precise idea of its nature, I shall employ the appellation proposed by its discoverers.

Olefiant gas is prepared by mixing in a capacious retort six measures of strong alcohol with sixteen of concentrated sulphuric acid, and heating the mixture as soon as it is made, by means of an Argand lamp. 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 potash.

The olefiant gas in this process is derived solely from the alcohol; and its production is owing to the strong affinity of sulphuric acid for water. Alcohol is composed of carbon, hydrogen, and oxygen; and from the proportion of its elements it is inferred to be a compound of 14 parts or one equivalent of oxygen gas, united with 9 parts or one equivalent of water. It is only necessary, therefore, in order to obtain olefiant gas, to deprive alcohol of the water which is essential to its constitution; and this is effected by sulphuric acid. The formation of ether, which occurs at the same time, will be explained hereafter. The other phenomena are altogether extraneous. They almost always ensue when substances derived from the animal and vegetable kingdoms are subjected to the action of sulphuric acid. They occur chiefly at the close of the preceding process, in consequence of the excess of acid which is then present.

Olefiant gas is a colourless elastic fluid, which has no taste, and scarcely any odour when pure. 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, Dr. 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. It hence follows that 100 cubic inches contain,

	Grains.
200 cubic inches of the vapour of carbon, which weigh	25.418
200 . . . hydrogen gas, which weigh	4.236;

and consequently

100 cubic inches of olefiant gas must weigh . 29.654.

Its specific gravity, accordingly, is 0.9722: whereas its specific gravity, as taken directly by Saussure, is 0.9852; by Henry, 0.967; and by Thomson, 0.97.

Olefiant gas, by weight, consists of

Carbon .	25.418	12 or two proportionals,
Hydrogen .	4.236	2 or two proportionals;

and its atomic weight is 14.

Olefiant gas, when a succession of electric sparks is passed through 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. Olefiant gas is decomposed by being passed 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.

Chlorine acts powerfully on olefiant gas. When these gases are mixed together in the proportion 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 muriatic 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. This substance is sometimes called *chloric ether;* but the term *hydrocarburet* of *chlorine*, as indicative of its composition, is more appropriate. The name hydrochloride of carbon has also been applied to it.

Hydrocarburet of chlorine was discovered by the Dutch chemists; but Dr. Thomson * first ascertained that it is a compound of olefiant gas and chlorine; and its nature has since been more fully elucidated by the researches of MM. Robiquet and Colin †. To obtain it in a pure and dry state, it should be well washed with water, and then distilled from chloride of calcium. Thus purified, it is a colourless volatile liquid, of a peculiar sweetish taste and ethereal odour. Its specific gravity at 45° F. is 1.2201. It boils at 152° F. and may be distilled without change. It suffers complete decomposition when its vapour is passed through a red-hot porcelain tube, being resolved into charcoal, light carburetted hydrogen, and muriatic acid gas.

The composition of hydrocarburet of chlorine is readily inferred from the fact, that in whatever proportions olefiant gas and chlorine may be mixed together, they always unite in equal volumes. Consequently they combine by weight according to the ratio of their densities, so that hydrocarburet of chlorine consists of

Chlorine . .	2.5 .	36	one proportion,
Olefiant gas .	0.9722	14	one proportion,
	3.4722	50	

and its atomic weight is 50. This estimate is confirmed by the analysis of Robiquet and Colin; but a different view of its composition has been lately proposed by M. Morin. (An. de Ch. et Ph. xliii. 244.) He contends that the chlorine, instead of uniting directly with olefiant gas, decomposes a portion of it, and is equally divided between its hydrogen and carbon, forming muriatic acid aud proto-chloride of carbon; and that the latter unites with the remaining elements of the olefiant gas which was employed. Hydro-carburet of chlorine would

* Memoirs of the Wernerian Society, vol. i.

† An. de Ch. et de Ph. vol. i. and ii.

hence consist of 1 equivalent of chlorine, 4 of carbon, and 3 of hydrogen; but the experiments on which this statement is founded require confirmation.

Hydrocarburet of chlorine forms a very dense vapour, its specific gravity, according to Gay-Lussac, being 3.4434. This is very near the united densities of chlorine and olefiant gas, a circumstance greatly in favour of the general opinion concerning the constitution of the hydrocarburet.

Dr. Henry has demonstrated that light is not essential to the action of chlorine on olefiant gas. On this he has founded an ingenious and perfectly efficacious method of separating olefiant gas from light carburetted hydrogen and carbonic oxide gases, neither of which is acted on by chlorine unless light is present. (Philos. Trans. for 1821.)

Olefiant gas unites also with iodine. This compound was discovered by Mr. Faraday (Philos. Trans. for 1821) by exposing olefiant gas and iodine, contained in the same vessel, to the direct rays of the sun. *Hydrocarburet of iodine*, or hydriodide of carbon, is a solid white crystalline body, which has a sweet taste and aromatic odour. It sinks rapidly in strong sulphuric acid. It is fused by heat, and then sublimed without change, condensing into crystals, which are either tabular or prismatic. On exposure to strong heat, it is decomposed, and iodine escapes. It burns, if held in the flame of a spirit lamp, with evolution of iodine and some hydriodic acid. It is insoluble both in water and in acid or alkaline solutions. Alcohol and ether dissolve it, and on evaporating the solution it crystallizes.

Hydrocarburet of iodine is composed, according to the analysis of Mr. Faraday, of 124 parts or one equivalent of iodine, and 14 parts or one equivalent of olefiant gas. (Quarterly Journal of Science, xiii.)

Hydrocarburet of Bromine.—This compound was formed by M. Serullas by adding one part of hydrocarburet of iodine to two parts of bromine contained in a glass tube. Instantaneous reaction ensues, attended with disengagement of caloric and a hissing noise, and two compounds, the bromuret of iodine and a liquid hydrocarburet of bromine are generated. By means of water the former is dissolved; while the latter, coloured by bromine, collects at the bottom of the liquid. The

decoloration is then effected by means of caustic potash. In order that the process should succeed, the hydrocarburet of iodine must not be in excess.

Hydrocarburet of bromine, after being washed with a solution of potash, is colourless, heavier than water, very volatile, of a penetrating ethereal odour, and of an exceedingly sweet taste, which it communicates to water in which it is placed, in consequence of being slightly soluble in that liquid. It becomes solid at a temperature between 21° and 23° F. This compound is identical with that which M. Balard formed by letting a drop of bromine fall into a flask full of olefiant gas. (An. de Ch. et Physique, xxxiv.)

ON THE NEW CARBURETS OF HYDROGEN DISCOVERED BY MR. FARADAY*.

In the process of compressing oil gas in Mr. Gordon's apparatus, during which operation the gas is subjected to a force equal to the pressure of thirty atmospheres, a considerable quantity of liquid collects, which retains its fluidity at the common atmospheric pressure. This liquid, when recently received from the vessel, boils at 60° F. But as soon as the more volatile portions are dissipated, which happens before one-tenth is thrown off, the point of ebullition rises to 100°; and the temperature gradually ascends to 250° before all the liquid is volatilized. This indicated the presence of several compounds, which differ in volatility; and Mr. Faraday remarked that the boiling point was more constant between 176° and 190° F. than at any other temperature. He was hence led to search for a definite compound in the fluid which came over at that period; and at length, by repeated distillations, and exposing the distilled liquid to a temperature of zero, he succeeded in obtaining a substance, to which he has applied the term of *bi-carburet of hydrogen*.

Bi-carburet of hydrogen, at common temperatures, is a colourless transparent liquid, which smells like oil gas, and has also a slight odour of almonds. Its specific gravity is nearly 0.85 at 60° F. At 32° it is congealed, and forms den-

* Philos. Transactions for 1825, Part II. or Annals of Philosophy, xxvii. 44.

dritic crystals on the sides of the glass. At zero it is transparent, brittle, and pulverulent, and is nearly as hard as loaf-sugar. When exposed to the air at the ordinary temperature it evaporates, and boils at 186°. The density of its vapour at 60°, and when the barometer stands at 29.98 inches, is nearly 2.7760.

Bi-carburet of hydrogen is very slightly insoluble in water; but it dissolves freely in fixed and volatile oils, in ether, and in alcohol, and the alcoholic solution is precipitated by water. It is not acted on by alkalies. It is combustible, and burns with a bright flame and much smoke. When admitted to oxygen gas, so much vapour rises as to make a powerfully detonating mixture. Potassium heated in it does not lose its lustre. On passing its vapour through a red-hot tube, it gradually deposits charcoal, and yields carburetted hydrogen gas. Chlorine, by the aid of sunshine, decomposes it with evolution of muriatic acid. Two triple compounds of chlorine, carbon, and hydrogen, are formed at the same time, one of which is a crystalline solid, and the other a dense thick fluid.

Bi-carburet of hydrogen was analyzed in two ways. In the first, its vapour was passed over oxide of copper heated to redness; and in the second, it was detonated with oxygen gas. Carbonic acid and water were the sole products: and as the absence of oxygen is established by the inaction of potassium, it follows that the bi-carburet consists of carbon and hydrogen only. Mr. Faraday infers from his analyses, that 100 measures of the inflammable vapour require 750 of oxygen for complete combustion; that 150 measures of oxygen unite with 300 of hydrogen; and that the remaining 600 combine with 600 of the vapour of carbon, forming 600 measures of carbonic acid gas. Consequently, 100 measures of the vapour are composed of

Carbon	. (0.4166×6)	. 2.4996	. 36	. 6 proportions.
Hydrogen	. (0.0694×3)	. 0.2082	. 3	. 3 proportions.

Its atomic weight is therefore 39; and its specific gravity by calculation, 2.7078.

The second carburet of hydrogen discovered by Mr. Faraday, to which he has not given a name, was derived from the same source as the preceding. It is obtained by heating with

the hand the condensed liquid from oil gas, and conducting the vapour which escapes through tubes cooled artificially to zero. A liquid is thus procured, which boils by slight elevation of temperature, and before the thermometer rises to 32° F. is wholly reconverted into vapour.

This vapour is highly combustible, and burns with a brilliant flame. Its specific gravity, at 60° F. and 29.94 of the barometer, is about 1.9065. On being cooled to zero, it is again condensed, and the specific gravity of this liquid at 54° is 0.627; so that among solids and liquids it is the lightest body known.

Water absorbs the vapour sparingly; but alcohol takes it up in large quantity, and the solution effervesces on being diluted with water. Alkalies and muriatic acid do not affect it. Sulphuric acid, on the contrary, absorbs more than 100 times its volume of the vapour. A dark coloured solution is formed, but no sulphurous acid is disengaged.

From the analysis of this vapour, made by detonating it with oxygen gas, Mr. Faraday infers that each volume requires six of oxygen for complete combustion, and yields four volumes of carbonic acid. It hence follows that 100 measures of the vapour contain 400 measures of the vapour of carbon and 400 of hydrogen gas, and that this carburet of hydrogen consists, by weight, of

Carbon	(0.4166 × 4)	1.6664	24	4 proportions.
Hydrogen	(0.0694 × 4)	0.2776	4	4 proportions.

Its equivalent is therefore 28. Its specific gravity must be 1.9440; and Mr. Faraday regards this estimate of its specific gravity as nearer the truth than that above stated. The composition of this substance was calculated by Dr. Thomson (Principles of Chemistry, vol. i. p. 151) before the compound itself had been obtained in an insulated form. He terms it *quadro-carburetted hydrogen*, and is of opinion that it exists in sulphuric ether, combined with one equivalent of water. This view is justified by the proportion in which the elements of ether are united.

The discovery of this substance has established a fact which is altogether new to chemists. The elements of the new carburet are united in the proportion of 24 to 4, and those of olefiant gas in that of 12 to 2; that is, the carbon and hydro-

gen in both are in the ratio of 6 to 1, and therefore each may be regarded as a compound of one atom of its component principles. Hence it appears that two substances may be identical with respect to the proportion of their constituents, and yet be quite distinct in their physical and chemical properties.

This peculiarity is explicable on the supposition that the ultimate atoms of such compounds are differently disposed. It is to be presumed that the smallest possible particle of olefiant gas contains two atoms of carbon and two atoms of hydrogen; and that, in like manner, an integrant particle of the new compound of Mr. Faraday contains four atoms of each element. Neither of these substances could, I conceive, be formed by direct union of a single atom of carbon and a single atom of hydrogen. If a combination of the kind were to occur, a new compound, different from any known at present, would be the result. Such appears to me the only satisfactory mode of accounting for the phenomena. A similar instance has already been noticed in the section on phosphorus.

NAPHTHA FROM COAL TAR.

This substance is obtained by the distillation of coal tar, and is termed *Naphtha* from its similarity to mineral naphtha. It has a strong and peculiar empyreumatic odour, and is highly inflammable. Potassium may be preserved in it without losing its lustre, which is a sufficient proof that it contains no oxygen. According to Dr. Thomson, one measure of the vapour of naphtha contains six measures of the vapour of carbon, and six of hydrogen gas; or, by weight, consists of 36 or six proportionals of carbon, and 6 or six proportions of hydrogen.

NAPHTHALINE.

This compound is likewise derived from coal tar. If the distillation is conducted at a very gentle heat, the naphtha, from its greater volatility, first passes over; and afterwards the naphthaline rises in vapour, and condenses in the neck of the retort as a white crystalline solid. (Dr. Kid in the Phil. Trans. for 1821, page 216 *.)

* See also a paper by Mr. Brande in the Quarterly Journal of Science, viii. 289; and Annals of Philosophy, N. S. vi. 136.

Pure naphthaline is heavier than water, has a pungent aromatic taste, and a peculiar, faintly aromatic, odour, not unlike that of the narcissus. It is smooth and unctuous to the touch, is perfectly white, and has a silvery lustre. It fuses at 180°, and assumes a crystalline texture in cooling. It volatilizes slowly at common temperatures, and boils at 410° F. Its vapour, in condensing, crystallizes with remarkable facility in thin transparent laminæ.

Naphthaline is not very readily inflamed; but when set on fire it burns rapidly, and emits a large quantity of smoke. It is insoluble in cold, and very sparingly dissolved by hot water. Its proper solvents are alcohol and ether, and especially the latter. It is likewise soluble in olive oil, oil of turpentine, and naphtha.

The alkalies do not act upon naphthaline. The acetic and oxalic acids dissolve it, forming pink coloured solutions. Sulphuric acid enters into direct combination with it, and forms a new and peculiar acid, which Mr. Faraday has described in the Philosophical Transactions for 1826, under the name of *Sulpho-naphthalic acid.*

Naphthaline, according to the analysis of Dr. Thomson, is a *sesquicarburet* of *hydrogen;* that is, a compound of 9 parts or an equivalent and a half of carbon and one equivalent of hydrogen. It is desirable, however, that this analysis should be repeated.

Sulpho-naphthalic acid is made by melting naphthaline with half its weight of strong sulphuric acid, when a red coloured liquid is formed, which becomes a crystalline solid in cooling. The mass is soluble in water, and the solution contains a mixture of sulphuric and sulpho-naphthalic acids. On neutralizing with carbonate of baryta, the insoluble sulphate subsides, while the soluble sulpho-naphthalate remains in solution; and on decomposing this salt by a quantity of sulphuric acid precisely sufficient for precipitating the baryta, pure sulpho-naphthalic acid is obtained.

The aqueous solution of the acid, as thus formed, reddens litmus paper powerfully, and has a bitter acid taste. On concentrating by heat, the liquid at last acquires a brown tint, and if then taken from the fire becomes solid as it cools. If the concentration is effected by means of sulphuric acid in an

exhausted receiver, the acid becomes a soft white solid, apparently dry, and at length hard and brittle. In this state it is chemically united with water, and deliquesces on exposure to the air; but in close vessels it undergoes no change during several months. Its taste, besides being bitter and sour, leaves a metallic flavour like that of cupreous salts. When heated in a tube at temperatures below 212°, it is fused without undergoing any other change, and crystallizes from centres in cooling. When more strongly heated, water is expelled, and the acid appears to be then anhydrous; but at the same time it acquires a red tint, and a minute trace of free sulphuric acid may be detected,—circumstances which indicate commencing decomposition. On raising the temperature still higher, the red colour first deepens, then passes into brown, and at length the acid is resolved into naphthaline, sulphurous acid, and charcoal; but in order thus to decompose all the acid, a red heat is requisite.

Sulpho-naphthalic acid is readily soluble in water and alcohol, and is also dissolved by oil of turpentine and olive oil, in proportions dependant on the quantity of water which it contains. By the aid of heat it unites with napththaline. It combines with alkaline bases, and forms neutral salts, which are called *sulpho-naphthalates*. All these salts are soluble in water, and most of them in alcohol, and when exposed to heat in the open air, take fire, leaving sulphates or sulphurets according to circumstances.

From Mr. Faraday's analysis of the neutral sulpho-naphthalate of baryta, it appears that 78 parts or one proportional of baryta are combined with 208 parts, or what may be regarded as one equivalent, of sulpho-naphthalic acid. These 208 parts were found to consist nearly of 80 parts or two equivalents of sulphuric acid, 120 parts or 20 equivalents of carbon, and 8 parts or 8 equivalents of hydrogen. It has not been demonstrated that sulphuric acid exists as such in the compound, nor is it known how its elements are arranged; but from some interesting facts noticed by Mr. Hennel, to be mentioned in the section on ether, it appears very probable that sulpho-naphthalic acid is composed of 2 proportionals of sulphuric acid united with 20 equivalents of carbon and 8 of hydrogen, the two latter existing as a carburet of hydrogen.

ON COAL AND OIL GAS.

The nature of the inflammable gases derived from the destructive distillation of coal and oil was first ascertained by Dr. Henry *, who showed, in several elaborate and able essays, that these gaseous products do not differ essentially from each other, but consist of a few well-known compounds, mixed in different and very variable proportions. The chief constituents were found to be light carburetted hydrogen and olefiant gases; but besides these ingredients, they contain an inflammable vapour, free hydrogen, carbonic acid, carbonic oxide, and nitrogen gases. The discoveries of Mr. Faraday have elucidated the subject still further, by proving that there exists in oil gas, and by inference in coal gas also, the vapour of several definite compounds of carbon and hydrogen, the presence of which, for the purposes of illumination, is exceedingly important.

The illuminating power of the ingredients of coal and oil gas is very unequal. Thus the carbonic oxide and carbonic acid are positively hurtful; that is, the other gases would give more light without them. The nitrogen of course can be of no service. The hydrogen is actually prejudicial; because, though it evolves a large quantity of caloric in burning, it emits an exceedingly feeble light. The carburets of hydrogen are the real illuminating agents, and the degree of light emitted by these is dependant on the quantity of carbon which they contain. Thus olefiant gas illuminates much more powerfully than light carburetted hydrogen; and for the same reason, the dense vapour of the quadrocarburet of hydrogen emits a far greater quantity of light, for equal volumes, than olefiant gas.

From these facts, it is obvious that the comparative illuminating power of different kinds of coal and oil gas may be estimated, approximately at least, by determining the relative quantities of the denser carburets of hydrogen which enter into their composition. This may be done in three ways. 1. By their specific gravity. 2. By the relative quantities of oxygen required for their complete combustion. 3. By the relative quantity of gaseous matter condensible by chlorine in the dark;

* Nicholson's Journal for 1805. Philosophical Transactions for 1808. Ibid. for 1821.

for chlorine, when light is excluded, condenses all the hydro-carburets, excepting light carburetted hydrogen. Of these methods, the last is, I conceive, the least exceptionable *.

The formation of coal and oil gas is a process of considerable delicacy. Coal gas is prepared by heating coal to redness in iron retorts. The quality of the gas, as made at different places, or at the same place at different times, is very variable, the specific gravity of some specimens having been found as low as 0.443, and that of others as high as 0.700. These differences arise in part from the nature of the coal, and partly from the mode in which the process is conducted. The regulation of the degree of heat is the chief circumstance in the mode of operating, by which the quality of the gas is affected. That the quality of the gas may be influenced from this cause is obvious from the fact, that all the dense hydro-carburets are resolved by a strong red heat either into charcoal and light carburetted hydrogen, or into charcoal and hydrogen gas. Consequently the gas made at a very high temperature, though its quantity may be comparatively great, has a low specific gravity, and illuminates feebly. It is therefore an object of importance that the temperature should not be greater than is required for decomposing the coal effectually, and that the retorts be so contrived as to prevent the gas from passing over a red-hot surface subsequently to its formation.

These remarks apply with still greater force to the manufacture of oil gas, because oil is capable of yielding a much larger quantity of the heavy hydro-carburets than coal. The quality of oil gas from the same material is liable to such great variation from the mode of manufacture, that the density of some specimens has been found as low as 0.464, and that of others as high as 1.110. The average specific gravity of good oil gas is 0.900, and it should never be made higher. The true interest of the manufacturer is to form as much olefiant gas as possible, with only a small proportion of the heavier hydro-carburets. If the latter predominate, the quantity of gas derived from a given weight of oil is greatly diminished; and a subsequent loss is experienced by the condensation of the

* For a discussion of this and other questions relative to oil and coal gas, the reader may consult an essay by Dr. Christison and myself in the Edinburgh Philosophical Journal for 1825.

inflammable vapours when the gas is compressed, or while it is circulating through the distributing tubes.

Coal gas, when first prepared, always contains sulphuretted hydrogen, and for this reason must be purified before being distributed for burning. The process of purification consists in passing the gas under strong pressure through milk of lime, or causing it to descend through successive layers of dry hydrate of lime. This latter method, which is practised with great success at Perth under the able direction of Mr. Anderson of that city, has this advantage over the former, that while it deprives the gas completely of sulphuretted hydrogen, there is no loss from absorption of olefiant gas or the heavy hydro-carburets, as invariably ensues when milk of lime is employed. But coal gas, after being thus purified, still retains some compound of sulphur, most probably, as Mr. Brande conjectures, sulphuret of carbon, owing to the presence of which a minute quantity of sulphurous acid is generated during its combustion. Oil gas, on the contrary, needs no purification; and as it is free from all compounds of sulphur, it does not yield any sulphurous acid in burning, and is therefore better fitted for lighting dwelling-houses than coal-gas.

With respect to the relative economy of the two gases, I may observe that the illuminating power of oil gas, of specific gravity 0.900, is about double that of coal gas, of 0.600. In coal districts, however, oil gas is fully three times the price of coal gas, and therefore in such situations, the latter is considerably cheaper. (Essay above quoted.)

A successful attempt has been made by Mr. Daniell to procure a gas, similar to that from oil in being free from sulphur, but made with cheaper materials. The substance employed for this purpose is a solution of common resin in oil of turpentine. The combustible liquid is made to drop into red-hot retorts in the same manner as oil; and the oil of turpentine, which from its volatility is driven off in vapour, is collected, and again used as a menstruum. For this process Mr. Daniell has taken out a patent, and the gas so prepared is employed by Mr. Gordon for filling his portable lamps. The gas, when properly made, is said to be of very superior quality, and nearly if not quite equal to oil gas. A patent has also been taken for the formation of gas from a volatile oil, prepared

during the destructive distillation of resin, and a manufacture both of the oil and gas is established at Hammersmith, near London.

SECTION III.

COMPOUNDS OF HYDROGEN AND SULPHUR.—SULPHURETTED HYDROGEN.

The best method of preparing pure sulphuretted hydrogen is by heating sulphuret of antimony in a retort, or any convenient glass flask, with four or five times its weight of strong muriatic acid. An interchange of elements takes place between water and the sulphuret of antimony, in consequence of which, sulphuretted hydrogen and protoxide of antimony are generated. The former escapes with effervescence, while the latter unites with muriatic acid. The affinities which determine these changes are the attraction of hydrogen for sulphur, of oxygen for antimony, and of muriatic acid for protoxide of antimony. This process may be explained differently. Instead of water, muriatic acid may be supposed to undergo decomposition, and, yielding its hydrogen to the sulphur and its chlorine to the metal, give rise to sulphuretted hydrogen and chloride of antimony. It is quite doubtful which explanation is the true one, and accordingly some chemists adopt one opinion, and others the other.

Sulphuretted hydrogen is also formed by the action of sulphuric or muriatic acid, diluted with three or four parts of water on protosulphuret of iron; and the theory of the phenomena is similar to the first of the two explanations just mentioned. Protosulphuret of iron may be procured either by igniting common iron pyrites (deuto-sulphuret of iron), by which means one proportional of 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 protosulphuret 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 quite immaterial.

Sulphuretted hydrogen is a colourless gas, 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 sulphur ousssprings. Under a pressure of 17 atmospheres, at 50° F. it is compressed into a limpid liquid, which resumes the gaseous state as soon as the pressure is removed.

Sulphuretted hydrogen is very injurious to animal life. According to the experiments of Dupuytren and Thenard, the presence of 1-1500th of sulphuretted hydrogen in air is instantly fatal to a small bird; 1-800th killed a middle-sized dog, and a horse died in an atmosphere which contained 1-150th of its volume.

Sulphuretted hydrogen 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 sulphuretted hydrogen 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. (Dr. Thomson.) From the result of this experiment, the composition of sulphuretted hydrogen may be inferred; for it is clear, from the composition of sulphurous acid, (page 261,) 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, sulphuretted hydrogen contains its own volume of the vapour of sulphur and of hydrogen gas; and since

	Grains.
100 cubic inches of the vapour of sulphur weigh .	33.888
100 cubic inches of hydrogen gas weigh . .	2.118
100 cubic inches of sulphuretted hydrogen gas must weigh	36.006

and its specific gravity is 1.1805.

The accuracy of this estimate is confirmed by several circumstances. Thus, according to Gay-Lussac and Thenard,

the weight of 100 cubic inches of sulphuretted hydrogen is 36.33 grains; and Sir H. Davy and Dr. Thomson found it somewhat lighter. When sulphur is heated in hydrogen gas, sulphuretted hydrogen 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. A similar effect is produced, though more slowly, by a succession of electric sparks. (Elements of Sir H. Davy, p. 282.) Gay-Lussac and Thenard have given ample demonstration of the same fact. Thus on heating tin in sulphuretted hydrogen gas, a 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.)

From the data above stated, it follows that sulphuretted hydrogen is composed, by weight, of

Sulphur	33.888	16	one proportional.
Hydrogen	2.118	1	one proportional.

Sulphuretted hydrogen has decidedly acid properties; for it reddens litmus paper, and forms salts with alkalies. It is hence sometimes called *hydro-sulphuric* acid. Its salts are termed *hydro-sulphurets* or *hydro-sulphates*. All the hydro-sulphurets are decomposed by muriatic or sulphuric acid, and sulphuretted hydrogen is disengaged with effervescence.

Recently boiled water absorbs its own volume of sulphuretted hydrogen, and acquires the peculiar taste and odour of sulphurous springs. The gas is expelled without change by boiling.

The elements of sulphuretted hydrogen may easily be separated from one another. Thus on putting a solution of sulphuretted hydrogen into an open vessel, the oxygen absorbed from the air gradually unites with the hydrogen of the sulphuretted hydrogen, water is formed, and sulphur deposited. Sulphuretted hydrogen and sulphurous acid mutually decompose each other, with formation of water and deposition of sulphur. If a drachm of fuming nitrous acid is poured into a bottle full of sulphuretted hydrogen gas, a bluish-white flame

passes rapidly through the vessel, sulphur and nitrous acid fumes make their appearance, and of course water is generated. Chlorine, iodine, and bromine decompose sulphuretted hydrogen, with separation of sulphur, and formation either of muriatic, hydriodic, or hydro-bromic acid. An atmosphere charged with sulphuretted hydrogen gas may be purified by means of chlorine in the space of a few minutes.

Sulphuretted hydrogen, from its affinity for metallic substances, is a chemical agent of great importance. It tarnishes gold and silver powerfully, forming with them metallic sulphurets. White paint, owing to the lead which it contains, is blackened by it; and the salts of nearly all the common metals are decomposed by its action. In most cases, the hydrogen of the sulphuretted hydrogen combines with the oxygen of the oxide, and the metal unites with the sulphur.

Sulphuretted hydrogen is readily distinguished from other gases by its odour. The most delicate chemical test of its presence is carbonate of lead (white paint) mixed with water and spread upon a piece of white paper. So minute a quantity of sulphuretted hydrogen may by this means be detected, that one measure of the gas mixed with 20,000 times its volume of air, hydrogen, or carburetted hydrogen, gives a brown stain to the whitened surface. (Dr. Henry.)

BISULPHURETTED HYDROGEN.

Though Scheele discovered this compound, it was first particularly described by Berthollet. (An. de Chimie, vol. xxv.) It may be made conveniently by boiling equal parts of recently slaked lime and flowers of sulphur with five or six of water, when a deep orange-yellow solution is formed, which contains a hydrosulphuret of lime with excess of sulphur. On pouring this liquid into strong muriatic acid, copious deposition of sulphur takes place; and the greater part of the sulphuretted hydrogen, instead of escaping with effervescence, is retained by the sulphur. After some minutes, a yellowish semifluid matter like oil collects at the bottom of the vessel, which is *bisulphuretted hydrogen*.

From the facility with which this substance resolves itself into sulphur and sulphuretted hydrogen, its history is imper-

fect, and in some respects obscure. It is viscid to the touch, and has the peculiar odour and taste of sulphuretted hydrogen, though in a slighter degree. It appears to possess the properties of an acid; for it unites with alkalies and the alkaline earths, forming salts which are termed *sulphuretted hydrosulphurets*. According to Mr. Dalton, bi-sulphuretted hydrogen consists of one equivalent of hydrogen and two equivalents of sulphur; and consequently its combining proportion is 33. This view of its composition is corroborated by Mr. Herschel's analysis of the sulphuretted hydrosulphuret of lime. (Edinburgh Philos. Journal, vol. i. p. 13.)

The salts of bisulphuretted hydrogen may be prepared by digesting sulphur in solutions of the alkaline or earthy hydrosulphurets. They are also generated when alkalies or alkaline earths are boiled with sulphur and water; but in this case, another salt is formed at the same time. Thus, on boiling together lime and sulphur, as in the preceding process, the only mode by which sulphuretted hydrogen can be formed at all, is by decomposition of water; but since no oxygen escapes during the ebullition, it is manifest that the elements of that liquid must have combined with separate portions of sulphur, and have formed two distinct acids. One of these, in all probability, is hyposulphurous acid; and the other is sulphuretted hydrogen.

The salts of bisulphuretted hydrogen absorb oxygen from the air, and pass gradually into hyposulphites. A similar change is speedily effected by the action of sulphurous acid. Dilute muriatic and sulphuric acids produce in them a deposition of sulphur, and evolution of sulphuretted hydrogen gas.

SECTION IV.

HYDROGEN AND SELENIUM.—HYDRO-SELENIC ACID.

Selenium, like sulphur, forms a gaseous compound with hydrogen, which has distinct acid properties, and is termed *seleniuretted hydrogen*, or *hydro-selenic acid*. This gas is disengaged when muriatic acid is added to a concentrated

solution of any hydro-seleniate. It may also be procured by heating seleniuret of iron in muriatic acid. By decomposition of water, oxide of iron and hydro-selenic acid are generated; and while the former unites with muriatic acid, the latter escapes in the form of gas.

Hydro-selenic acid gas is colourless. Its odour is at first similar to that of sulphuretted hydrogen; 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 hydro-selenic acid, and selenium, in the form of a red powder, subsides.

All the salts of the common metals are decomposed by hydro-selenic acid. The hydrogen of that acid combines with the oxygen of the oxide, and a seleniuret of the metal is generated.

Hydroselenic acid gas is composed, according to the analysis of Berzelius, of one equivalent of each of its constituents.

SECTION V.

COMPOUNDS OF HYDROGEN AND PHOSPHORUS.

Much uncertainty still prevails concerning the nature of these compounds. Even their number is doubtful; though two are generally admitted by chemists. Some of the difficulties have, however, been lately removed. The observations of Dumas, relative to the constitution of protophosphuretted hydrogen, have been confirmed by M. Buff; and, therefore, the unexpected statement of Rose, that this compound contains more phosphorus than perphosphuretted hydrogen, may be inferred to be incorrect. (An. de Ch. et Ph. xxxi. 113. et xli. 220; and Poggendorff's Annalen, viii. 192.)

Proto-phosphuretted hydrogen. This gas, which was discovered in 1812 by Sir H. Davy, is colourless, and has a dis-

agreeable odour, somewhat like that of garlic. Water absorbs about one-eighth of its volume. It does not take fire spontaneously, as perphosphuretted hydrogen does, when mixed with air or oxygen at common temperatures; but the mixture detonates with the electric spark, or by a temperature of 300° F. 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. Admitted into a vessel of chlorine it inflames instantly, and emits a white light, a property which it possesses in common with perphosphuretted hydrogen. Its specific gravity was found by Dumas to be 1.214, and 100 cubic inches weigh 37.027 grains.

Sir H. Davy prepared this gas by heating hydrated phosphorous acid in a retort (page 280); and it is also evolved from hydrous hypophosphorous acid by similar treatment. It is also formed, according to Dumas, by the action of strong muriatic acid on phosphuret of lime; and likewise by the spontaneous decomposition of per-phosphuretted hydrogen.

Dr. Thomson states that when sulphur is heated in 100 measures of protophosphuretted hydrogen, sulphuret of phosphorus and 200 measures of sulphuretted hydrogen are generated; and he hence infers that the former contains twice its volume of hydrogen gas. But this mode of analysis is inaccurate, since a considerable quantity of sulphuretted hydrogen is always absorbed by the excess of sulphur employed in the experiment. Dumas, who detected this error, has also proved protophosphuretted hydrogen to contain once and a half its volume of hydrogen. His experiments were made by introducing into a tube containing the gas a fragment of bichloride of mercury (corrosive sublimate), and applying heat so as to convert it into vapour. Mutual decomposition instantly took place: phosphuret of mercury and muriatic acid were generated; and 100 measures of gas, thus decomposed, yielded 300 measures of muriatic acid gas, corresponding to 150 of hydrogen. The quantity of hydrogen contained in any given volume of protophosphuretted hydrogen is thus given; and by subtracting the weight of the former from that of the latter, the compound is found to consist of 1 part of hydrogen to 10.65 of phosphorus. But though this calculation is

founded on data which appear to be correct, the equivalent of phosphorus, deducible from it, does not correspond with that formerly stated. (Page 277.)

It is affirmed by Dr. Thomson that when protophosphuretted hydrogen is detonated with 1.5 its volume of oxygen gas, the only products are water and phosphorous acid; but 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 protophosphuretted 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 277.) The elements of the calculation have been confirmed both by Dumas and Buff.

It frequently happens in the preparation of protophosphuretted hydrogen, especially when heat is incautiously applied, that it is mixed with variable quantities of free hydrogen, which has been doubtless often overlooked, and thus the frequent cause of error. Dumas obviated this source of fallacy by agitating portions of the gas, which he employed, with a cold, saturated, solution of sulphate of copper. This substance has the property of absorbing both the compounds of phosphorus and hydrogen entirely, with production of phosphuret of copper; while the free hydrogen is left, and the purity of the gas ascertained. Sulphuric acid and chloride of lime act in a similar manner.

Perphosphuretted hydrogen. The gas, to which this name is applied, was discovered in the year 1783 by M. Gengembre, and has since been particularly examined by Mr. Dalton, Dr. Thomson, M. Dumas, and Professor H. Rose. It may be prepared in several ways. The first method is by heating phosphorus in a strong solution of pure potash. The second consists in heating a mixture made of small pieces of phosphorus and recently slaked lime, to which a quantity of water is added sufficient to give it the consistence of thick paste. The third method is by the action of dilute muriatic acid,

aided by moderate heat, on phosphuret of lime. In these processes, three compounds of phosphorus are generated;—phosphoric acid, hypophosphorous acid, and perphosphuretted hydrogen—all of which are produced by decomposition of water, and the union of its elements with separate portions of phosphorus. The last method appears to yield the purest gas.

The gas obtained by either of these processes is said by Mr. Dalton to be generally, and by M. Dumas to be always, mixed with variable proportions of hydrogen; but Rose denies that free hydrogen gas is evolved, except when the heat is so great as to decompose the hypophosphite, a temperature which is never attained so long as the materials are moist. It has a peculiar odour, resembling that of garlic, and a bitter taste. Its specific gravity according to Dr. Thomson is 0.9027, according to Dalton 1.1 nearly, and 1.761 according to Dumas. It does not support flame or respiration.

Recently boiled water, according to Dalton, absorbs fully one-eighth of its bulk of this gas, most of which is again expelled by boiling or agitation with other gases; but Dr. Thomson states that water takes up only about five per cent of its volume. The aqueous solution does not redden litmus paper, nor does the gas itself possess any of the properties of acids. The gas is freely and completely absorbed by a solution of sulphate of copper or chloride of lime, by which means its purity may be ascertained, and the presence of hydrogen detected.

This, as well as the other compound of phosphorus and hydrogen sometimes decomposes metallic solutions in the same manner as sulphuretted hydrogen, giving rise to the formation of water and a phosphuret of the metal. But if the metal has 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.

The most remarkable character of this compound, by which it is distinguished from all other gases, is the spontaneous combustion which it undergoes 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—phosphoric 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, and be then mixed with oxygen, the combustion is perfect. Mr. Dalton observed that it may be mixed with pure oxygen in a tube of 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 lime 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 lately mentioned to me by Mr. 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.

Perphosphuretted hydrogen gas is resolved into its elements by exposure to strong heat, or by successive sparks of electricity; and when sulphur is volatilized in this gas, the phosphuretted is converted into sulphuretted hydrogen. Dr. Thomson states that the pure hydrogen in the former case, and in the latter the sulphuretted hydrogen, retain precisely the same volume as the gas from which they were derived. He hence infers that the phosphuretted hydrogen contains its

own volume of hydrogen gas; but this fact is disputed by other chemists, and particularly by M. Dumas, who finds that 100 measures of the former contain 150 of the latter. (An. de Ch. et Ph. xxxi. 153.) The quantity of oxygen required to effect the complete combustion of phosphuretted hydrogen, that is, to convert it into water and phosphoric acid, is also uncertain. Dalton and Dumas agree in the opinion that phosphuretted hydrogen requires about twice its volume for this purpose; while Dr. Thomson states that only one and a half times its volume are requisite.

When perphosphuretted hydrogen is allowed to stand for a few days over water, it deposits part of its phosphorus without change of volume, and ceases to be spontaneously combustible when mixed with atmospheric air. According to Dr. Thomson the perphosphuretted hydrogen parts with 1-4th of its phosphorus under these circumstances, and a peculiar gas, which he has called *sub-phosphuretted hydrogen*, is generated; but M. Dumas maintains that 1-3d of the phosphorus is deposited, and that the new gas is identical with protophosphuretted hydrogen.

Perphosphuretted hydrogen, according to Dr. Thomson, is composed of 1 part of hydrogen to 12 of phosphorus; the proportion as stated by Rose is as 1 to 10.52; and according to Dumas, it is as 1 to 16.1. Such results, it is manifest, prove nothing but the uncertainty of our chemical knowledge relative to this subject. The cause of the discordance is, indeed, fully explained by M. Buff, for the gas is not only always mixed with more or less free hydrogen at the moment of its formation, but is so extremely liable to spontaneous decomposition, even at common temperatures, that the same specimen will vary in its constitution during the course of an hour.

SECTION VI.

COMPOUNDS OF NITROGEN AND CARBON.

BICARBURET OF NITROGEN, OR CYANOGEN GAS.

Cyanogen gas, the discovery of which was made in 1815 by M. Gay-Lussac, (Annales de Chimie, vol. xcv.) is prepared by heating cyanuret of mercury, carefully dried, in a small glass retort, by means of a spirit lamp. This cyanuret which, on the supposition of its being a compound of oxide of mercury and prussic acid, was formerly called *prussiate of mercury*, is in reality composed of metallic mercury and cyanogen. On exposing it 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 charcoal, derived from the cyanogen itself, a portion of which is decomposed by the temperature employed in its formation; but Gay-Lussac states that no free nitrogen is disengaged till towards the close of the process.

Cyanogen gas is colourless, and has a strong pungent and very peculiar odour. At the temperature of 45° F. and under a pressure of 3.6 atmospheres, it is a limpid liquid, which resumes the gaseous form when the pressure is removed. 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° F., 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 a recent observation of Wöhler, that two of the products are cyanous acid and ammonia; which, uniting together, generate urea. (An. de Ch. et de 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 . .	29.652
200 the vapour of carbon weigh	25.418
100 cubic inches of cyanogen gas must weigh .	55.070

And it consists by weight of

Nitrogen .	29.652 .	14 .	one equivalent.
Carbon .	25.418 .	12 .	two equivalents.

The specific gravity of a gas so constituted is 1.8054; whereas Gay-Lussac found it, by weighing, to be 1.8064.

Cyanogen, from this view of its composition, is a *bicarburet of nitrogen;* but for the sake of convenience I shall employ the term *cyanogen*, proposed by its discoverer *. All the compounds of cyanogen, which are not acid, are called *cyanurets* or *cyanides*.

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 cyanuret 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.

HYDROCYANIC OR PRUSSIC ACID.

Prussic acid was discovered in the year 1782 by Scheele,

* From κύανος, *blue*, and γιννάω, *I generate;* because it is an essential ingredient of Prussian blue.

and Berthollet afterwards ascertained that it contains carbon, nitrogen, and hydrogen; but Gay-Lussac first procured it in a pure state, and by the discovery of cyanogen was enabled to determine its real nature. The substance prepared by Scheele was merely a solution of prussic acid in water.

Pure hydrocyanic or prussic acid may be prepared by heating cyanuret of mercury in a glass retort with two-thirds of its weight of concentrated muriatic acid. By an interchange of elements similar to that which was explained in the first process for forming sulphuretted hydrogen (p. 364), the cyanogen of the cyanuret unites with the hydrogen either of water or muriatic acid, forming hydrocyanic acid; while a solution of corrosive sublimate remains in the retort. The vapour of hydrocyanic acid, as it rises, is mixed with moisture and muriatic acid. It is separated from the latter by being conducted through a narrow tube over fragments of marble, with the lime of which the muriatic acid unites. It is next dried by means of chloride of calcium, and is subsequently collected in a tube surrounded with ice or snow.

Vauquelin proposes the following process as affording a more abundant product than the preceding. It consists in filling a narrow tube, placed horizontally, with fragments of cyanuret of mercury, and causing a current of dry sulphuretted hydrogen gas to pass slowly along it. The instant that gas comes in contact with the cyanuret, double decomposition ensues, and hydrocyanic acid and bi-sulphuret of mercury are generated. The progress of the sulphuretted hydrogen along the tube may be distinctly traced by the change of colour, and the experiment should be closed as soon as the whole of the cyanuret has become black. It then only remains to expel the hydrocyanic acid by a gentle heat, and collect it in a cool receiver. This process is elegant, easy of execution, and productive.

Pure hydrocyanic acid is a limpid colourless fluid, of a strong odour, similar to that of peach-blossoms. It excites at first a sensation of coolness on the tongue, which is soon followed by heat; but when diluted, it has the flavour of bitter almonds. Its specific gravity at 45° F. is 0.7058. It is so exceedingly volatile, that its vapour during warm weather may be collected over mercury. Its point of ebullition is

79° F., and at zero it congeals. When a drop of it is placed on a piece of glass, it becomes solid, because the cold produced by the evaporation of one portion is so great as to freeze the remainder. It unites with water and alcohol in every proportion.

Pure hydrocyanic acid is a powerful poison, producing in poisonous doses insensibility and convulsions, which are speedily followed by death. A single drop of it placed on the tongue of a dog causes death in the course of a very few seconds; and small animals, when confined in its vapour, are rapidly destroyed. On inspiring the vapour, diluted with atmospheric air, headach and giddiness supervene; and for this reason the pure acid should not be made in close apartments during warm weather. The distilled water from the leaves of the *Prunus lauro-cerasus* owes its poisonous quality to the presence of this acid. Its effects are best counteracted by diffusible stimulants, and of such remedies solution of ammonia appears to be the most beneficial. The aqueous solution of chlorine may be used as an antidote, which decomposes prussic acid instantly, with formation of muriatic acid. In some experiments recently described by MM. Persoz and Nonat, symptoms of poisoning, induced by prussic acid applied to the globe of the eye, ceased on the internal administration of chlorine. It would hence appear, that both substances were absorbed into the circulating fluids, and there reacted on each other. (An. de Ch. et de Ph. xliii. 324.)

Pure hydrocyanic acid, even when excluded from air and moisture, is very liable to spontaneous changes, owing to the tendency of its elements to form new combinations. These changes sometimes commence within an hour after the acid is made, and it can rarely be preserved for more than two weeks. The commencement of decomposition is marked by the liquid acquiring a reddish-brown tinge. The colour then gradually deepens, a matter like charcoal subsides, and ammonia is generated. On analyzing the black matter, it was found to contain carbon and nitrogen. The acid may be preserved for a longer period if diluted with water, but even then it undergoes gradual decomposition.

Hydrocyanic acid reddens litmus paper feebly, and unites with most alkaline bases, forming salts which are termed

prussiates or *hydrocyanates*. It is a weak acid; for it does not decompose the carbonates, and no quantity of it can destroy the alkaline reaction of potash. Its salts are poisonous; they are all decomposed by carbonic acid, and have the odour of hydrocyanic acid, a character by which the hydrocyanates may easily be recognised.

Hydrocyanic acid is resolved by galvanism into hydrogen and cyanogen, the former of which appears at the negative, and the latter at the positive pole. When its vapour is conducted through a red-hot porcelain tube, partial decomposition ensues. Charcoal is deposited, and nitrogen, hydrogen, and cyanogen gases are set at liberty; but the greater part of the acid passes over unchanged. Electricity produces a similar effect. The vapour of hydrocyanic acid takes fire on the approach of flame; and with oxygen gas it forms a mixture which detonates with the electric spark. The products of the combustion are nitrogen, water, and carbonic acid.

The composition of hydrocyanic acid is shown by the following simple but decisive experiment of Gay-Lussac. If a quantity of potassium, precisely sufficient for absorbing 50 measures of pure cyanogen gas, is heated in 100 measures of hydrocyanic acid vapour, cyanuret of potassium is generated, diminution of 50 measures takes place, and the residue is pure hydrogen. From this it appears, that hydrocyanic acid vapour is composed of equal volumes of cyanogen and hydrogen, united without any condensation; and, consequently, these two gases combine, by weight, according to the ratio of their densities. The composition of hydrocyanic acid may, therefore, be thus stated:—

	By Volume.		By Weight.	
Cyanogen	50	.	1.8054—26,	one equivalent,
Hydrogen	50	.	0.0694 1,	one equivalent,
	100 acid vapour.			

The atomic weight of hydrocyanic acid is 27. The specific gravity of its vapour is, of course, intermediate between that of its constituents, or 0.9374; as determined directly by Gay-Lussac its density is 0.9476.

From the powerful action of hydrocyanic acid on the animal

economy, this substance, in a diluted form, is sometimes employed in medical practice to diminish pain and nervous irritability. It may be procured of any given strength by dissolving cyanuret of mercury in water, and transmitting a current of sulphuretted hydrogen gas through the solution till the whole of the cyanuret is decomposed. The decomposition is known to be complete by the filtered liquid remaining colourless and transparent when mixed with a solution of sulphuretted hydrogen; for should any undecomposed cyanuret of mercury be present, a black precipitate, bi-sulphuret of mercury, will be formed. This test of the complete decomposition of the cyanuret of mercury should never be neglected. The excess of sulphuretted hydrogen is removed by agitation with carbonate of lead, and the hydrocyanic acid is then separated from the insoluble matters by filtration. The process adopted at Apothecaries' Hall, London, is to mix in a retort one part of cyanuret of mercury, one part of muriatic acid of specific gravity 1.15, and six parts of water; and to distil the mixture until a quantity of acid, equal to that of the water employed, is collected. The product has a density of 0.995. (Brande's Manual of Chemistry.) In this process a little muriatic acid is apt to pass over into the recipient, and render the product impure. Its presence, in a medical point of view, cannot be very material; but it may be separated by mixing the impure acid with a little chalk, and distilling to dryness. The muriatic acid unites with lime, and is retained in the retort, where it may be detected by its appropriate test. Muriatic when mixed with hydrocyanic acid cannot be detected by nitrate of silver; because cyanuret of silver is very similar to the chloride both in its appearance, and in several of its leading properties.

The quality of dilute hydrocyanic acid, however prepared, is very variable, owing to the volatility of the acid, and its tendency to spontaneous decomposition. On this account, it should be made only in small quantities at a time, kept in well-stopped bottles, and excluded from light. The best way of estimating the strength of any solution is that proposed by Dr. Ure. To 100 grains, or any other convenient quantity of the acid, contained in a phial, small quantities of peroxide of mercury in fine powder are successively added, till

it ceases to be dissolved. The weight of the peroxide which is dissolved, divided by four, gives the quantity of real hydrocyanic acid present. (Quarterly Journal, vol. xiii.)

The presence of free hydrocyanic acid is easily recognised by its odour. Chemically it may be detected by agitating the fluid supposed to contain it with oxide of mercury in fine powder. Double decomposition ensues, by which water and cyanuret of mercury are generated; and on evaporating the solution slowly, the latter is obtained in the form of crystals.

A test of far greater delicacy, originally noticed by Scheele, is the following. To the liquid supposed to contain hydrocyanic acid, add a solution of green vitriol, throw down the protoxide of iron by a slight excess of pure potash, and after exposure to the air for four or five minutes, acidulate with muriatic or sulphuric acid, so as to redissolve the precipitate. Prussian blue will then make its appearance, if prussic acid had been originally present. The nature of the chemical change will be explained in the section on the salts of ferrocyanic acid, when describing the manufacture of Prussian blue. M. Lassaigne, who has written an essay on the tests of this acid, (An. de Ch. et Ph. xxvii. 200,) speaks of the *per*-sulphate as the proper re-agent for this experiment; but according to my observation, the presence of the protoxide is essential to its success. If the iron is strictly at its maximum of oxidation, Prussian blue will not be formed at all, as was proved long ago by Scheele and Proust.

As hydrocyanic acid is sometimes administered with criminal designs, the chemist may be called on to search for its presence in the stomach after death. This subject has been investigated experimentally by MM. Leuret and Lassaigne, and the process they have recommended is the following. The stomach or other substances to be examined are cut into small fragments, and introduced into a retort along with water; the mixture being slightly acidulated with sulphuric acid. The distillation is then conducted at a temperature of 212° F., the volatile products are collected in a receiver surrounded with ice, and the presence of hydrocyanic acid in the distilled matter is tested by the method above mentioned. These gentlemen found, that prussic acid may be thus detected two or three days after death; but not after a longer period. The disappearance of the acid appears owing partly to its volatility, and

partly to the facility with which it undergoes spontaneous decomposition. (Journal de Chimie Medicale, &c. ii. p. 561.)

CYANIC ACID.

In the last edition of this work two compounds were described under the name of *cyanic acid*, one discovered by Wöhler, and the other by Liebig, both consisting of the same elements in the same proportion, and yet essentially different from each other in their chemical properties. The discovery of another compound of cyanogen and oxygen, containing twice as much oxygen as the others, has since been made by Serullas, and hence a change of nomenclature is necessary. The acids formerly described under the name of *cyanic* must now be termed *cyanous acid;* and the new compound will receive its proper appellation of *cyanic acid.* (An. de Ch. et de Ph. xxxviii. 379.)

When bi-chloride of cyanogen, which consists, as its name implies, of two equivalents of chlorine and one of cyanogen, is gently boiled with water, mutual decomposition ensues; and each equivalent of the bi-chloride reacts on two equivalents of water. Every 72 parts of chlorine combine with two parts of hydrogen, yielding two equivalents of muriatic acid; while the corresponding 26 parts, or one equivalent, of cyanogen, unite with 16 parts of oxygen, and constitute one equivalent of cyanic acid. The solution is then evaporated until nearly all the muriatic acid is expelled, and on cooling the cyanic acid is deposited in oblique rhomboidal prisms. They are purified by a second solution and crystallization.

These crystals are colourless and transparent when recent, but become opaque by exposure to the air, and if gently heated, lose 23.4 per cent of water. They are insoluble in cold water; but they are dissolved by this menstruum, as also by sulphuric, nitric, and muriatic acid, with the aid of heat. They have little taste, redden litmus paper, and are rather lighter than sulphuric acid. One of the most remarkable characters of the acid is its permanence. For instance, it may be boiled in strong nitric or sulphuric acid without decomposition; and by evaporating its solution in the former, it is obtained very white and pure. It is volatile at a lower temperature than boiling mercury, and condenses, unchanged, in the form of acicular crystals. When heated with potassium it is decom-

posed, yielding potash and cyanuret of potassium. With metallic oxides it forms permanent salts, which do not detonate.

Anhydrous cyanic acid, first noticed by Wöhler, is obtained by cooling from a hot concentrated solution of the crystals in sulphuric or muriatic acid. The figure of its crystals, when they are regularly formed, is that of an octohedron with a square base. When the anhydrous acid is sharply heated, part of it sublimes without change; but part is decomposed, and pure cyanous acid is formed in considerable quantity.

Liebig and Wöhler have remarked, that the substance called pyro-uric acid, which sublimes when uric acid is decomposed by heat, is cyanic acid. This compound is also formed, according to Liebig, by transmitting chlorine gas through water in which cyanite of silver is suspended; chloride of silver, carbonic acid, and ammonia being generated at the same time. To this result the elements of water manifestly contribute, by yielding oxygen to the carbon, and hydrogen to the nitrogen, of a portion of cyanogen. Liebig also states, that on heating dry uric acid in dry chlorine gas a large quantity of cyanic and muriatic acids is generated. He adds, further, that cyanite of potash, when heated in strong acetic acid, is converted into cyanate of potash. (An. de Ch. et de Ph. xli. 225. and xliii. 64.)

Cyanous acid of Wöhler.—It was stated by Gay-Lussac in the essay already quoted, that cyanogen gas is freely absorbed by pure alkaline solutions; and he expressed his opinion that the alkali combines directly with the cyanogen. It appears, however, from the experiments of Wöhler, that hydrocyanic and cyanous acids are formed under these circumstances; and, consequently, that alkaline solutions act upon cyanogen in the same manner as on chlorine, iodine, bromine, and sulphur. But the salts of cyanic acid cannot conveniently be procured in this way, owing to the difficulty of separating the cyanite from the hydrocyanate with which it is accompanied. Wöhler finds that cyanite of potash may be procured in large quantity by mixing ferrocyanate of potash with an equal weight of peroxide of manganese in fine powder, and exposing the mixture to a low red heat. The cyanogen of the ferrocyanic acid receives oxygen from the manganese,

and is converted into cyanous acid, which unites with the potash. The ignited mass is then boiled in alcohol of 86 per cent; and as the solution cools, the cyanite is deposited in small tabular crystals resembling chlorate of potash. The only precaution necessary in this process is to avoid too high a temperature.

Cyanous acid is characterized by the facility with which it is resolved by water into carbonic acid and ammonia. This change is effected merely by boiling an aqueous solution of cyanite of potash; and it takes place still more rapidly when an attempt is made to decompose the cyanite by means of another acid. If the acid is diluted, cyanous acid is instantly decomposed, and carbonic acid escapes with effervescence. But, on the contrary, if a concentrated acid is employed, then the cyanous acid resists decomposition for a short time, and emits a strong odour of vinegar. According to Liebig, the acid may be obtained in a free state by transmitting sulphuretted hydrogen gas through water, in which cyanite of silver is suspended; but the operation should be discontinued before all the cyanite is decomposed, otherwise the free sulphuretted hydrogen would react on the cyanous acid, and effect its decomposition. The acid thus formed is permanent only for a few hours. Wöhler has himself lately procured it by distilling anhydrous cyanic acid, and transmitting the products through a cool dry receiver; when a clear, colourless, and very volatile liquid collected, which was pure anhydrous cyanous acid. (An. de Ch. et de Ph. xxxiii. 207. and xliii. 64.)

Cyanous acid forms a soluble salt with baryta, but insoluble ones with oxide of lead, mercury, and silver. If cyanite of potash is quite pure, it gives a white precipitate with nitrate of silver, and the cyanite of silver so formed dissolves without residue in dilute nitric acid. With ammonia it forms a compound which has all the properties of urea.

Cyanous acid, according to the analysis of Wöhler, is composed of 26 parts or one equivalent of cyanogen, and eight parts or one equivalent of oxygen. The accuracy of this result was at first doubted by Liebig, but it is now admitted to be correct. (An. de Ch. et de Ph. xx. and xxvii.)

The existence of cyanic acid was suspected by M. Vauquelin before it was actually discovered by Wöhler. The

experiments of the former chemist led him to the opinion that a solution of cyanogen in water is gradually converted into hydrocyanic, cyanic, and carbonic acids, and ammonia; and he supposed alkalies to produce a similar change. He did not establish the fact, however, in a satisfactory manner. (An. de Ch. et de Ph. vol. ix.)

Cyanous acid of M. Liebig.—A powerfully detonating compound of mercury was described in the Philosophical Transactions for 1800 by Mr. E. Howard. It is prepared by dissolving 100 grains of mercury in a measured ounce and a half of nitric acid of specific gravity 1.3; and adding, when the solution has become cold, two ounces by measure of alcohol, the density of which is 0.849. The mixture is then heated till moderately brisk effervescence takes place, during which the fulminating compound is generated. A similar substance may be made by treating silver in the same manner. The conditions necessary for forming these compounds are, that the silver or mercury be dissolved in a fluid which contains so much free nitric acid and alcohol, that on the application of heat, nitric ether shall be freely disengaged.

Fulminating silver and mercury bear the heat of 212° or even 260 F., without detonating; but a higher temperature or slight percussion between two hard bodies, causes them to explode with violence. The nature of these compounds was discovered in 1823 by Liebig *, who demonstrated that they are salts composed of a peculiar acid, which he termed *fulminic acid*, in combination with oxide of mercury or silver. According to an analysis of fulminating silver made by Liebig and Gay-Lussac †, the acid of the salt is composed of 26 parts or one proportional of cyanogen, and 8 parts or one proportional of oxygen. It is therefore a real *cyanous acid*, and its salts are cyanites; but in order not to apply the same appellation to two different compounds, it will be convenient to retain the term of *fulminic acid* originally proposed by Liebig. Fulminating silver, therefore, is a fulminate of the oxide of silver; and it is found to contain one equivalent of each constituent.

It is remarkable that the oxide of silver cannot be entirely

* An. de Ch. et de Ph. vol. xxiv. † Ibid. xxv.

separated from fulminic acid by means of an alkali. On digesting fulminate of silver in potash, for example, one equivalent of oxide of silver is separated, and a double fulminate is formed, which consists of two equivalents of fulminic acid, one of oxide of silver, and one equivalent of potash. Similar compounds may be procured by substituting other alkaline substances, such as baryta, lime, or magnesia, for the potash. These double fulminates are capable of crystallizing; and they all possess detonating properties.

From the presence of oxide of silver in the double fulminates, it was at first imagined that this oxide actually constitutes a part of the acid; but since several other substances, such as oxide of mercury, zinc, and copper, may be substituted for that of silver, this view can no longer be admitted.

Fulminic acid has not hitherto been obtained in an insulated form; for while some acids do not decompose the fulminates, others act on fulminic acid itself, and give rise to new products. Muriatic acid, for example, causes the formation of hydrocyanic acid, and of a new acid containing chlorine, carbon, and nitrogen, the nature of which has not been determined. Hydriodic acid acts in a similar manner; and a peculiar acid is likewise produced by the action of sulphuretted hydrogen. From subsequent researches Liebig suspects that this acid is composed of sulphur, cyanogen, and oxygen in the ratio of two equivalents of the first substance, one of the second, and one of the third; but the accuracy of this view has not been demonstrated in a conclusive manner.

CHLORIDE OF CYANOGEN.

The existence of this compound was first noticed by Berthollet, who named it *oxy-prussic acid*, on the supposition of its containing prussic acid and oxygen; and it was afterwards described by Gay-Lussac, in his essay on cyanogen, under the appellation of *chloro-cyanic acid*. It was procured by this chemist by transmitting chlorine gas into an aqueous solution of hydrocyanic acid until the liquid acquired bleaching properties, removing the excess of chlorine by agitation with mercury, and then heating the mixture, so as to expel the gaseous chloride of cyanogen. The chemical changes which take place during this process are complicated. At first the

elements of hydrocyanic acid unite with separate portions of chlorine, and give rise to muriatic acid and chloride of cyanogen; and when heat is applied, the elements of the chloride and water react on each other, in consequence of which muriatic acid, ammonia, and carbonic acid are generated. Owing to this circumstance the chloride of cyanogen was always mixed with carbonic acid, and its properties imperfectly understood.

During the course of last year M. Serullas succeeded in procuring this compound in a pure state, by exposing cyanuret of mercury, in powder and moistened with water, to the action of chlorine gas contained in a well stopped phial. The vessel is kept in a dark place; and after ten or twelve hours the colour of the chlorine is no longer perceptible, bichloride of mercury is found at the bottom of the phial, and its space is filled with the vapour of chloride of cyanogen. The bottle is then cooled down to zero by freezing mixtures of snow and salt, at which temperature chloride of cyanogen is solid. Some chloride of calcium is then introduced, the stopper replaced, and the bottle kept in a moderately warm situation, in order that the moisture within may be completely absorbed. The chloride of cyanogen is then again solidified by cold, the phial completely filled with dry and cold mercury, and a bent tube adapted to its aperture by means of a cork. The solid chloride, which remains adhering to the inner surface of the phial, is converted into gas by gentle heat, and, passing along the tube, is collected over mercury. Exposure to the direct solar rays interferes with the success of this process. Muriate of ammonia, together with a little carbonic acid, is then generated, and a yellow liquid collects, which appears to be a mixture of chloride of carbon and chloride of nitrogen.—(An. de Ch. et Ph. xxxv. 291.)

Chloride of cyanogen is solid at zero of Fahrenheit's thermometer, and in congealing crystallizes in very long slender needles. At temperatures between 5° F. and 10.5° it is liquid, and also at 68° under a pressure of four atmospheres; but at the common pressure, and when the thermometer is above 10.5° or 11° F. it is a colourless gas. In the liquid state it is as limpid and colourless as water. It has a very offensive

odour, irritates the eyes, is corrosive to the skin, and highly injurious to animal life.

Chloride of cyanogen is very soluble in water and alcohol. The former under the common pressure, and at 68° F., dissolves twenty-five times its volume. Alcohol takes up 100 times its volume, and the absorption is effected almost with the same velocity as that of ammoniacal gas by water. These solutions are quite neutral with respect to litmus and turmeric paper, and may be kept without apparent change. The gas may even be separated without decomposition by boiling. The chloride of cyanogen, accordingly, does not possess the characters of an acid.

The changes induced by the action of alkalies do not appear to be very clearly understood. M. Serullas agrees with Gay-Lussac in stating, that if to a solution of chloride of cyanogen a pure alkali is added, and then an acid, effervescence ensues from the escape of carbonic acid gas. Ammonia, and probably muriatic and hydrocyanic acid, is also generated.

The statement of Gay-Lussac relative to the composition of chloride of cyanogen is confirmed by the analysis of M. Serullas. According to these chemists, it is composed of equal measures of chlorine and cyanogen gases, united without any condensation; and, by weight, of 36 parts or one equivalent of chlorine, and 26 parts or one equivalent of cyanogen. Its equivalent is therefore 62, and its specific gravity in the gaseous state 2.1527.

Bichloride of Cyanogen.—This compound, which contains twice as much chlorine as the preceding, was prepared by Serullas by the action of dry chlorine on anhydrous prussic acid, muriatic acid being generated at the same time. It is solid at common temperatures, and occurs in white acicular crystals. At 284° F. it fuses, and enters into ebullition at 374°. Its vapour is acrid and excites a flow of tears, and it is very destructive to animals. Its odour somewhat resembles that of chlorine, and is very similar to that of mice. It is very soluble in alcohol and ether, and is precipitated from them by water, which dissolves it in small quantity. When boiled in water, or solution of potash, it is converted into muriatic and cyanic acids. (An. de Ch. et Ph. xxxviii. 370.)

IODIDE OF CYANOGEN.

Iodide of Cyanogen, which was discovered in 1824 by M. Serullas, (An. de Ch. et de Ph. vol. xxvii.) may be prepared by the following process:—Two parts of cyanuret of mercury and one of iodine are intimately and quickly mixed in a glass mortar, and the mixture is introduced into a phial with a wide mouth. On applying heat, the violet vapours of iodine appear; but as soon as the cyanuret of mercury begins to be decomposed, the vapour of iodine is succeeded by white fumes, which, if received in a cool glass receiver, condense upon its sides into flocks like cotton wool. The action is found to be promoted by the presence of a little water.

Iodide of cyanogen, when slowly condensed, occurs in very long and exceedingly slender needles, of a white colour. It has a very caustic taste and penetrating odour, and excites a flow of tears. It sinks rapidly in sulphuric acid. It is very volatile, and sustains a temperature much higher than 212° F. without decomposition; but it is decomposed by a red heat. It dissolves in water and alcohol, and forms solutions which do not redden litmus paper. Alkalies act upon it in the same manner as on chloride of cyanogen, a compound to which it is very analogous.

Sulphurous acid, when water is present, has a very powerful action on iodide of cyanogen. On adding a few drops of this acid, iodine is set free, and hydrocyanic acid produced; but when more of the sulphurous acid is employed, the iodine disappears, and the solution is found to contain hydriodic acid. These changes are of course accompanied with formation of sulphuric acid, and decomposition of water.

Iodide of cyanogen has not been analyzed with accuracy; but M. Serullas infers from an approximative analysis, that it is composed of one equivalent of iodine and one of cyanogen.

BROMIDE OF CYANOGEN.

This substance has been prepared by Liebig by a process very similar to that described for procuring iodide of cyanogen. At the bottom of a small tubulated retort, or a rather long tube,

is placed some cyanuret of mercury slightly moistened, and after cooling the apparatus by cold water, or still better by a freezing mixture, a precaution which is indispensable in summer, half its weight of bromine is introduced. Strong reaction instantly ensues, and caloric is so freely evolved, that a considerable quantity of the bromine would be dissipated, unless the temperature of the retort had been previously reduced. The new products are bromide of mercury and bromide of cyanogen, the latter of which collects in the upper part of the tube in the form of long needles. After allowing any vapour of bromine, which may have risen at the same time, to condense and fall back upon the cyanuret of mercury, the bromide of cyanogen is expelled by a gentle heat, and collected in a recipient carefully cooled.

As thus formed, the bromide is crystallized, sometimes in small regular colourless and transparent cubes, and sometimes in long and very slender needles. In its physical properties it is so very similar to iodide of cyanogen, that they may easily be mistaken for each other, especially when the crystals of the bromide possess the acicular form. They agree closely in odour and volatility, but the bromide is even more volatile than the iodide of cyanogen. It is converted into vapour at 59° F., and crystallizes suddenly on cooling. Its solubility in water and alcohol is likewise greater than that of iodide of cyanogen. By a solution of caustic potash it is converted into hydrocyanate and hydrobromate of potash.

Bromide of cyanogen is highly deleterious. A grain of it dissolved in a little water, and introduced into the œsophagus of a rabbit, proved fatal on the instant, acting with the same rapidity as prussic acid. In consequence of the volatility and noxious qualities of this substance, experiments with it should be conducted with great circumspection. The danger from this cause, together with a deficient supply of bromine, prevented M. Serullas from continuing the investigation of its properties. (Edin. Journal of Science, VII. 189.)

FERROCYANIC ACID.

Ferrocyanic acid has, within these few years, been the

subject of able researches by Mr. Porrett *, Berzelius †, and M. Robiquet ‡. Mr. Porrett recommends two methods for obtaining ferrocyanic acid, by one of which it is procured in crystals, and by the other in a state of solution. The first process consists in dissolving 58 grains of crystallized tartaric acid in alcohol, and mixing the liquid with 50 grains of ferrocyanate of potash dissolved in the smallest possible quantity of hot water. Bitartrate of potash is precipitated, and the clear solution, on being allowed to evaporate spontaneously, gradually deposits ferrocyanic acid in the form of small cubic crystals of a yellow colour. In the second process, ferrocyanate of baryta, dissolved in water, is mixed with a quantity of sulphuric acid precisely sufficient for combining with the baryta; when the insoluble sulphate of baryta subsides, and ferrocyanic acid remains in solution. According to Mr. Porrett, every ten grains of ferrocyanate of baryta require so much liquid sulphuric acid as is equivalent to 2.53 grains of real acid.

Ferrocyanic acid is neither volatile nor poisonous in small quantities, and has no odour. It is gradually decomposed by exposure to the light, forming hydrocyanic acid and Prussian blue; but it is far less liable to spontaneous decomposition than hydrocyanic acid. It differs also from this acid in possessing the properties of acidity in a much greater degree. Thus it reddens litmus paper permanently, neutralizes alkalies, and separates the carbonic and acetic acids from their combinations. It even decomposes some salts of the more powerful acids. Peroxide of iron, for example, unites with ferrocyanic in preference to sulphuric acid, unless the latter is concentrated.

Different opinions have prevailed as to the nature of ferrocyanic acid. Berzelius maintains that it is a super-hydrocyanate of the protoxide of iron; but M. Robiquet has shown by arguments which appear to me unanswerable, that this supposition is inconsistent with the phenomena. The view which is now commonly taken of the composition of this acid was

* Philosophical Transactions for 1814 and 1815. Annals of Philosophy, vol. xiv.

† Annales de Chimie et de Physique, vol. xv.

‡ Ibid. vol. xvii.

suggested by an experiment made by Mr. Porrett. On exposing ferrocyanate of soda to the agency of galvanism, the soda was observed to collect at the negative pole, while oxide of iron, together with the elements of hydrocyanic acid, appeared at the opposite end of the battery. From this he inferred, that the iron does not act the part of an alkali in the salt, for on that supposition it should have accompanied the soda, but that it enters into the constitution of the acid itself. Mr. Porrett at first considered the iron to be in the state of an oxide; but he concludes from subsequent researches, that ferrocyanic acid contains no oxygen, and that its sole elements are carbon, hydrogen, nitrogen, and metallic iron. To the acid thus constituted, he proposes the name of *ferruretted* * *chyazic acid*; but the term *ferro-cyanic acid* introduced by the French chemists is more generally employed.

This view has the merit of accounting for the fact, that iron, though contained in ferrocyanic acid and all its salts, cannot be detected in them by the usual tests of iron. For the liquid tests are fitted only for detecting oxide of iron as existing in a salt, and therefore cannot be expected to indicate the presence of metallic iron while forming one of the elements of an acid. We may now also understand how it happens that ferrocyanic should actually contain the elements of hydrocyanic acid, and yet differ from it totally in its properties.

According to the experiments of Mr. Porrett, ferrocyanic acid is composed of one equivalent of iron, one of hydrocyanic acid, and two equivalents of carbon. M. Robiquet states, however, that its elements are in such proportion as to form cyanuret of iron, and hydrocyanic acid; and the result of his researches, together with the analysis of Berzelius, appears to justify the conclusion that ferrocyanic acid is composed of

Hydrogen . .	2 equivalents.
Iron . . .	1 equivalent.
Cyanogen . .	3 equivalents.

or of

Hydrocyanic acid .	2 equivalents.
Cyanuret of iron .	1 equivalent †.

* *Chyazic* from the initials of carbon, hydrogen, and azote.

† See a notice on the Triple Prussiates in the An. de Ch. et de Ph. vol. xxii.

Ferrocyanic acid is, therefore, analogous to several acids, such as the muriatic, hydriodic, and hydrosulphuric acids, all of which contain hydrogen as an essential element, and which for this reason are termed *hydracids*. Under this point of view, ferrocyanic acid may be regarded as a compound of a certain *radical* and hydrogen. This radical, which has not been obtained in an insulated state, is composed of

Cyanogen 3 equiv.
Iron . 1 equiv.

or of

Cyanogen 2 equiv.
Cyanuret of iron 1 equiv.;

and the acid itself consists of one equivalent of the radical and two of hydrogen.

The salts of ferrocyanic acid were once called *triple prussiates*, on the supposition that they were composed of prussic or hydrocyanic acid in combination with oxide of iron and some other alkaline base. They are now termed *ferro-cyanates*. The beautiful dye, Prussian blue, is a ferrocyanate of the peroxide of iron. It is always formed when ferrocyanic acid or its salts are mixed in solution with a per-salt of iron; and for this reason the per-salts of iron, provided no free alkali is present, afford a certain and an extremely delicate test of the presence of ferrocyanic acid.

SULPHOCYANIC ACID.

This acid was discovered in the year 1808 by Mr. Porrett, who ascertained that it is a compound of sulphur, carbon, hydrogen, and nitrogen, and described it under the name of *sulphuretted chyazic acid*. It is now more commonly called *sulpho-cyanic* acid, and its salts are termed *sulpho-cyanates*.

Sulphocyanic acid is obtained by mixing so much sulphuric acid with a concentrated solution of sulphocyanate of potash as is sufficient to neutralize the alkali, and then distilling the mixture. An acid liquor collects in the recipient, which is sulphocyanic acid dissolved in water, and sulphate of potash remains in the retort.

Sulphocyanic acid, as thus prepared, is a transparent liquid, which is either colourless or has a slight shade of pink. Its odour is somewhat similar to that of vinegar. The strongest solution of it which Mr. Porrett could obtain had a specific gravity of 1.022. It boils at 216°.5 F.; and at 54°.5 crystallizes in six-sided prisms.

Sulphocyanic acid reddens litmus paper, and forms neutral compounds with alkalies. Its presence, whether free or combined, is easily detected by a per-salt of iron, with the oxide of which it unites, forming a soluble salt of a deep blood-red colour. With the protoxide of copper it yields a white salt, which is insoluble in water.

According to the analysis of Mr. Porrett, (Annals of Philosophy, vol. xiii.) which is confirmed by that of Berzelius, (An. de Ch. et de Ph. vol. xvi.) sulphocyanic acid is composed of

Cyanogen	26	.	one equivalent.
Sulphur	32	.	two equivalents.
Hydrogen	1	.	one equivalent.

or of

Bisulphuret of Cyanogen	58	.	or one equivalent.
Hydrogen	1	.	or one equivalent.

Bisulphuret of Cyanogen.—Sulpho-cyanic acid may be regarded as a hydracid, of which bisulphuret of cyanogen, lately described by Liebig, is the radical. (An. de Ch. et Ph. xli. 187.) It was prepared by exposing fused sulphocyanuret of potassium to a current of dry chlorine gas. Reaction readily ensued, and at first chloride of sulphur and bichloride of cyanogen distilled over; but at length a red vapour appeared, which collected as a red or orange-coloured substance in the upper part of the tube. In this state it contained some free sulphur, which was in a great measure removed by heating it in dry chlorine gas; when it acquired an orange tint, and in powder was yellow. It had then so nearly the constitution of bisulphuret of cyanogen, that there can be little doubt of its being such. When heated with potassium the action is exceedingly violent, and three compounds, sulphocyanuret, sulphuret, and cyanuret of potassium, are generated.

If a solution of sulphocyanic acid is exposed to the air, a yellow matter gradually collects, which Wöhler conceived to be a compound of sulphur and sulphocyanic acid, but which Liebig considers bisulphuret of cyanogen. It is formed freely by boiling sulphocyanate of potash with dilute nitric acid, the best proportions being 1 part of the salt, 3 of water, and 2 or 2.5 of nitric acid; for if the nitric acid is too strong or in too great excess, the yellow compound will not be formed. It is

also generated by the action of chlorine on a strong solution of the salt. In fact, the oxygen of the air, nitric acid, and chlorine, act upon sulphocyanic acid in the same manner as on hydriodic and hydrosulphuric acids. The yellow matter retains water with obstinacy.

Sulphuret of Cyanogen.—Another sulphuret of cyanogen, different from that just described, was discovered in 1828 by M. Lassaigne. It was prepared by the action of cyanuret of mercury in fine powder with half its weight of bichloride of sulphur, confined in a small glass globe, and exposed for two or three weeks to day-light. A small quantity of crystals, biting to the tongue and of a penetrating odour, collected in the upper part of the vessel, which formed red-coloured compounds with per-salts of iron. Its constitution has not been accurately determined; and the attempts of Liebig to prepare it were unsuccessful. (An. de Ch. et Ph. xxxix.)

Selenio-cyanic Acid.—This substance was obtained by Berzelius in combination with potash, but he could not obtain it in a separate state. It may be regarded as a hydracid, of which seleniuret of cyanogen is the radical.

SECTION VII.

COMPOUNDS OF SULPHUR.

BISULPHURET OF CARBON.

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. (Philos. Trans. for 1813.)

Sulphuret 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 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.

Bisulphuret of carbon is a transparent colourless liquid, which is remarkable for its high refractive power. Its specific gravity is 1.272. It has an acid, pungent, and somewhat aromatic taste, and a very fetid odour. It is exceedingly volatile;—its vapour at 63.5° F. supports a column of mercury 7.36 inches long; and at 110° F. it enters into brisk ebullition. From its great volatility it may be employed for producing intense cold.

Bisulphuret of carbon 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 deutoxide 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. With the alkalies it unites slowly, forming compounds which Berzelius calls *carbo-sulphurets*. It is converted by strong nitro-muriatic acid into a white crystalline substance like camphor, which Berzelius considers to be a compound of muriatic, carbonic, and sulphurous acid gases.

Xanthogen and Hydroxanthic acid.—M. Zeise, Professor of Chemistry at Copenhagen, has discovered some novel and interesting facts, relative to bicarburet of sulphur. When this fluid is agitated with a solution of pure potash in strong alcohol, the alkaline properties of the potash disappear entirely; and on exposing the solution to a temperature of 32° F. numerous acicular crystals are deposited. M. Zeise attributes these phenomena to the formation of a new acid, the elements of which are derived, in his opinion, partly from the alcohol and partly from the bisulphuret of carbon. He regards the acid as a compound of carbon, sulphur, and hydro-

gen. He supposes it to be a hydracid, and that its radical is a sulphuret of carbon. To the radical of this hydracid he applies the term *Xanthogen* (from ξανθος *yellow*, and γενναω *I generate*), expressive of the fact that its combinations with several metals have a yellow colour. The acid itself is called *hydroxanthic acid*, and its salts *hydroxanthates*. The crystals deposited from the alcoholic solution are the hydroxanthate of potash.

There is no doubt of a new acid being generated under the circumstances described by M. Zeise; but since he has not procured xanthogen in an insulated form, nor determined with certainty the constituent principles of hydroxanthic acid, there exists considerable uncertainty as to its real nature. On this account I refer to the original essay for more ample details concerning it. (An. de Ch. et de Ph. vol. xxi.; and Annals of Philosophy, N. S. vol. iv.)

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 thirty or forty grains. The phosphorus is placed in a glass tube, five or six 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. Caloric is evolved at the moment of combination, and sulphuretted hydrogen and phosphoric acid, 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° F.; for otherwise sulphuretted hydrogen and phosphoric acid 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 Mr. Faraday with about five parts of sulphur and seven of phosphorus, was quite fluid at 32° F., and did not solidify at 20° F. (Quarterly Journal, vol. iv.)

SECTION VIII.

COMPOUNDS OF SELENIUM.

SULPHURET OF SELENIUM.

When sulphuretted hydrogen gas is conducted into a solution of selenic acid, an orange-coloured precipitate subsides, which is a sulphuret of selenium. It fuses at a heat a little above 212° F., and at a still 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 alkaline hydrosulphurets dissolve it. Nitric acid acts upon it with difficulty; but the nitro-muriatic converts it into sulphuric and selenious acids. (Annals of Philosophy, vol. xiv.) According to Berzelius, this sulphuret is composed of 40 parts or one proportional of selenium, and 24 parts or one proportional and a half of sulphur.

Selenium and sulphur combine readily by the aid of heat, but it is difficult in this way to obtain a definite compound.

PHOSPHURET OF SELENIUM.

Phosphuret of selenium may be prepared in the same manner as 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 phosphuret 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. (Annals of Philosophy, vol. xiv.)

METALS.

GENERAL PROPERTIES OF METALS.

METALS are distinguished from other substances by the following properties. They are all conductors of electricity and caloric. 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-one. 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	Known to the Ancients.	
Silver		
Iron		
Copper		
Mercury		
Lead		
Tin		
Antimony	Described by Basil Valentine	15th century
Zinc	Described by Agricola in	1520
Bismuth	First mentioned by Paracelsus	16th century
Arsenic	Brandt, in	1733
Cobalt		
Platinum	Wood, assay-master, Jamaica	1741
Nickel	Cronstedt	1751
Manganese	Gahn and Scheele	1774
Tungsten	M. M. D'Elhuyart	1781
Tellurium	Müller	1782
Molybdenum	Hielm	1782

Names of Metals.	Authors of the Discovery.	Dates of the Discovery.
Uranium	Klaproth	1789
Titanium	Gregor	1791
Chromium	Vauquelin	1797
Columbium	Hatchett	1802
Palladium, Rhodium	Dr. Wollaston	1803
Iridium	Descotils and Smithson Tennant	1803
Osmium	Smithson Tennant	1803
Cerium	Hisinger and Berzelius	1804
Potassium, Sodium, Barium, Strontium, Calcium	Sir H. Davy	1807
Cadmium	Stromeyer	1818
Lithium	Arfwedson	1818
Silicium, Zirconium	Berzelius	1824
Aluminium, Glucinium, Yttrium	Wöhler	1828
Thorium	Berzelius	1829
Magnesium	Bussy and Wöhler	1829

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 nineteen times heavier than an equal bulk of water. Great specific gravity 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 specific gravity 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	Gay-Lussac and Thenard

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. Dr. Wollaston has described 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 $\frac{1}{30.000}$th of an inch. (Philos. Transactions for 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

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 when they do crystallize, they always 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 caloric 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. (Page 260.)

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 will appear by inspecting the following table. (Thenard's Chemistry, vol. i.)

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	430	Newton.
	Bismuth	493	
	Lead	500	Biot.
	Tellurium—rather less fusible than lead		Klaproth.
	Arsenic—undetermined.		
	Zinc	698	Brongniart.
	Antimony—a little below a red heat.		
	Cadmium		Stromeyer.

		Pyrometer of Wedgwood.	
Infusible below a red heat.	Silver	20°	Kennedy.
	Copper	27°	Wedgwood.
	Gold	32°	
	Cobalt—rather less fusible than iron		
	Iron	130	Wedgwood.
		158	Mackenzie.
	Manganese	160	Guyton.
	Nickel—the same as Manganese		Richter.
	Palladium.		
	Molybdenum, Uranium, Tungsten, Cromium — Almost infusible, and not to be procured in buttons by the heat of a smith's forge. — Fusible before the oxy-hydrogen blow-pipe.		
	Titanium, Cerium, Osmium, Iridium, Rhodium, Platinum, Columbium — Infusible in the heat of a smith's forge, but fusible before the oxy-hydrogen blow-pipe.		

Metals differ also in volatility. Some are readily volatilized by caloric, 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. There is not a single fact in support of the opinion that one elementary principle can 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. Chemists are not acquainted with any instance of a metal forming a definite compound either with a metallic oxide or with an acid. They unite readily, on the contrary, with elementary substances. Thus, under favourable circumstances, they combine with each other, yielding compounds termed *alloys*, which possess all the characteristic physical properties of pure metals. They unite likewise with the simple substances not metallic, 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 as 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 treating the metallic bodies has already been explained in the introduction. Before proceeding, however, to describe the metals individually, 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 blow-pipe.

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 potash, and projecting the mixture into a red-hot crucible. Most metals may be oxidized by digestion in nitric acid; and nitro-muriatic 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° F. 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 silver for oxygen is still weaker than that of mercury; for it cannot be oxidized by the sole agency of caloric at any temperature.

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. Potash 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 and *black flux* 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. 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.

The distinguishing feature of metallic oxides is the property which many possess of entering into combination with acids. All salts, those of ammonia excepted, are composed of an acid and a metallic oxide. In some instances all the oxides of the same metal are capable of forming salts with acids, as is

exemplified by the oxides of iron. More commonly, however, 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 and deutoxide of manganese, 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, potash, 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.

All the metallic chlorides are solid at the common temperature, except the bichlorides of tin and arsenic, which are liquid. 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; but all the others are more or less soluble in water.

Two only of the metallic chlorides, those namely of gold and platinum, are decomposable by heat. All the chlorides

of the common metals are decomposed at a red heat by hydrogen gas, muriatic acid being disengaged while the metal is set free. Pure charcoal does not effect their decomposition; but if moisture be present at the same time, muriatic 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 muriatic acid gas. The change is accompanied with decomposition of water, the hydrogen of which combines with chlorine, and its oxygen with the metal. All chlorides, when in solution, may be recognised by yielding with nitrate 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 evaporating a solution of the muriate of a metallic oxide to dryness, and applying heat so long as any water is expelled. Metallic chlorides are often deposited from such solutions by crystallization.

Chlorine manifests a feeble affinity for metallic oxides. No combination of the kind occurs at a red heat, and no chloride of a metallic oxide can be heated to redness without decomposition. Such compounds can only be formed at low temperatures; and they are possessed of little permanency. It is well known that chlorine may combine under favourable circumstances with the alkalies and alkaline earths; and M. Grouvelle has succeeded in making it unite with magnesia, and the oxides of zinc, copper, and iron. (An. de Ch. et de Ph. vol. xvii.) Of these chlorides, that of potash may be taken as an example. If chlorine is conducted into a dilute and cold solution of pure potash, the chloride of that alkali will be produced; but the affinity which gives rise to its formation is not sufficient for rendering it permanent. It is destroyed by most substances that act on either of its constituents. The addition of an acid produces this effect by combining with the alkali, and hence the chlorine is separated by the carbonic acid of the atmosphere. Animal or vegetable colouring matters are fatal to the compound by giving chlorine an opportunity to exert its bleaching power; and, indeed, the colour is removed by the chloride of potash almost as readily as by a solution of chlorine in pure

water. It is also destroyed by the action of heat; nor can its solution be concentrated without decomposition; for, in either case, muriatic and chloric acids are generated. (Page 293.)

Berzelius has published some ingenious remarks in order to prove that chlorine does not unite with metallic oxides, and that the bleaching compounds supposed to be examples of such a mode of combination are mixtures of a metallic chloride and a chlor*ite* of an oxide. The tendency of the supposed chlorite is to pass into a chlorate and chloride, as by the application of heat; but if colouring matter or an oxidable substance be present, the chlorous acid yields its oxygen, and a metallic chloride results. The bleaching power of the compound is of course attributed to the oxygen which is set at liberty. This point is powerfully argued by Berzelius, and supported on well-contrived experiments; but since no decisive proof of the existence of such a compound as chlorous acid has as yet been given, there appears to be no sufficient reason for rejecting the explanation generally adopted by chemists. (An. de Ch. et de Ph. xxxviii. 208.)

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 potash, soda, protoxide of lead, or oxide of bismuth, heated to redness, oxygen gas is evolved, and an iodide of these metals will be formed. 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 recognised either by the colour of its vapour, or by its action on starch. (Page 316.) The metallic iodides are generated under circumstances analogous to those above mentioned for procuring the chlorides.

When the vapour of iodine is conducted over red-hot lime,

baryta, or strontia, oxygen is not disengaged, but an iodide of those oxides, according to Gay-Lussac, is generated. The iodides of these oxides are therefore more permanent than the analogous compounds with chlorine. Iodine does not combine with any other oxide under the same circumstances; and indeed all other such iodides very few of which exist, are, like the chlorides of oxides, possessed of little permanency, and are decomposed by a red heat.

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, water is decomposed, and hydriodic and iodic acids 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 iodurets 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 disengagement of caloric. These compounds have as yet been but partially examined. They may be formed either by the action of bromine on the pure metals, or by dissolving metallic oxides in hydrobromic acid, and evaporating the solution to dryness. Bromine unites with potash, 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 potash and soda, is by dissolving the carbonate of these alkalies in hydrofluoric acid, and evaporating the

solution to perfect dryness. The insoluble fluorides are easily formed from the hydrofluates of potash and soda by double decomposition. These compounds are without exception decomposed by concentrated sulphuric acid with the aid of heat; and the hydro-fluoric 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 caloric; and in several instances the heat evolved 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. The sulphurets of the common metals may be made by this process. The elements of the oxide unite with separate portions of sulphur, forming sulphurous acid gas, which is disengaged, and a metallic sulphuret which remains in the retort.

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 sulphuretted hydrogen, or an alkaline hydrosulphuret. Nearly all the salts of the common metals are decomposed when a current of sulphuretted hydrogen gas is conducted into their solutions. The salts of uranium, iron, manganese, cobalt, and nickel, are well-known exceptions; but these also are precipitated by hydrosulphuret of ammonia or potash.

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 which are formed of the metallic bases of the alkalies and earths, are insoluble in water.

Most of the protosulphurets are capable of supporting intense heat without decomposition; but 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 heat and air or oxygen gas; and the products depend entirely on the degree of heat and the nature of the metal. The sulphuret is 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, then 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 action of hydrogen gas at a red heat, the pure metal being set free and sulphuretted hydrogen evolved. M. 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 in the essays which he published in the *Journal de Physique*. In the 53d volume of that work, he demonstrated that sulphuret of iron (magnetic pyrites), as well as the common cubic pyrites or bisulphuret, are compounds of sulphur and metallic iron without any oxygen. He showed the same also with respect to the sulphurets of other metals, such as those of 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.

It was the general belief at that time, also, that the compounds formed by heating sulphur with an alkali or alkaline earth are sulphurets of a metallic oxide. Thus, the old *hepar sulphuris*, *sulphuretum potassæ* of the Edinburgh Pharmacopœia, which is made by fusing together a mixture of sulphur and dry carbonate of potash, was regarded as a sulphuret of potash. In the year 1817 M. Vauquelin published an essay in the 6th volume of the *Annales de Chimie et de Physique*, wherein he detailed some experiments, the object of which was to determine the state of the alkali in that compound. The late Count Berthollet had observed that when *hepar sulphuris* is dissolved in water, the solution always contains a considerable portion of sulphuric acid, which he conceives to be generated at the moment of solution. He supposed that water is then decomposed; and that its elements combine with different portions of sulphur, the oxygen giving rise to the formation of sulphuric acid, and the hydrogen to sulphuretted hydrogen. The accuracy of this explanation was called in question by Vauquelin in the paper above mentioned, who contended that the sulphuric acid is generated, not during the process of solution, but by the action of heat during the formation of the sulphuret. One portion of potash, according to him, yields its oxygen at a high temperature to some of the sulphur, converting it into sulphuric acid, while the potassium unites with pure sulphur. Two combinations therefore result —sulphuret of potassium and sulphate of potash, which are mixed together. Though the experiments adduced in favour of this opinion were not absolutely convincing, yet they made it the more probable of the two; and M. Vauquelin, admitting however the want of actual proof, inferred from them that when an alkaline oxide is heated to redness with sulphur, the former loses oxygen, and a sulphuret of the metal itself is produced.

The sixth volume of the Annals likewise contains a paper by Gay-Lussac, who offered additional arguments in favour of Vauquelin's opinion, and I believe most chemists held them to be satisfactory. But the more recent labours of Berthier and Berzelius have given still greater insight into the nature of these compounds. One of Vauquelin's chief argu-

ments was drawn from the action of charcoal on sulphate of potash. 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 sulphoret is left, analogous both in appearance and properties to that which may be made by igniting carbonate of potash 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 potash would be decomposed by charcoal at a high temperature; and that, consequently, the product must be a sulphuret of potassium.

Berthier has proved in the following manner that these changes do actually occur. (An. de Ch. et de Ph. vol. 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, potash, and soda; but from the 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 de Ph. vol. xx.) He transmitted a current of dry hydrogen gas over a known quantity of sulphate of potash, heated to redness. It was expected from 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 relations 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.

Cyanogen, as already mentioned at page 376, has an affinity for metallic substances. Few of the cyanurets, however, have been hitherto obtained in a separate state, excepting those of potassium, mercury, silver, and palladium. The three latter are readily decomposed by a red heat.

Cyanogen unites also with some of the metallic oxides When hydrocyanic acid vapour is transmitted over pure baryta contained in a porcelain tube, and heated till it begins to be luminous, hydrogen gas is evolved, and cyanuret of baryta, according to Gay-Lussac, is generated. The same chemist succeeded in forming the cyanurets of potash and soda by a similar process. These compounds exist only in the dry state.

A change is produced in them by the action of water, the nature of which has already been explained. (Page 383.)

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 of these compounds is the radical of a hydracid, that is, it 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 potash and muriatic acid have a strong affinity for each other, the solution would of course contain muriate of potash. 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, chemists are in doubt whether they are dissolved as such, or whether they may not be converted, by decomposition of water, into hydriodate, hydrosulphate, and hydrocyanate of potash. 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 muriatic or hy-

driodic acid, is mixed with potash or any similar metallic oxide, the acid and salifiable base do not unite, as happens in other cases, 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 sulphuretted hydrogen acts upon a salt 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 muriate of potash, 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 or cyanuret of potassium, metallic silver is said to unite with chlorine or cyanogen, while the oxygen of the oxide of silver combines with potassium; so that nitrate of potash and chloride or cyanuret of silver are generated. On adding sulphuric acid to a solution of chloride of potassium, production of muriatic acid and potash, which did not previously exist, instantly ensues, in consequence of water being decomposed, and yielding its hydrogen to chlorine, and its oxygen to potassium; and this explanation is justified by the circumstance, that the same change certainly occurs when concentrated sulphuric acid is brought into contact with solid chloride of potassium. It is further believed that the crystallized muriate 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 muriate of potash 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 muriate 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 muriate 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 muriate of potash, the oxygen of the oxide of silver unites with the hydrogen of the muriatic acid; chloride of silver is precipitated, and nitrate of potash remains in the liquid. On adding sulphuric acid to a muriate, muriatic acid is simply displaced, 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, for example, 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 muriatic acid for metallic oxides, co-operate in determining the decomposition of water, and the production of a muriate. Neither view has materially the advantage in point of simplicity; for while some phenomena are more simply explained by one mode of reasoning, others are more easily explicable according to the other. It is certainly an objection to the latter view, that it supposes the frequent decomposition and reproduction of water, without there being any direct proof of its occurrence; for the solution of chlorides and similar compounds often takes place, even without disengagement of caloric. The circumstances which may be mentioned as appearing to indicate decomposition of water, are the following:—1. The solution of some compounds, such as sulphuret and cyanuret of potassium, actually emit an odour of sulphuretted hydrogen and hydrocyanic 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; and this effect could scarcely be expected to occur, unless the protoxide of iron were contained 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 sul-

phuretted hydrogen gas disengaged with effervescence. In like manner chloride and sulphuret of silicium are converted by water into silica and muriatic acid and sulphuretted hydrogen. 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.

The first argument is not perhaps to be trusted, because the production of sulphuretted hydrogen and hydrocyanic acid is probably occasioned by the carbonic acid of the atmosphere. The three latter, though not amounting to demonstration, give a high degree of probability to the existence of salts of muriatic and hydriodic acid; and if this be admitted, the same view may be extended to other hydracids. This opinion, which is preferred by many chemists, is adopted in the present work. Considering how much the affinity of metals for oxygen, and that of the radicals of the hydracids for hydrogen, differ in force, it is likely that some of the chlorides and similar compounds dissolve without change, while others give rise to decomposition of water. But as in general chemists possess no means of determining the nature of the change in particular instances, it has been thought most consistent to apply the same view to all, except in some special cases when the contrary is mentioned.

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. (An. de Chimie, vol. i. and xiii.)

The metallic phosphurets may be prepared in several ways. The most direct method is by bringing phosphorus in contact with metals at a high 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. 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 Professor Rose the phosphurets of copper, nickel, cobalt, and iron are the only ones which admit of being advantageously prepared by this method. (Poggendorff's Annalen, vi. 205.) When chlorides are employed, muriatic acid gas, and with sulphurets sulphuretted hydrogen gas, is of course generated.

Phosphorus is said to unite with metallic oxides. For example, phosphuret of lime is 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 mixture 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 known are those of zinc, potassium, arsenic, and tellurium. No 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 two 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 13 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 at common temperatures they decompose water 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 alkaline earths. These are four in number; namely,

Barium, Strontium, Calcium, Magnesium.

These metals, like the preceding, 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 six in number; namely,

Aluminium, Glucinium, Yttrium,
Zirconium, Silicium, Thorinum.

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. Silica is even considered by several chemists as an acid, and its chemical relations appear to justify the opinion. For reasons to be afterwards mentioned, the propriety of placing silicium among the metals is exceedingly doubtful.

Class II. The number of the metals included in this class

amounts to 28. 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, molybdenum, tungsten, antimony, columbium, titanium, tellurium, and gold.

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,

Manganese,	Tin,	Cobalt,
Zinc,	Cadmium,	Nickel.
Iron,		

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 thirteen in number; namely,

Arsenic,	Uranium,	Bismuth,
Molybdenum,	Columbium,	Copper,
Chromium,	Cerium,	Tellurium,
Tungsten,	Titanium,	Lead.
Antimony,		

Order 3. Metals, the oxides of which are decomposed by a red heat. These are

Mercury,	Platinum,	Osmium,
Silver,	Palladium,	Iridium.
Gold,	Rhodium,	

CLASS I.

METALS WHICH BY OXIDATION YIELD ALKALIES OR EARTHS.

ORDER I.

METALLIC BASES OF THE ALKALIES.

SECTION I.

POTASSIUM.

Potassium was discovered in the year 1807 by Sir H. Davy, and the circumstances which led to the discovery have already been described. (Page 128.) It was prepared by that philosopher by causing hydrate of potash, slightly moistened for the purpose of increasing its conducting power, to communicate with the opposite poles of a galvanic battery of 200 double plates; when the oxygen both of the water and the potash passed over to the opposite pole, while the hydrogen of the former, and the potassium of the latter, made their appearance at the negative wire. 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 potash in contact with turnings of iron heated to whiteness in a gun-barrel. The iron, under these circumstances, deprives the water and potash 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 M. Curaudau, by mixing dry carbonate of potash 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 M. Brunner, who decomposes potash by means of iron and

charcoal. From eight ounces of fused carbonate of potash, 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 potash solely by means of charcoal. The material employed for the purpose is carbonate of potash prepared by heating cream of tartar to redness in a covered crucible. (Poggendorff's Annalen, iv. 23.)

Potassium is 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° F. 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° F. It sublimes at a 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. 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 electricity and caloric.

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 white flame and great evolution of caloric. 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 the emission of light, and pure hydrogen gas is evolved.

OXIDES OF POTASSIUM.

Potassium unites with oxygen in two proportions. The protoxide, commonly called *potash* or *potassa*, 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 performing the last-mentioned process, the potassium should be cut into very thin slices; for otherwise the oxidation is incomplete. The product, when partially oxidized, was once suspected to be a distinct oxide; but it is now admitted to be a mixture of potash and potassium.

As potash is the protoxide of potassium, it is supposed to contain one atom of each of its elements. Its composition is best determined by collecting and measuring the quantity of hydrogen which is evolved when potassium is plunged under water. From the experiments of Sir H. Davy, and Gay-Lussac and Thenard, it appears that forty grains of potassium decompose precisely nine grains of water; and that while one grain of hydrogen escapes in the gaseous form, the corresponding eight grains of oxygen combine with the metal. The protoxide of potassium is therefore composed of

Potassium	.	40, or one equivalent,
Oxygen	.	8, or one equivalent;

And its equivalent is 48.

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. According to Gay-Lussac and Thenard, it consists of

Potassium	.	40, or one equivalent.
Oxygen	.	24, or three equivalents.

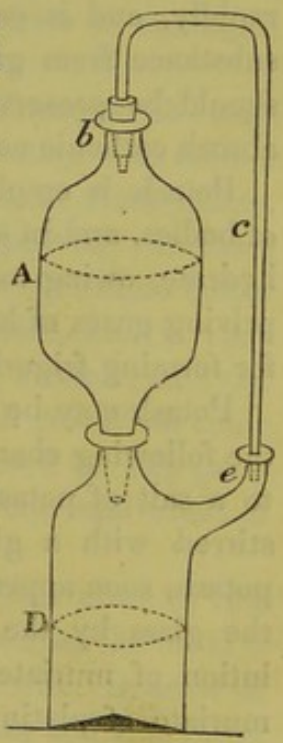
Anhydrous potash can only be prepared by the slow oxidation of potassium, as already mentioned. In its pure state, it is a white solid substance, highly caustic, which fuses at a temperature somewhat above that of redness, and bears the strongest heat of a wind furnace without being decomposed or volatilized. It has a powerful affinity for water, and intense heat is disengaged during the act of combination. With a certain portion of that liquid it forms a solid hydrate, the elements of which are united by an affinity so energetic, that no degree of heat hitherto employed can effect their separation. This substance was long regarded as the pure alkali, but it is in reality a *hydrate of potash*. It is composed of forty-eight parts or one equivalent of potash, and nine parts or one equivalent of water.

Hydrate of potash is solid at common temperatures. It fuses at a heat rather below redness, and assumes a somewhat crystalline texture in cooling. 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 it is now termed *potassa* and *potassa fusa* by the Colleges of Edinburgh and London. This preparation is made by evaporating the aqueous solution of potash 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 potash. It is purified from these substances by dissolving it in alcohol, and evaporating the solution 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 potash of the druggists is dissolved in water, a number of small bubbles of gas are disengaged, which is pure oxygen. Mr. Graham finds its quantity to be variable in different specimens, and to depend apparently on the impurity of the specimen.

The aqueous solution of potash, *aqua potassæ* of the Pharmacopœia, is prepared by decomposing carbonate of potash by lime. To effect this object completely, it is advisable to employ equal parts of quicklime and carbonate of potash.

After slaking the lime in an iron vessel, the carbonate of potash, dissolved in its own weight of hot water, is added, and the mixture boiled briskly for about ten minutes. The liquid, after subsiding, is filtered through a funnel, the throat of which is obstructed by a piece of clean linen. This process is founded on the fact that lime deprives carbonate of potash of its acid, forming an insoluble carbonate of lime, and setting the pure alkali at liberty. If the decomposition is complete, the filtered solution should not effervesce when neutralized with an acid.

As pure potash 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 Mr. 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 by 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 Mr. 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.

Solution of potash is highly caustic, and its taste intensely acrid. It possesses 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. For the same reason it should be preserved in well-closed bottles, that it may not absorb carbonic acid from the atmosphere.

Potash 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 59.)

Potash may be distinguished from all other substances by the following characters. 1. If tartaric acid be added in excess to a salt of potash dissolved in water, and the solution be stirred with a glass rod, a white precipitate, bitartrate of potash, soon appears, which forms peculiar white streaks upon the glass by the pressure of the rod in stirring. 2. A solution of muriate of platinum causes a yellow precipitate, muriate of platinum and potash. This is the most delicate test, provided the mixture be gently evaporated to dryness, and a little cold water be afterwards added. Muriate of platinum and potash then remains in the form of small shining yellow crystals. 3. By being precipitated by no other substance.

The following test has been recommended by M. Harkort for distinguishing between potash 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 potash, becomes blue, an effect which is not produced by the presence of soda.

Chloride of potassium.—Potassium takes fire spontaneously in an atmosphere of chlorine, and burns with greater brilliancy than in oxygen gas. This chloride is also generated when potassium is heated in muriatic acid gas, hydrogen being evolved at the same time. It is the residue of the decomposition of chlorate of potash by heat; and it is obtained in the form of colourless cubic crystals, when a solution of muriate of potash evaporates spontaneously.

Chloride of potassium has a saline and rather bitter taste. It requires three parts of water at 60° F. for solution, and is still more soluble in hot water. Its solution probably contains muriate of potash. (Page 418.) It is composed of 36 parts or one equivalent of chlorine, and 40 parts or one equivalent of potassium.

Iodide of potassium.—This compound is formed with emission of light, when potassium is heated in contact with iodine. It may likewise be obtained by means of heat from iodate, and by crystallization from hydriodate of potash. It fuses readily when heated, and is volatilized at a temperature below redness. It deliquesces in a moist atmosphere, and is very soluble in water. It dissolves also in strong alcohol; and the solution, when gently evaporated, yields small colourless cubic crystals of iodide of potassium. It is composed of 124 parts or one equivalent of iodine, and 40 parts or one equivalent of potassium.

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 hydroguret of potassium was made by Gay-Lussac and Thenard, by heating potassium in hydrogen gas. It is a gray solid substance, which is readily decomposed by

heat or contact with water. It does not inflame spontaneously in oxygen gas.

Sulphuret of potassium.—Sulphur unites readily with potassium by the aid of heat; and so much caloric is evolved at the moment of combination, that the mass becomes incandescent. The best method of obtaining a sulphuret in definite proportion is by decomposing sulphate of potash according to the process of Berthier or Berzelius. (Page 414.) This sulphuret is composed of 16 parts or one equivalent of sulphur, and 40 parts or one equivalent of potassium. It has a red colour, fuses below the temperature of ignition, and assumes a crystalline texture in cooling. It is dissolved by water, being probably converted, with evolution of caloric, into hydrosulphuret of potash.

Besides this protosulphuret, Berzelius has described four other compounds, which he obtained by igniting carbonate of potash with different proportions of sulphur. These are composed of one equivalent of potassium with 2, 3, 4, and 5 equivalents of sulphur.

Phosphuret of potassium.—This compound may be formed by the action of potassium on phosphorus with the aid of a moderate heat. It is converted by water into potash and perphosphuretted hydrogen gas, which inflames at the moment of its formation.

SECTION II.

SODIUM.

Sir H. Davy made the discovery of sodium in the year 1807, a few days after he had discovered 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.

Sodium 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° F. and rises in vapour at a full red heat. Its specific gravity is 0.972.

Sodium soon tarnishes on exposure to the air, though less rapidly than potassium. When thrown into water it swims upon its surface, occasions violent effervescence and a hissing noise, and is rapidly oxidized; but no light is visible. The action is stronger with hot water, and a few scintillations appear; but still there is no flame. In each case, soda is generated, owing to which the water acquires an alkaline reaction, and pure hydrogen gas is disengaged.

Oxides of Sodium.—Chemists are acquainted with two definite compounds only of sodium and oxygen. The protoxide, or *soda*, is a gray white solid, difficult of fusion, which is obtained by burning sodium in dry atmospheric air. It is also formed when sodium is oxidized by water; and its composition may be determined by collecting the hydrogen which is then disengaged. According to the experiments of Sir H. Davy, the results of which differ little from those of Gay-Lussac and Thenard, soda consists of 24 parts of sodium and 8 parts of oxygen. For this reason, 24 is regarded as the atomic weight of sodium, and 32 the combining proportion of soda.

When sodium is heated to redness in excess of pure oxygen, an orange-coloured substance is formed, which is peroxide of sodium. It is resolved by water into oxygen and soda; and it is composed, according to Gay-Lussac and Thenard, of two equivalents of sodium and three of oxygen. It is partially reconverted into soda by a very strong heat.

With water soda 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 potash. It is prepared from the solution of pure soda, exactly in the same manner as the corresponding preparations of potash. The solid hydrate is composed of 32 parts or one equivalent of soda, and 9 parts or one equivalent of water.

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 recognised as glauber 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 blow-pipe flame, they communicate to it a rich yellow colour.

Chloride of Sodium.—This compound may be formed directly by burning sodium in chlorine, or by heating it in muriatic acid gas. It is deposited in crystals, when a solution of muriate of soda is evaporated; for this salt, like muriate of potash, exists only while in solution, and is converted into a chloride during the act of crystallizing. Hence sea water, the chief ingredient of which is muriate of soda, yields chloride of sodium by evaporation; and from this source is derived most of the different kinds of common salt, such as fishery salt, stoved salt, and bay salt, substances essentially the same, and between which the sole difference depends on the mode of preparation. Chloride of sodium is known likewise as a natural product under the name of rock or mineral salt.

The common varieties of salt, of which rock and bay salt are the purest, always contain small quantities of sulphate of magnesia and lime, and muriate of magnesia. These earths may be precipitated as carbonates by boiling a solution of salt for a few minutes with a slight excess of carbonate of soda, filtering the liquid, and neutralizing with muriatic 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.

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° F. for solution, and its solubility is not increased by heat. Like the soluble chlorides in general, it passes into a muriate while in the act of dissolving. (Page 417.) Sulphuric acid decomposes it with evolution of muriatic acid gas, and formation of sulphate of soda. In composition it is analogous to chloride of potassium, consisting of one equivalent of chlorine and one of sodium.

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 muriatic acid and chloride of lime.

The compounds of sodium with iodine, sulphur, and phosphorus are so analogous to those which potassium forms with the same elements, that a particular description of them is unnecessary. Sodium does not unite with hydrogen.

According to Gmelin of Tübingen sulphuret of sodium is the colouring principle of *lapis lazuli*, to which the colour of ultra-marine is owing; and he has succeeded in preparing artificial ultra-marine by heating sulphuret of sodium with a mixture of silica and alumina. (An. de Ch. et Ph. xxxvii. 409.)

Chloride of Soda.—This compound has lately acquired the attention of scientific men under the name of Labarraque's *disinfecting soda liquid*, which was announced by M. Labarraque as a compound of chlorine and soda, analogous to the well-known bleaching powder, chloride of lime. The nature of this liquid has been since investigated by Mr. Phillips and Mr. Faraday, especially by the latter; and it appears from the experiments of this chemist, that while chloride of soda is the active ingredient, its properties are considerably modified by the presence of carbonate of soda. (Quarterly Journal of Science, N. S. II. 84.)

Pure chloride of soda is easily prepared, by transmitting to saturation a current of chlorine gas into a cold and rather dilute solution of caustic soda. Common carbonate of soda may be substituted for the pure alkali; but considerable excess of chlorine must then be employed in order to displace the whole of the carbonic acid. It may also be formed easily, cheaply, and of uniform strength, by decomposing chloride of lime with carbonate of soda, as proposed by M. Payen. (Quarterly Journal of Science, N. S. I. 236.) However prepared, its properties are the same. As its constituents are retained in combination by a feeble affinity, the compound is easily destroyed. It emits an odour of chlorine, and possesses the bleaching properties of that substance in a very high degree. When kept in open vessels, it is slowly decomposed by the carbonic acid of the atmosphere with evolution of chlorine; and the change is more rapid in air charged with putrid

effluvia, because the carbonic acid produced during putrefaction promotes the decomposition of the chloride. On this, as was proved by M. Gaultier de Claubry, depends the efficacy of an alkaline chloride in purifying air loaded with putrescent exhalations. When the solution is heated to the boiling point, or concentrated by means of heat, the chloride undergoes a change previously explained, (page 293.) and is converted into chlorate and muriate of soda.

Chloride of soda may be employed in bleaching, and for all purposes to which chlorine gas or its solution was formerly applied. It is now much used in removing the offensive odour arising from drains, sewers, or all kinds of animal matter in a state of putrefaction. Bodies disinterred for the purpose of judicial inquiry, or parts of the body advanced in putrefaction, may by its means be rendered fit for examination; and it is employed in surgical practice for destroying the fetor of malignant ulcers. Clothes worn by persons during pestilential diseases are disinfected by being washed with this compound.

It is also used in fumigating the chambers of the sick; for the disengagement of chlorine is so gradual, that it does not prove injurious or annoying to the patient. In all these instances chlorine appears actually to decompose noxious exhalations by uniting with the elements of which they consist, and especially with hydrogen.

In preparing the disinfecting liquid of Labarraque, it is necessary to be exact in the proportion of the ingredients employed. The quantities used by Mr. Faraday, founded on the directions of Labarraque, are the following. He dissolved 2800 grains of crystallized carbonate of soda in 1.28 pints of water, and through the solution, contained in Woulfe's apparatus, was transmitted the chlorine evolved from a mixture of 967 grains of sea-salt and 750 grains of peroxide of manganese, when acted on by 960 grains of sulphuric acid, diluted with 750 grains of water. In order to remove any accompanying muriatic acid gas, the chlorine before reaching the soda was conducted through pure water, by which means nearly a third part was dissolved, but the remaining two-thirds were fully sufficient for the purpose. The gas was readily absorbed by the solution, and from the beginning to the end of the process, not a particle of carbonic acid gas was evolved;

whereas by employing an excess of chlorine, the carbonic acid may be entirely expelled.

The solution thus prepared has all the characters of Labarraque's soda liquid. Its colour is pale yellow, and it has but a slight odour of chlorine. Its taste is at first sharp, saline, and scarcely at all alkaline; but it produces a persisting biting effect upon the tongue. It first reddens and then destroys the colour of turmeric paper. When boiled it does not give out chlorine, nor is its bleaching power perceptibly impaired; and if carefully evaporated, it yields a mass of damp crystals, which, when redissolved, bleach almost as powerfully as the original liquid. When rapidly evaporated to dryness, the residue contains scarcely any chlorate of soda or chloride of sodium; but it has nevertheless lost more than half of its bleaching power, and therefore chlorine must have been evolved during the evaporation. The solution deteriorates gradually by keeping, chloric acid and chloride of sodium being generated. When allowed to evaporate spontaneously, chlorine gas is gradually evolved, and crystals of carbonate of soda remain.

In some respects the nature of this liquid is still obscure; but from the preceding facts, drawn from the essay of Mr. Faraday, two points seem to be established. First, that the liquid contains chlorine, carbonic acid, and soda. Secondly, that the chlorine is not simply combined either with water or soda; for by boiling, the gas is neither expelled as it would be from an aqueous solution, nor does the liquid yield chloric acid and chloride of sodium as when pure chloride of soda is heated. It may perhaps be regarded as a compound of chloride and bicarbonate of soda. Its production may be conceived by supposing, that when chlorine is introduced in due quantity into a solution of carbonate of soda, it combines with half of the alkali, while the remainder with all the carbonic acid constitutes bicarbonate of soda. Should this salt unite, though by a feeble affinity, with chloride of soda, both may thence derive a degree of permanence which neither singly possesses. During spontaneous evaporation, the tendency of the common carbonate to crystallize may occasion its reproduction, and the disengagement of chlorine. These remarks, however, are merely speculative.

SECTION III.

LITHIUM.

In the year 1818 M. Arfwedson of Sweden *, in analyzing the mineral called petalite, discovered the existence of a new alkali, 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 λίθειος, *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 silica and alumina, whereas potash is likewise present in lepidolite and lithion-mica, and therefore lithia should be prepared solely from the former.

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 silica 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.

Sir H. Davy succeeded, by means of galvanism, in obtaining a white-coloured metal like sodium from lithia; but it was oxidized, and thus reconverted into the alkali, with such rapidity that it could not be collected. Lithia may therefore be regarded as the protoxide of *lithium*; and, according to the analysis of sulphate of lithia by Stromeyer and Thomson, lithia

* An. de Ch. et de Ph. vol. x.

is inferred to be composed of 10 parts or one equivalent of lithium, and 8 parts or one equivalent of oxygen. Its equivalent is, therefore, 18; but the accuracy of this estimate is rendered doubtful by some late experiments of M. Hermann, from whose researches the equivalent of lithia may be estimated, in round numbers, at 14.

Lithia is distinguished from potash and soda by its greater neutralizing power, by forming sparingly soluble salts with carbonic and phosphoric acids, and by chloride of lithium being highly deliquescent, and dissolving freely in strong alcohol. This alcoholic solution burns with a red flame; and all the salts of lithia, when heated on platinum wire before the blow-pipe, tinge the flame of a red colour. Further, when lithia is fused on platinum foil, it attacks that metal, and leaves a dull yellow trace round the spot on which it lay. (Berzelius on the Blow-pipe. Children's Translation.)

Lithia is distinguished from the alkaline earths by forming soluble salts with sulphuric and oxalic acids; and by the circumstance that carbonate of lithia, though sparingly soluble in water, forms with it a solution which gives a brown stain to turmeric paper.

CLASS I.

ORDER II.

METALLIC BASES OF THE ALKALINE EARTHS.

SECTION IV.

BARIUM.

Sir H. 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, and placing a globule of mercury in a little hollow made in its surface. The paste was laid upon a platinum tray which communicated with the positive pole of a galvanic battery of 100 double plates, while the negative wire was brought into contact with the mercury. The baryta was decomposed, and its barium entered into combination 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.

Barium, thus procured, is of a dark-gray colour, 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.

Oxides of Barium.—Barytes, or *Baryta*, so called from the great density of its compounds, (from βαρὺς, 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 nitrate of baryta at a red heat; or, as was ascertained by Dr. Hope, 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. Baryta is a gray powder, the specific gravity of which is about 4. It requires a very high temperature for fusion. It 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 potash or soda; but it is much less caustic and less soluble in water 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 luminousness. 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 78 parts or one equivalent of baryta, and 9 parts or one equivalent of water.

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.) A saturated solution of baryta in boiling water deposits in cooling transparent, flattened prismatic crystals, which are composed, according to Mr. Dalton, of 78

parts or one equivalent of baryta, and 180 parts or 20 equivalents of water.

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.

The exact combining proportion of barium is not known with certainty; for while Dr. Thomson estimates its equivalent at 70, Berzelius states it at 68.66. Were I to venture an opinion from some experiments at present in progress, and of which unforeseen hindrances have for some time delayed the conclusion, I should select 69 as the equivalent of barium; but as the subject is still under investigation, I shall continue for the present to use the number stated by Dr. Thomson, being that which is generally employed in this country. Accordingly, baryta is regarded as a compound of 70 parts or one equivalent of barium, and 8 parts or one equivalent of oxygen.

Deutoxide of barium may be formed by conducting dry oxygen gas over pure baryta at a low red heat. An easier process, according to M. Quesneville, junr., is to introduce nitrate of baryta into a luted retort of porcelain, to which is attached a Welter's safety tube terminating under an inverted jar full of water. Heat is gradually applied to the retort, and a red heat continued as long as there is any disengagement of nitric oxide or nitrogen gas. When these have ceased and pure oxygen passes over, which is a proof of all the nitrate being decomposed, the process is discontinued. The peroxide of barium is then found in the retort. This statement, however, is declared by Berzelius to be quite inaccurate, and that the residue is a compound of baryta and protoxide of nitrogen. (Yahres-bericht for 1828, 107.) Deutoxide of barium, according to Thenard, contains twice as much oxygen as baryta; or is composed of one equivalent of barium and two equivalents of oxygen. This is the substance employed by Thenard in the formation of deutoxide of hydrogen.

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 forming with muriatic acid a salt, which crystallizes readily by evaporation in the form of four, six, or eight-sided tables, is insoluble in alcohol, and does not undergo any change on exposure to the air.

The readiest method of forming the salts of baryta is by the action of moderately dilute acids on the native or artificial carbonate.

All the soluble salts of baryta are poisonous. The carbonate, from being dissolved by the juices of the stomach, likewise acts as a poison. The sulphate, from its perfect insolubility, is inert.

Chloride of Barium.—This compound is generated when chlorine gas is conducted over baryta at a red heat, and oxygen gas is disengaged. It may also be formed by heating to redness the crystallized muriate of baryta. It consists of one equivalent of each of its constituents. It requires five times its weight of water at 60° F. for solution, and is much more soluble in boiling water. At a strong red heat it fuses.

Bromide of Barium.—It was prepared by M. Henry, junr., who has examined it, by boiling proto-bromide 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. It resists decomposition by heat, and consists of one equivalent of each of its elements.

Sulphuret of Barium.—The protosulphuret may be prepared from sulphate of baryta by the action of charcoal or hydrogen gas at a high temperature. (Page 411.) It dissolves readily in hot water, forming hydrosulphuret of baryta. By means of this solution all the chief salts of baryta may be procured. Thus by adding an alkaline carbonate, carbonate of baryta is precipitated; and when muriatic acid is added, sulphuretted hydrogen is evolved, and muriate of baryta produced. A solution of pure baryta may also be obtained from the hydrosulphuret, by boiling it with peroxide of copper, until the filtered solution no longer gives a dark precipitate with acetate of lead. The crystallized hydrate of baryta is easily procured by means of this solution.

The combinations of barium with the other non-metallic substances have not yet been carefully examined.

SECTION V.

STRONTIUM.

The metallic base of strontia, called *strontium*, was discovered by Sir H. Davy 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.

From the close resemblance between baryta and strontia, these substances were once supposed to be identical. Dr. Crawford, however, and M. Sulzer noticed a difference between them; but the existence of strontia was first established with certainty in the year 1792 by Dr. 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.

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 52 parts or one equivalent of strontia, and 9 parts or one equivalent of water. Hydrate of strontia fuses readily at a red heat, but sustains the strongest heat of a wind furnace without decomposition. 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. These crystals are composed, according to the analysis of Dr. Hope, of 52 parts or one equivalent of strontia,

* Edinburgh Philosophical Transactions, iv. 3.

† Klaproth's Contributions, vol. i.

and 108 parts or 12 equivalents of water. They are converted by heat into the protohydrate. They require 50 times their weight of water at 60° F. for solution, and twice their 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 atomic weight of strontia, as deduced from the analyses of Berzelius, Stromeyer, and Thomson, is 52; and consequently strontia, regarded as the protoxide of strontium, is composed of 44 parts or one equivalent of strontium, and one equivalent of oxygen.

Deutoxide of strontium is prepared in the same manner as the corresponding preparation of baryta. It may likewise be formed by pouring an aqueous solution of strontia into deutoxide of hydrogen. According to Thenard it contains twice as much oxygen as the protoxide.

The soluble salts of strontia, like those of baryta, are precipitated by alkaline carbonates, and by sulphuric acid or soluble sulphates. Strontia is distinguished from baryta by forming with muriatic acid a salt, which crystallizes in the form of slender hexagonal prisms, deliquesces in a moist atmosphere, and dissolves freely in pure alcohol. The alcoholic solution, when set on fire, burns with a blood-red flame; and the salts of strontia, when exposed to the blow-pipe flame on platinum wire, impart to it a red tinge. They are also distinguished by a difference in the solubility of their sulphates. On adding glauber salt in excess to a soluble salt of baryta, that base is so completely precipitated, that its presence cannot be afterwards detected in the solution by any reagent. But when a salt of strontia is thus treated, so much sulphate of strontia remains in solution, that the filtered liquid yields a white precipitate with carbonate of potash or soda.

The salts of strontia are most conveniently prepared from the carbonate. These compounds are not poisonous.

Chloride of strontium is formed under precisely the same circumstances as chloride of barium, and its composition is analogous. It is exceedingly soluble in boiling water, and

requires twice its weight of water at 60° F. for solution. As already mentioned, it is soluble in alcohol.

Sulphuret of strontium may be prepared by the processes referred to in the last section. It may be advantageously employed for forming the solution and salts of strontia, in the same manner as those of baryta are prepared from sulphuret of barium. It consists of 44 parts or one equivalent of strontium, and 16 parts or one equivalent of sulphur.

SECTION VI.

CALCIUM.

The existence of calcium, the metallic base of lime, was demonstrated by Sir H. 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.

When carbonate of lime is exposed to a white or even to a very strong red heat, carbonic acid is expelled, and pure lime, commonly called *quicklime*, remains. 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 lime-stone is employed. The expulsion of carbonic acid is facilitated by mixing the carbonate with combustible substances, in which case carbonic oxide is generated. (Page 255.)

Lime is a brittle white earthy solid, the specific gravity 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 blow-pipe. 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 composed of 28 parts or one equivalent of lime, and 9 parts or one equivalent of water. The process of *slaking* lime consists in forming this hydrate, and the hydrate itself is called *slaked* lime. It differs from the hydrates of strontia and 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 Mr. 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, or *lime water*, which has been prepared in the cold, deposition of lime ensues. This fact was determined experimentally by Mr. Phillips, who has likewise observed that water at 32° F. 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. Gay-Lussac succeeded, however, in obtaining crystals of lime by evaporating lime water under the exhausted receiver of an air-pump by means of sulphuric acid, as in Mr. Leslie's process for freezing water. (Page 70.) Small transparent crystals, in the form of regular hexahedrons, are 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 atomic weight of lime, as deduced from the experiments of Dr. Thomson, is 28; and therefore lime, regarded as the protoxide of calcium, is composed of 20 parts or one equivalent of calcium, and 8 parts or one equivalent of oxygen.

Deutoxide of calcium may be formed in the same way as deutoxide of strontium. According to Thenard it consists of one equivalent of calcium and two equivalents of oxygen.

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 is oxalate of ammonia or potash; 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 muriatic acid.

The best characters for distinguishing lime from baryta and strontia are the following. Nitrate of lime yields prismatic crystals by evaporation, is deliquescent in a high degree, and very soluble in alcohol. 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 very moist, and do not dissolve in pure alcohol.

The salts of lime, when heated before the blow-pipe, or when their solutions in alcohol are set on fire, communicate to the flame a dull brownish-red colour.

Chloride of Calcium.—This compound is formed in the same manner as chloride of strontium. In decomposing muriate of lime by heat, a little muriatic acid is sometimes expelled as well as water. Chloride of calcium is soluble in alcohol, and deliquesces rapidly on exposure to the atmosphere. On account

of its strong affinity for water, it is much employed to deprive gases and other substances of their moisture. For a like reason, it may be used for forming frigorific mixtures with snow; but for this purpose crystallized muriate of lime, which contains six equivalents of water of crystallization, is far preferable.

Chloride of calcium contains one proportional of each of its elements.

Chloride of Lime.—This compound, commonly called *oxymuriate of lime*, or *bleaching powder*, is prepared by exposing thin strata of recently slaked lime in fine powder to an atmosphere of chlorine. The gas is absorbed in large quantity, and combines directly with the lime.

Chloride of lime 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, muriatic, and I presume chloric, acid are formed; and by long keeping, the dry chloride appears to undergo a similar change, at least muriatic acid is produced in large quantity. Chloride of lime 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 calcium was first carefully investigated by Mr. Dalton *, and it has since been analyzed by Dr. Thomson †, M. Welter ‡, and Dr. Ure §. The three first-mentioned chemists infer from their researches that bleaching powder is a hydrated *subchloride* or *dichloride* of lime, in which thirty-six parts or one equivalent of chlorine are united with fifty-six parts or two equivalents of lime. They are also of opinion, that on mixing this subchloride with water, a real chloride is dissolved, and one equivalent of lime separated as an insoluble powder. Dr. Ure, on the contrary, denies that bleaching powder is a subchloride; and maintains,

* Annals of Philosophy, i. 15. and ii. 6.
† Ibid. xv. 401.
‡ An. de Ch. et de Ph. vol. viii.
§ Quarterly Journal, xiii. 1.

according to the result of his own analysis, that the elements of this compound 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 which is present. The following is the result of his analysis of three specimens, No. 1 being good commercial bleaching powder, No. 2 made by himself with pure protohydrate of lime, and No. 3 prepared by himself with lime containing more water than in No. 2.

	No. 1.	No. 2.	No. 3.
Chlorine	23	40.32	39.5
Lime	46	45.40	39.9
Water	31	14.28	20.6
	100	100	100

The experiments of Dr. Ure appear to have been made with great care, and his results to be entitled to equal if not greater confidence than those of the other chemists. Upon the whole it is probable, that common commercial bleaching powder consists of chloride of lime, a compound of 36 parts or one equivalent of chlorine, and 28 parts or one equivalent of lime; and that this, the essential ingredient, is mixed with variable quantities of hydrate of lime.

Several methods have been proposed for estimating the value of different specimens of chloride of lime. 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 muriatic acid. Muriate of lime is generated, and the chlorine being set free, its quantity may easily be measured.

Bromide of Calcium.—It was prepared by M. Henry by the action of hydrate of lime on protobromide of iron. It crystallizes in acicular crystals, which are very deliquescent,

and extremely soluble both in water and alcohol. Its taste resembles that of chloride of calcium. It is partially decomposed by heat, and consists of one equivalent of each of its elements.

Protosulphuret of Calcium is procured by processes similar to those for forming sulphuret of barium.

The phosphorescent substance called *Canton's phosphorus*, which is made by exposing a mixture of calcined oyster shells and sulphur to a red heat, is supposed to be a sulphuret of lime; but its real composition has not been determined.

Phosphuret of Lime.—This compound is formed by passing the vapour of phosphorus over fragments of quicklime at a red heat. The true nature of the product is not known with certainty. It is either a phosphuret of lime, or a mixture of phosphate of lime and phosphuret of calcium. When it is put into water, mutual decomposition ensues, and phosphuretted hydrogen, hypophosphorous acid, and phosphoric acid are generated.

SECTION VII.

MAGNESIUM.

The galvanic researches of Sir H. Davy demonstrated the existence of magnesium, though he obtained it in a quantity too minute for determining its properties. It has lately been prepared by M. Bussy by the action of potassium on chloride of magnesium heated to redness in a tube of porcelain. The magnesium, separated by washing from chloride of potassium, had the appearance of small brown scales, which, when pressed by a pestle in an agate mortar, left a metallic trace, the colour of which resembled that of lead. Diluted nitric acid does not act upon it, but it is dissolved by muriatic acid and potash. It burns with difficulty even at a high temperature, and yields magnesia by the combustion.

Magnesia, the only known oxide of magnesium, is 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 specific gravity 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 caloric, and the product is readily decomposed by a red heat. There probably exist several different compounds of water and magnesia, but the native hydrate is the only one known with certainty. According to the analysis of Stromeyer, this hydrate contains one equivalent of each of its constituents; and the results of the analyses of Berzelius and Dr. Fyfe accord very nearly with this proportion.

Magnesia dissolves very sparingly in water. According to Dr. 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.

The atomic weight of magnesia, as determined by Dr. Thomson, is 20. Consequently this alkaline base, regarded as the protoxide of magnesium, is composed of

Magnesium	.	12 or one equivalent.
Oxygen	.	8 or one equivalent.

Magnesia is characterized by the following properties. With nitric and muriatic 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 precipitated from its salts as a bulky hydrate by the pure alkalies. It is precipitated as carbonate of magnesia, by the carbonates of potash 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 compounds of magnesium with the other simple substances have little interest. The chloride is formed by decomposing muriate of magnesia by heat; but it is apt to lose a portion of muriatic acid during the process. It is very deliquescent, and is soluble in alcohol. It is composed of thirty-six parts or one equivalent of chlorine, and twelve parts or one equivalent of magnesium. The bromide crystallizes in small acicular prisms, which have a bitter sharp taste, are deliquescent, and very soluble in water and alcohol. It is decomposed by a strong heat.

CLASS I.

ORDER III.

METALLIC BASES OF THE EARTHS.

SECTION VIII.

ALUMINIUM.

That alumina is an oxidized body was proved by Sir H. Davy, who found that potash 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 lately procured *aluminium*, the metallic base of alumina, in a pure state. (Edinburgh Journal of Science, No. xvii. 178.)

The preparation of this metal 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 disengagement of heat and light, that the process cannot be safely conducted in glass vessels. Wöhler succeeded in effecting the decomposition in 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 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 gray 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 gray powder separates, which on close inspection, especially in sunshine, is found to consist solely of minute scales of metal. After being well washed with *cold* water, it is pure aluminium. The solution is neutral, and contains a quantity of alumina, owing to a combination being formed between chloride of aluminium and choride of potassium during the action.

Aluminium, as thus formed, is a gray 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 perfectly distinct by pressure on steel, or in an agate mortar; so that the lustre of aluminium is decidedly metallic. In its 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.

Aluminium 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 muriatic and sulphuric acid it is dissolved with evolution of hydrogen gas. It is easily and completely dissolved even by a dilute solution of potash, hydrogen gas being evolved at the same time. Ammonia produces a similar effect, and renders soluble a large quantity of alumina. The hydrogen gas which makes its appearance is of course derived from water, the oxygen of which combines with aluminium.

Alumina 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 earthen-ware are made, consist of hydrate 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 potash. This salt, as purchased in the shops, is frequently contaminated with oxide of iron, and consequently unfit for many chemical purposes; but it may be separated from this impurity by repeated crystallization. The absence of iron is proved by the alum being soluble without residue in a solution of pure potash; whereas when oxide 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 potash 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 sub-sulphate. 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 muriatic 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.) 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.

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. (Page 40.)

Alumina most probably forms several different hydrates with water. Dr. Thomson has described two different compounds of this kind. One is the bi-hydrate, composed of one equivalent of alumina and two of water; and it is procured by exposing, for the space of two months, alumina, precipitated by means of an alkali, to a dry air, the temperature of which does not exceed 60° F. The other compound is a protohydrate, obtained by drying the bi-hydrate at a temperature of 100° F., by which means half of its water is expelled.

Alumina, owing to its insolubility, 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 potash, 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.

Chemists are not agreed as to the combining proportion of alumina; but Dr. Thomson, after comparing the results of a considerable number of analyses, has fixed upon 18 as its equivalent. The composition of alumina is still more uncertain, for as yet no direct experiment has been made on the subject. Dr. Thomson considers it a compound of one proportional of aluminium and one of oxygen, and on this supposition 10 is the equivalent of the former; but Berzelius believes its constitution to be analogous to that of peroxide of iron, and a strong argument may be adduced in favour of this view.

Alumina is easily recognised 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 potash or soda, but the precipitate is completely re-dissolved by an excess of the alkali.

Chloride of Aluminium.—This compound was discovered some years ago, by Professor Oersted, 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.

To procure chloride of aluminium, Wöhler precipitated aluminous earth from a hot solution of alum by means of potash, 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.

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 muriatic 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 the common muriate of alumina, formed by decomposition of water. According to Oersted it is volatile at a temperature a little higher than 212°, and fuses nearly at the same degree.

Sulphuret 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 vivid emission of light. The resulting sulphuret is a partially vitrified, semi-metallic mass, which acquires an iron-black metallic lustre when burnished. On exposure to the air it emits a strong odour of sulphuretted hydrogen, swells up gradually, and falls into a

gray powder, sulphuretted hydrogen gas and alumina being obviously generated at the expense of the watery vapour floating in the atmosphere. Applied to the tongue, it excites a pricking warm taste of sulphuretted hydrogen. When thrown into pure water sulphuretted hydrogen gas is rapidly disengaged, and gray alumina deposited.

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.

Phosphuret 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 gray pulverulent mass, which by friction acquires a dark gray 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 explosive. The effervescence is less rapid than with the sulphuret, but is increased by heat.

Seleniuret 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 seleniuretted hydrogen; 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, euclase, beryl, and emerald. It is the 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 grayish 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 muriatic acid with the aid of heat; and the same ensues with disengagement of hydrogen gas, in solution of potash. 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.)

Glucina is commonly prepared from beryl, in which it exists to the extent of about 14 per cent, combined with silica 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 potash, 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 muriatic acid, and the solution evaporated to perfect dryness; by which means the silica is rendered quite insoluble. The alumina and glucina are then redissolved in water acidulated with muriatic 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.

Glucina is a white powder, which has neither taste nor odour, and is quite insoluble in water. Its specific gravity 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 γλυκὺς, sweet.) According to the analysis of Dr. Thomson and Berzelius, 26 is the atomic weight

of glucina; but the composition of the oxide has not yet been determined.

Glucina may be known chemically by the following characters. 1. Pure potash or soda precipitates glucina from its salts, but an excess of the alkali redissolves it. 2. It is precipitated permanently by pure ammonia as hydrate, and by fixed alkaline carbonates as 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.

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 grayish-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, as 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 potash; 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, as well as many of its salts, has 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 it 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 potash,

and by yielding a precipitate with ferrocyanate of potash. (Berzelius.) The equivalent of yttria, as deduced by Dr. Thomson from the analysis of Berzelius, is 42; but the composition of this earth is unknown.

THORIUM.

The earthy substance formerly called *thorina*, was found by Berzelius to be phosphate of yttria; but during last year 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. Thorina was procured from a rare Norwegian mineral, now called *thorite*, which was sent to Berzelius by M. Esmark. It consitutes 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 muriatic acid; when a gelatinous mass is formed, from which silica 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 sulphuretted hydrogen, 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 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.)

The metallic base of thorina (thorium) was procured by the action of potassium on chloride of thorium, 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-gray colour; and when pressed in an agate mortar, it acquires metallic lustre and an iron-gray 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 muriatic acid.

Thorina, when formed by the oxidation of thorium, or after being strongly heated, is a white earthy substance, of specific gravity 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 equivalent is about 67.6.

Thorina is distinguished from alumina and glucina by its insolubility in pure potash; from yttria by forming with sulphate of potash a double salt which is quite insoluble in a cold saturated solution of sulphate of potash; and from zirconia by the circumstance that this earth, after being precipitated from a hot solution of sulphate of potash, is almost insoluble in water and the acids. Thorina is precipitated, also, by ferrocyanate of potash, 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.

The experiments of Sir H. Davy proved zirconia to be an oxidized body, and afforded a presumption that its base, *zir-*

conium, is of a metallic nature. The decomposition of this earth, however, had not been effected in a satisfactory manner till the year 1824, when Berzelius succeeded in obtaining zirconium in an insulated state.

Zirconium is procured by heating a mixture of potassium and hydrofluate of zirconia and potash, carefully dried, in a tube of glass or iron, by means of a spirit-lamp. The reduction takes place at a temperature below redness, and without emission of light. The mass is then washed with boiling water, and afterwards digested for some time in dilute muriatic acid. The residue is pure zirconium.

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, muriatic, or nitro-muriatic acids; but it is dissolved readily, and with disengagement of hydrogen gas, by hydro-fluoric acid. Heated in the open air it takes fire at a temperature far below luminousness, 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 gray 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 *.

Zirconia 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. It is an earthy substance, resembling alumina in appearance, of specific gravity 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 great 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

* Poggendorff's Annalen, vol. iv. or Quarterly Journal of Science, xviii. 157.

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 potash, the zirconia subsiding as a sub-salt, and the potash 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 on 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 atomic weight of this earth is about 30 or 33.

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 chesnut-brown colour, and without lustre. It is insoluble in sulphuric, nitric, and muriatic acid; and it is slowly attacked by nitro-muriatic acid, even with the aid of heat. It is readily dissolved by hydrofluoric acid, with disengagement of hydrogen gas.

SECTION X.

SILICIUM.

That silica or siliceous earth is composed of a combustible body united with oxygen, was demonstrated by Sir H. Davy;

for on bringing the vapour of potassium in contact with pure silica heated to whiteness, a compound of silica and potash resulted, through which was diffused the inflammable base of silica 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 Dr. 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 wants the metallic lustre, and is a non-conductor of electricity, cannot be regarded as a metal. It may not be improper, however, to have the absence of these qualities more completely ascertained, before separating silica from a class of bodies with which, in several respects, it is so nearly allied.

Pure silicium was first procured by Berzelius in the year 1824 by the action of potassium on fluo-silicic acid gas; but it is more conveniently prepared from the double hydro-fluate of silica and potash or soda, previously dried by a temperature near that of redness. In this state the compound may be regarded as a double fluoride, in which neither oxygen nor hydrogen are present; and when heated in a glass tube with potassium, this metal unites with fluorine, and silicium 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 siliciuret of potassium. The silicium 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 hydro-fluoric acid to dissolve adherent particles of silica. (Annals of Philosophy, XXVI. 116.)

Silicium 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 blow-pipe without fusing or undergoing any other change. It is neither dissolved nor oxidized by the sulphuric, nitric, muriatic, or hydrofluoric acids; but a mixture of the nitric and hydrofluoric acids dissolves it readily even in the cold.

Silicium is not changed by ignition with chlorate of potash. 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 silica co-operating with the attraction of oxygen for silicium. For a similar reason it burns vividly when brought into contact with carbonate of potash 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 potash, soda, or baryta.

OXIDE OF SILICIUM OR SILICA.

Silica exists in the earth in great quantity. 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 in sandstones; and flint, calcedony, rock crystal, and other analogous substances, consist almost entirely of silica. Siliceous earth of sufficient purity for most purposes may, indeed, be procured by igniting transparent specimens of rock crystal, throwing them while red-hot into water, and then reducing them to powder.

Pure silica, in this state, is a light white powder, which feels rough and dry when rubbed between the fingers, and is both insipid and inodorous. It is fixed in the fire, and is very infusible; but fuses before the oxy-hydrogen blow-pipe with greater facility than lime or magnesia.

In its solid form it is quite insoluble in water; but Berzelius has shown that, when silica in the nascent state is in contact with that fluid, it is dissolved in large quantity. On evaporating the solution gently, a bulky gelatinous substance separates, which is a hydrate of silica. This hydrate is partially decomposed by a very moderate temperature; but a red heat is required for expelling the whole of the water. Ac-

cording to Dr. Thomson, silica unites with water in several proportions. (First Principles, vol. i. p. 191.)

Silica, most likely from its insolubility, does not change the blue vegetable colours. It appears to possess the properties of an acid rather than of an alkali. Thus, no acid acts upon silica except hydrofluoric acid; whereas it is dissolved by solutions of the fixed alkalies, and combines with many of the metallic oxides. On this account silica is termed *silicic acid* by some chemists, and its compounds with alkaline bases *silicates*. The compound earthy minerals that contain silica may be regarded as native silicates.

The combination of silica with the fixed alkalies is best effected by mixing pure sand with carbonate of potash 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 silica with three of carbonate of potash, 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 silica 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 silica. When a solution of this kind is evaporated to dryness, the silica is rendered quite insoluble, and may thus be obtained in a pure form.

But if the proportion of silica 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 glass is composed of silica and an alkali, 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 pearlashes. 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.

Berzelius ascertained the composition of silica by oxidizing a known quantity of silicium, and weighing the product carefully; and according to this synthetic experiment, 100 parts of silica are composed of 48 parts of silicium and 52 parts of oxygen. The atomic weight of silica, deduced apparently with great care by Dr. Thomson, is precisely 16. Chemists are not agreed about the atomic constitution of silica. Berzelius considers it a compound of one atom of silicium and three atoms of oxygen; but the opinion of Dr. Thomson, that it is composed of an atom of each element, is both more simple and agrees better with the combining proportion of silica. According to this view, and adopting 16 as the equivalent of silica, 8 is of course the equivalent of silicium, an inference which accords very nearly with the experimental result of Berzelius.

Chloride of Silicium.—When silicium 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 has a suffocating odour not unlike that of cyanogen, and when put into water is converted into muriatic acid and silica, the latter being easily obtained in the gelatinous form. (Berzelius.)

Sulphuret of Silicium.—This compound is formed by heating silicium in the vapour of sulphur, and the union is attended with the phenomena of combustion. The product is a white earthy-looking substance, which is instantly converted by the action of water into sulphuretted hydrogen and silica; and while the former escapes with effervescence, the latter is dissolved in large quantity. In open vessels, owing to the moisture of the atmosphere, it undergoes a similar change; but in dry air it may be kept unaltered.

FLUOSILICIC ACID GAS.

This gas is formed whenever hydrofluoric acid comes in contact with siliceous earth; and this is the reason why 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 the gas 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 silica; so that the resulting compound consists of silica and fluoric acid. But for reasons already stated, (page 338) fluor spar is here 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 silica, and give rise to the production of water and fluosilicic acid gas. This gas is therefore a fluoride of silicium; and though in compliance with the usage of other chemists, I have retained its ordinary name, its title to be considered an acid is questionable. It may occur to some whether hydrofluoric acid does not unite directly with silica; but this idea is inconsistent with the proportion in which the elements of the gas are found to be united.

This compound 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 specific gravity, according to Dr. Thomson, is 3.6111; and 100 cubic inches of it, at 60° F. and when the barometer stands at 30 inches, weigh 110.138 grains.

Water acts powerfully on fluosilicic acid gas, of which it condenses, according to Dr. John Davy, 365 times its volume.

(Philos. Trans. for 1812.) The gas suffers decomposition at the moment of contact with water, depositing part of its silica in the form of a gelatinous hydrate, 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 silica 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 silica is deposited. On this fact is founded the mode of analyzing fluosilicic acid gas, adopted by Dr. Davy and Dr. Thomson. According to the results obtained by Thomson, which appear more correct than those of Dr. Davy, this gas is composed of 18.86 parts or one equivalent of fluorine, and 8 parts or one equivalent of silicium. Considered as a compound of fluoric acid and silica, it consists of 10.86 parts or one equivalent of fluoric acid, and 16 parts or one equivalent of silica.

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*. According to the experiments of Berzelius, it appears to be a definite compound of hydrofluoric acid and silica in the ratio of three equivalents of the former to two of the latter. If evaporated before separation from the silica deposited by the action of water on fluosilicic acid gas, this compound is reproduced. But if the solution is poured off from the silica 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 silica is rendered insoluble. By exactly neutralizing with carbonate of potash, nearly all the silica and acid are precipitated in the form of a sparingly soluble double hydrofluate of silica and potash; and

a still more complete precipitation is effected by muriate of baryta in excess, when hydrofluate of silica and baryta is generated. A variety of similar compounds may be obtained either by double decomposition, or by the action of silicohydrofluoric acid on metallic oxides. Most of these salts are soluble in water, those of potash, soda, lime, baryta, and yttria, being the only sparingly soluble ones noticed by Berzelius. They have in general a sour bitter taste, redden litmus paper, and are decomposed at a high temperature with disengagement of fluosilicic acid gas. These salts were formerly known by the name of *fluosilicates*, in which silica and fluoric acid were thought to act the part of a compound acid; but Berzelius has shown that this view is inaccurate, and that they may be regarded as double salts, consisting of two proportionals of hydrofluate of silica, and one proportional of a hydrofluate of some other base.

Most of the facts contained in the preceding account of silicohydrofluoric acid are drawn in part from an Essay of Berzelius in the Annals of Philosophy, XXIV. 450, but chiefly from his *Lehrbuch der Chemie*, I. 631.

CLASS II.

METALS, THE OXIDES OF WHICH ARE NEITHER ALKALIES NOR EARTHS.

ORDER I.

METALS WHICH DECOMPOSE WATER AT A RED HEAT.

SECTION XI.

MANGANESE.

The black oxide of manganese was described in the year 1774 by Scheele as a peculiar earth, and Gahn subsequently showed that it contained 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 *man-*

ganium 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.

Manganese is a hard brittle metal, of a grayish-white colour, and granular texture. Its specific gravity, according to John, is 8.013. When pure it is not attracted by the magnet.

It is exceedingly infusible, requiring a heat of 160° Wedgwood for fusion. It soon tarnishes on exposure to the air, and absorbs oxygen with rapidity when heated to redness in open vessels. It is said to decompose water at common temperatures with disengagement of hydrogen gas, though the process is exceedingly slow; but at a red heat decomposition is rapid, and protoxide of manganese is generated. Decomposition of water is likewise occasioned by dilute muriatic or sulphuric acid, and the muriate or sulphate of protoxide of manganese is the product.

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, if not three, of the five compounds enumerated as oxides of manganese, have a similar constitution. The composition of these oxides has been particularly investigated by Berzelius, Dr. Thomson, (First Principles, I.) M. Arfwedson *, M. Berthier †, and myself ‡. The following table, drawn up by Mr. Phillips, correctly represents the relative quantities of oxygen and manganese contained in these oxides.

* Letter from Berzelius in the An. de Ch. et de Ph. vi.

† Ibid. xx.

‡ Philos. Trans. of Edin. for 1828; or Phil. Mag. and Annals, IV.

	Mang.		Oxy.		Mang.		Oxy.
Protoxide .	28	+	8	or	1	+	1 equiv.
Deutoxide .	28	+	12		2	+	3
Peroxide .	28	+	16		1	+	2
Red Oxide .	28	+	10.66		3	+	4
Varvicite .	28	+	14		4	+	7

Peroxide.—This is 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. 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 one equivalent of water and two of the oxide. The peroxide may be made artificially by exposing nitrate 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 expel some oxygen from the peroxide.

Peroxide of manganese undergoes no change on exposure to the air. It 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. (Page 194.) With muriatic acid, a muriate of the protoxide is generated, and chlorine is evolved. (Page 290.) 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 seems owing to a small quantity of deutoxide of manganese held in solution by a large excess of free sulphuric acid. 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 protoxide of manganese. (Page 190.)

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 procuring chlorine and oxygen gases, and in the preparation of the salts of manganese.

Deutoxide.—This oxide occurs nearly pure in nature, 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.

The colour of the deutoxide 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 deutoxide, has a brown tint; but when prepared from nitrate of manganese, it is nearly as black as the peroxide, and the native deutoxide is of the same colour. With sulphuric and muriatic 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, as observed by Berthier; and when boiled with dilute sulphuric acid, it undergoes a similar change. From the proportion of oxygen and manganese in this oxide, it may be regarded as a compound of 44 parts or one equivalent of peroxide, and 36 parts or one equivalent of protoxide of manganese.

Protoxide.—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, as was shown by Berthier, by exposing the peroxide, deutoxide, or red oxide of manganese to the combined agency of charcoal and a white heat; and Dr. Forchhammer, in the Annals of Philosophy, XVII. 52, has described an elegant mode of preparation, 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 manganese; for some of the 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.

Protoxide of manganese, when pure, is of a light-green colour, very near the mountain green. According to Forchhammer 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° F. 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; but this phenomenon is by no means constant. It unites readily with acids without effervescence, producing the same salts as when the same acids act on carbonate 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 muriatic 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.

In order to prepare a pure salt of manganese from the common peroxide of commerce, either of the following processes should be employed. The impure deutoxide left in the process for procuring oxygen gas from the peroxide by means of heat, is mixed with a sixth of its weight of charcoal in powder, and exposed to a white heat for half an hour in a covered crucible. The protoxide thus formed is to be dissolved in muriatic acid, the solution evaporated to dryness, and the residue kept for a quarter of an hour in perfect fusion; being protected as much as possible from the air. By this means the chlorides of iron, calcium, and other metals are decomposed. The fused chloride of manganese is then poured out on a clean sandstone, dissolved in water, and the solution separated from insoluble matters by filtration. If free from iron, it will give a white precipitate with ferrocyanate of potash, without any appearance of green or blue, and a flesh-coloured precipitate with hydrosulphuret of ammonia. The

manganese is then thrown down as a white carbonate by bicarbonate of potash or soda; and from this salt, after being well washed, all the other salts of manganese may be prepared. The other method of forming a pure muriate was suggested by Mr. Faraday, and consists of heating to redness a mixture of peroxide of manganese with half its weight of muriate of ammonia. Owing to the volatility of the sal-ammoniac it is necessary to apply the required heat as rapidly as possible, and this is best done by projecting the mixture in small portions at a time into a crucible kept red hot. In this process the chlorine of the muriatic acid unites with the metal of the oxide to the exclusion of every other substance, provided an excess of manganese be present. The resulting chloride is then dissolved in water, and the insoluble matters separated by filtration. (Faraday in Quarterly Journal, vol. vi.)

In preparing manganese of great purity, the operator should bear in mind that the precipitated carbonate sometimes contains muriatic acid, retained probably in the form of submuriate. It may likewise contain traces of lime; for oxalate of lime, insoluble as it is in pure water, does not completely subside from a strong solution of chloride of manganese, and therefore a small quantity of that earth may be present, although not indicated by oxalate of ammonia.

The salts 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. The protoxide is precipitated from its solutions, as a white hydrate by ammonia, or the pure fixed alkalies; as white carbonate of manganese by alkaline carbonates and bicarbonates; and as white ferrocyanate of manganese by ferrocyanate of potash, 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, muriatic, or sulphuric, are precipitated by sulphuretted hydrogen. With an alkaline hydrosulphuret, on the contrary, a flesh-coloured precipitate is formed, which is either a hydrosulphuret of the protoxide,

or a hydrated protosulphuret of metallic manganese. When heated in close vessels, it yields a dark-coloured sulphuret, and water is evolved.

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 or deutoxide 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 blow-pipe; and it is the cause of the rich colour of the amethyst. It is acted on by strong sulphuric and muriatic acids, with the aid of heat, in the same manner as the peroxide and deutoxide, 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 protomuriate of tin, or sulphurous and phosphorous acids, protosulphate of manganese being generated. The pink colour which the salts of manganese generally possess, is owing to the presence of a small quantity of red oxide. By strong nitric acid, or when boiled with dilute sulphuric acid, it undergoes the same kind of change as the deutoxide.

The red oxide of manganese contains more oxygen than the protoxide and less than the deutoxide. Its elements are in such proportion, that it may be regarded as a compound either of

Deutoxide 80 or two equiv.		Peroxide 44 or one equiv.	
Protoxide 36 or one equiv.	or	Protoxide 72 or two equiv	
116		116	

It contains 27.586 per cent of oxygen, and loses 6.896 per cent of oxygen when converted into the green oxide.

Varvicite. This compound is known only as a natural production, having been first noticed a year or two ago, by Mr. Phillips, among some ores of manganese found 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 during last winter by Professor Stromeyer. Varvicite was at first mistaken for peroxide of manganese, to which both in the colour of its powder and its degree of hardness it bears considerable resemblance; but it is readily distinguished from that ore by its stronger lustre, its highly lamellated texture, which is very similar to that of manganite, and by yielding water freely when heated to redness. Its specific gravity is 4.531. It has not been found regularly crystallized; but my specimen from Jhlefeld is in *after-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 one equivalent of peroxide and one of deutoxide of manganese, united in the mineral with half an equivalent 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.

Manganese is one of those metals which is capable of forming an acid with oxygen. When peroxide of manganese is mixed with an equal weight of nitre or carbonate of potash, and the mixture is exposed to a red heat, a green-coloured fused mass is formed, which has been long known under the name of *mineral chameleon*. On putting this substance into water, a green solution is obtained, the colour of which soon passes into blue, purple, and red; and ultimately, a brown flocculent matter, red oxide of manganese, subsides, and the liquid becomes colourless. These changes take place more rapidly by dilution, or by employing hot water. We are indebted to MM. Chevillot and Edwards for a consistent ex-

planation of these phenomena*. They demonstrated that peroxide of manganese, when fused with potash, absorbs oxygen from the atmosphere, and is thereby converted into an acid, the *manganesic*, which unites with the alkali. They attributed the different changes of colour above mentioned to the combination of this acid with different proportions of potash. By evaporating the red solution rapidly, they succeeded in obtaining a manganesiate of potash in the form of small prismatic crystals of a purple colour. This salt yields oxygen to combustible substances with great facility, and detonates powerfully with phosphorus. It is decomposed when in solution by very slight causes, being converted into red oxide of manganese.

The subsequent researches of Dr. Forchhammer render it probable that the green and red colours are produced by two distinct acids, the *manganeseous* and manganesic, the former giving rise to the green, and the latter to the red tint. He succeeded in forming a solution of manganesic acid in the following manner. By heating a mixture of nitrate of baryta with peroxide of manganese, manganesite of baryta was generated; and to this salt, after having been well washed with water, a quantity of dilute sulphuric acid was added, precisely sufficient for combining with its base. The manganeseous acid, at the moment of being set free, resolved itself into deutoxide of manganese and manganesic acid; and the latter, dissolving in the water, formed a beautiful red solution. Dr. Forchhammer infers from his analysis of these compounds, that manganeseous acid contains three and manganesic four atoms of oxygen united with one atom of manganese. (Annals of Philosophy, vol. xvi.)

Chloride of Manganese.—This compound is best prepared by evaporating a solution of muriate of manganese to dryness by a gentle heat, and heating the residue to redness in a glass tube, while a current of muriatic 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, being converted by that fluid, with evolution

* An. de Ch. et de Ph. vol. viii.

of caloric, into muriate of manganese. It is composed of 28 parts or one equivalent of manganese, and 36 parts or one equivalent of chlorine.

A new chloride of manganese, remarkable for its volatility, has been described by M. Dumas. (Edinburgh Journal of Science, viii. 179.) It is readily formed by putting a solution of manganesic into strong sulphuric acid, and then adding fused sea-salt. The muriatic and manganesic 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 convert it into red by means of sulphuric acid. The solution, when evaporated, leaves a residue of sulphate and manganesiate of potash. This mixture, treated by strong sulphuric acid, yields a solution of manganesic acid, into which are added small fragments of sea-salt, as long as coloured vapour continues to be evolved.

The new chloride, when first formed, appears as a vapour of a copper or greenish colour; but on traversing a glass tube cooled to 5° or —4° F., 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 muriatic and manganesic acids are generated. From this it is manifest, that the new chloride is proportional to manganesic acid; that is, when its chlorine unites with hydrogen, the oxygen required to constitute water with that hydrogen exactly suffices for forming manganesic acid with the manganese. It is hence supposed to consist of 28 parts or one equivalent of manganese, and 144 parts or four equivalents of chlorine.

Fluoride of Manganese.—A gaseous compound of fluorine and manganese has been discovered by M. Dumas and Dr. Wöhler. (Edinburgh Journal of Science, ix.) It 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 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 manganesic 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 manganesic 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. It hence consists of one equivalent of manganese, and four equivalents of fluorine.

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 sulphuretted hydrogen 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 muriatic acid, with disengagement of very pure sulphuretted hydrogen gas.

SECTION XII.

IRON.

Iron has a peculiar gray 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. (Page 401.) 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 specific gravity 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 a temperature of 158° of Wedgwood's pyrometer. 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 cobalt and nickel.

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 protocarbonate of iron, either pure, or in the form of clay iron ore, when it is mixed with siliceous, aluminous, and other foreign substances. The three former occur most abundantly in primary districts, and supply the finest kinds of iron, as those of 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.

The extraction 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, 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 silica acts the part of an acid, and lime, alumina, magnesia, protoxide of manganese, and sometimes oxide of iron, act as bases. The most usual combination, according to Mitscherlich, is bisilicate of lime and magnesia, sometimes with a little bisilicate of the black oxide of iron; a compound which he has obtained in crystals, having the precise form of pyroxen. 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 de 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 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

remains 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 silicium. 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. M. Magnus has observed that the reduction takes place at a heat considerably below that of redness; and 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 is 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.

But iron, in its ordinary state, has a strong affinity for oxygen. In a perfectly dry atmosphere it undergoes no change; but when moisture is likewise present, its oxidation, or *rusting*, is rapid. The first part of the change appears to consist in the formation of protocarbonate of iron; 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 M. Chevallier 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. It 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 154-5.)

OXIDES OF IRON.

Iron combines with oxygen in two proportions only, forming the blue or protoxide, and the red or peroxide of iron. Both these compounds are capable of yielding regular crystallizable salts with acids.

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 Stromeyer first obtained it in an insulated form by transmitting dry hydrogen gas over peroxide of iron at a very low temperature. (Edinburgh Journal of Science, No. x.)

Protoxide of iron has a dark-blue colour, and when melted with vitreous substances communicates to them a tint of blue. It is attracted by the magnet, though less powerfully than metallic iron. It is exceedingly combustible; for when fully exposed to air at common temperatures, it suddenly takes fire and burns vividly, being reconverted into the peroxide. 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 or muriatic acid; and its composition may be determined by collecting and measuring the gas which is dis-

engaged. According to Gay-Lussac it is composed of 8 parts of oxygen, and 28.3 parts of iron; but Dr. Thomson infers from an analysis of protosulphate of iron, that the quantity of iron united with 8 parts of oxygen is 28 precisely. The atomic weight of the protoxide is therefore 36.

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 ferrocyanate by ferrocyanate of potash. 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. Sulphuretted hydrogen does not act if the protoxide is united with any of the stronger acids; but alkaline hydrosulphurets cause a black precipitate, protosulphuret of iron.

Peroxide.—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-muriatic 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 40 parts or one equivalent of the peroxide, and 9 parts or one equivalent of water.

Peroxide of iron 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 ferrocyanate of potash it forms Prussian blue, ferrocyanate of the peroxide of iron. Sulphocyanate of potash causes a deep blood-red, and infusion of gall-nuts a black colour. Sulphuretted hydrogen converts the peroxide into protoxide of iron, and deposition of sulphur takes place at the same time. These reagents, and especially ferrocyanate and sulphocyanate of potash, 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 researches of several chemists, such as Gay-Lussac, Berzelius, Bucholz, and Thomson, leave no doubt that the oxygen contained in the blue and red oxides of iron is in the ratio of one to one and a half. Consequently, the peroxide consists of 28 parts or one equivalent of iron, and 12 parts or an equivalent and a half of oxygen.

Black oxide.—This substance, long supposed to be protoxide of iron, contains more oxygen than the blue, 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 united in a proportion which is by no means constant. It occurs native, frequently crystallized in the form of a regular octohedron; 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 may be regarded as a compound of one equivalent of the protoxide and two equivalents of the peroxide; and Berzelius is of opinion that the composition of magnetic iron ore is similar. 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 one equivalent of peroxide to two of the protoxide, and in the latter are contained one equivalent of peroxide to three equivalents 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 further 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.) These mixed salts give 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.

Chlorides of iron.—Chlorine unites in two proportions with iron, forming compounds which were described in 1812 by Dr. John Davy. The protochloride is made by evaporating a solution of the protomuriate to dryness, and heating it to redness in a glass tube from which the air is excluded. The resulting chloride has a gray colour, a lamellated texture, and metallic lustre. It is composed of one proportional of each element, and is converted by water into protomuriate of iron.

The perchloride is formed by burning iron wire in an atmosphere of chlorine. It is of a bright yellowish brown colour, crystallizes in small iridescent plates, and is volatile at a temperature a little above 212° F. It consists of one equivalent of iron and an equivalent and a half of chlorine, and forms with water a red-coloured solution, which is permuriate of iron.

Bromides of iron.—Into a porcelain capsule put any quantity of bromine with about twenty times its weight of water, and add iron filings as long as any action continues, promoting union by gentle heat and agitation. If the solution is made and evaporated to dryness in close vessels, a protobromide is obtained; but if freely exposed to the air, the perbromide is left. In order to obtain it pure, it should be redissolved in water, filtered to remove a little peroxide, and again evaporated. A red perbromide remains, which is deliquescent, soluble in water and alcohol, and according to M. Henry consists of one equivalent of iron and two of bromine. The accuracy of this estimate is surely very doubtful.

By exactly decomposing a solution of perbromide of iron by means of alkalies or alkaline earths, the hydrobromates of those bases are easily prepared.

Iodide of iron may be formed by heating the metal in the vapour of iodine, or by evaporating a solution of the hydriodate prepared as in the process just described for procuring bromide of iron.

Sulphurets of iron.—There are two compounds of iron and

sulphur, both of which are natural products. The protosulphuret is the magnetic iron pyrites of mineralogists. It is a brittle yellow substance, of a metallic lustre, and is feebly attracted by the magnet. By exposure to air and moisture, it is gradually converted into protosulphate of iron. It may be made artificially by igniting protosulphate of iron with charcoal; or still more conveniently by heating a mixture of iron filings and sulphur. (Page 364.) It is dissolved completely and readily by dilute sulphuric or muriatic acid, with disengagement of sulphuretted hydrogen. It is composed of 28 parts or one equivalent of iron, and 16 parts or one equivalent of sulphur.

The bisulphuret, which contains two equivalents of sulphur, is common iron pyrites. When heated to redness, it loses half its sulphur, and is converted into the protosulphuret. It is insoluble in sulphuric and muriatic acid.

Phosphuret of iron.—This compound may be formed by heating phosphate of iron with charcoal. It is sometimes contained in metallic iron, to the properties of which it is exceedingly injurious by causing it to be brittle at common temperatures.

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 Dr. 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-gray 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 a full red heat, and in cooling acquires a crystalline granular texture. The quality of different specimens is by no means uniform; and two kinds, white and gray 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 gray by exposure to a strong heat and cooling slowly, and the gray 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. Gray 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. Mr. Mackintosh of Glasgow has introduced an elegant process of forming steel by exposing heated iron to a current of coal gas, when carburetted 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 red 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 XIII.

ZINC.—CADMIUM.

ZINC.

The zinc of commerce, sometimes called *spelter*, is obtained either from *calamine*, native carbonate 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.

Zinc has a strong metallic lustre, and a bluish-white colour. Its texture is lamellated, and its density 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° F. 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 680° F., and when slowly cooled crystallizes in four or six-sided prisms. Exposed in close vessels to a white heat, it sublimes unchanged.

Zinc undergoes little change by the action of air and moisture. 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. Zinc is readily oxidized by dilute sulphuric or muriatic acid, and the hydrogen which is evolved contains a small quantity of metallic zinc in combination.

Oxides of Zinc.—Chemists are not agreed as to the number of the oxides of zinc; but there is certainly only one oxide of importance, that, namely, which is formed under the circumstances above mentioned, and which is the base of the salts of zinc. 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. According to the ex-

periments of Berzelius and Thomson, 42 is its equivalent; and it may be regarded as a compound of 34 parts or one equivalent of zinc, and 8 parts or one equivalent of oxygen.

The presence of zinc is easily recognised by the following characters.—The oxide is precipitated from its solutions as a white hydrate by pure potash 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 zinc. Hydrosulphuret of ammonia causes a white precipitate, which is either a hydrosulphuret of the oxide of zinc, or a hydrated sulphuret of the metal. Sulphuretted hydrogen 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.

When metallic zinc is exposed for some time to air and moisture, or is kept under water, it acquires a superficial coating of a gray matter, which Berzelius describes as a suboxide. It is probably a mixture of metallic zinc and the white oxide, into which it is resolved by the action of acids. The superoxide 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, called *butter of zinc* from its soft consistence, is formed, with evolution of heat and light, when zinc filings are introduced into chlorine gas. It was prepared by Dr. John Davy by evaporating muriate of zinc to dryness, and heating the residue to redness in a glass tube. It deliquesces on exposure to the air, being reconverted into a muriate. It consists of one equivalent of each of its elements.

Bromide and iodide may be formed by processes similar to those for preparing the analogous compounds of iron. (Page 486.)

Native sulphuret of zinc, or zinc blende, is frequently found in dodecahedral crystals, or in forms allied to the dodecahedron. Its structure is lamellated, its lustre adamantine, and its colour variable, being sometimes yellow, red, brown,

or black. It may be made artificially by heating to redness a mixture of oxide of zinc and sulphur, by decomposing sulphate of zinc by charcoal, or by drying the white precipitate obtained on adding hydrosulphuret of ammonia to a salt of zinc.

Sulphuret of zinc is composed of one proportional of each of its constituents, and is dissolved with disengagement of sulphuretted hydrogen gas by dilute muriatic or sulphuric acid.

CADMIUM.

Cadmium was discovered in the year 1817 by Stromeyer in an oxide of zinc which had been prepared for medical purposes*; 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. Mr. 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 twelve to twenty per cent of cadmium.

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 muriatic acid, and after adding a portion of free acid, a current of sulphuretted hydrogen gas is transmitted through the liquid by means of which the cadmium is precipitated as 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 of cadmium is dissolved in water, and an excess of carbonate of ammonia added. The white carbonate of cadmium subsides, which, when heated to redness, yields a pure oxide. By mixing this oxide with char-

* Annals of Philosophy, vol. xiv. † Ibid. N. S. vol. iii.

coal, and exposing the mixture to a red heat, metallic cadmium is sublimed.

A very elegant process for separating zinc from cadmium was proposed by Dr. 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 muriatic acid.

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 specific gravity 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 muriatic acids act upon it less easily, and the oxygen is then derived from water.

Cadmium combines with oxygen, so far as is yet known, in one proportion only; and this oxide is conveniently procured in a separate state by igniting the carbonate. It has an orange colour, and is fixed in the fire. It is insoluble in water, and does not change the colour of violets; but it is a powerful salifiable base, forming neutral salts with acids. This oxide, according to the analysis of Stromeyer, is composed of 56 parts of cadmium and 8 parts of oxygen. It is of course regarded as a compound of one equivalent of each element, and consequently 56 is the equivalent of cadmium.

Oxide of cadmium is precipitated as a white hydrate by pure ammonia, but is redissolved by excess of the alkali. It is precipitated permanently by pure potash as a hydrate, and by all the alkaline carbonates as carbonate of cadmium.

Sulphuret of cadmium, which occurs native in some kinds of zinc blende, is easily procured by the action of sulphuretted hydrogen on a salt of cadmium. It has a yellowish orange colour, and is distinguished from sulphuret of arsenic by being insoluble in pure potash, and by sustaining a white

heat without subliming. It is composed of 56 parts or one equivalent of cadmium and 16 parts or one equivalent of sulphur. (Stromeyer.)

Chloride of cadmium may be prepared by decomposing the muriate by heat.

SECTION XIV.

TIN.

The tin of commerce, known by the names of *block* and *grain* tin, is 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.

Tin has a white colour, and a lustre resembling that of silver. The brilliancy of its surface is soon impaired by exposure to the atmosphere, though it is not 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 specific gravity is about 7.9. At 442° F. it fuses, and if exposed at the same time to the air, its surface tarnishes, and a gray powder is formed. When heated to whiteness, it takes fire and burns with a white flame, being converted into peroxide of tin.

Oxides of Tin.—Tin is susceptible of two degrees of oxidation. Both the oxides of tin form salts by uniting with acids; but they are likewise capable of combining with alkalies. From data furnished by the experiments of Berzelius, Gay-Lussac,

and Thomson, these oxides are inferred to be thus constituted:—

	Tin.	Oxygen.
Protoxide	58 or one equivalent.	8 or one equivalent.
Peroxide	58	16 or two equivalents.

The protoxide is of a gray colour, and is formed when tin is kept for some time in a state of fusion in an open vessel. It may also be procured by precipitation from protomuriate of tin. This salt is made by boiling tin in strong muriatic acid, when the metal is oxidized by decomposition of water; and if atmospheric air be carefully excluded, a pure protomuriate results. From this solution the hydrated protoxide may be precipitated either by pure potash or its carbonate; but an excess of the former must be carefully avoided, as otherwise the precipitate would be redissolved. It is essential likewise to the success of the process that the protoxide should be both washed and dried without exposure to the air.

Protoxide of tin is remarkable for its powerful affinity for oxygen. When heated in open vessels, it is converted into peroxide with evolution of heat and light. Its salts not only attract oxygen from the air, but act as powerful deoxidizing agents. Thus, protomuriate of tin converts the peroxide of copper or iron into protoxides, and precipitates silver, mercury, and platinum from their solutions in the metallic state. Added to a solution of gold, it occasions a purple-coloured 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 recognised with certainty. It is thrown down by sulphuretted hydrogen as black protosulphuret of tin.

Peroxide of tin is most conveniently prepared by the action of nitric acid on metallic tin. Nitric 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 deutoxide 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 have been decomposed.

Peroxide of tin acts the part of a weak acid, uniting with alkalies, and forming soluble compounds with them. Its affinity for acids is feeble. As prepared by the preceding method it is insoluble in acids; but if precipitated from permuriate of tin by a pure alkali, when the oxide falls as a gelatinous hydrate, it is readily dissolved by muriatic and sulphuric acid.

Peroxide of tin is separated from its solution in muriatic acid as a bulky hydrate by potash, ammonia, or the alkaline carbonates, and the precipitate is easily and completely redissolved by the pure fixed alkali in excess. Sulphuretted hydrogen occasions a yellow precipitate, which is either hydrosulphuret of peroxide of tin, or bisulphuret of the metal.

Peroxide of tin, when melted with glass, forms white enamel.

Chlorides of Tin.—Tin unites in two proportions with chlorine, and the researches of Dr. Davy leave no doubt of these compounds being analogous in composition to the oxides of tin.

The protochloride, which consists of one equivalent of tin and one equivalent of chlorine, may be made either by evaporating the muriate of the protoxide to dryness and fusing the residue in a close vessel, or by heating an amalgam of tin with calomel. (Dr. Davy.) It is a gray solid substance, of a resinous lustre, which fuses at a heat below redness, and when heated in chlorine gas is converted into the bichloride.

The bichloride, composed of one equivalent of tin and two equivalents of chlorine, may be prepared either by heating metallic tin or the protochloride in an atmosphere of chlorine, or by distilling a mixture of eight parts of tin in powder with twenty-four of corrosive sublimate. It is a colourless volatile liquid, which emits copious white fumes when exposed to the atmosphere. It has a very strong attraction for water, and is converted by that fluid into the permuriate. It was formerly called the *fuming liquor* of *Libavius*.

Sulphurets of Tin.—The protosulphuret is best formed by heating sulphur with metallic tin. A brittle compound of a bluish-gray colour and metallic lustre results, which is fusible at a red heat, and assumes a lamellated structure in cooling.

It is dissolved by muriatic acid, with disengagement of sulphuretted hydrogen. According to the analysis of Dr. Davy and Berzelius, it is composed of one equivalent of tin and one equivalent of sulphur.

The bisulphuret, formerly called *aurum musivum*, has a golden yellow colour, and is made by heating a mixture of sulphur and peroxide of tin in close vessels. The elements of the latter unite with separate portions of sulphur, forming sulphurous acid and bisulphuret of tin. This compound was supposed by Proust to be the hydrosulphuret of the peroxide of tin, and its real nature was first made known by Dr. Davy. (Philos. Trans. for 1812, page 198.) It consists of one equivalent of tin and two equivalents of sulphur.

By exposing a mixture of sulphur and protosulphuret of tin to a low red heat, Berzelius obtained a compound consisting of 58 parts or one equivalent of tin, and 24 parts or one equivalent and a half of sulphur. If it is really a definite compound, it should be termed a *sesquisulphuret*.

SECTION XV.

COBALT.—NICKEL.

COBALT.

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; at least Professor Stromeyer informs me that he has analysed several varieties, in every one of which he has detected the presence of cobalt.

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. On heating this substance with a mixture of sand and potash, a beautiful blue-coloured glass is obtained, which, when reduced to powder, is known by the name of *smalt*.

Metallic cobalt may be obtained by dissolving zaffre in

muriatic acid, and transmitting through the solution a current of sulphuretted hydrogen gas until the arsenious acid is completely separated in the form of sulphuret of arsenic. 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 potash is added. The precipitate consisting of peroxide of iron and carbonate of cobalt, after being well washed with water, is digested in a solution of oxalic acid, which dissolves the iron and leaves the cobalt in the form of an insoluble oxalate. (Laugier.) On heating the oxalate of cobalt 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 (page 482).

A solution of cobalt may also be made by acting on the native arseniuret with sulphuric mixed with a fourth part of nitric acid, separating as much arsenious acid as possible by evaporation, and conducting the remainder of the process as above described. The arseniuret from Tünaberg should be preferred for this purpose, as it is in general free from nickel, which always accompanies the cobalt ores of Germany.

Cobalt is a brittle metal, of a reddish-gray colour, and weak metallic lustre. Its density, according to my observation, is 7.834. It fuses at about 130° of Wedgwood, and when slowly cooled it crystallizes. It is attracted by the magnet, and is susceptible of being rendered permanently magnetic. It undergoes little change in the air, but absorbs oxygen when heated in open vessels. It is attacked with difficulty by sulphuric or muriatic 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.)

Oxides of Cobalt.—Chemists are acquainted with two oxides of cobalt. According to the experiments of Rothoff*, the

* Annals of Philosophy, vol. iii. p. 356.

protoxide is composed of 29.5 parts of cobalt and eight parts of oxygen, so that the atomic weight of cobalt is 29.5. Dr. Thomson, on the contrary, infers from his analysis of sulphate of cobalt, that twenty-six is the equivalent of this metal. From this discordance it may be doubted if the atomic weight of cobalt is known with certainty. According to Rothoff, the oxygen contained in the two oxides is as 1 to 1.5.

The protoxide is of an ash-gray 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 may be prepared by decomposing carbonate of cobalt by heat in a vessel from which atmospheric air is excluded. It is easily recognised 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.

Protoxide of cobalt is precipitated from its salts by pure potash as a blue hydrate, which absorbs oxygen from the air, and gradually becomes black. 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 potash, soda, or ammonia; but an excess of the last redissolves it with facility. Sulphuretted hydrogen produces no change, unless the solution is quite neutral, or the oxide is combined with a weak acid. Alkaline hydrosulphurets always precipitate it as black sulphuret of cobalt.

Muriate of cobalt is celebrated as a sympathetic ink. When diluted with water so as to form a pale pink solution, and then employed as ink, the letters, which are invisible in the cold, become blue if gently heated.

Peroxide of cobalt is of a black colour, and is easily formed from the protoxide in the way already mentioned. It does not unite with acids; and when digested in muriatic acid, the protomuriate of cobalt is generated with disengagement of chlorine. When strongly heated in close vessels, it gives off oxygen, and is converted into the protoxide.

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 gradually

dissolved. If nitrate of cobalt is used, a double salt may be obtained in crystals which L. Gmelin, to whom we are indebted for these remarks, believes to consist of nitrate and *cobaltate* of ammonia. The existence of this acid, however, has not yet been satisfactorily established.

Cobalt appears to unite with sulphur in three proportions; the first being a protosulphuret, the second a sesquisulphuret, and the third a deutosulphuret. The protosulphuret has a gray colour, a metallic lustre, and a crystalline texture. It may be formed in the dry way either by throwing fragments of sulphur on red-hot cobalt, or by igniting oxide of cobalt with sulphur; and it is thrown down as a black precipitate from the salts of cobalt by alkaline hydrosulphurets, or even by sulphuretted hydrogen gas if the salt is quite neutral, or the oxide united with any of the feebler acids.

Arfwedson has observed that when hydrogen gas is transmitted over sulphate of cobalt heated to redness, water and sulphurous acid are evolved, and a compound remains, called an *oxisulphuret*, consisting of oxide of cobalt united with sulphuret of cobalt. When this substance is exposed to sulphuretted hydrogen gas at a red heat, the oxide is decomposed, and the sesquisulphuret is formed.

The deutosulphuret is prepared, according to Setterberg, by heating carbonate of cobalt in a state of intimate mixture with one and a half of its weight 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.

The compounds of cobalt with the other non-metallic bodies have hitherto been little examined.

NICKEL.

Nickel is a constituent of meteoric iron. It occurs likewise in the copper-coloured mineral of Westphalia, termed *copper-nickel*, a native arseniuret of nickel, which in addition to its chief constituents contains sulphur, iron, cobalt, and copper. The preparations of nickel may either be made from this mineral 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 potash, and set aside to crystallize spontaneously; when a double salt, sulphate of nickel and potash, is deposited. Dr. 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 easily precipitated as sulphuret by a current of sulphuretted hydrogen 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 sulphuretted hydrogen, and the oxides of nickel and cobalt precipitated by carbonate of potash. The separation of these oxides may then be effected by the method suggested by M. Berthier. The mixed hydrates, after being well washed, are suspended in water through which chlorine 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 muriate, and may be removed from the insoluble peroxides by filtration.

Metallic nickel, which 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, 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 and cobalt may be rendered magnetic. Its specific gravity after fusion is about 8.279, and is increased to near 9.0 by hammering.

Nickel is very infusible, but less so, according to my observation, 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. Muriatic 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.

Nickel is susceptible of two stages of oxidation. According to the experiments of Berzelius, Berthier, and Thomson, the combining proportion of nickel is 26, and that of its protoxide 34. The protoxide may hence be regarded as a compound of one equivalent of each element. (Edinburgh Journal of Science, No. XIII. 157.) Peroxide of nickel has been less fully examined than the protoxide; but from some experiments of Rothoff, it appears to consist of 26 parts or one equivalent of nickel, and 12 parts or one equivalent and a half of oxygen.

Protoxide of nickel may be formed by heating the carbonate, oxalate, or nitrate to redness in an open vessel, and is then of an ash-gray colour; but after being heated to whiteness, its colour is a dull olive-green. It is said to be reducible by heat unaided by combustible matter; but I have exposed it to intense heat in a wind furnace, without its reduction being effected. 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 hydrosulphurets. Sulphuretted hydrogen occasions no precipitate, unless the solution is quite neutral, or the oxide combined with a weak acid.

Peroxide of nickel has a black colour, and is formed by transmitting chlorine gas through water in which the hydrate of the protoxide is suspended. The peroxide does not unite with acids, is decomposed by a red heat, and with hot muriatic acid forms a protomuriate with disengagement of chlorine gas.

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.

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 muriatic acid with evolution of sulphuretted hydrogen; while that procured in the dry way is of a grayish yellow colour, and requires for solution nitric or nitro-muriatic acid. It occurs as a natural production in very delicate acicular crystals, the *haarkies* of the Germans.

Arfwedson obtained another sulphuret by transmitting hydrogen gas over sulphate of nickel at a red heat. It is of a lighter yellow and more fusible than the former, and appears to be a disulphuret, consisting of one equivalent of sulphur and two of nickel.

Phosphorus unites readily with nickel, forming a white fusible phosphuret. When nickel and charcoal are heated together, and the uncombined metal removed by muriatic acid, a carburet of nickel remains, similar in appearance to graphite. (Berzelius.)

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 XVI.

ARSENIC.

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.

Arsenic is an exceedingly brittle metal, of a strong metallic lustre, and white colour, running into steel gray. Its structure is crystalline, and its density, according to my observation, is 5.8843. When heated to 356° F. 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. 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. 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. (Lehrbuch der Chemie, II. 32.)

COMPOUNDS OF ARSENIC AND OXYGEN.

Chemists are acquainted with two compounds of arsenic and oxygen; and as they both possess the properties of an acid, the terms *arsenious* and *arsenic* acid have been properly applied to them. Considerable difference of opinion exists as to their composition. Dr. Thomson believes 38 to be the combining proportion of metallic arsenic, and that arsenious acid consists of one atom of metal to two atoms of oxygen, and arsenic acid of one atom of metal to three atoms of oxygen. According to Berzelius, 37.627 is the equivalent of the metal, and the oxygen in the two acids is in the ratio of 3 to 5. Arsenious acid is stated by the former to contain 29.63, and by the latter

24.18 per cent of oxygen, a difference which is very considerable. The results of Dr. Thomson are commonly adopted in this country; but as several circumstances induce me to suspect their accuracy, I shall employ those of Berzelius by preference. As the atomic weight of metallic arsenic was found nearly the same by both chemists, 38 may be adopted as the most convenient. The composition of the two acids of arsenic may accordingly be thus stated:—

	Arsenic.	Oxygen.
Arsenious acid	38 or one equivalent	12 or $1\frac{1}{2}$ equivalents.
Arsenic acid	38 or one equivalent	20 or $2\frac{1}{2}$ equivalents.

Arsenious acid.—This compound, frequently called *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. 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, preserves its transparency in a perfectly dry atmosphere, but in ordinary states of the air gradually becomes opaque and white. Its specific gravity is 3.7. At 380° F. it is volatilized, yielding vapours which do not possess the odour of garlic, and which condense unchanged on cold surfaces. If the sublimation is slowly conducted, the vapour collects in the form of distinct octohedral crystals of adamantine lustre and perfectly transparent. Its point of fusion is rather higher than that at which it sublimes; and therefore, in order to be vitrified, it must either be heated under pressure, or the temperature rapidly raised beyond 380°.

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. (Dr. Christison on the Taste of Arsenic in the Edinburgh Medical and Surgical Journal for July, 1827.) 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 thirty 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, 177.)

When metallic arsenic is sharply heated with hydrate of potash, pure hydrogen gas is evolved, and a mass is left consisting of arseniuret of potassium and arsenite of potash; facts, which prove that a portion of arsenic is oxidized, and derives its oxygen partly from water and partly from potash. 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 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.)

The tests commonly recommended for detecting the presence of arsenious acid are four in number; namely, lime water, ammoniacal nitrate of silver, ammoniacal sulphate of copper, and sulphuretted hydrogen.

1. When lime water is added in excess to a solution of arsenious acid, a white precipitate subsides, which is arsenite of lime. On drying this salt, mixing it with powdered charcoal or black flux, and heating the mixture contained in a glass

tube to redness by means of a spirit-lamp, the arsenic is reduced, sublimes, and condenses in a cool part of the tube. The process of reduction is absolutely necessary, since several other acids as well as the arsenious, such as carbonic, phosphoric, oxalic, and tartaric acid, yield white precipitates with lime water. Arsenite of lime is soluble in all acids which are capable of dissolving lime itself; and indeed all the arsenites are dissolved by those acids with which their bases do not form insoluble compounds.

Lime water is of little service for discovering arsenious acid in mixed fluids; for arsenite of lime is so light a powder, that when formed in gelatinous or oleaginous solutions, such as in broth or tea made with milk, it remains suspended in the liquid, and cannot be separated from it.

2. Arsenious acid is not precipitated by nitrate of silver unless an alkali is present, to neutralize the nitric acid. Ammonia is commonly employed for the purpose; but as arsenite of silver is very soluble in ammonia, an excess of the alkali would retain the arsenite in solution. To remedy this inconvenience, Mr. Hume proposes to employ the ammoniacal nitrate of silver, which is made by dropping ammonia into a 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 silver. Ammoniacal nitrate of silver likewise diminishes the risk of fallacy that might arise from the presence of phosphoric acid. Phosphate of silver is so very soluble in ammonia, that when a neutral phosphate is mixed with the ammoniacal nitrate of silver, the resulting phosphate of silver is held almost entirely in solution by the free ammonia.

The test of nitrate of silver, however, even in its improved state, is still liable to objection. For when arsenious acid in small proportion is mixed with salts of muriatic acid, or animal and vegetable infusions, the arsenite 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

Dr. Christison has shown, as I conceive quite satisfactorily, that this test cannot be relied on in practice.

3. Ammoniacal sulphate of copper, which is made by adding ammonia to a solution of sulphate 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. Dr. 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; but arsenite of copper is also dissolved by tannin and perhaps by other vegetable as well as some animal principles.

4. When a current of sulphuretted hydrogen 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, yellow sulphuret of arsenic. The precipitate is at first partially suspended in the liquid; but as soon as free sulphuretted hydrogen is expelled by boiling, 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 potash or ammonia. To avoid this source of fallacy, it is necessary to acidulate the solution with a little acetic or muriatic acid. Sulphuretted hydrogen likewise acts on arsenic in all vegetable and animal fluids if previously boiled, filtered, and acidulated.

But it does not necessarily follow, because sulphuretted hydrogen causes a yellow precipitate, that arsenic is present; for there are not less than four other substances, namely, selenium, cadmium, tin, and antimony, the sulphurets of which, judging from their colour alone, might be mistaken for orpi-

ment. From these and all other substances whatever, the sulphuret of arsenic may be thus distinguished.—When heated with black flux in the manner described for reducing arsenite of lime, a metallic crust of an iron-gray colour externally, and crystalline on its inner surface, is deposited on the cool part of the tube. This character alone is quite satisfactory; 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 abundant, they should be removed before sulphuretted hydrogen is employed; and this object is accomplished by slightly acidulating the solution with nitric acid, adding nitrate of silver as long as a precipitate appears, filtering, removing excess of silver by muriate of soda, neutralizing the filtered solution with an alkali, and lastly, acidulating as usual with acetic acid. The object of these directions will readily appear. The organic substances form an insoluble compound with oxide of silver, while the arsenic, excess of nitrate of silver, and the acid of the decomposed nitrate, remain in the liquid. Now silver and free nitric acid would interfere with the action of sulphuretted hydrogen. The former is precipitated as a black sulphuret by this reagent; while free nitric acid decomposes the gas, and throws down sulphur, which, if mixed in any quantity with sulphuret of arsenic, prevents its reduction. (Christison on Poisons, 199.)

It hence appears, that of the various tests for arsenic, the

only one which gives uniform results, and is applicable to every case, is sulphuretted hydrogen:—all the rest may be dispensed with. For this great improvement in the mode of testing for arsenious acid, we are indebted to Dr. Christison. By this process he discovered the presence of arsenious acid when mixed with complex fluids, such as tea, porter, and the like, in the proportion of one-fourth of a grain to an ounce; and more recently he has twice obtained so small a quantity as the 20th of a grain from the stomachs of people who had been poisoned with arsenic. (Edinburgh Medical and Surgical Journal for October, 1824; and second volume of the Transactions of the Medico-Chirurgical Society of Edinburgh.)

The black flux employed in the processes for reducing arsenic, is prepared by deflagrating a mixture of bitartrate of potash with half its weight of nitre. The nitric and tartaric acid undergo decomposition, and the solid product is charcoal derived from tartaric acid, and pure carbonate of potash. 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.

Arsenic acid.—This compound is made by dissolving arsenious acid in concentrated nitric, mixed with a little muriatic acid, and distilling the solution to perfect dryness. 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 sulphuretted hydrogen 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 or 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.

Chloride of Arsenic.—When arsenic in powder is thrown into a jar full of dry chlorine gas, it takes fire, and a chloride 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 muriatic and arsenious acids. According to Dr. J. Davy it is composed of 60.48 parts of chlorine and 39.52 of arsenic, a proportion which does not correspond with the laws of combination, and therefore is doubtless inexact.

The following process has been lately proposed by M. Dumas. Into a tubulated retort is introduced 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 muriatic 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. M. 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.)

Iodide 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.)

Bromide 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 collected in a cool receiver. (An. de Ch. et Ph. xxxviii. 318.)

This compound is solid at or below 68° F., liquefies between 68° and 77°, and boils at 428°. As a liquid it is transparent and slightly yellow, and yields long prisms by evaporation. It is composed of one equivalent of arsenic and one and a half of bromine; and by contact with water it is converted into arsenious and hydrobromic acids.

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 muriatic acid; but as thus prepared it is always mixed with free hydrogen. M. Soubeiran, who has lately written on this compound, generated it by fusing arsenic with its own weight of granulated zinc, and decomposing the alloy with strong muriatic acid. The gas, thus developed, is quite free from hydrogen, being absorbed without residue by a saturated solution of sulphate of copper. Its specific gravity, calculated by Soubeiran, is 4.1828. 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. Water absorbs one-fifth of its volume, and acquires the odour of the gas. It wants altogether 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, muriatic 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 products are water and sulphuret of copper; and with several other metallic salts its action is similar.

M. 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 equivalent 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.)

A solid compound of arsenic and hydrogen, of a brown colour, was discovered by Sir H. Davy and 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. M. Soubeiran, in his late experiments, succeeded in forming it by the latter process, but not by that of Davy. It appears to be a compound of one equivalent of arsenic and one of hydrogen.

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. It is composed of 38 parts or one equivalent of arsenic, and 16 parts or one equivalent of sulphur.

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 sulphuretted hydrogen 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. In composition it is proportional to arsenious acid; that is, it consists of 38 parts or one equivalent of arsenic, and 24 parts or one equivalent and a half of sulphur.

Orpiment is employed as a pigment, and is the colouring principle of the paint called *King's yellow*. M. Braconnot has proposed it likewise for dyeing silk, woollen, or cotton stuffs of a yellow colour. For this purpose the cloth is 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 fibres of the cloth. (An. de Ch. et de Ph. vol. xii.)

Persulphuret of arsenic is prepared by transmitting sulphuretted hydrogen gas through a moderately strong solution of arsenic acid; or by saturating a solution of arseniate of potash or soda with the same gas, and acidulating with muriatic 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 disssolved by pure alkalies, fuses by heat, and may be sublimed in close vessels without decomposition. It is proportional, in composition, to arsenic acid; that is, it consists of one equivalent of arsenic and two equivalents and a half of sulphur.

The experiments of Orfila have proved that the sulphurets of arsenic are poisonous, though in a much less degree than arsenious acid. The precipitated sulphuret is more injurious than native orpiment.

SECTION XVII.

CHROMIUM.—MOLYBDENUM.—TUNGSTEN.—COLUMBIUM.

CHROMIUM.

Chromium* was discovered in the year 1797 by Vauquelin in a beautiful red mineral, the native di-chromate of lead.

* From Χρῶμα, *colour*, indicative of its remarkable tendency to form coloured compounds.

(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.)

Chromium, which has hitherto been procured in very small quantity, owing to its powerful attraction for oxygen, may be obtained by exposing the oxide of chromium mixed with charcoal to the most intense heat of a smith's forge. Its colour is white with a shade of yellow, and distinct metallic lustre. It is a brittle metal, very infusible, and with difficulty attacked by acids, even by the nitro-muriatic. Its specific gravity has been stated at 5.9; but Dr. Thomson found it a little above 5. When fused with nitre it is oxidized, and converted into chromic acid.

Chromium unites with oxygen in two proportions, forming the green oxide, and chromic acid. Dr. Thomson some years ago ascertained that the combining proportion of chromic acid is 52; and according to the results of an elaborate investigation, published in the Philosophical Transactions for 1827, the oxide and acid are thus constituted:—

	Chromium.	Oxygen.
Green oxide	32 or one equivalent	8 or 1 equivalent.
Chromic acid	32 . .	20 or 2½ equivalents.

Protoxide.—This oxide is easily prepared by dissolving chromate of potash in water, and mixing it with a solution of protonitrate of mercury, when an orange-coloured precipitate, protochromate of mercury, 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 protoxide of chromium.

Protoxide of chromium is of a green colour, exceedingly infusible, and suffers no change by heat. It is insoluble in water, and after being strongly heated, resists the action of the most powerful acids. Deflagrated with nitre, 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.

Protoxide 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 potash in water, equal measures of strong muriatic 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 one equivalent of the protoxide and 26 equivalents of water. (Thomson.) The oxide, in this state, is readily dissolved by acids.

The anhydrous oxide is formed when bichromate of potash is briskly boiled with sugar and a little muriatic 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 muriatic acid, the brown matter is the only solid product, and on boiling this compound with a little carbonate of potash, a 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.

Chromic acid.—This acid is prepared by digesting chromate of baryta, precipitated from a mixture of nitrate of baryta and chromate of potash, in a quantity of dilute sulphuric acid exactly sufficient for combining with the baryta. The sulphate of baryta subsides, and a solution of chromic acid is obtained. Another method has been lately proposed by M. Arnold Maus, which consists in decomposing a hot concentrated solution of bichromate of potash by silicated hydrofluoric acid. The chromic acid, after being separated from the sparingly soluble hydrofluate of silica and potash, 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. 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 potash. (Edinburgh Journal of Science, viii. 175.)

Chromic acid has a dark ruby-red colour, and forms irregular crystals when its solution is concentrated. It is very soluble in water, has a sour taste, and possesses all the properties of an acid. It is converted into the green oxide, with evolution of oxygen, by exposure to a strong heat. It yields a muriate of the protoxide when boiled with muriatic acid and alcohol, and the direct solar rays have a similar effect when muriatic acid is present. With sulphurous acid it forms a sulphate of the protoxide; and it is more or less completely converted into protoxide 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 lead, which is found native in small quantity, and is easily prepared by mixing chromate of potash with a soluble salt of lead. It is of a rich yellow colour, and is employed in the arts of painting and dyeing to great extent.

When sulphurous acid gas is transmitted into a solution of chromate or bichromate of potash, a brown precipitate subsides, which was long regarded as a distinct oxide of chromium; but Dr. Thomson, in the essay above cited, 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 muriatic acid, and then precipitate the green oxide by ammonia. The brown compound may be formed by boiling a solution of bichromate of potash with alcohol; and it

is also rapidly generated, when bichromate of potash is gently boiled with sugar and a little muriatic acid.

Fluochromic acid gas.—When a mixture of fluor-spar and chromate of lead is distilled with fuming or even common sulphuric acid in a leaden retort, a red-coloured gas is disengaged. This gas acts rapidly upon glass, with deposition of chromic acid and formation of fluo-silicic acid gas. It is absorbed 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. This gas may be regarded as a compound either of fluorine and chromium, or of hydrofluoric and chromic acids; but from the circumstance of its being decomposed so readily by moisture, the first view is the more probable.

Chlorochromic acid gas.—This compound is formed by the action of fuming sulphuric acid on a mixture of chromate of lead and chloride of sodium. It is a red-coloured gas which may be collected in glass vessels over mercury. It is decomposed instantly by water, and yields a solution of muriatic and chromic acids. It may be regarded either as a compound of muriatic and chromic acids, or of chlorine and chromium.

These gases were discovered in the year 1825 by M. Unverdorben. (Edinburgh Journal of Science, No. vii. 129.)

Dr. Thomson, in the essay already referred to, has described a red-coloured liquid under the name of chlorochromic acid, which he obtained by the action of concentrated sulphuric acid on a mixture of dry bichromate of potash and sea-salt. It obviously contains chromic acid and chlorine; but its exact nature has not been satisfactorily established, and according to Dr. Thomson's description, it can scarcely be regarded as a definite compound.

Protochloride of chromium.—This compound is best prepared, according to the method of forming chlorides suggested by Oersted, by transmitting dry chlorine over a mixture of protoxide of chromium and charcoal heated to redness in a tube of porcelain. The chloride gradually collects as a crystalline sublimate of a purple colour, which is transparent in thin layers, but when in thicker masses is opaque. It is slowly

dissolved by water, yielding a green solution, possessed of all the properties of the proto-muriate.

Sulphuret of chromium may be formed by transmitting the vapour of bisulphuret of carbon over protoxide of chromium at a white heat; by heating in close vessels an intimate mixture of sulphur and hydrated protoxide; or by fusing the protoxide with a persulphuret of potassium, and dissolving the soluble parts in water. It cannot be prepared in the moist way. It is of a dark-gray 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-muriatic acid. It consists of an equivalent of each of its elements.

Phosphuret of chromium.—This compound is best prepared by exposing phosphate of chromium in a covered crucible lined with charcoal to a strong heat. It is a porous friable substance of a light-gray colour, undergoes little change in the open fire, and is very slightly affected even by nitro-muriatic acid.

MOLYBDENUM.

When native sulphuret of molybdenum, in fine powder, is digested in nitro-muriatic acid until the ore 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.) The sulphuret, which was long mistaken for graphite, was distinguished in the year 1778 by Scheele; but the metal was first obtained in a separate state by Hjelm. It likewise occurs in nature in the form of molybdate of lead.

Molybdenum is a brittle metal, of a white colour, and so very infusible, that hitherto it has only been obtained in a state of semi-fusion. In this form it has a specific gravity varying between 8.615 to 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-muriatic acid. It has three degrees of oxidation, forming two oxides and one acid. The molybdic acid, ac-

cording to Bucholz, is composed of 48 parts of molybdenum and 24 parts of oxygen; and consequently, on the supposition that this acid contains three atoms of oxygen, 48 is the atomic weight of the metal itself.

Molybdic acid is a white powder, of specific gravity 3.4. It has a sharp metallic taste, reddens litmus paper, and forms salts with alkaline bases. It is very sparingly soluble in water; but the molybdates of potash, soda, and ammonia, dissolve in that fluid, and the molybdic acid is precipitated from the solutions by any of the strong acids.

Berzelius has lately described the two oxides of molybdenum. (Edinburgh Journal of Science, iv.133.) The *protoxide* is black, and consists of one equivalent of oxygen and one equivalent of molybdenum. The *deutoxide* is brown, and contains twice as much oxygen as the protoxide. They both form salts with acids. Berzelius states that the blue *molybdous acid* of Bucholz is a bimolybdate of the deutoxide of molybdenum.

Berzelius has likewise succeeded in forming three *chlorides* of molybdenum, the composition of which is analogous to the compounds of this metal with oxygen.

The native *sulphuret* of molybdenum, according to the analysis of Bucholz, is composed of 48 parts or one equivalent of molybdenum, and 32 parts or two equivalents of sulphur. Berzelius has lately discovered another sulphuret, of a ruby-red colour, transparent, and crystallized. It is proportional to the molybdic acid; that is, contains three equivalents of sulphur to one equivalent of the metal.

TUNGSTEN.

Tungsten 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 grayish-white colour, and considerable lustre. It is brittle, nearly as hard as steel, and less fusible than manganese. Its specific gravity 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 de Ph. xvii.) the oxygen of the former is to that of the latter in the ratio of two to three. It is hence inferred, that the real protoxide of tungsten is yet unknown, and that tungstic acid contains three atoms of oxygen to one atom of the metal. Now, Bucholz ascertained that this acid consists of 96 parts of tungsten and 24 parts of oxygen, and consequently 96 is the atomic weight of tungsten, and 120 the equivalent of its acid. The brown oxide is composed of 96 parts or one equivalent of metal, and 16 parts or two equivalents of oxygen.

A convenient method of preparing tungstic acid is 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 muriatic acid on *Wolfram*, native tungstate of iron and manganese. It is also obtained by heating the brown oxide to redness in open vessels.

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.

The oxide of tungsten is formed 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 potash, and fusing the mixture in a platinum crucible. The resulting tungstate of potash is dissolved in hot water, mixed with about half its weight of muriate 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 potash to remove any tungstic acid. The residue is oxide of tungsten. It appears that in this process the tungstate of potash and muriate 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 muriatic 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.

Oxide of tungsten, when prepared by means of hydrogen gas, 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.

Chlorides of Tungsten.—According to Wöhler tungsten and chlorine unite in three proportions. The perchloride is generated by heating the oxide of tungsten in chlorine gas. The action is attended with the appearance of combustion, dense fumes arise, and a thick sublimate is obtained in the form of white scales, like native boracic acid. It is volatile at a low temperature without previous fusion. It is converted by the action of water into tungstic and muriatic acids, and must therefore, in composition, be proportional to tungstic acid; that is, it consists of 96 parts or one equivalent of tungsten, and 108 parts or three equivalents of chlorine.

When metallic tungsten is heated in chlorine gas, it takes fire, and yields the deutochloride. The compound appears in the form of delicate fine 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 muriatic acid and oxide of tungsten. It is entirely dissolved by solution of pure potash, with disengagement of hydrogen gas, yielding muriate and tungstate of potash. A similar change is produced by ammonia, except that some oxide of tungsten is left undissolved.

Another chloride has been described by Wöhler. It is formed at the same time as the first; and though it is converted into muriatic and tungstic acids by the action of water, and would thus seem identical with the perchloride in the proportion of its elements, its other properties are nevertheless different. 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 has not yet been discovered.

The compounds of tungsten with the other simple substances have been very little or not at all examined.

COLUMBIUM.

This metal was discovered in 1801 by Mr. Hatchett, who detected it in a black mineral belonging to the British Museum, supposed to have come from Massachussets 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 Dr. Wollaston.

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

iu the preparation of zirconium and silicium, namely, by heating potassium with the double fluoride of potassium and columbium. (*Lehrbuch der Chemie*, II. 120.) 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. In this state it does not conduct electricity; but in a denser state it is a perfect conductor. By pressure it acquires metallic lustre, and has an iron-gray 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, muriatic, or nitro-muriatic 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 potash, the hydrogen gas of the water being evolved.

Columbium unites with oxygen in two proportions, giving rise to an oxide and an acid. The oxygen in these compounds is in the ratio of 2 to 3, and the experiments of Berzelius lead to the inference that the oxide is formed of 185 parts or one equivalent of columbium, united with 16 parts or two equivalents of oxygen; and the acid of one equivalent of the metal and three of oxygen. But the combining proportion of the acid is not known with such certainty as altogether to establish the accuracy of this opinion.

The oxide of columbium 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-gray colour, very hard and coherent. When reduced to powder, its colour is dark brown. It is not attacked by any acid, even by nitro-hydrofluoric acid; but it is converted into columbic acid either by fusion with hydrate of potash, or deflagration with nitre. When heated to low redness it takes fire, and glows, yielding a light-gray powder; but in this way it is never completely oxidized. Berzelius states that this oxide, in union with pro-

toxide 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.

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 potash, 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 potash.

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, muriatic, 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.

Chloride 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 muriatic acids.

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.

Berzelius has also described a compound of columbium and fluorine. The other compounds of columbium have been scarcely or not at all examined.

SECTION XVIII.

ANTIMONY.

ANTIMONY sometimes occurs native; but its only ore which is abundant, and from which the antimony of commerce is derived, is the sulphuret. This sulphuret was long regarded as the metal itself, and was called *antimony*, or *crude antimony;* while the pure metal was termed the *regulus* of *antimony*.

Metallic antimony may be obtained 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 at 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.

Antimony is a brittle metal, of a white colour running into bluish-gray, and is possessed of considerable lustre. Its density is about 6.7. At 810° F. it fuses; and when slowly cooled, sometimes crystallizes in octohedral or dodecahedral crystals. Its structure is highly lamellated. It has the character of being a volatile metal; but Thenard found that it bears an intense white heat without subliming, provided atmospheric air be perfectly excluded, and no gaseous matters, such as carbonic acid or watery vapour, be disengaged during the process. 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 real protoxide and metallic antimony. Heated to a white or even full-red heat in a covered crucible, and then suddenly exposed 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 deutoxide of antimony; but according to Berzelius they are a protoxide, an opinion which I believe to be correct.

The chemists who have paid most attention to the oxides of antimony are Thenard*, Proust†, Berzelius‡, and Thomson§. The former maintained the existence of six, the second of two, the third of four, and the last of three oxides of antimony. The opinion of Dr. Thomson is now admitted by most chemists; and there is reason to believe that the proportions which he has assigned to these oxides are very near the truth.

	Antimony.	Oxygen.
Protoxide	. 44, or one equivalent,	8, = 52
Deutoxide	. 44, . . .	12, = 56
Peroxide	. 44, . . .	16, = 60

Protoxide.—When muriate of the protoxide of antimony, made by boiling the sulphuret in muriatic acid, (page 364,) is poured into water, a white curdy precipitate, formerly called *powder of Algaroth*, subsides, which is a submuriate of the protoxide. On digesting this salt in a solution of carbonate of potash, and then edulcorating it with water, the protoxide is obtained in a state of purity. It may also be procured directly by adding carbonate of potash or soda to a solution of tartar emetic. It is also generated during the combustion of metallic antimony; but as thus formed, I apprehend it is not quite pure.

Protoxide of antimony, when prepared in the moist way, 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 grayish crystalline mass on cooling. It is very volatile, and if protected from atmospheric air may be sublimed completely without change. When heated in open vessels it absorbs oxygen; and when the temperature is suddenly raised,

* An. de Chimie, vol. xxxii. † Journal de Physique, vol. lv.
‡ An. de Chimie, vol. lxxxiii; and An. de Ch. et de Ph. vol. xvii.
§ First Principles, vol. ii.

and the oxide is porous, it takes fire and burns. In both cases the deutoxide 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 muriate 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 potash is an exception; for it dissolves readily in water without change. By excess of tartaric or muriatic acid, the insoluble salts of antimony may be rendered soluble in water.

The presence of antimony in solution is easily detected by sulphuretted hydrogen. This gas occasions an orange-coloured precipitate, hydrated protosulphuret of antimony, which is soluble in pure potash, and is dissolved with disengagement of sulphuretted hydrogen gas by hot muriatic acid, forming a solution from which the white submuriate is precipitated by water *.

Deutoxide. When metallic antimony is digested in strong nitric acid, the metal is oxidized at the expense of the acid, and a white hydrate of the peroxide is formed; and on exposing this substance to a red heat, it gives out water and oxygen gas, and is converted into the deutoxide. It is also generated when the protoxide is exposed to heat in open vessels. Thus, on heating sulphuret of antimony with free exposure to the air, sulphurous acid and protoxide of antimony are generated; but on continuing the roasting until all the sulphur is burned, the protoxide gradually absorbs oxygen and passes into the deutoxide. Hence this oxide is formed in the process of preparing the *pulvis antimonialis* of the pharmacopœia.

Deutoxide of antimony is white, infusible, and fixed in the fire, two characters by which it is readily distinguished from the protoxide. It is insoluble in water, and likewise in acids after being heated to redness. It combines with alkalies, and

* For an account of the means of detecting antimony in mixed fluids, for the purpose of judicial inquiry, the reader may consult an essay on that subject in the Medical and Surgical Journal for 1827.

for this reason it has been called *antimonious acid*, and its salts *antimonites*, by Berzelius. Antimonious acid is precipitated from these salts by acids as a hydrate, which reddens litmus paper, and is dissolved by muriatic and tartaric acids, though without appearing to form with them definite compounds.

Peroxide of antimony, or *antimonic acid*, is obtained as a white hydrate, either by digesting the metal in strong nitric acid, or by dissolving it in nitromuriatic acid, concentrating by h at 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 muriatic 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 pure peroxide of a yellow colour remains. In this state it resists the action of muriatic acid. When exposed to a red heat, it parts with oxygen, and is converted into the deutoxide.

Chlorides of Antimony.—When antimony in powder is thrown into a jar of chlorine gas, combustion ensues, and the protochloride 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 chloride 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, is converted into muriatic acid and protoxide of antimony. If a large quantity of water is employed, the whole of the oxide subsides as the submuriate.

The bichloride 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 muriatic acid and the hydrated peroxide, which subsides. It contains twice as much chlorine as the protochloride, or is composed of one equivalent of antimony, and two equivalents of chlorine. (Rose in the Annals of Philosophy, N. S. x.)

Dr. Thomson, in his "First Principles," has described an-

other chloride of antimony, composed of one equivalent of chlorine and two equivalents of the metal. It is, therefore, a *dichloride.*

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° F., and boils at 518° F. It is colourless, and crystallizes in needles; it attracts moisture from the air, and is decomposed by water.

Sulphurets of Antimony.—The native sulphuret of antimony is of a lead-gray colour, and though generally compact, sometimes occurs in acicular crystals, or in rhombic prisms. When heated in close vessels, it enters into fusion without undergoing any other change. Boiled in hot muriatic acid, it is dissolved with disengagement of sulphuretted hydrogen. The experiments of Berzelius, Dr. Davy, and Thomson, leave no doubt of its being analogous in composition to the protoxide of antimony, that is, consisting of one equivalent of each of its elements. It may be formed artificially by fusing together antimony and sulphur, or by transmitting a current of sulphuretted hydrogen gas through a solution of tartar emetic. The orange precipitate, which subsides in the last-mentioned process, is commonly regarded as hydrosulphuret of the oxide of antimony. In my opinion it is a hydrated sulphuret of the metal; for when well washed and treated by sulphuric acid it does not yield a trace of sulphuretted hydrogen. The accuracy of this view has been lately confirmed by Gay Lussac. (An. de Ch. et Ph. xlii. 87.)

The *sesquisulphuret* is formed, according to Rose, by transmitting sulphuretted hydrogen gas through a solution of deutoxide of antimony in dilute muriatic acid. (An. of Phil. N. S. x.)

Rose formed the *bisulphuret*, consisting of one equivalent of antimony and two of sulphur, by the action of sulphuretted hydrogen on a solution of the peroxide. The golden sulphuret, prepared by boiling sulphuret of antimony and sulphur in solution of potash, a process which is not adopted by either of our colleges, is a bisulphuret.

M. Rose has likewise demonstrated that the *red antimony*

of mineralogists *(rothspiesglanzerz)* is a compound of one equivalent of the protoxide combined with two equivalents of the protosulphuret of antimony; and it may hence be called an *oxy-sulphuret*. The pharmaceutic preparations known by the terms of *glass*, *liver*, and *crocus* of antimony, are of a similar nature, though less definite in composition, owing to the mode by which they are prepared. They are made by roasting the native sulphuret, so as to form sulphurous acid and oxide of antimony, and then vitrefying 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 potash 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 alkaline carbonate, and treating the product with hot water; or by boiling the mineral in a solution of carbonate of soda or potash. The finest Kermes is obtained, according to M. Cluzel, from a mixture of 4 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 twenty-four hours the deposite is collected on a filter, moderately washed with cold water, and dried at a temperature of 70° or 80° F. Kermes is considered by Berzelius and Rose as a hydrated protosulphuret, and it was described as such in the last edition of this work; but from the observations lately published by Gay-Lussac, it appears to be a hydrated oxy-sulphuret identical, when deprived of its water, with the red antimony above referred to. When digested in a solution of cream of tartar or tartaric acid, oxide of antimony is dissolved, and a pure sulphuret remains; and on reducing it by means of heat and hydrogen gas, sulphuretted hydrogen and *water* are generated. The golden sulphuret has a similar constitution; but its colour inclines more to the orange, and it commonly contains a little free sulphur.

The theory of the formation of Kermes, as given by Gay-Lussac, is the following. A portion of potash and sulphuret of antimony exchange elements with each other, yielding sulphuret of potassium and oxide of antimony: the latter, combining with undecomposed sulphuret of antimony, constitutes the oxy-sulphuret, which is freely dissolved by the hot alkaline solution, and is deposited as it cools. The addition of an acid throws down an additional quantity of the same substance, accompanied with evolution of sulphuretted hydrogen, arising from decomposed sulphuret of potassium. Of course the oxygen which unites with antimony, and which Gay-Lussac derives from potash, may be ascribed to decomposition of water, the hydrogen of which gives rise to sulphuretted hydrogen.

SECTION XIX.

URANIUM.—CERIUM.

URANIUM.

Uranium was discovered in the year 1789 by Klaproth in 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 sulphuretted hydrogen 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 sulphuretted hydrogen, and after being concentrated by evaporation, is set aside to crystallize. The nitrate of uranium is gradually deposited in flattened four-sided prisms of a beautiful lemon-yellow colour.

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.

Chemists are acquainted with two compounds of uranium and oxygen, the composition of which has been minutely studied by Arfwedson * and Thomson. (First Principles, ii.) According to the chemist last mentioned, whose experiments are the most recent, the equivalent of uranium is 208, and its oxides are composed of

	Uranium.	Oxygen.		
Protoxide	208	8	=	216
Peroxide	208	16	=	224

According to the analyses of Arfwedson, 216 is the atomic weight of uranium, and the oxygen in its two oxides is in the ratio of 1 to 1.5; and Berzelius, from the composition of three salts of uranium, has arrived at a similar conclusion.

The protoxide of uranium is of a very dark green colour, and is obtained by decomposing nitrate of the peroxide by 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, and yields a yellow solution which is a pernitrate. The protoxide is employed in the arts for giving a black colour to porcelain.

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 by pure alkalies, fixed or volatile; but retains a portion of these bases in combination. It is thrown down as a carbonate by carbonate of potash; but it is

* Annals of Philosophy, N. S. vii.

not precipitated at all by the carbonates of soda or ammonia, a circumstance which affords an easy method of separating uranium from iron. It is not precipitated by sulphuretted hydrogen. With ferrocyanate of potash it gives a brownish-red precipitate, not unlike ferrocyanate of the peroxide 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.

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-gray or nearly black colour, is converted into protoxide when heated in the open air, and is readily dissolved by nitric acid. Muriatic acid attacks it feebly.

CERIUM.

Cerium was discovered in the year 1803 by MM. Hisinger and Berzelius, in a rare Swedish mineral known by the name of cerite, and its existence was recognised about the same time by Klaproth. Dr. Thomson has since found it to the extent of thirty-four per cent in a mineral from Greenland, called *Allanite*, in honour of Mr. Allan, who first distinguished it as a distinct species.

The properties of cerium are in a great measure unknown. It appears from the experience of Vauquelin, who obtained it in minute buttons not larger than the head of a pin, that it is a white brittle metal, which resists the action of nitric, but is dissolved by nitro-muriatic acid. According to an experiment made by Mr. Children and Dr. Thomson, metallic cerium is volatile in very intense degrees of heat. (Annals of Philosophy, vol. ii.)

Oxides of Cerium.—Cerium unites with oxygen in two proportions, and the composition of the resulting oxides has been particularly studied by M. Hisinger. (An. of Phil. iv.) Dr. Thomson has likewise made experiments on the subject, and infers from data furnished partly by himself and partly by M. Hisinger, that 50 is the atomic weight of cerium, and that its oxides are thus constituted (First Principles, i.) : —

	Cerium.		Oxygen.		
Protoxide	50	.	8	=	58
Deutoxide	50	.	12	=	62

Protoxide of cerium is a white powder, which is insoluble in water, and forms salts with acids, all of which, if soluble, have an acid reaction. Exposed to the air at common temperatures it suffers no change; but if heated in open vessels, it absorbs oxygen and is converted into the peroxide. It is precipitated from its salts as a white hydrate by pure alkalies; as a white carbonate by alkaline carbonates, but is redissolved by the precipitant in excess; and as a white oxalate by oxalate of ammonia.

Peroxide of cerium is of a fawn-red colour. It is dissolved by several of the acids, but is a weaker base than the protoxide. Digested in muriatic acid, chlorine is disengaged and a protomuriate results.

The most convenient method of extracting pure oxide of cerium from cerite is by the process of Laugier. After reducing cerite to powder, it is dissolved in nitro-muriatic acid, and the solution is evaporated to perfect dryness. The soluble parts are then redissolved by water, and an excess of ammonia is added. The precipitate thus formed, consisting of the oxides of iron and cerium, is well washed and afterwards digested in a solution of oxalic acid, which dissolves the iron, and forms an insoluble oxalate with the cerium. By heating this oxalate to redness in an open fire, the acid is decomposed, and the peroxide of cerium is obtained in a pure state.

Sulphuret of Cerium.—Dr. Mosander has succeeded in forming this compound by two different processes. The first method is by transmitting the vapour of sulphuret of carbon over carbonate of cerium at a red heat; and the second is by fusing oxide of cerium at a white heat with a large excess of sulphuret of potassium (*hepar-sulphuris*), and afterwards removing the soluble parts by water. The product of the first operation is porous, light, and of a red colour like red lead; and that of the second is in small brilliant scales, and of a yellow colour, like *aurum musivum*. These sulphurets, though different in appearance, are similar in point of composition,

containing 26 per cent of sulphur. They are insoluble in water, but are dissolved in acids with evolution of sulphuretted hydrogen gas, without any residuum of sulphur. (Philos. Mag. and Annals, i. 71.)

SECTION XX.

BISMUTH.—TITANIUM.—TELLURIUM.

BISMUTH.

Bismuth is found 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.

Bismuth has a reddish-white colour and considerable lustre. Its structure is highly lamellated, and when slowly cooled, it crystallizes in octohedrons. Its density is about 10. It is brittle when cold, but may be hammered into plates while warm. At 476° F. it fuses, and sublimes in close vessels at about 30° Wedgwood. It is a less perfect conductor of caloric 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 gray 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 muriatic or sulphuric acid, but it is readily oxidized and dissolved by nitric acid.

Oxide of Bismuth.—This metal unites with oxygen in one proportion only, forming a yellow-coloured oxide, which may be easily procured by heating the subnitrate to redness. At a full red heat it is fused, and yields a transparent yellow glass. At a still higher temperature it is sublimed. It unites with

acids, and most of its salts are white. According to the experiments of Dr. J. Davy*, it is composed of 72 parts of bismuth, and 8 parts of oxygen; and therefore 72 is the atomic weight of bismuth, and 80 the equivalent of its oxide. This result is confirmed by the researches of Dr. Thomson†.

When nitrate 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 pigment, owing to the facility with which it is blackened by sulphuretted hydrogen. If the nitrate with which it is made contains no excess of acid, and a large quantity of water is employed, the whole of the bismuth is separated as a subnitrate.—By this character bismuth may be both distinguished and separated from other metals.

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 grayish-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. (Dr. Davy.) From the experiments of Drs. Davy and Thomson, it appears to consist of one equivalent of each of its elements.

Bromide of Bismuth is prepared by heating the metal with a large excess of bromine in a long tube; when a gray-coloured bromide results, similar in its aspect to fused iodine. At 392° F. 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 oxy-bromide. (Serullas.)

Sulphuret of Bismuth.—This sulphuret is found native, and may be formed artificially by fusing bismuth with sul-

* Philosophical Transactions for 1812. † First Principles, vol. i.

phur. It is of a lead-gray colour, and metallic lustre. The experiments of Dr. Davy, Thomson, and Lagerhielm* leave no doubt of its being composed of one equivalent of bismuth and one equivalent of sulphur. I apprehend the dark-brown precipitate caused by the action of sulphuretted hydrogen on the salts of bismuth is likewise a protosulphuret.

TITANIUM.

Titanium was first recognised as a new substance by Mr. Gregor of Cornwall, and its existence was afterwards established by Klaproth†. But the properties of the metal were not ascertained in a satisfactory manner until the year 1822, when Dr. 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 the Rev. Dr. Buckland. 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 conduct electricity, and are attracted slightly by the magnet, a property which seems owing to the presence of a minute quantity of iron. Their specific gravity 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-muriatic 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 peroxide of titanium. By this character they are proved to be metallic titanium.

Oxides of Titanium.—This metal has probably two degrees of oxidation. The *protoxide* is of a purple colour, and is supposed to exist pure in the mineral called *Anatase;* but its composition and chemical properties are unknown. The *peroxide* exists in a nearly pure state in titanite or rutile. Menaccanite, in which titanium was originally discovered by Mr. Gregor, is a compound of the oxide of titanium, iron, and

* Annals of Philosophy, vol. iv. † Contributions, vol. i.
‡ Philosophical Transactions for the year 1823.

manganese. This oxide 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 gray mass remains, which consists of potash and oxide of titanium. This compound is dissolved in concentrated muriatic acid; and on diluting with water, and boiling the solution, the greater part of the oxide of titanium is thrown down. It is then collected on a filter, and well washed with water acidulated with muriatic acid. In this state, the oxide 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 hydrosulphuret of ammonia, which converts the oxides of iron and manganese into sulphurets, but does not act on the oxide of titanium. The two sulphurets are readily dissolved by dilute muriatic acid; and the oxide of titanium, after being collected on a filter and well washed, as before, may be dried and heated to redness. This method was proposed by Professor Rose of Berlin. (An. de Ch. et de Physique, xxiii.)

Rose has since simplified the process in the following manner. 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 sulphuretted hydrogen 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 muriatic acid to remove the iron, and the oxide of titanium 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. xxxviii. 131.)

Oxide of titanium, when pure, is quite white. It is exceedingly infusible and difficult of reduction; and after being once ignited, it ceases to be soluble in acids. M. Rose has observed that, like silica, it possesses weak acid properties. Thus he finds that it unites readily with alkalies, and denies its power of acting as an alkaline base. On this account he proposes for it the name of *titanic acid*. In the state of hydrate, as when precipitated from muriatic acid by boil-

ing, 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 a salt, prevents this inconvenience. After exposure to a red heat it is not attacked by acids, except by the hydrofluoric.

If previously ignited with carbonate of potash, oxide of titanium is soluble in dilute muriatic 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 the presence of titanium; an effect which appears owing to tannin 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 reconverted into the peroxide.

The atomic weight of titanium, as deduced by Dr. Thomson from experiments made by Rose and by himself, is 32. Titanic acid is inferred, from the same data, to be composed of 32 parts or one equivalent of titanium, and 16 parts or two equivalents of oxygen. The peroxide of titanium, and its chemical constitution, have not, however, been ascertained with certainty.

Chloride of Titanium.—This substance was first prepared in the year 1824 by Mr. George of Leeds, by transmitting dry chlorine gas over metallic titanium at a red heat. At common temperatures it is a transparent colourless fluid, of considerable specific gravity, boils violently at a temperature a little above 212° F., and condenses again without change. 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, a very rapid, almost explosive, disengagement of chlorine gas ensues, attended with considerable increase of temperature; and if the water is not in excess, a solid residue is obtained. This substance is deliquescent, and soluble in water; and its solution possesses all the characters of muriate of titanium.

The composition of this chloride has not been satisfactorily established; but it contains more chlorine than is capable of

uniting with the hydrogen derived from water, when the oxygen of that fluid converts titanium into the peroxide.

Sulphuret of Titanium.—This compound was discovered by Rose, who prepared it by transmitting the vapour of bisulphuret of carbon over peroxide of titanium 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 acid and oxide of titanium. By acids it is slowly decomposed, and is dissolved by muriatic acid with disengagement of sulphuretted hydrogen gas. According to the experiments of Rose it is proportional to peroxide of titanium, consisting of 32 parts or one equivalent of titanium, and 32 parts or two equivalents of sulphur.

TELLURIUM.

Tellurium is 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*. It occurs in the metallic state, chiefly in combination with gold and silver.

Tellurium has a tin-white colour running into lead-gray, a strong metallic lustre, and lamellated texture. It is very brittle, and its density is 6.115. It fuses at a temperature below redness, and at a red heat is volatile. When heated before the blow-pipe it takes fire, burns rapidly with a blue flame bordered with green, and is dissipated in gray-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.

Oxide of Tellurium.—Tellurium is rapidly oxidized by nitric acid, and a soluble nitrate of the oxide results. The oxide is likewise formed during the combustion of the metal. It is of a gray colour, fuses at a red heat, and at a temperature still higher sublimes. When heated before the blow-pipe on charcoal it is decomposed with violence. It has the pro-

* Contributions, vol. iii.

perty of forming salts both with acids and alkalies. It is precipitated from its solution in acids, as a hydrate, by all the alkalies both pure and carbonated; but it is redissolved by an excess of the precipitant. Alkaline hydrosulphurets occasion a black precipitate, which is probably a sulphuret of tellurium. It is reduced to the metallic state, and thrown down as a black powder, by insertion of a rod of zinc, tin, antimony, or iron.

According to Berzelius oxide of tellurium is composed of nearly 32 parts of the metal, and 8 parts of oxygen; so that 32 may be regarded as the atomic weight of tellurium, and 40 of its oxide. This result, however, differs considerably from that of Klaproth, and therefore requires confirmation.

Tellurium unites in one proportion with chlorine, and in two proportions with hydrogen. The most interesting of these compounds is telluretted hydrogen gas, discovered in the year 1809 by Sir H. Davy. This gas is colourless, has an odour similar to that of sulphuretted hydrogen, and is absorbed by water, forming a claret-coloured solution. As it unites with alkalies, it may be regarded as a feeble acid. It reddens litmus paper at first; but loses this property after being washed with water.

SECTION XXI.

COPPER.

Native copper is by no means uncommon. It occurs in large amorphous masses in some parts of America, and is sometimes found in octohedral crystals, or in forms allied to the octohedron. The metallic 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 oxide 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 silica, and rises as a fusible slag to the surface; while most of the copper returns to the state of sulphuret. It is then subject 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.

Copper is 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. In fusibility it stands between silver and gold.

Copper 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, carbonate of the peroxide of copper. At a red heat it absorbs oxygen, and is converted into the peroxide, which appears in the form of black scales. It is attacked with difficulty by muriatic and sulphuric acids, and not at all by the vegetable acids, if atmospheric air be excluded; but if air has 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 peroxide.

Oxides of Copper.—The oxides of this metal have been studied by Proust, Chenevix, Dr. Davy, and Berzelius, and especially by the former*. From the labours of these chemists, it appears that there are but two oxides of copper, and that they are thus constituted:—

	Copper.	Oxygen.		
Protoxide . .	64 . . .	8	=	72
Peroxide . .	64 . . .	16	=	80

Consequently, if the first be regarded as a compound of one equivalent of each element, 64 is the atomic weight of copper.

* Journal de Physique, vol. lix.

The *red* or *protoxide* 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 mixing 64 parts of metallic copper in a state of fine division with 80 parts of the peroxide, and heating the mixture to redness in a close vessel; or by boiling a solution of acetate of copper with sugar, when the peroxide is partially deoxidized, and subsides as a red powder.

Protoxide of copper combines with the muriatic, sulphuric, and probably with several other acids, forming salts, most of which are colourless, and from which the protoxide is precipitated as an orange-coloured hydrate by alkalies. They attract oxygen rapidly from the atmosphere, by which they are converted into persalts. The protomuriate is easily formed by putting a solution of the permuriate with free muriatic acid and copper filings into a well-closed glass phial. The protoxide 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 peroxide.

Peroxide of copper, *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 persalts of copper by means of pure potash, and by heating nitrate of copper to redness.

Peroxide of copper varies in colour from a dark brown to a bluish-black, according to the mode of formation. It undergoes no change by heat alone, but is readily reduced to the metallic state by heat and combustible matter. It is insoluble in water, and does not affect the vegetable blue colours. It combines with nearly all the acids, and most of its salts have a green or blue tint. It is soluble likewise in ammonia, forming with it a deep-blue solution, a property by which the peroxide of copper is distinguished from all other substances.

Peroxide of copper is precipitated by pure potash as a blue hydrate, which is rendered black by boiling, the hydrate being decomposed at that temperature. Pure ammonia at first throws down a greenish-blue insoluble sulphate, which is redissolved by the precipitant in excess, and forms the deep-blue

ammoniacal sulphate of copper. Alkaline carbonates cause a bluish-green precipitate, carbonate of copper, which is redissolved by an excess of carbonate of ammonia. It is precipitated as a dark-brown bisulphuret by sulphuretted hydrogen, and as a reddish-brown ferrocyanate by ferrocyanate of potash. 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 muriatic acid, is chemically pure.

The best mode of detecting copper, when supposed to be present in mixed fluids, is by sulphuretted hydrogen. The sulphuret, after being collected, and heated to redness in order to char any organic substances, should be placed on a piece of porcelain, and be digested in a few drops of nitric acid. Sulphate of copper is formed, which, when evaporated to dryness, strikes the characteristic deep blue on the addition of ammonia.

The red oxide of copper is by some chemists supposed to be a suboxide or a compound of two atoms of copper and one atom of oxygen; while the elements of the black oxide are thought to be in the ratio of one atom of each. According to this view the atomic weight of copper is 32 or half that above stated. This opinion, which is adopted by Dr. Thomson, is certainly supported by the tendency of the red oxide to absorb oxygen and pass into the state of black oxide; and other arguments may be adduced in its favour. But, nevertheless, as the red oxide is unquestionably a definite compound, capable of uniting with acids, and proportional to several other compounds, such as the protosulphuret and protochloride of copper, it appears to me more consistent to consider it as the real protoxide, composed of one atom of each of its elements.

Some chemists admit the existence of a third oxide, which Thenard prepared 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. It is said to contain twice as much oxygen as the black oxide; but as the latter is so commonly known by the term peroxide, the former may

be conveniently distinguished by the name of *superoxide*. This is the more necessary, as its existence is by no means unequivocally established.

Chlorides of Copper.—The chlorides of copper have been minutely studied by Proust and Dr. Davy. From the able researches of these chemists, and especially of the latter, there is no doubt that the two chlorides are proportional to the two oxides of copper, or that they are composed of

	Copper.	Chlorine.
Protochloride .	64 .	36
Perchloride .	64 .	72

When copper filings are introduced into an atmosphere of chlorine gas, the metal takes fire spontaneously, and both the chlorides are generated.

The *protochloride* may be conveniently prepared by heating copper filings with twice their weight of corrosive sublimate. In this way it was originally made by Mr. Boyle, who termed it *resin of copper*, from its resemblance to common resin. Proust procured it by the action of protomuriate of tin on permuriate of copper; and also by decomposing the permuriate by heat. He gave it the name of *white muriate of copper*.

Protochloride 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 muriatic 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.

The *perchloride* is best formed by exposing permuriate of copper to a temperature not exceeding 400° F. (Dr. Davy.) It is a pulverulent substance of a yellow colour, deliquesces on exposure to air, and is reconverted by water into the permuriate. It parts with half its chlorine when strongly heated, and protochloride of copper is generated.

Sulphurets of Copper.—The protosulphuret is a natural production, well known to mineralogists under the name of *copper glance;* and in combination with sulphuret of iron, it is a constituent of variegated copper ore. It is formed arti-

ficially by heating copper filings with a third of their weight of sulphur, the combination being attended with such free disengagement of caloric, that the mass becomes vividly luminous. According to the analysis of Berzelius, it is composed of 64 parts or one equivalent of copper, and 16 parts or one equivalent of sulphur.

Bisulphuret of copper is a constituent of copper pyrites, in which it is combined with protosulphuret of iron. It may be formed artificially by the action of sulphuretted hydrogen on a persalt of copper. When exposed to a red heat in a close vessel it loses half of its sulphur, and is converted into the protosulphuret.

Phosphuret of copper may be formed by the contact of heated metallic copper and vapour of phosphorus, by transmitting perphosphuretted hydrogen over chloride or sulphuret of copper with the aid of heat, or by the action of the same gas on salts of copper. It is probable that there are several different phosphurets of copper; but their composition has not been fully determined.

SECTION XXII.

LEAD.

Native lead is an exceedingly rare production; but in combination, especially with sulphur, it occurs in large quantity. All the metallic 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 lead, sulphurous acid, which is evolved, and free oxide of lead. These oxidized portions then react on sulphuret of lead: by the reaction of two equivalents of oxide of lead and one of the sulphuret, two equivalents of metallic lead and one of sulphurous acid result; while one equivalent of the sulphuret and one of sulphate of lead mutually decompose each other, giving rise to two equivalents 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 lead, and is decomposed by the addition of quicklime, the oxide so sepa-

rated reacting as before on sulphuret of lead. The lead of commerce commonly contains silver, iron, and copper.

Lead has a bluish-gray colour, and when recently cut, a strong metallic lustre; but it soon tarnishes by exposure to the air, acquiring a superficial coating of carbonate of lead. (Christison.) Its density is 11.358. 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° F., and when slowly cooled forms octohedral crystals. It may be heated to whiteness in close vessels without subliming. Most of the compounds of lead are poisonous.

Lead absorbs oxygen quickly at high temperatures. When fused in open vessels, a gray 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 yellow oxide of lead. 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 lead, 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 lately been minutely investigated by Dr. 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, hydriodates, muriates, and sulphates are highly preservative; so small a quantity as 1-30,000th part of phosphate of soda or hydriodate of potash 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, may be safely collected in leaden cisterns. Of this, the water of Edinburgh is a remarkable instance.

Lead is not attacked by the muriatic 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.

Oxides of Lead.—Lead has three degrees of oxidation; and the composition of its oxides, as determined with great care by Berzelius, is as follows (An. of Phil. xv.):—

	Lead.	Oxygen.	
Protoxide	104	8	= 112
Deutoxide	104	12	= 116
Peroxide	104	16	= 120

Protoxide.—This oxide is prepared on a large scale by collecting the gray 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 deutoxide. It may be obtained pure by heating the carbonate or nitrate to low redness in a vessel from which atmospheric air is excluded.

Protoxide of lead has a yellow colour, is insoluble in water, fuses at a red heat, and in close vessels is fixed and unchangeable in the fire. 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.

Protoxide of lead is precipitated from its solutions by pure alkalies as a white hydrate, which is redissolved by potash 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 sulphuretted hydrogen; and as yellow iodide of lead by hydriodic acid or hydriodate of potash.

M. Orfila has proved experimentally that sulphate of lead, owing to its insolubility, is not poisonous; and therefore sulphate of magnesia, or any soluble sulphate, renders the soluble poisonous salts of lead inert.

The best method of detecting the presence of lead in wine or other suspected mixed fluids is by means of sulphuretted hydrogen. 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 nitrate of lead 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 hydriodate of potash 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 earthen ware 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 lead in twenty-four 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*. This is a convenient method of obtaining very pure metallic lead.

Deutoxide.—Deutoxide of lead is the *minium* or *red lead* of commerce, which is employed as a pigment, and in the manufacture of flint glass. It is formed by heating litharge in open vessels while a current of air is made to play upon its surface.

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.

Peroxide.—This oxide may be obtained by the action of nitric acid on minium, as just mentioned; but the most convenient method of preparing it is by transmitting a current of chlorine gas through a solution of acetate of lead. In this process water is decomposed;—its hydrogen uniting with chlorine, and its oxygen with protoxide of lead, gives rise to muriatic acid and peroxide of lead.

Peroxide of lead is of a puce colour, and does not unite with acids. It is resolved by a red heat into the protoxide and oxygen gas.

Chloride of Lead.—This compound, sometimes called *horn lead* or *plumbum corneum*, is slowly formed by the action of chlorine gas on thin plates of lead, and may be obtained more easily by adding muriatic acid or a solution of sea-salt to acetate or nitrate of lead dissolved in water. This chloride dissolves to a considerable extent in hot water, especially when acidulated with muriatic acid. In solution it is probably a muriate of the oxide of lead; but in cooling, the chloride separates in the form of small acicular crystals of a white colour. It fuses at a temperature below redness, and forms as it cools a semi-transparent horny mass. It bears a full red heat in close vessels without subliming. According to the analysis of Dr. Davy, it is composed of one equivalent of lead and one equivalent of chlorine.

The pigment called *mineral* or *patent yellow* is a compound of chloride and protoxide of lead. It is prepared for the purposes of the arts by the action of moistened sea-salt on litharge, by which means a portion of the protoxide is converted into chloride of lead, and then fusing the mixture. Soda is set free during this process, and is converted into a carbonate by absorbing carbonic acid from the atmosphere.

Iodide of Lead is easily formed by mixing a solution of hydriodic acid or hydriodate of potash with acetate or nitrate 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. It is composed of one equivalent of iodine and one equivalent of lead.

Sulphuret of Lead may be made artificially, either by heating together lead and sulphur, or by the action of sulphuretted hydrogen on a salt of lead. It is an abundant natural product, well known by the name of galena. It consists of one equivalent of lead and one equivalent of sulphur.

Phosphuret of Lead has been little examined. It may be formed by heating phosphate of lead with charcoal, by mixing a solution of phosphorus in alcohol or ether with a 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 vegetable acid, are decomposed by heat in close vessels. (Berzelius.)

CLASS II.

ORDER III.

METALS, THE OXIDES OF WHICH ARE REDUCED TO THE METALLIC STATE BY A RED HEAT.

SECTION XXIII.

MERCURY OR QUICKSILVER.

Mercury is found in the native state, but it occurs more commonly in combination with sulphur as cinnabar. From this ore the mercury of commerce may be 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.

Mercury is 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, evinces a strong tendency to crystallize in octohedrons. It contracts greatly at the moment of congelation; for while its density at 47° F. is 13.545, the specific gravity of frozen mercury is 15.612. When solid it is malleable, and may be cut with a knife. At 680° F., 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. Mercury 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 mercury is 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 peroxide of nitrogen.

OXIDES OF MERCURY.

Mercury is susceptible of two stages of oxidation, and both its oxides are capable of forming salts with acids. It appears from the researches of Donovan* and Sefstrom†, whose results are confirmed by the experiments of Dr. Thomson, that these oxides are formed in the following proportions:—

	Mercury.	Oxygen.	
Protoxide	200 or one equivalent.	8	= 208
Peroxide	200	16	= 216

Protoxide.—This oxide, which is a black powder, insoluble

* Annals of Philosophy, vol. xiv. † Ibid. vol. iii. p. 355.

in water, is best prepared by the process recommended by Donovan. This consists in mixing calomel briskly in a mortar with pure potash in excess, so as to effect its decomposition as rapidly as possible. The protoxide is then to be 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.

This oxide is precipitated from its salts, of which the nitrate is the most interesting, as the black protoxide by pure alkalies; as a white carbonate, which soon becomes dark from the loss of carbonic acid, by alkaline carbonates; as calomel by muriatic acid or any soluble muriate; and as the black protosulphuret by sulphuretted hydrogen. Of these tests, the action of muriatic acid is the most characteristic. The oxide is reduced to the metallic state by copper, phosphorous acid, or protomuriate of tin.

Peroxide.—This oxide may be formed 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.*

Peroxide of mercury, thus prepared, is commonly in the form of shining crystalline scales of a red 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, and into soluble colourless persalts. The oxide is separated from all acids as a red, or when hydratic as a yellow precipitate, by the pure and carbonated fixed alkalies. Ammonia and its carbonate cause a white precipitate, which is a double salt, consisting of

one equivalent of the acid, one equivalent of the peroxide, and one equivalent of ammonia. The oxide is readily reduced to the metallic state by metallic copper. Sulphuretted hydrogen, phosphorous acid, and protomuriate 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 sulphuretted hydrogen 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 bibromuret and biniodide of mercury in a similar manner. (An. de Ch. et Ph. xl. 46.)

CHLORIDES OF MERCURY.

Mercury unites with chlorine in two proportions; and the researches of Sir H. Davy and Mr. Chenevix leave no doubt that these compounds are analogous in composition to the oxides of mercury, that is, are composed of

	Mercury.		Chlorine.	
Protochloride	200	. .	36	= 236
Bichloride	200	. .	72	= 272

Bichloride.—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 peroxide of mercury, with chloride of sodium or sea-salt. The exact quantities required for mutual decomposition are 296 parts or one equivalent of the bisulphate, to 120 parts or two equivalents of the chloride. Thus,

One equivalent of bisulphate of mercury consists of		Two equivalents of chloride of sodium consist of	
Sulphuric acid . .	80 or two equivalents.	72 or two equiv. of chlorine.	
Peroxide of mercury	216 or one equivalent.	48 or two equiv. of sodium.	
	296		120

And the products are,

One equivalent of bichloride of mercury consisting of		Two equivalents of sulphate of soda consisting of	
Mercury	200 or one equivalent.	Sulphuric acid	80 or two equivalents.
Chlorine	72 or two equivalents.	Soda	64 or two equivalents.
	272		144

Bichloride of mercury, when obtained by sublimation, 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 specific gravity is 5.2. It sublimes at a red heat without change. 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 muriatic acid at the temperature of 70° Fahr. With the muriates of ammonia, potash, soda, and several other bases, it enters into combination, forming double salts, which are more soluble than the chloride itself.

Bichloride of mercury is probably converted at the moment of solution into a muriate of the peroxide; at least this view may safely be admitted, since alkalies and other reagents act upon it precisely in the same manner as on other persalts of mercury. Its aqueous solution is gradually decomposed by light, calomel being deposited.

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 potash. 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, Dr. 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 at a boiling

temperature by protomuriate of tin. 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 digested with protomuriate of tin. The organic substances are then dissolved in a hot solution of caustic potash, and the insoluble parts washed and sublimed to separate the mercury. (Christison on Poisons, p. 281.)

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 Mr. Sylvester, and has since been simplified by Dr. Paris. (Medical Jurisprudence, by Paris and Fonblanque.)

Many animal and vegetable solutions convert bichloride of mercury into calomel, a portion of muriatic 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.

Protochloride.—Protochloride of mercury, or *calomel*, is always generated when chlorine comes in contact with mercury at common temperatures. It may be made by precipitation, by mixing muriatic acid or any soluble muriate with a solution of protonitrate of mercury. It is more commonly prepared by sublimation. This is conveniently done by mixing 272 parts or one equivalent of the bichloride with 200 parts or one equivalent 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.

Protochloride of mercury is a rare mineral production, called *horn quicksilver*, which occurs crystallized in quadrangular prisms, terminated by pyramids. When obtained by sublimation it is in semi-transparent crystalline cakes; but as formed by precipitation, it is a white powder. Its density is 7.2. 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 and uniting with muriatic acid,—products which necessarily imply decomposition of water. When calomel is boiled in a solution of muriate of ammonia, it is converted into corrosive sublimate and metallic mercury. Muriate of soda has a similar effect, though in a less degree.

Iodides of Mercury.—The protiodide is formed by mixing a solution of protonitrate of mercury with hydriodate of potash; and the deutiodide by the action of the same hydriodate on any persalt of mercury. The former is yellow, and is composed of one equivalent of iodine and one equivalent of mercury. The other is of an exceedingly rich red colour, and may be used with advantage in painting. It contains twice as much iodine as the yellow iodide. Both these compounds are insoluble in pure water, but are dissolved by a solution of hydriodate of potash.

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° F. it forms a yellow fluid, which slowly sublimes in small transparent scales, or in large rhombic tables when in quantity. The crystals remain unchanged in the air; but they quickly become red when rubbed or touched.

Cyanuret of Mercury.—This compound is best prepared by boiling, in any convenient quantity of water, eight parts of finely levigated ferrocyanate of peroxide of iron, quite pure and well dried on a sand-bath, with eleven parts of peroxide of mercury in powder, until the blue colour of the ferrocyanate entirely disappears. A colourless solution is formed, which,

when filtered and concentrated by evaporation, yields crystals of cyanuret of mercury in the form of quadrangular prisms. In this process, the oxygen of the oxide of mercury unites with the iron and hydrogen of the ferrocyanic acid; while the metallic mercury enters into combination with the cyanogen. The brown insoluble matter is peroxide of iron. Pure ferrocyanate of iron is easily procured by digesting common Prussian blue of commerce with muriatic acid diluted with ten parts of water, so as to remove the subsulphate of iron and alumina and other impurities which it commonly contains, and then edulcorating the insoluble ferrocyanate till the free acid is removed. (Edinburgh Journal of Science, v.)

Cyanuret of mercury, when pure, is colourless and inodorous, has a very disagreeable metallic taste, and is highly poisonous. It does not affect the colour of litmus or turmeric paper; and when strongly heated it is converted into cyanogen and metallic mercury. (Page 375.) It is more soluble in hot than in cold water, and appears to dissolve in that liquid without change; for its solution has not the characteristic odour of the salts of hydrocyanic acid, nor do alkalies throw down oxide of mercury. It is composed of 200 parts or one equivalent of mercury, and 52 parts or two equivalents of cyanogen.

Sulphurets of Mercury.—The protosulphuret may be prepared by transmitting a current of sulphuretted hydrogen gas through a dilute solution of protonitrate of mercury, or through water in which calomel is suspended. It is a black-coloured substance, convertible into sulphate of mercury by digestion in strong nitric acid. When exposed to heat it is resolved into the bisulphuret and metallic mercury. It is composed of 200 parts or one equivalent of mercury, and 16 parts or one equivalent of sulphur.

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 hydrosulphuret of ammonia. A black precipitate subsides, which acquires the usual red colour of cinnabar when

sublimed. I apprehend the black precipitate, formed by the action of sulphuretted hydrogen on cyanuret 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-muriatic, with formation of sulphuric acid and oxide of mercury. M. Guibourt has shown that it is composed of one equivalent of mercury and two equivalents of sulphur*.

SECTION XXIV.

SILVER.

This metal frequently occurs native in silver mines, both massive and in octohedral or cubic crystals. It is also found in combination with several other metals, such as gold, antimony, copper, and arsenic, and with sulphur. In the state of sulphuret it so frequently accompanies galena, that the lead of commerce is rarely quite free from traces of silver.

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

* An. de Ch. et de Ph. vol. i. See also some very judicious observations on the paper of M. Guibourt by Mr. Brande, in the Journal of Science, xviii. 291.

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.

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. 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, through the pores of which the pure mercury passes, while the amalgam of silver is retained. 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 uses by placing a clean piece of copper into a solution of nitrate 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 potash. For this purpose precipitate a solution of nitrate of silver with muriate of soda, wash the precipitate with water, and dry it. Then put twice its weight of carbonate of potash 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.

Silver 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 20° or 22° of Wedgwood's pyrometer it fuses.

Pure silver does not rust by exposure to air and moisture, nor is it oxidized by fusion in open vessels. It appears, indeed, that a film of oxide is formed when melted silver is exposed to a current of air or oxygen gas; but it spontaneously parts with the oxygen as it becomes solid. When silver in the form of leaves or fine wire is intensely heated by means of electricity, galvanism, or the oxy-hydrogen blow-pipe, 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 silver. It is not attacked by sulphuric acid unless by the aid of heat. Nitric acid is its proper solvent, and forms with it a salt, which, in its fused state, is known by the name of *lunar caustic.*

Oxide of Silver.—This oxide is best procured by mixing a solution of pure baryta with nitrate of silver dissolved in water. It is of a brown colour, insoluble in water, and is completely reduced by a red heat. According to Sir H. Davy, it is composed of 110 parts of silver and 8 parts of oxygen; and, therefore, regarding it as the real protoxide, 110 is the atomic weight of silver.

Oxide of silver 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 sulphuretted hydrogen; and as a white curdy chloride of silver, which is turned violet by light, and is very soluble in ammonia, by muriatic acid or any soluble muriate. 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 twenty grains of lunar caustic to six 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 ten or twelve 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, vol. 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 Mr. 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.

Chloride of Silver.—This compound, which sometimes occurs native in silver mines, is always generated when silver is heated in chlorine gas, and may be prepared conveniently by mixing muriatic acid, or any soluble muriate, with a solution of nitrate 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. Muriatic acid is set free during this change, and, according to Berthollet, the dark colour is owing to a separation of oxide of silver. (Statique Chimique, vol. i. p 195.)

Chloride of silver, sometimes called *luna cornea* or *horn silver*, 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° F. it fuses, and forms a semitransparent horny mass on cooling. 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 muriatic acid. According to the experiments of Berzelius and Dr. Thomson it is composed of 110 parts or one equivalent of silver, and 36 parts or one equivalent of chlorine.

Iodide of Silver.—This compound is formed when hydriodate of potash is mixed with a solution of nitrate of silver. It is of a greenish yellow colour, is insoluble in water and ammonia, and contains one equivalent of each of its elements.

Cyanuret of Silver is formed by mixing hydrocyanic acid with nitrate of silver. It is a white curdy substance, similar in appearance to chloride of silver, insoluble in water and nitric acid, and soluble in a solution of ammonia. It is decomposed by muriatic acid with formation of hydrocyanic acid and chloride of silver. It consists of one equivalent of each of its elements.

Sulphuret of Silver.—Silver has a strong affinity for sulphur. This metal tarnishes rapidly when exposed to an atmosphere containing sulphuretted hydrogen gas, owing to the formation of a sulphuret. On transmitting a current of sulphuretted hydrogen 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.

Sulphuret of silver, according to the experiments of Berzelius, is a compound of 110 parts or one equivalent of silver, and 16 parts or one equivalent of sulphur.

Silver unites also by the aid of heat with phosphorus, forming a soft, brittle, crystalline compound.

SECTION XXV.

GOLD.

Gold has hitherto been found only in the metallic state, either pure or in combination with other metals. It occurs massive, capillary, in grains, and crystallized in octohedrons and cubes, or their allied forms. It is sometimes found in primary mountains; but more frequently in alluvial deposi-

tions, especially among sand in the beds of rivers, having been washed by water out of disintegrated rocks in which it originally existed. The richest gold mines of Europe are in Hungary. It is 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. This metal is left in the form of chloride when the gold is dissolved in nitro-muriatic acid.

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 at 32° of Wedgwood's pyrometer.

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 blow-pipe, 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 only solvents are chlorine and nitro-muriatic acid; and it appears from the observations of Sir H. Davy that chlorine is the agent in both cases, since nitro-muriatic acid does not dissolve gold, except when it gives rise to the formation of chlorine. (Page 299.) It is to be inferred, therefore, that the chlorine unites directly with the gold. Whether the resulting solution is really a chloride of the metal, or a muriate of its oxide, generated by decomposition of water, is uncertain; but from the observations of M. Pelletier, which will be mentioned immediately, I conceive the former opinion to be the more probable. There is no inconvenience, however, in regarding it as a muriate, because reagents act upon it as if it were such.

The most convenient method of forming a solution of gold is to digest fragments of the metal in a mixture composed of two measures of muriatic and one of nitric acid, until the acid

is saturated. The orange-coloured solution is then evaporated to dryness by a regulated heat, in order to expel the free acid without decomposing the residual chloride of gold. On adding water, the chloride is dissolved, forming a neutral solution of a reddish-brown colour.

Oxides of Gold.—The chemical history of the oxides of gold is as yet very imperfect. Berzelius is of opinion that there are three oxides. His protoxide is obtained by decomposing the protochloride of gold by a solution of pure potash, and is of a dark green colour. The deutoxide or purple oxide is the product of the combustion of gold. The composition of these oxides has not yet been satisfactorily determined, and the very existence of the first, though probable, may be questioned. The only well-known oxide is that which is supposed to exist in the solution of gold combined with muriatic acid. It may be prepared by mixing with a concentrated neutral solution of gold a quantity of pure potash exactly sufficient for combining with the muriatic acid. A reddish-yellow coloured precipitate, the hydrous peroxide, subsides, which is rendered anhydrous by boiling, and assumes a brownish-black colour*. The best method of forming it, according to M. Pelletier, is by digesting the muriate with pure magnesia, washing the precipitate with water, and removing the excess of magnesia by dilute nitric acid.

Peroxide of gold is yellow in the state of hydrate, and nearly black when pure, is insoluble in water, and completely decomposed by solar light or a red heat. Muriatic 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 potash and baryta, apparently forming regular salts, in which it acts the part of a weak acid. These circumstances have induced M. Pelletier to deny that the peroxide is a salifiable base, and to contend that the muriatic solution of gold is in reality a chloride of the metal. On this supposition he proposes the term *auric acid* for peroxide

* M. Pelletier in the An. de Ch. et de Ph. vol. xv.

of gold, and to its compounds with alkalies he gives the denomination of *aurates*.

Peroxide of gold is thrown down of a yellow colour by ammonia, and the precipitate is an aurate of that alkali. It is a highly detonating compound, analogous to the fulminating silver described in the last section.

According to the experiments of Berzelius*, which are confirmed by those of Javal† and Thomson, 100 parts of gold unite with 12.077 to constitute the peroxide; and if this oxide be regarded as consisting of three equivalents of oxygen and one of metal, 200 will be the equivalent of gold, and 224 that of its peroxide. It is therefore a tritoxide; and this opinion is corroborated by the constitution of the chlorides of gold.

Chlorides of Gold.—On concentrating the solution of gold to a sufficient extent by evaporation, the perchloride may be obtained in red prismatic crystals, which become brown when brought to perfect dryness. It deliquesces on exposure to the air, and is dissolved readily by water without residue. At a temperature far below that of redness, it is converted, with evolution of two-thirds of its chlorine, into the yellow insoluble protochloride, from which the chlorine is entirely expelled by a red heat. This protochloride is converted, by being boiled in water, into the soluble perchloride and metallic gold.

The composition of the chlorides of gold has been ascertained by Berzelius, and Mr. W. Johnston has lately confirmed the accuracy of his observations. (Brewster's Journal, N. S. iii. 131.) The insoluble chloride consists of one equivalent of gold and one of chlorine; while the soluble compound is a terchloride, consisting of one equivalent of gold and three of chlorine. When mixed with sea-salt, and the solution is evaporated, a double chloride of a reddish-yellow colour is obtained, which crystallizes either in prisms or four-sided tables. They consist, according to Berzelius and Johnston, of one equivalent of terchloride of gold, one of chloride of sodium, and four of water. A double chloride of gold and potassium may be formed in the same manner as the foregoing, and its constitution is analogous. It crystallizes sometimes in four-sided prisms and needles, and sometimes in large brilliant

* An. de Ch. lxxxiii. † An. de Ch. et Ph. xvii.

thin plates. A similar compound may be obtained with muriate of ammonia, and with several metallic chlorides, such as those of barium, strontium, calcium, magnesium, manganese, zinc, cobalt, and nickel.

The solution of gold is decomposed by substances which have a strong affinity for oxygen. On adding protosulphate of iron dissolved in water, the iron is oxidized to a maximum, and a copious brown precipitate subsides, which is metallic gold in a state of very minute division.—This precipitate, when duly washed with dilute muriatic 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. When a piece of charcoal is immersed in solution of gold, and exposed to the direct solar rays, its surface acquires a coating 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*.

When protomuriate of tin is added to a dilute aqueous solution of gold, a purple-coloured precipitate, called the *purple of Cassius*, is thrown down, which is the substance employed in painting on porcelain for giving a pink colour. It appears to be a compound of peroxide of tin and purple oxide of gold, in which the former is supposed to act as an acid.

Sulphuret of Gold.—On transmitting a current of sulphuretted hydrogen 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, and appears from the analysis of Oberkampf to be composed of 200 parts or one equivalent of gold, and 48 parts or three equivalents of sulphur.

The compounds of gold with the other non-metallic bodies have been little examined.

* 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.

SECTION XXVI.

PLATINUM.

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. Two years ago, however, M. Boussingault discovered it in a syenitic rock in the province of Antioquia in North America, where it occurs in veins associated with gold. Rich mines of gold and platinum have also been recently discovered in the Uralian mountains. (Edinburgh Journal of Science, v.)

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, admits of being welded at a high temperature. Dr. Wollaston * has observed that it is a less perfect conductor of caloric than most 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 blow-pipe, it is fused, and afterwards

* 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.

burns with the emission of sparks. The late Mr. Smithson Tennant showed that it is oxidized when ignited with nitre, (Philos. Trans. for 1797); and a similar effect is occasioned by pure potash and lithia.

Platinum is not attacked by any of the pure acids. Its only solvents are chlorine and nitro-muriatic acid, which act upon it with greater difficulty than on gold. The resulting orange-red coloured liquid, from which the excess of acid should be expelled by cautious evaporation, may be regarded as containing either chloride of platinum, or the muriate of its oxide.

Oxides of Platinum.—According to Berzelius there are two oxides of platinum, the oxygen of which is in the ratio of 1 to 2. The protoxide, prepared by the action of potash on protochloride of platinum, is of a black colour, and is reduced by a red heat. According to the earlier experiments of Berzelius, this oxide consists of 8 parts of oxygen and 96.5 of platinum; but he now estimates the equivalent of platinum at 98.6 or 99, while the number of Dr. Thomson is 96. The binoxide is obtained with difficulty; for on attempting to precipitate it from the muriate by means of an alkali, it either falls as a sub-salt, or is held altogether in solution. Berzelius recommends that it should be prepared by exactly decomposing sulphate 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. Like peroxide of gold it is a very feeble base, and is much disposed to unite with alkalies.

Another oxide was described by Mr. E. Davy in the Philosophical Transactions for 1820. It is of a gray colour, and is prepared by heating fulminating platinum with nitrous acid. It appears from his analysis to be composed of one equivalent of platinum, and an equivalent and a half of oxygen. Mr. Cooper has likewise described an oxide of platinum; but its existence as a definite compound distinct from those above described has not, I conceive, been satisfactorily demonstrated.

Chlorides of Platinum.—The perchloride is procured by evaporating muriate of platinum to dryness at a gentle heat.

It is deliquescent, and is soluble in water, alcohol, and ether. The ethereal solution is decomposed by the agency of light, metallic platinum being deposited. It is probable, from the analysis of the double chloride of potassium and platinum by Dr. Thomson and Berzelius, that perchloride of platinum is composed of one equivalent of metal and two equivalents of chlorine. It is therefore a bichloride, and corresponds with the peroxide.

When the bichloride is heated to the temperature of melting lead or a little higher, it parts with half of its chlorine, and is converted into a protochloride, which is resolved by a red heat into platinum and chlorine. It is insoluble in pure water, but is dissolved by a solution of the perchloride.

Platinum is distinguished from all other substances by the following circumstances. When pure potash or a salt of potash is added to a concentrated solution of platinum, a yellow crystalline precipitate subsides, which is very sparingly soluble in water. When heated to full redness chlorine gas is disengaged, and the residue consists of metallic platinum and chloride of potassium. It is composed of one equivalent of bichloride of platinum and one of chloride of potassium.

Ammonia, or its salts, produce a similar precipitate, which consists of one equivalent of the bichloride, and one of muriate of ammonia.

When this compound, which is generally called the *muriate* of *platinum* and *ammonia*, is heated to redness, chlorine and muriate of ammonia are evolved, and pure platinum remains 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. (Page 204.) This salt affords an easy method of procuring platinum in a metallic state and of separating it from other metals.

Soda forms with muriate of platinum a double salt, which is soluble in water and alcohol, and crystallizes in flattened, oblique, four-sided prisms of an orange-red colour. According to Dr. Thomson it is a compound of one equivalent of bichloride of platinum, one equivalent of chloride of sodium, and eight equivalents of water.

Sulphuret of Platinum.—When sulphuretted hydrogen gas

is transmitted through a solution of muriate of platinum, a black precipitate is thrown down, which was regarded by Vauquelin as a hydrosulphuret of oxide of platinum. It absorbs oxygen from the air while in a moist state, giving rise to the formation of sulphuric acid. Its composition has not been determined with accuracy.

A black sulphuret of platinum was procured by Mr. E. Davy by heating the metal with sulphur, and Vauquelin obtained a similar compound by igniting the yellow muriate of platinum and ammonia with twice its weight of sulphur. According to the analysis of these chemists, it contains about 16 per cent of sulphur.

Hydrosulphuret of platinum is converted by the action of nitric acid into a sulphate which possesses remarkable properties. On boiling it in strong alcohol, a black powder is precipitated, which consists, according to Mr. E. Davy, of 96 per cent of platinum, together with a little oxygen, nitrous acid, and carbon, the last of which is supposed to be accidental. When this powder is placed on bibulous paper moistened with alcohol, a strong action accompanied with a hissing noise ensues, and the powder becomes red-hot, and continues so until the alcohol is consumed. The substance which remains is pure platinum.

Fulminating platinum may be prepared by the action of ammonia in slight excess on a solution of sulphate 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-muriatic acid, the platinum, together with palladium, rhodium, iron, copper, and lead, is dissolved; while a black powder is left consisting of osmium and iridium.

PALLADIUM.

This metal was discovered in 1803 by Dr. Wollaston *. On adding cyanuret of mercury dissolved in water to a neutral solution of the ore of platinum, either before or after the separation of that metal by muriate 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 Dr. Wollaston supposed to arise from a small remnant of sulphur. (Phil. Trans. 1829. p. 7.)

Palladium resembles platinum in colour and lustre. It is ductile as well as malleable, and is considerably harder than platinum. Its specific gravity varies from 11.3 to 11.8. (Wollaston.) In fusibility it is intermediate between gold and platinum, and is dissipated in sparks when intensely heated by the oxy-hydrogen blow-pipe. 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.

Palladium is oxidized and dissolved by nitric acid, and even the sulphuric and muriatic acids act upon it by the aid of heat; but its proper solvent is nitro-muriatic acid. Its oxide forms beautiful red-coloured salts, from which metallic palladium is precipitated by protosulphate of iron and all the metals described in the foregoing sections, excepting silver, gold, and platinum.

* Philosophical Transactions, for 1804 and 1805.

Oxide of palladium is precipitated by pure potash, as an orange-coloured hydrate, which becomes black when dried, and is decomposed by a red heat. It may be regarded as the protoxide, and according to the late researches of Berzelius consists of one equivalent of oxygen, and 53 parts, or what he considers one equivalent of palladium. An oxide with twice as much oxygen may be thrown down by alkalies from a solution of the bichloride. It falls as a hydrate of a deep yellowish brown colour, which retains a little alkali in combination; but on heating the solution to 212° F., the alkali is dissolved, and a black oxide separates. (An. de Ch. et Ph. xl. 72.)

Berzelius describes two chlorides. The protochloride is formed by evaporating the nitro-muriatic solution to dryness. When crystallized in solution with chloride of potassium it forms a double chloride, which crystallizes either in small needles of a golden yellow tint, or in larger prisms of a brownish-yellow colour. It is soluble in water and alcohol; but in distilling the spirituous solution, most of the palladium is reduced. It contains an equivalent of each chloride.

On evaporating this double compound with nitro-muriatic acid, deutoxide of nitrogen is disengaged, and microscopic crystals of a cinnabar-red colour are deposited; but when large enough to be appreciated, their colour appears reddish-brown, and their form that of the regular octohedron. They consist of one equivalent of bichloride of palladium and one of chloride of potassium. It is converted by heat into the double protochloride, with evolution of chlorine; and water occasions a similar change.

RHODIUM.

This metal was discovered by Dr. 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-muriatic acid, and the solution, after being mixed with some muriate of soda, 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.

Rhodium, thus procured, 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 specific gravity 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-muriatic 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 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; and the rose-red tint of the muriate suggested the name of rhodium. (From ῥόδον, a rose.) According to Dr. Thomson, the equivalent of rhodium is 44, and the oxygen in its two oxides is in the ratio of 1 to 2; but the number selected by Berzelius, as the result of his recent researches, is about 52; and the oxygen in the two oxides is as 1 to 1·5. (An. de Ch. et Ph. xl. 51.)

Berzelius succeeded in preparing two chlorides, the composition of which is similar to that of the oxides of rhodium, that is, an equivalent of the metal is united in one of them with one equivalent, and in the other with one equivalent and a half of chlorine. The latter, or sesqui-chloride, forms a double chloride both with chloride of potassium and sodium. The former consists of one equivalent of each chloride; but in the

latter one equivalent of sesqui-chloride of rhodium is combined with an equivalent and a half of chloride of sodium.

IRIDIUM AND OSMIUM.

These metals were discovered by the late Mr. Tennant in the year 1803*, and the discovery of iridium was made about the same time by M. Descotils in France. The black powder mentioned at the beginning of this section is a compound of iridium and osmium, an alloy which Dr. Wollaston has detected in the form of flat white grains among fragments of crude platinum. This alloy, which is quite insoluble in nitro-muriatic acid, is the source from which iridium and osmium are extracted.

Osmium.—This metal is separated from the alloy just mentioned by fusion with soda or nitre; and the following process, given by Dr. Wollaston, may be resorted to with advantage. (Phil. Trans. 1829. p. 8.) The pulverulent alloy 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 potash, 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 oxide 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 oxide becomes solid and crystallizes.

Osmium is precipitated from the solution of its oxide by all the metals, excepting gold and silver. A convenient mode of reduction is to agitate it with mercury, adding muriatic 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. If it has been exposed to a very gentle heat, its

* Philosophical Transactions for 1804.

specific gravity 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 specific gravity to be 10. (An. de Ch. et Ph. xl. 257. and xlii. 185.)

Oxides.—Recent researches have induced Berzelius to consider the equivalent of osmium as identical with that of platinum, being about 99. He has enumerated five degrees of oxidation. The protoxide is precipitated by pure alkalies from the protochloride, and falls of a deep green, nearly black, colour, as a hydrate, which is soluble in acids, and detonates when heated with combustible matter. The deutoxide 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 muriatic acid, without the oxide being dissolved. The tritoxide is prepared in like manner from the ter-chloride. The sesqui-oxide has not been obtained in a separate state; but it is procured in combination with ammonia when the deutoxide 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 oxide, which consists of four equivalents of oxygen and one of osmium. (Berzelius.) It 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**. 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. It is hence sometimes called *osmic acid*. When touched it communicates a stain which cannot be removed by washing. With the infusion of

* From ὀσμή, odour.

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 sesqui-oxide 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 sulphuretted hydrogen. The sulphurets correspond to the number of the oxides. (Berzelius.)

Iridium.—In the process already described for separating osmium from its ore, oxide of iridium is left in combination with potash, after the soluble compound of osmium has been removed by the action of water. On digesting the mass in muriatic 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, is owing to the metal passing through different stages of oxidation. In general, after treatment with muriatic acid, some undecomposed ore remains, which, from its refratory nature, often requires repeated fusion with nitre.

Muriate of iridium, when deprived of its excess of acid by heat, may be procured by evaporation in crystals of a deep brown colour. This compound, which is probably rather a chloride than a muriate, is distinguished by forming with water a red solution, which is rendered colourless by the pure alkalies or alkaline earths, by sulphuretted hydrogen, infusion of gall-nuts, or ferrocyanate of potash. It is decomposed by nearly all the metals except gold and platinum, iridium being

thrown down in the metallic state. The metal may also be procured by exposing the chloride to a red heat.

Iridium is 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: Mr. 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. Its greatest specific gravity in the unfused state is 15.8629. 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-muriatic acid.

According to the late researches of Berzelius, the equivalent of iridium is identical with that of platinum, and it is capable of forming four oxides corresponding to analogous chlorides. The protoxide, sesqui-oxide, and tritoxide are precipitated by alkalies from the chloride to which they are respectively proportional. The protoxide is greenish-gray as a hydrate, and black when anhydrous. The sesqui-oxide is bluish-black in the dry state, and deep-brown as a hydrate. The hydrated tritoxide is of a yellowish-brown or greenish colour. The deutoxide 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 sesqui-oxide. 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.

Besides forming four simple chlorides, proportional to the oxides above mentioned, iridium forms double chlorides with sodium and potassium, for an account of which I refer to the Essays of Berzelius already cited in the history of osmium.

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.

PLURANIUM AND RHUTENIUM.

From some observations by M. Osann, it appears that the insoluble residue left after the action of nitro-muriatic acid on the Uralian ore of platinum, contains two new metals, to which he has given the names of *Pluranium* and *Rhutenium*. Of their properties little is known, and the certainty that they are new metals has not yet been established. (Phil. Mag. and Annals, v. 233.)

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 200 to 110, that the amalgam may be inferred to contain one equivalent of each of its elements. It is indeed possible that the variety of proportion 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.

Alloys are analogous to metals in their chief physical properties. They are opaque, possess the metallic lustre, and are good conductors of electricity and caloric. 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 alloys 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 con-

spicuous when dense metals are liquefied by combination with quicksilver, and is manifestly owing to the loss of their cohesive power. 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, Mr. 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.

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 potash 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 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 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 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 muriatic 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. Equal parts of these metals constitute an alloy which is more fusible than either separately, and is the common solder of the

glaziers. Its point of fusion is about 360° F. M. Kupfer has observed that most of the alloys of tin and lead, made in atomic proportion, have a specific gravity 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 by a temperature below 212° Fahr. The best proportion, according to M. D'Arcet, is eight parts of bismuth, five of lead, and three of tin.

An alloy of three parts of lead to one of antimony constistutes the substance of which types for printing are made.

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 zinc 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*, *Dutch-gold*, and *Pinchbeck*. The *white copper* of the Chinese is composed, according to the analysis of Dr. 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 mutual 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. (Philos. 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 silicium 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.

SALTS.

GENERAL REMARKS ON SALTS.

In the preceding pages I have been chiefly occupied with the description either of elementary principles, or of compounds immediately resulting from their union. The class of bodies now to be described is of a different nature, being exclusively compounds derived from the combination of other compound bodies.

The term *salt* is often somewhat vaguely employed in chemistry, but according to the usage of most chemists, it denotes a definite compound of an acid, and an alkaline or salifiable base, both of which are in every case composed of at least two simple substances. Sulphate of potash, for instance, is a salt, the acid of which consists of oxygen and sulphur, and the base of oxygen and potassium. A different view may indeed be formed of the nature of a salt. Thus, to employ the example already adduced, sulphate of potash contains sulphur, oxygen, and potassium; and it may be thought that these three elements do not exist in the salt as sulphuric acid and potash, but are combined directly and indiscriminately with each other. But such an opinion is gratuitous and untenable. Sulphate of potash is said to contain sulphuric acid and potash, because, in the first place, it is formed by the direct mixture of these two substances; secondly, because the acid and the alkali, after combination, may be separated and again procured in their original state by the agency of galvanism; and, thirdly, because no known affinity is in operation by which the tendency of potassium to constitute potash with oxygen, or of sulphur to form sulphuric acid with the same element, may be counteracted. It is probable, indeed, that all compounds consisting of three or more elementary principles are composed of binary compounds united with each other.

In studying the salts, it is important to set out with correct ideas concerning the nature of an acid and of an alkaline base,

and therefore a few preliminary remarks will be made concerning the nature and characteristic properties of these two classes of compounds.

An acid is commonly regarded as a substance which has a sour taste, reddens litmus paper, and neutralizes alkalies. But these properties, though very conspicuous in all the powerful acids, are not altogether general, and therefore cannot serve the purpose of a definition. Thus insoluble acids, owing to their insolubility, do not taste sour, nor redden litmus paper; and some bodies, such as carbonic acid and sulphuretted hydrogen, the title of which to be placed among the acids cannot be called in question, are unable to destroy the alkaline reaction of potash. The most correct definition of an acid with which I am acquainted is the following:—an acid is a compound which is capable of uniting in definite proportion with alkaline bases, and which, when liquid or in a state of solution, has either a sour taste, or reddens litmus paper.

Most of the acids contain oxygen as one of their elements, a circumstance which induced Lavoisier to suppose that oxygen possesses some specific power of causing acidity, and for this reason he regarded it as the *acidifying principle*. The acquisition of new facts, however, has shown the fallacy of his opinion. Acids may and do exist which contain no trace of oxygen, nor does its presence necessarily give rise to acidity. The compounds of oxygen are frequently alkaline instead of acid; and in many instances they are neither acid nor alkaline. No substance, excepting deutoxide of hydrogen, contains a larger proportional quantity of oxygen than water, and yet this fluid does not possess the slightest degree of acidity. The progress of science, indeed, seems to justify the opinion that there is no body to which the term acidifying principle is strictly applicable. The acidity of any substance cannot be referred to one of its elements rather than the other; but it is a new property peculiar to the compound, and to which each of its constituents contributes.

An alkali is characterized by a peculiar pungent taste, by its alkaline reaction on vegetable colours, and by neutralizing acids. There are many salifiable bases, however, which do not possess these characters. Thus pure magnesia, though it is a strong alkaline base and forms neutral salts with acids,

is insipid, and barely produces an appreciable effect on yellow turmeric paper,—an inaction obviously owing to its insolubility. Some compounds neutralize the properties of acids in an imperfect manner, although they form perfect salts. For these reasons it is desirable to define precisely what is meant by a salifiable base, and the following definition appears to me to answer the purpose. Every compound may be regarded as an alkaline or salifiable base, which forms definite compounds with acids, and which, when liquid or in a state of solution, has an alkaline reaction. All alkaline bases, with the exception of ammonia and the vegetable alkalies, are metallic oxides.

The nomenclature of the salts was explained on a former occasion. (Page 141.) 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 lead, for instance, has the property of reddening litmus paper; whereas it consists of one equivalent of oxide of lead and one equivalent of nitric acid, and therefore in composition is precisely analogous to nitrate of potash, 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.

As every 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 groups, placing together those saline combinations which consist of the same acid, united with different salifiable bases. The salts of each group, 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 group, and may therefore be omitted.

Nearly all salts are solid, and most of them assume crystalline forms when their solutions are spontaneously evaporated.

The colour of salts is very variable. Those that are composed of a colourless base and acid are always colourless.—There is no necessary connexion between the colour of an oxide or an acid and that of its salts. A salt, though formed of a coloured oxide or acid, may be colourless; and if it is 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 only one which is remarkable 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 be-

come 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 the degree of 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 which 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, and is termed the *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.

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 of lead, which contain no water of crystallization.

The atmospheric pressure is said to have considerable influence on the crystallization 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 re-admitting 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, pro-

vided 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 Mr. Graham, published in the Philosophical Transactions of Edinburgh for 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 dissolving in water, 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 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 composition of salts is subject to the laws of chemical union; and, indeed, the study of these compounds by Wenzel, Richter, and Berzelius, together with the facts ascertained by Dr. Wollaston and Dr. Thomson, tended materially to establish the doctrine of definite proportion. All salifiable bases, consisting of one equivalent of a metal and one equivalent of oxygen, are converted into neutral salts, that is, into salts without excess either of acid or base, by uniting with one equivalent of an acid. When a metal forms two salifiable bases with oxygen, the peroxide manifests a tendency to unite with more acid than the protoxide, and Gay-Lussac has demonstrated the existence of the following law:—*that the quantity of acid which the oxides of the same metal require for*

saturation, is in the same ratio as the quantity of oxygen contained in their oxides. (Mémoirs D'Arcueil, vol. ii.) Thus, while protosulphate of iron contains one equivalent of each of its elements, the soluble persulphate is composed of one equivalent of peroxide of iron, and one equivalent and a half of sulphuric acid. In like manner, the peroxides of mercury and copper are disposed to unite with two equivalents of acid, or twice as much as would form a neutral salt with the protoxides of those metals. Hence, when a peroxide unites with one equivalent of an acid, the product is commonly a subsalt.

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 most probably of two different acids and two different bases. Nearly all the double salts hitherto examined consist of the same acid and two different bases.

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 regularly limited 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.*

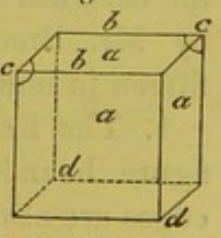
Most bodies crystallize under favourable circumstances. The condition by which the process is peculiarly favoured is the slow and gradual change of a fluid into a solid, the arrangement of the particles being at the same time undisturbed by motion. This is exemplified during the slow cooling of a fused 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.

Crystallographers have observed that certain crystalline forms are peculiar to certain substances. Thus, calcareous spar crystallizes in rhombohedrons, fluor spar in cubes, and quarz in six-sided pyramids; and these forms are so far peculiar to those substances, that fluor spar is never found in rhombohedrons or six-sided pyramids, nor does calcareous spar or quarz ever occur 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 an enumeration of the primary forms. To those who are desirous of more ample information, I may recommend Mr. Brooke's "Familiar Introduction to Crystallography," or the translation of Mohs's Treatise on Mineralogy by Mr. Haidinger.

The surfaces which limit the figure of crystals are called *planes* or *faces*, and are generally flat. The lines formed by the junction of two planes are called *edges;* and the angle formed by two such edges is a *plane angle*. A *solid angle* is the point formed by the meeting of at least three planes. Thus in the cube or hexahedron, figure 1, *aaa* are planes, *bb* are edges, and *cc* solid angles. The cube it is apparent has six planes or faces, twelve edges, and eight solid angles. Each of the faces has four angles, which are rectangular.

Fig. 1.



The forms of crystals are exceedingly diversified. They are divided by crystallographers into what are called *primitive*, *primary*, *derivative*, or *fundamental* forms, and into *secondary* or *derived* forms. This distinction is founded on the fact, that the same substance frequently assumes different crystalline forms; which, however, though actually different, are in ge-

neral geometrically allied to each other. A body, for instance, whose ordinary figure is a cube, may assume a shape represented by figure 2, where the general outline is cubic, but the solid angles are replaced by triangular faces; just as if the crystal had been originally a perfect cube, and its eight solid angles subsequently removed by mechanical means. Instead of the solid angles the edges of the cube may be wanting, and a new form, such as figure 3, be produced. If the new planes are small, the crystal will preserve its cubic appearance; but if they are larger, the outline of the cube will be less distinct; and should the faces of the original cube wholly disappear, a form altogether different will result.—Secondary crystals are those which may be thus deduced by the substitution of planes for the edges or angles of some primary form; and the primary or fundamental form is that from which the former are derived. The replacement is commonly produced by a *tangent plane*, by which, in reference to the edge of a crystal, is meant a plane inclined equally to the two adjacent primary planes, and parallel to the edge which it replaces. In allusion to a solid angle, a tangent plane is equally inclined on all the primary planes of which the solid angle is constituted.

Fig. 2.

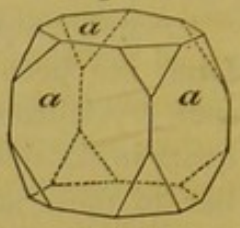
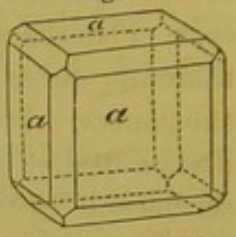


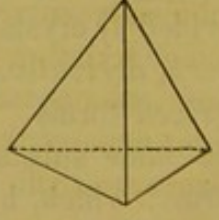
Fig. 3.



The number and kind of primary forms are stated differently by different crystallographers, according to the system which they adopt; but I apprehend it will be most advantageous to the chemical student to be acquainted with those enumerated by Mr. Brooke in the work above mentioned. They are fifteen in number.

1. The first is the hexahedron or cube of geometricians, a figure bounded by six square faces. All the angles of its edges are also equal to 90 degrees. (Fig. 1.)

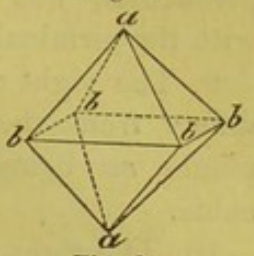
Fig. 4.



2. The tetrahedron, a regular solid of geometry, is contained under four equilateral triangles, and therefore all its plane angles are equal to 60 degrees. The faces incline to each other at the edges at an angle of 70° 31′ 44″. (Fig. 4.)

3. The regular octohedron is contained under eight equilateral triangles, figure 5, and consequently all its plane angles are equal to 60 degrees. The base of the octohedron *bbbb* is a square, and the planes incline on each other at the edges at an angle of 109° 28′ 16″. The octohedron is a regular solid of geometry.

Fig. 5.



4. The rhombic dodecahedron (fig. 6) is limited by twelve similar rhombic faces, the plane angles of which are equal to 109° 28′ 16″ and 70° 31′ 44″. The faces incline to each other at the edges at an angle of 120°.

Fig. 6.

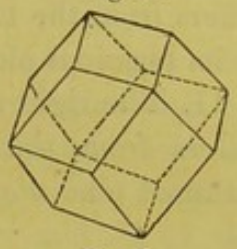


Fig. 7.

5. The octohedron with a square base, fig. 7, is bounded by eight faces which are similar isosceles triangles. The base *bbbb* is always a square, and this is the only part of the figure which is constant.

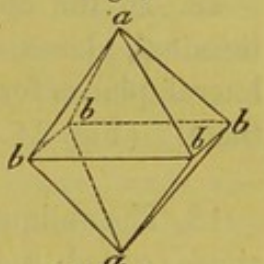


Fig. 8.

6. The rectangular octohedron, figure 8, is limited by eight isosceles triangles, four of which are different from the other four. The base *bbbb* is always a rectangle; but the ratio of its two sides, as well as all the other dimensions of the figure, is variable.

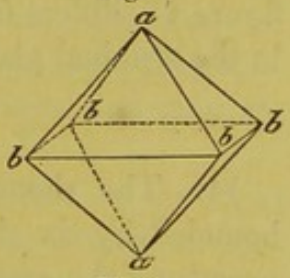


Fig. 9.

7. The rhombic octohedron, figure 9, is contained under eight faces which are similar scalene triangles, and the base *bbbb* is a rhomb. All its dimensions are variable.

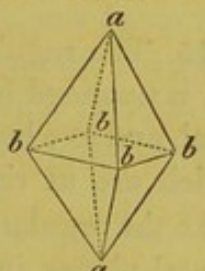
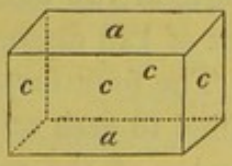


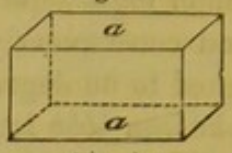
Fig. 10.

8. The right square prism, figure 10, is a six-sided figure, which differs from the cube only in its four *lateral* planes *cccc* being rectangles. The extreme or *terminal* planes *aa* are square. The term *right* denotes that the lateral and terminal planes are inclined to each other at a right angle. It is used in opposition to *oblique*, which signifies that the sides are not per-



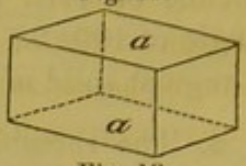
pendicular, but form an oblique angle with the terminal planes.

Fig. 11.



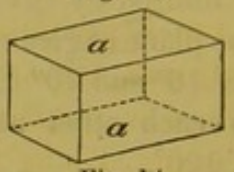
9. The right rectangular prism, fig. 11, differs from the former in the terminal planes *aa* being rectangular instead of cubic.

Fig. 12.



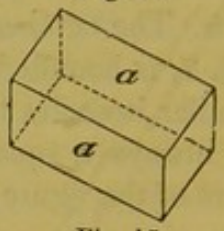
10. The right rhombic prism, figure 12, differs from the two preceding forms only in its terminal planes *aa* being rhombs.

Fig. 13.



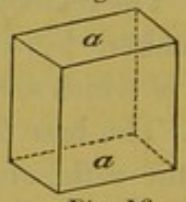
11. The right rhomboidal prism, fig. 13, differs from the preceding form in the terminal planes *aa* being rhomboids.

Fig. 14.



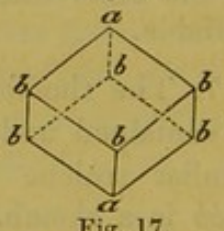
12. In the oblique rhombic prism the terminal planes *aa* are rhombic, and the lateral planes form an oblique angle with them. (Fig. 14.)

Fig. 15.



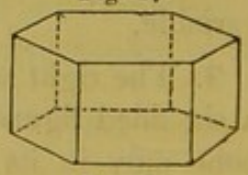
13. The oblique rhomboidal prism, sometimes called the doubly oblique prism, figure 15, differs from the preceding form in the terminal planes *aa* being rhomboids.

Fig. 16.



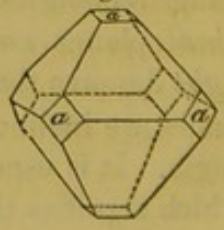
14. The rhombohedron, figure 16, is bounded by six rhombic faces, which are exactly of the same size and form.

Fig. 17.



15. The regular hexagonal prism, figure 17, is bounded by six perpendicular or lateral, and two horizontal or terminal planes, which are at right angles to the former. Like the regular hexagon of geometry, the lateral planes incline to each other at an angle of 120 degrees. If these angles are not of 120 degrees, the prism is irregular.

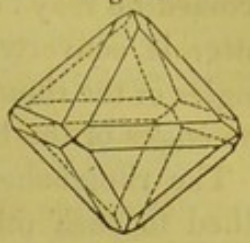
Fig. 18.



The four first forms are geometrically allied to each other. Thus, if the six solid angles of the regular octohedron are replaced by tangent planes, as in figure 18, and these are enlarged until they intersect

each other, and the faces of the octohedron disappear, a perfect cube is produced. If the twelve edges of the octohedron are replaced by tangent planes, as in figure 19, and these are extended till they mutually intersect, the rhombic dodecahedron will be formed. The cube may by analogous changes be converted into the octohedron, tetrahedron, and rhombic dodecahedron. For if the eight solid angles of the cube be replaced by equilateral triangles, (fig. 2.) and these are enlarged till the planes of the original cube are destroyed, the octohedron results. The tetrahedron may be formed by replacing the four solid angles *cc* and *dd* of the cube (fig. 1.) by tangent planes, so that all its original faces disappear. By replacing the twelve edges of the cube with tangent planes as in figure 3, until the new faces intersect each other, the rhombic dodecahedron will be produced. By the combination of the planes of different primary forms, various secondary ones are created, as is made obvious by the figures, and will be rendered still clearer by making the transitions above described with an apple or potato. The study of such allied forms is very important, because the same substance often occurs in several of these figures, and may assume all of them.

Fig. 19.



The octohedron with a square base is allied to the right square prism. Thus if in figure 7 two tangent planes are substituted for the solid angles *aa*, and the edges of the base are replaced by faces perpendicular to the former, new forms will result. If the faces of the octohedron disappear, the right square prism is formed; but if traces of them remain, secondary forms intermediate between the two primary ones will be produced.

The rectangular and rhombic octohedrons and the right rectangular and rhombic prisms are associated with each other. Thus on replacing the solid angles *aa*, and the four edges of the base of the rectangular octohedron, by tangent planes, and extending them till the planes of the octohedron disappear, the right rectangular prism is formed; and the rhombic octohedron by a similar change is converted into the right rhombic prism. By applying tangent planes to all the edges of the

rhombic octohedron except those of the base, the rectangular octohedron may be produced; and by a reversed operation the latter is converted into the former. In this case the solid angles of the rhombic octohedron must be so placed as to bisect the edges of the base of the rectangular octohedron.

The rhombohedron and six-sided or hexagonal prism are allied to each other. If tangent planes are laid on the two solid angles *aa* of the rhombohedron, (fig. 16.) and either the six solid lateral angles marked *b*, or the edges between them, are replaced by equal planes perpendicular to the former, a six-sided prism results; and the six-sided prism may be reconverted into the rhombohedron by replacing all its alternate solid angles by equal and similar rhombic planes.

The six-sided prism is often associated in nature with a double six-sided pyramid, formed by all its terminal edges being replaced by isosceles triangles. If the faces of the prism disappear, the double six-sided pyramid results.

The crystalline forms which have an intimate geometrical connexion with each other, are considered by crystallographers as constituting certain groups, which are termed *Systems of Crystallization*. Thus, of the fifteen primary forms above described, the Tessular System of Mohs comprehends the cube, the tetrahedron, the regular octohedron, and the rhombic dodecahedron, together with several others not enumerated; his Pyramidal System contains the octohedron with a square base, and the right square prism; the Prismatic System contains the rectangular and rhombic octohedron, and the right rectangular and right rhombic prisms; the Hemiprismatic System includes the right rhomboidal and the oblique rhombic prisms; the oblique rhomboidal prism belongs to the Tetarto-prismatic System; and the Rhombohedral System comprehends the rhombohedron and the regular hexagonal prism. This distinction is so far important, that all the forms which a salt, or any substance, almost always assumes, belong to the same system of crystallization.

Besides the distinction arising from external form, minerals are further distinguished by differences in the mechanical connexion 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 at 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 spliting 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 primary 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 may be converted.

Cleavage not only affords a useful character for distinguishing minerals, but is frequently employed by mineralogists for detecting the primary forms of crystals. If a mineral occur in two or more of those forms which have been enumerated as primary, that one is usually selected as fundamental, which

may be produced by cleavage. Thus fluor spar is met with in cubes, in the form of the regular octohedron, and as the rhombic dodecahedron. Of these the cube is by far the most frequent; and yet the octohedron is usually adopted as the fundamental form, because fluor has four equally distinct cleavages parallel to the planes of that figure. It is, indeed, a practice very common among mineralogists, not only to consider cleavage as the most influential circumstance in fixing the primary form of a crystal, but to adopt as such no figure which is inconsistent with its cleavages.

Since the forms above enumerated as belonging to the tessular 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 tessular 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 tessular 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 Professor Mitscherlich of Berlin, relative to the connexion between the crystalline form and composition of bodies. It appears from his researches*, that certain substances are capable of being substituted for each other in combination, without influencing the form of the compound. This singular circumstance has been ably traced by Professor Mitscherlich in the salts of phosphoric and arsenic acids. Thus, neutral phosphate and biphosphate of soda have exactly the same form as arseniate and binarseniate of soda. Phosphate and

* Annales de Ch. et de Physique, vol. xiv. 172, xix. 350, and xxiv. 264 and 355.

biphosphate of ammonia correspond in like manner to arseniate and binarseniate of ammonia. The neutral phosphate and arseniate of potash could not be obtained in crystals fit for examination; but the biphosphate and binarseniate of that alkali have the same form. Each arseniate has a corresponding phosphate, possessed of the same form, and containing the same number of equivalents of acid, alkali, and water. These series of salts, in fact, differ in nothing but in one containing arsenic and the other phosphoric acid.

From these and analogous facts it appears that certain substances, when similarly combined with the same body, are disposed to affect the same crystalline form. This discovery has led to the formation of groups, each comprehending substances which crystallize in the same manner, and which are hence said to be *isomorphous*. The salts of arsenic acid are isomorphous with those of phosphoric acid. The oxide of lead, baryta, and strontia, when combined with the same acid, yield salts which are said by Professor Mitscherlich to be isomorphous. The salts of lime are isomorphous with those of magnesia, protoxide of manganese, iron, cobalt, and nickel, oxide of zinc, and peroxide of copper. The salts of selenic and sulphuric acids, when similarly united with water and the same base, assume the same form; and the salts of peroxide of iron are isomorphous with those of alumina.

The similarity of the chemical constitution of isomorphous bodies is peculiarly striking. The first singularity of the kind, which merits notice, is the tendency of some isomorphous salts to combine with the same quantity of water of crystallization. This is especially remarkable in the salts of arsenic and phosphoric acids. The biphosphate and binarseniate of potash crystallize with two equivalents of water. The neutral phosphate and arseniate of soda contain twelve and a half equivalents of water; and in the biphosphate and binarseniate of soda four equivalents of water are present. The quantity of water contained in the arseniates of ammonia corresponds to that of the phosphates of ammonia. Indeed scarcely any crystallized artificial arseniate is known, to which a corresponding phosphate has not been discovered. If, on the contrary, two isomorphous salts crystallize with different

equivalent quantities of water, their forms are found to differ also. The common sulphates of manganese and copper differ in form from the sulphates of iron and zinc; whereas when their crystals contain the same number of equivalents of water, their form is identical. Mitscherlich has remarked that isomorphous salts, which when pure combine with different proportional quantities of water, are disposed in crystallizing together to unite with the same number of equivalents of water, and assume the same form. The mixed sulphates of iron and copper crystallize together with great facility; and the crystals, though containing a considerable quantity of copper, have the same proportional quantity of water and the same form as pure protosulphate of iron. According to Mitscherlich, the sulphates of zinc and copper, of copper and magnesia, of copper and nickel, of zinc and manganese, and of magnesia and manganese, crystallize together with six equivalents of water of crystallization, (the same number he states as in protosulphate of iron), and have the same form as green vitriol, without containing a trace of iron. In these instances the isomorphous salts do not occur in definite proportions; so that though they crystallize together, they do not appear to be chemically united.

The similarity in the chemical constitution of isomorphous substances may be illustrated in a different way. Thus, in isomorphous salts the proportional quantities of acid and base are the same. A neutral phosphate does not correspond to a binarseniate, nor a biphosphate to a neutral arseniate. There is in general also an exact similarity in the composition of the constituents of isomorphous substances. Thus all chemists agree that the atomic constitution of arsenic and phosphoric acids is the same; and the fact is still further evinced by the composition of selenic and sulphuric acids. This singular coincidence led Professor Mitscherlich to believe, that the form of crystals depends on their atomic constitution. He at first suspected that identity of crystalline form is determined solely by the number of atoms, and the mode in which they are united, 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 acids 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.

The discovery of Professor Mitscherlich, while it serves as a caution to mineralogists against too exclusive reliance on crystallographic character, is in several respects of deep interest to the chemist.—It tends to lay open fields of inquiry which may not otherwise have been thought of, and thus lead to the discovery of new substances.—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 may afford a useful guide in discovering the atomic constitution of compounds. Thus, two isomorphous oxides are most likely composed of the same number of atoms of metal and oxygen; so that if, as Berzelius supposes, peroxide of iron consists of two atoms of iron and three atoms

of oxygen, alumina, which is isomorphous with it, will probably have a similar atomic constitution. The similarity in the composition of several other isomorphous compounds gives considerable weight to the argument; but our knowledge of this subject is as yet too limited to excite much confidence. It is possible that aluminium and iron may not be isomorphous, and yet yield isomorphous oxides by uniting with oxygen in different proportions.—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 connexion 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.

In one of the essays above referred to, Professor Mitscherlich observed that biphosphate of soda is capable of yielding two distinct kinds of crystals, which, though different in form, in composition appeared 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; and infers from his observations that a body, whether simple or compound, may assume two different crystalline forms. The cause of this unexpected fact is not yet ascertained.

The same close observer has noticed, that the form of salts is sometimes changed by heat, without their losing the solid state. This change was first noticed in sulphate of magnesia, and also in sulphate 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.

SULPHATES.—SULPHITES.—HYPOSULPHATES.—HYPOSULPHITES.

SULPHATES.

The salts of sulphuric acid in solution may be detected by muriate of baryta. 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 recognised. 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 potash 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 muriatic, nitric, or acetic acid, and adding muriate of baryta, 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, tin, antimony, bismuth, lead, and mercury. The sparingly soluble sulphates are those of strontia, lime, zirconia, yttria, cerium, and silver. All the others are soluble in water.

All the sulphates, those of potash, soda, lithia, baryta, strontia, and lime excepted, are decomposed in 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 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 sulphuretted hydrogen. In some instances the hydrogen entirely deprives the metal of its sulphur.

The composition of the sulphates, so far as they are subject to general laws, has already been described. (Page 190.)

Sulphate of Potash.—This salt is easily prepared artificially by neutralizing carbonate of potash with sulphuric acid; and it is procured abundantly by neutralizing with carbonate of potash the residue of the operation for preparing nitric acid. (Page 242.) Its taste is saline and bitter. It generally crystallizes in six-sided prisms, bounded by pyramids with six sides; the size of which is said to be much increased by the presence of a little carbonate of potash. Its primary form, according to Mitscherlich, is a rhombic octohedron, and it is isomorphous with chromate and seleniate of potash. (Poggendorff's Annalen, xviii. 168.) The crystals contain no water of crystallization, 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° F. and five of boiling water for solution.

Sulphate of potash is composed of 40 parts or one equivalent of sulphuric acid, and 48 parts or one equivalent of potash.

Bisulphate of potash, which contains twice as much acid as the foregoing salt, is easily formed by digesting 88 parts or one equivalent of the neutral sulphate, with water containing about 50 parts of concentrated sulphuric acid, and evaporating the solution. The primary form of its crystals is a right rhombic prism, but which is in general so flattened as to be tabular. 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.

Mr. Phillips has described a sesquisulphate, obtained in the form of acicular crystals from the residue of the process for making nitric acid. The conditions for ensuring its production have not been determined. (Phil. Mag. and Annals, ii. 421.)

Sulphate of Soda.—This compound, commonly called *Glau-*

ber'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 muriatic acid and chlorine. (Pages 290 and 295.)

Sulphate of soda has a cooling, saline, and bitter taste. It commonly yields four and six-sided prismatic crystals, but its primary form is a rhombic octohedron. Its crystals effloresce rapidly when exposed to the air, losing the whole of their water, and, according to Berzelius, are composed of 72 parts or one equivalent of the neutral sulphate, and 90 parts or ten equivalents of water. The crystals readily undergo the watery fusion when heated. At 32° F. 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, the primary form of which is a rhombic octohedron. Its specific gravity in this state is 2.462. (Haidinger.)

Bisulphate of soda may be formed in the same manner as the analogous salt of potash.

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 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 Ammonia.—This salt is easily prepared by neutralizing carbonate of ammonia with dilute sulphuric acid; and 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. It is sublimed by heat, but is partially decomposed at the same time. The crystals are composed of 40 parts or one equivalent of acid, and 17 parts or one equivalent of ammonia, combined according to Dr. Thomson with one and according to Berzelius with two equivalents of water.

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. Its primary form is 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. It consists of an equivalent of each ingredient.

Sulphate of Strontia.—This salt, the *celestine* of mineralogists, is less abundant than heavy spar. It occurs in prismatic crystals of peculiar beauty in Sicily, and its primary form is a right rhombic prism. 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. It requires about 3840 times its weight of boiling water for solution. According to Dr. Thomson it consists of 52 parts or one equivalent of strontia, and one equivalent of sulphuric acid.

Sulphate of Lime.—This salt is easily formed by mixing a solution of muriate 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 salt, 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 are generally flattened prisms, the primary form of which is a rhombic prism. The anhydrous compound consists of one equivalent of acid, and 28 parts or one equivalent of lime; and pure gypsum, according to Dr. Thomson, is composed of 68 parts or one equivalent of sulphate of lime, and 18 parts or two equivalents of water. The hydrous salt is deprived of its water by a low red heat, and in this state forms plaster of Paris. Its property of becoming hard, when made into a thin paste with water, is owing to the anhydrous sulphate combining chemically with that liquid, and thus depriving it of its fluidity.

Sulphate of lime has hardly any taste. It is considerably more soluble than the sulphates 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 freshly precipitated, it may be dissolved completely by dilute nitric acid. It is commonly believed to sustain a white heat without decomposition; but Dr. 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, which are irregular six-sided prisms, terminated by six-sided summits. Its primary form 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. The crystals are composed, according to Gay-Lussac, of 60 parts or one equivalent of the dry sulphate, and 63 parts or seven equivalents of water.

On mixing solutions of sulphate of magnesia and sulphate of potash in atomic proportion, and evaporating, a double salt is formed, which consists of one equivalent of each of the salts and six equivalents of water. The crystals are prismatic, but of a complicated nature, and are connected with an oblique rhombic prism. A similar double salt, isomorphous with the preceding, is formed by spontaneous evaporation from the mixed solutions of sulphate of ammonia and sulphate of magnesia. The crystals contain one equivalent of each of the two salts, and eight equivalents of water.

Sulphate of Alumina.—The pure sulphate is a compound of little interest; but with sulphate of potash it forms an interesting double salt, the well-known alum of commerce.

Alum has a sweetish astringent taste. It is soluble in five parts of water at 60° F., and in little more than its own weight of boiling water. The solution reddens litmus paper; but it is doubtful whether this is owing to an excess of acid, or to the weak affinity existing between alumina and sulphuric acid. (Page 589.) It crystallizes readily in octohedrons, or in segments of the octohedron, and the crystals contain 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.

There is some doubt as to the real composition of alum. According to Dr. Thomson, it is composed of

Sulphate of alumina,	174	3 equivalents.
Sulphate of potash,	88	1 equivalent.
Water,	225	25 equivalents.

Mr. Phillips, on the contrary, regards it as a compound of two equivalents of sulphate of alumina, one equivalent of bisulphate of potash, and 25 equivalents of water.

Sulphate of alumina forms with sulphate of ammonia, and with sulphate of soda, double salts, which are very analogous to common alum.

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; when it is 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 lampblack, four of burned alum, and eight of carbonate of potash. 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 potash 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.)

Sulphate 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 salt, and occur in flat rhombic prisms. It is insoluble in alcohol, but dissolves in twice and a half times its weight of cold water. If gradually heated it may be long exposed to a moderate red heat, without losing any of its acid. The crystals are composed of 40 parts or one equivalent of sulphuric acid, 36 parts or one equivalent of protoxide of manganese, and according to Mitscherlich of 45 parts or five equivalents of water.

With sulphate of ammonia this salt yields a double sulphate of ammonia and manganese, consisting of one equivalent combined with eight of water. It is isomorphous with the analogous salts of magnesia and protoxide of iron.

Sulphate of Iron.—Sulphate of the protoxide of iron, commonly called *green vitriol*, is formed by the action of dilute sulphuric acid on metallic iron (page 208), or by exposing protosulphuret of iron in fragments to the combined agency of air and moisture. This salt has a strong styptic, inky taste. Though neutral in composition, being composed of one equivalent of each element, it reddens the vegetable blue colours. It is insoluble in alcohol, but soluble in two parts of cold, and in three-fourths of its weight of boiling water. It occurs in right rhombic prisms, which are transparent, and of a pale-green colour. It consists of 76 parts or one equivalent of the dry salt, combined according to Thomson with seven, and according to Mitscherlich with six, equivalents of water. In the anhydrous state it is of a dirty white colour. It is this salt which is employed in the manufacture of fuming sulphuric acid. (Page 264.)

Protosulphate of iron forms double salts with sulphate of potash and sulphate of ammonia, the former of which contains

six and the latter eight equivalents of water. They are isomorphous with the analogous double sulphates of magnesia.

Protosulphate of iron absorbs oxygen from the air, especially when in solution, by which an insoluble subsulphate of the peroxide of iron is generated, consisting, according to Berzelius, of one equivalent of sulphuric acid, and four equivalents of peroxide of iron.

When a solution of protosulphate of iron is boiled with a little nitric acid, until the liquid acquires a red colour, and is then evaporated to dryness by a moderate heat, a salt remains, the greater part of which is soluble both in alcohol and water, and which attracts moisture from the atmosphere. The analysis of Berzelius has proved it to be a compound of 40 parts or one equivalent of peroxide of iron, and 60 parts or an equivalent and a half of sulphuric acid. It is, therefore, a sesquisulphate of the peroxide of iron.

By mixing sulphate of potash with persulphate of iron, and allowing the solution to crystallize by spontaneous evaporation, crystals are obtained similar to common alum in form, colour, taste, and composition. In this double salt sulphate of alumina is replaced by persulphate of iron, with which it is isomorphous.

A similar double salt may be made with a mixture of sulphate of ammonia and persulphate of iron.

Sulphate 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 made, for the purposes of commerce, by roasting native sulphuret of zinc. It crystallizes by spontaneous evaporation in transparent flattened four-sided prisms, and the primary form of the crystals is a right rhombic prism. 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 a strictly neutral salt, consisting of one equivalent of each of its elements. The crystals are composed of 82 parts or one equivalent of the anhydrous sulphate, and 63 parts or seven equivalents of water. Sulphate of potash crystallizes with sulphate of zinc as a double salt in flat rhombic prisms, the acute edges of which are replaced by planes.

Sulphate 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 primary form of sulphate of zinc. If an excess of sulphuric acid is present, the crystals are square prisms, which according to Messrs. 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.) Dr. Thomson says he analyzed both kinds, and found their composition identical. They consist of one equivalent of the anhydrous salt and seven equivalents of water. It is soluble in about three times its weight of water at 60° F.

This salt crystallizes with great facility when mixed with sulphate of potash, as a double sulphate of potash and nickel. The crystals are of an emerald-green colour, soluble in nine parts of cold water, and are composed of one equivalent of sulphate of nickel, one equivalent of sulphate of potash, and six equivalents of water. Its primary form is an oblique rhombic prism; but the general outline of the crystals is sometimes that of a six-sided prism. It is isomorphous with similar double salts of iron and manganese.

Sulphate of Chromium.—This salt may be formed by saturating dilute sulphuric acid with hydrated oxide of chromium. It crystallizes readily as a double salt, in octohedral crystals, with sulphate of potash and sulphate of ammonia. The double sulphate with ammonia, which has lately been prepared by my assistant, Mr. Warrington, appears almost black by reflected, but ruby-red by transmitted light. Sulphate of chromium and potash is similar in its appearance, and is described in his *Lehrbuch* by Berzelius, who states its composition to be exactly analogous to that of common alum.

Sulphates of Copper.—Sulphate of the protoxide of copper has not been obtained in a separate state. The sulphate of the peroxide, *blue vitriol*, employed by surgeons as an escharotic and astringent, may be prepared for chemical purposes by dissolving peroxide of copper in dilute sulphuric acid; but it is procured for sale by roasting the native sulphuret, so as to bring both its elements to a maximum of oxidation. This salt forms regular crystals of a blue colour, reddens litmus paper, and is soluble in about four of cold, and in two parts of boiling water. According to the researches of Proust, Thom-

son, and Berzelius, it is composed of eighty parts or one equivalent of peroxide of copper, eighty parts or two equivalents of acid, and ninety parts or ten equivalents of water. It is therefore, strictly, a bisulphate.

When pure potash is added to a solution of bisulphate of copper in a quantity insufficient for separating the whole of the acid, a pale bluish-green precipitate, the subsulphate, is thrown down, which is composed of one equivalent of acid and one equivalent of the peroxide.

Sulphate of copper and ammonia is generated by dropping pure ammonia into a solution of the bisulphate, until the subsalt 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 bisulphate 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 *ammoniaret of copper* of the pharmacopœia, contains sulphuric acid, peroxide 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 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 pure sulphate of the peroxide results*. The former is composed of one equivalent of sulphuric acid and one equivalent of the protoxide; and the latter of two equivalents of acid and one equivalent of the peroxide. (Thomson.) When this bisulphate, which is the salt employed in making corrosive sublimate, is thrown into hot water, decomposition ensues, and a yellow subsalt, formerly called *turpeth mineral*, subsides. This salt is composed of one equivalent of the acid and one equivalent of the peroxide. The hot water

* Donovan in the Annals of Philosophy, vol. xiv.

retains some of the sulphate in solution, together with free sulphuric acid.

Sulphate of Silver.—As this salt is rather sparingly soluble in water, it may be formed by double decomposition from concentrated solutions of nitrate 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 silver is isomorphous with the sulphate.

Sulphate 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 one equivalent of oxide of silver, one of acid, and two of ammonia; and it is formed by dissolving sulphate 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 arseniate of silver, which have a similar constitution, and are formed in the same manner. (Mitscherlich in An. de Ch. et Ph. xxxviii. 62.)

Double Sulphates by Fusion.—Berthier has remarked that some sulphates fuse together readily at a red heat, yielding uniform crystalline masses, which appear to be definite compounds. Thus sulphate of soda and sulphate of lime, when mixed in the ratio of their equivalents, fuse readily, and yield a mass similar to the mineral Glauberite. Sulphate of soda, fused in similar proportions with the sulphate of magnesia, baryta, and lead, gives analogous compounds. In all these instances, however, the affinity is so feeble, that it is overcome by the action of water. (An. de Ch. et Ph. xxxviii. 255.)

SULPHITES.

The salts of sulphurous acid have not hitherto been minutely examined. The sulphites of potash, 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, muriatic, phosphoric, and arsenic acids, decompose all the sulphites with effervescence, owing to the escape of sulphurous acid, which may easily be recognised 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 one equivalent of the acid and one equivalent of the base.

The hyposulphates and hyposulphites are of little importance, and their general character has already been sufficiently described. (Pages 269 and 271.) For a particular description of the hyposulphates, the reader is referred to an essay by Dr. Heeren (An. de Ch. et Ph. xl. 30).

SECTION II.

NITRATES.—NITRITES.—CHLORATES.—IODATES.

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 three following characters:—1st, by deflagrating with red-hot charcoal; 2d, by their power of dissolving gold leaf on

the addition of muriatic acid; 3d, by the evolution, when mixed with sulphuric acid, of dense, white, acid vapours, which are easily recognised to be nitric acid by their odour.

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 palladium is decomposed at such a moderate temperature, that a great part of the acid passes off unchanged. Nitrate of lead requires a red heat, by which it is resolved, as already mentioned, (page 238) into oxygen and nitrous acid. In some instances the changes are more complicated. With nitre, for example, a nitrite of potash is at first generated, with escape of oxygen gas: as the heat increases, the nitrous acid is converted into deutoxide of nitrogen and oxygen, the former of which remains in combination with potash; the deutoxide 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 potash. The preceding facts have been chiefly collected from the observations of Phillips and Berzelius. The tendency of potash and soda to unite with protoxide of nitrogen was first observed by Sir H. Davy; and M. Hess has lately remarked that similar compounds are obtained with soda, baryta, and lime, as well as potash, 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-muriatic 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 potash. 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 one equivalent of nitric acid, and one equivalent 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 only nitrates found native are those of potash, soda, lime, and magnesia.

Nitrate of Potash.—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 shaded situation, is moderately exposed to the air, nitric acid is gradually generated, and unites with the potash, lime, and magnesia which are commonly present in the mixture. On dissolving these salts in water, and precipitating the two earths by carbonate of potash, a solution is formed, which yields crystals of nitre by evaporation. The nitric acid is probably 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, where it is gradually generated.

Nitrate of potash 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° F., 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° F. 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 for 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, which is its primary form. (Mr. Brooke.) It is plentifully found in the soil in some parts of India.

Nitrate of Ammonia.—Nitrate of ammonia 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 Sir H. Davy. (Researches concerning the nitrous oxide.) If the evaporation is conducted at a temperature not exceeding 100° F., the salt is obtained in prismatic crystals which are composed, according to the experiments of Davy, Berzelius, and Thomson, of 67 parts or one equivalent of neutral nitrate of ammonia, and 9 parts or one equivalent of water. If the solution is evaporated at 212° F., fibrous crystals are procured; and if the heat be gradually increased to 300° F., 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 are deliquescent, and very soluble in water.

The change which nitrate of ammonia undergoes at a temperature varying between 400° and 500° of F. has already been explained. (Page 230.) When heated to 600°, it explodes with violence, being resolved into water, nitrous acid, deutoxide of nitrogen, and nitrogen. The fibrous variety was found by Sir H. 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 re-

agent, and for preparing pure baryta. It is easily prepared by digesting the native carbonate, reduced to powder, in nitric acid diluted with eight or ten times its weight of water. The salt crystallizes readily by evaporation in transparent octohedrons. Its crystals contain no water of crystallization, and are very apt to decrepitate by heat unless previously reduced to powder. They require twelve parts of water at 60° F., and three or four of boiling water for solution. They undergo the igneous fusion in the fire before being decomposed. They are insoluble in alcohol.

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 is anhydrous, crystallizes in the form of the regular octohedron, and undergoes no change in a moderately dry atmosphere. On some occasions this salt contains water of crystallization; and then assumes the form of a prism with ten sides and two summits. The hydrous salt, according to Mr. Cooper, contains 27.8 per cent of water.

Nitrates of Lime and Magnesia.—These salts are very deliquescent, and soluble in alcohol. By this character nitrate of lime is easily distinguished and separated from the nitrates of baryta and strontia. (Page 445.)

Nitrate of Copper.—This salt is prepared by the action of nitric acid on copper. (Page 232.) It crystallizes, though with some difficulty, in prisms, which are of a deep-blue colour, and deliquesce on exposure to the air. The crystals are composed of 108 parts or two equivalents of acid, 80 or one equivalent of the peroxide, and 126 or 14 equivalents of water. (Thomson.) It is therefore strictly a binitrate. The green insoluble subsalt, procured by exposing the binitrate to heat, contains, exclusive of water, one equivalent of acid and one equivalent of the peroxide. When heated to redness it yields pure peroxide of copper.

Nitrate of Lead.—This salt is formed by digesting litharge in dilute nitric acid. It crystallizes readily in octohedrons, which are almost always opaque. These crystals are anhydrous. This salt has an acid reaction, but is neutral in composition, consisting of 54 parts or one equivalent of acid, and 112 or one equivalent of protoxide of lead.

A di-nitrate of lead, composed of one equivalent of acid to

two equivalents of the protoxide, 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 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, (Poggendorff's 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 M. 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. The crystals are composed of 208 parts or one equivalent of the protoxide, 54 parts or one equivalent of acid, and two equivalents of water. These salts dissolve completely 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 deutoxide of nitrogen, and transparent prismatic crystals of the pernitrate are deposited as the solution cools. It is composed, according to Thomson, of one equivalent of the peroxide and one of the acid; and when put into hot water it is resolved into a soluble salt, the composition of which is unknown, and into a yellow subsalt. The latter was found by M. Grouvelle to consist of one equivalent of acid to two of the peroxide. (An. de Ch. et Phys. xix.)

Nitrate 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° F., 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.

Pure nitrate of silver, 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 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 clear glass vessels, 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 silver constitutes an extremely delicate test of the presence of organic matter, and has been properly recommended as such by Dr. John Davy. Its solution is always kept in the laboratory as a test for chlorine and muriatic acid.

Nitrate of silver, even after fusion, reddens vegetable colouring matters; but it is neutral in composition, consisting of one equivalent of acid and one of the oxide.

NITRITES.

Little is known with certainty concerning the compounds of nitrous acid with alkaline bases. Nitrite of potash 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. Two nitrites

of lead have been described in the Annales de Chimie, vol. 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 one equivalent of chloric acid and one equivalent of a protoxide, 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 potash 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. The mixture employed in the percussion locks for guns consists of sulphur and chlorate of potash; and is improved by the addition of charcoal.

All the chlorates hitherto examined are soluble in water, excepting the protochlorate of mercury, which is of sparing solubility. These salts are distinguished by the action of strong muriatic 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 potash and baryta.

Chlorate of Potash.—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 primary form is stated by Mr. Brooke to be an oblique rhombic prism. It is soluble in sixteen times its weight of water at 60° F., and in two and a half of boiling water. It is quite anhydrous, and when exposed to a temperature of 400° or 500° F.

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.

Chlorate of potash is made by transmitting chlorine gas through a concentrated solution of pure potash, until the alkali is completely neutralized. The solution which, after being boiled for a few minutes, contains nothing but muriate and chlorate of potash (page 293), 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 muriate 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 Mr. Wheeler. On digesting for a few minutes a concentrated solution of chlorate of potash with a slight excess of silicated hydrofluoric acid, the alkali is precipitated in the form of an insoluble double hydrofluate of silica and potash, while chloric acid remains in solution. The liquid after filtration is neutralized by carbonate of baryta, which likewise throws down the excess of hydrofluoric acid and silica. The silicated hydrofluoric acid employed in the process is made by conducting fluosilicic acid gas into water.

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 recognised by the facility with which their acid is decomposed by deoxidizing agents. Thus, sul-

phurous, phosphorous, muriatic, and hydriodic acids, deprive iodic acid of its oxygen, and set iodine at liberty. Sulphuretted hydrogen not only decomposes the acid of these salts, but occasions the formation of hydriodic acid by yielding hydrogen to the iodine. Hence an iodate may be converted into a hydriodate by transmitting a current of sulphuretted hydrogen 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 Potash.—This salt is easily procured by adding iodine to a concentrated hot solution of pure potash, until the alkali is completely neutralized. The liquid, which contains iodate and hydriodate of potash (page 316), is evaporated to dryness by a gentle heat, and the residue, when cold, is treated by strong alcohol. The iodate, which is insoluble in that menstruum, is left, while the hydriodate of potash is dissolved.

All the insoluble iodates may be procured from this salt by double decomposition. Thus iodate of baryta may be formed by mixing muriate of baryta with a solution of iodate of potash.

A biniodate of potash has lately been described by Serullas. It is formed by incompletely neutralizing chloride of iodine with potash or its carbonate, and setting it aside to cool. A peculiar compound of chloride of potassium and biniodate of potash falls; but on dissolving this substance, filtering, and exposing the solution to a temperature of 77° F., 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 of potash may be formed by mixing a large excess of sulphuric acid with a moderately dilute solution of iodate of potash. On evaporating at 77° F., 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 potash, above mentioned, may be formed by the action of muriatic acid on iodate of potash. By spontaneous evaporation it is obtained, sometimes in brilliant, transparent,

elongated prisms, and at another in hexagonal laminæ; but generally it crystallizes in right quadrangular prisms with its 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.

SECTION III.

SALTS OF THE ACIDS OF PHOSPHORUS AND ARSENIC.

PHOSPHATES.

The neutral salts of phosphoric acid with fixed bases sustain a red heat without losing any of their acid, and are all fusible at a high temperature; but from the effects of heat on phosphate of soda, it is probable that the phosphates generally, by a strong heat, are converted into pyrophosphates. The phosphates of the third class of metals, at least the greater part of them, are resolved into phosphurets by the combined agency of heat and charcoal. The alkaline phosphates are only partially decomposed under these circumstances, and the phosphates of lime, baryta, and strontia, undergo no change. The neutral phosphates, excepting those of potash, soda, and ammonia, are of sparing solubility in pure water; but they are all dissolved without effervescence in an excess of phosphoric or nitric acid, and are precipitated, for the most part unchanged, from the acid solutions by pure ammonia. Of all the phosphates, those of baryta, lime, and lead, and especially the latter, are the most insoluble.

The presence of a neutral phosphate in solution may be distinguished by the tests already mentioned in the section on phosphorus. (Page 276.) The insoluble phosphates are decomposed when boiled with a strong solution of carbonate of potash or soda, the acid uniting with the alkali so as to form a soluble phosphate. The earthy phosphates yield to this treatment with some difficulty, and require continued ebullition.

Several phosphates are met with in the native state, such as those of lime, manganese, iron, uranium, copper, and lead.

Phosphate of Potash.—This salt may be prepared by a process analogous to that described for the formation of phosphate of soda. It is deliquescent, and has not been procured in regular crystals. It consists of 35.71 parts or one equivalent of phosphoric acid, and 48 parts or one equivalent of potash.

The biphosphate may be formed by adding phosphoric acid to carbonate of potash until the liquid ceases to yield a precipitate with muriate of baryta, and setting aside the solution to crystallize. The primary form of the crystals is an octohedron with a square base; but they commonly occur in square prisms terminated with the planes of the primary form. They are composed of one equivalent of potash, two of phosphoric acid, and two equivalents of water. (Mitscherlich.)

Phosphate of Soda.—Of the alkaline phosphates, that with base of soda is the one generally employed, owing to the facility with which it is obtained in crystals. It is prepared on a large scale in chemical manufactories, by neutralizing the superphosphate of lime, procured by the action of sulphuric acid on burned bones (page 272), with carbonate of soda. The precipitated phosphate of lime is separated by filtration, and the clear liquid, after being duly concentrated, deposits crystals of phosphate of soda in cooling. It commonly contains traces of sulphuric acid, from which it may be purified by repeated solution in distilled water, and crystallization. It is customary in this process to employ a slight excess of the alkali, the presence of which facilitates the formation of crystals. On this account phosphate of soda has commonly an alkaline reaction; but when carefully prepared, Dr. Thomson says it is quite neutral.

This salt crystallizes in oblique rhombic prisms, which effloresce on exposure to the air, and require four parts of cold or two of boiling water for solution. According to the analysis of Mitscherlich, it may be inferred to consist of 35.71 parts or one equivalent of acid, 32 parts or one equivalent of soda, and 112.5 parts or $12\frac{1}{2}$ equivalents of water. This salt is employed in medicine as a laxative, and in chemistry as a reagent. By the action of heat it is converted into pyrophosphate of soda, which will be described in the course of this section.

Mr. Clarke of Glasgow has described a new phosphate of soda, different from the foregoing, in so far as it contains $7\frac{1}{2}$ instead of $12\frac{1}{2}$ equivalents of water. It was formed by exposing a solution of the common phosphate to a uniform temperature of about 90° F. The crystals are permanent in the air, and quite different in form from the common phosphate.

Biphosphate of soda is prepared by adding phosphoric acid to carbonate of soda until the solution ceases to precipitate muriate of baryta. 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. (Page 606.) 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 primary form of its ordinary crystals is a right rhombic prism, the smaller angle of which is 93° 54′.

A double phosphate of potash and soda may be formed by neutralizing biphosphate of potash with carbonate of soda. The primary form of its crystals is an oblique rhombic prism, which frequently occurs without any modification. The crystals consist of one equivalent of each base, and two of acid.

Phosphate of Soda and Ammonia.—This salt is easily prepared by dissolving one equivalent of muriate of ammonia and two equivalents of phosphate of soda in a small quantity of boiling water. As the liquid cools, prismatic crystals of the double phosphate are deposited, while muriate of soda remains in solution. Their primary 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 blow-pipe. When heated it parts with its water and ammonia, and a very fusible biphosphate of soda remains. It is composed of one equivalent of phosphate of soda, one equivalent of phosphate of ammonia, and ten equivalents of water.—(Mitscherlich.)

Phosphate of Ammonia.—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 primary form of the crystals is an oblique rhombic

prism, the smaller lateral angle of which is 84° 30′. They often occur in rhombic prisms with dihedral summits. They appear to contain an equivalent and a half of water. (Mitscherlich.)

The biphosphate is made in the same manner as the preceding biphosphates. The crystals are less soluble than the neutral phosphate, and undergo no change on exposure to the air. Their primary form is an octohedron with a square base; but the right square prism, terminated by the faces of the primary form, is the most frequent. They consist of one equivalent of ammonia, two of acid, and three of water.

Phosphate of Lime.—Chemists differ exceedingly as to the number of compounds which phosphoric acid is capable of forming with lime. There seems no doubt, however, from the researches of Berzelius and others, that phosphate of lime, as it exists in bones, or as obtained by mixing muriate of lime with neutral phosphate of soda in excess, is composed of 35.71 parts or one equivalent of phosphoric acid, and 28 or one equivalent of lime. This is the compound of which many urinary concretions consist.

Biphosphate of lime may be prepared by dissolving phosphate of lime in a slight excess of phosphoric acid. It is very soluble in water, but does not crystallize. A superphosphate is also formed by the action of sulphuric acid on phosphate of lime; but whether it is really a biphosphate mixed with free phosphoric acid, or some supersalt with a still larger proportion of acid, is as yet uncertain. The biphosphate exists in the urine.

Phosphate of Ammonia and Magnesia.—The simple phosphate of magnesia, which is prepared by mixing a solution of sulphate of magnesia with phosphate of soda, is of little interest; but the double phosphate is of importance as constituting a distinct species of urinary concretion. It is easily procured by adding carbonate of ammonia and afterwards phosphate of soda to a solution of sulphate of magnesia, when the double phosphate subsides in the form of minute crystalline grains. This salt is insoluble in pure water; but is dissolved by most acids, even by the acetic, and is precipitated unchanged when the solution is neutralized by ammonia.

The composition of this salt has not been satisfactorily de-

termined. On exposure to heat it emits water and ammonia, and a compound of phosphoric acid and magnesia is left, which is insoluble in water, but is dissolved by strong acids. When strongly heated it undergoes the igneous fusion, and yields a white enamel. According to Stromeyer, the salt, after being exposed to a red heat, contains 37 per cent of magnesia.

Pyrophosphates.—The only pyrophosphates which have been carefully studied are those of soda and silver. The former is readily prepared by the action of heat on phosphate of soda, as was mentioned in the section on phosphorus. (Page 278.) When the ignited mass is dissolved in water, and the solution set aside to evaporate spontaneously, crystals are obtained, having the general outline of an irregular six-sided prism, and the primary form of which is a rhombic octohedron. (Haidinger.) These crystals are permanent in the air, much less soluble in water than the common phosphate, and contain five equivalents of water.

The oxides of most metals of the second and third classes yield with pyrophosphoric acid insoluble or sparingly soluble salts, which may be prepared by double decomposition with pyrophosphate 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 pyrophosphate of soda; and that some of them, such as the pyrophosphate of lead, copper, nickel, cobalt, uranium, bismuth, manganese, and protoxide of mercury, are dissolved by it with great facility.

Stromeyer has lately made a comparative examination of phosphate and pyrophosphate of silver. The former is prepared by double decomposition from nitrate of silver and phosphate of soda, the characteristic yellow phosphate being generated. (Page 276.) The residual liquid contains free nitric acid as well as nitrate of soda, phosphoric acid uniting with more than an equivalent of oxide of silver;—a tendency to the formation of a subphosphate being manifested by phosphoric acid in regard to baryta and some other bases, as well as to oxide of silver. The yellow phosphate is speedily blackened by exposure to light; but when protected from this agent, it yields on drying an anhydrous powder, which has a specific gravity of 7.321. Its colour changes on the appli-

cation of heat to a reddish brown; but as it cools, the original tint returns. It sustains a red heat without fusion; but it fuses at a white heat, and if kept for some time in a fused state, a portion of pyrophosphate is generated. Pyrophosphate of silver is formed by double decomposition from pyrophosphate of soda and nitrate of silver, the remaining solution being neutral as at first. The white precipitate acquires a reddish tint by the agency of light, and on drying yields an anhydrous powder, which has a density of 5.306. It fuses with extreme facility, even at a temperature below that of redness, forming a dark-brown coloured liquid which, without suffering any appreciable decomposition, becomes a crystalline mass in cooling. It acquires a brownish-yellow tint on the first impression of heat, and, when cold, retains a shade of the same colour. By digestion in phosphate of soda, it is rapidly converted into phosphate of silver. The composition of both salts was formerly stated. (Page 279.)

Phosphites and Hypophosphites.—These compounds have hitherto been little examined, and are of no material importance. They do not, therefore, require a particular description. (Page 280.)

ARSENIATES.

All the arseniates are sparingly soluble in water, excepting those of potash, soda, ammonia, and perhaps lithia; but they are all dissolved without effervescence by dilute nitric acid as well as most other acids which do not precipitate the base of the salt, and are thrown down again unchanged by pure ammonia. Most of them bear a red heat without decomposition; but they are all decomposed by being 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 common metals, such as those 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 lead is the most insoluble.

The soluble arseniates are easily recognised by the tests described in the section on arsenic (page 510); and the insoluble arseniates, when boiled in a strong solution of the fixed alka-

line 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, nickel, cobalt, iron, copper, and lead, are natural productions.

Arsenic acid unites in two proportions with potash, soda, and ammonia, forming neutral and bi-salts, all of which, the neutral arseniate of potash excepted, may be obtained in crystals. They are all formed by adding arsenic acid to the alkaline carbonates in the manner described for forming the phosphates. Binarseniate of potash may be formed conveniently by heating to redness equal parts of nitrate of potash and arsenious acid, and continuing the heat until the effervescence arising from the nitre has ceased. These salts are so similar to the corresponding phosphates both in form and composition, that a particular description is unnecessary.

ARSENITES.

The only soluble compounds of arsenious acid and salifiable bases known to chemists are the arsenites of potash, soda, and ammonia, which may be prepared by boiling a solution of these alkalies in arsenious acid. The other arsenites are insoluble, or, at most, 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 the way of double decomposition.

On exposing the arsenites to heat in close vessels, the arsenious acid is 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. (Page 510.)

The soluble arsenites, if quite neutral, are characterized by forming a yellow arsenite of silver when mixed with the nitrate of that base, and a green arsenite of copper, *Scheele's green*, with sulphate of copper. When acidulated with acetic or muriatic acid, sulphuretted hydrogen causes the formation of orpiment. The insoluble arsenites are all decomposed when boiled in a solution of carbonate of potash or soda.

The arsenite of potash is the active principle of Fowler's arsenical solution.

SECTION IV.

CHROMATES.—BORATES.—FLUOBORATES.

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 the common 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 chromates are in general sufficiently distinguished by their colour. They may be known chemically by the following character:—On boiling a chromate in muriatic acid mixed with alcohol, the chromic acid is at first set free, and is then decomposed, a green muriate of the oxide of chromium being generated.

The only native chromate hitherto discovered is the red chromate of lead from Siberia, in the examination of which Vauquelin made the discovery of chromium.

Chromates of Potash.—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 potash, 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 its potash 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, the primary form of which, according to Mr. Brooke, is a right rhombic prism.

Chromate of potash 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° Fah.; but it is insoluble in alcohol. It has an alkaline reaction, and on this account M. Tassaert* regards it as a subsalt; but Dr. Thomson has proved that it is neutral in composition, consisting of fifty-two parts or one equivalent of chromic acid, and forty-eight parts or one equivalent of potash †.

Bichromate of potash, 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 primary form of which is an oblique rhombic prism. They have an exceedingly rich red colour, are anhydrous, and consist of one equivalent of the alkali, and two equivalents of chromic acid. (Thomson.) They are soluble in about ten times their weight of water at 60° F., and the solution reddens litmus paper.

The insoluble salts of chromic acid, such as the chromates of baryta, lead, protoxide of mercury, and silver, are prepared by mixing the soluble salts of those bases with a solution of chromate of potash. The two former are yellow, the third orange-red, and the fourth deep red or purple. The yellow chromate, which consists of one equivalent of acid, and one equivalent of oxide, is now extensively used as a pigment.

A dichromate of lead, composed of one equivalent of chromic acid, and two equivalents of protoxide of lead, may be formed by boiling carbonate of lead with excess of chromate of potash. It is of a beautiful red colour, and has been recommended by Mr. Badams as a pigment. (Annals of Philosophy, N. S. vol. ix. p. 303.) It may be also made by boiling chromate of lead with ammonia or lime water.

* An. de Ch. et de Ph. vol. xxii. † Annals of Philosophy, vol. xvi.

BORATES.

As the boracic is a feeble acid, it neutralizes alkalies imperfectly, and hence the borates of soda, potash, and ammonia 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 muriatic, 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 all 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. (Page 283.)

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 hexahedral prisms, 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, according to the analysis of Dr. Thomson, are composed of forty-eight parts or two equivalents of boracic acid, thirty-two or one equivalent of soda, and seventy-two or eight equivalents 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 M. 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 specific gravity of the solution is at 30° or 32° of Beaume's hydrometer; the solution is then very slowly cooled; and when the temperature descends to about 133° F. 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.)

Fluoborates.—The compounds of this acid with salifiable bases are as yet almost entirely unknown. Dr. Davy ascertained that it unites with ammoniacal gas in three proportions, forming salts, one of which is solid, and the two others liquid.

SECTION V.

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.

All the carbonates, excepting those of potash, soda, and lithia, may be deprived of their acid by heat. The carbonate of baryta and strontia, especially the former, requires 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 excepting those of potash, 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.

The former nomenclature of the salts is peculiarly excep-

tionable as applied to the carbonates. The two well-known carbonates of potash, for example, are distinguished by the prepositions *sub* and *super*, as if the one had an alkaline, and the other an acid reaction; whereas, in fact, according to their action on test paper, they are both subsalts. I shall adopt the nomenclature which has been employed with other salts, applying the generic name of carbonate to those salts which contain one equivalent of carbonic acid, and one equivalent of the base,—compounds which may be regarded as neutral in composition, however they may act on the colouring matter of plants.

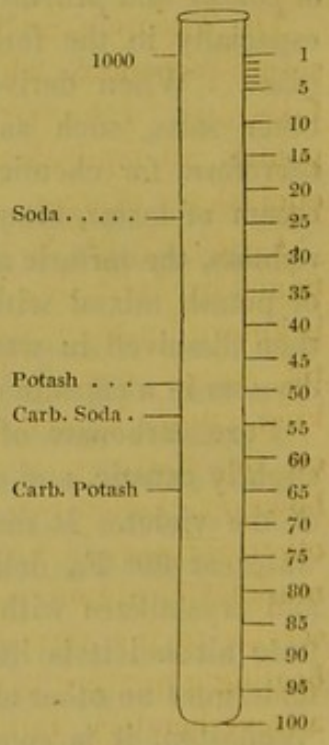
Several of the carbonates occur native, among which may be enumerated the carbonates of soda, baryta, strontia, lime, magnesia, manganese, protoxide of iron, copper, lead, and the double carbonate of lime and magnesia.

Carbonate of Potash.—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 of potash, thus obtained, is known in commerce by the names of *potash* and *pearlash*, and is employed in many of the arts, especially in the formation of soap and the manufacture of glass. When derived from this source it always contains other salts, such as sulphate and muriate of potash; and therefore, for chemical purposes, it should be prepared from cream of tartar, bitartrate of potash. On heating this salt to redness, the tartaric acid is decomposed, and a pure carbonate of potash 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 potash has a taste strongly alkaline, is slightly caustic, and communicates a green to the blue colour of the violet. It dissolves in less than an equal weight of water at 60° F., 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. According to the analysis of Dr. Wollaston, it is composed of 22 parts or one equivalent of carbonic acid, and 48 parts or one equivalent of potash.

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 potash contained in a given weight of impure carbonate. A convenient mode of effecting this object is described by Mr. Faraday in his excellent work on *Chemical Manipulation*. Into a tube sealed at one end, 9½ 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 wood-cut. Opposite to the numbers 23.44, 48.96, 54.63, and 65, draw a line, and at the first write soda, at the second potash, at the third carbonate of soda, and at the fourth carbonate of potash. 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 eight measures of distilled water. This is the standard acid to be used in all the experiments; and if this acid is poured into the tube till it reaches either of the four marks just mentioned, we shall obtain the exact quantity which is necessary for neutralizing 100 grains of the alkali written opposite to it. If, when the acid reaches the word *carb. potash*, 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 potash. 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 Potash is made by transmitting a current of carbonic acid gas through a solution of carbonate of potash; and it is also prepared by evaporating a mixture of carbonate of ammonia and carbonate of potash, the ammonia being dissipated in a pure state. By slow evaporation, the bicarbonate is deposited from the liquid in prisms with eight sides, terminated with dihedral summits. Its primary form is a right rhomboidal prism.

Bicarbonate of potash, 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° F. for solution, and is much more soluble at 212° F.; but it parts with some of its acid at that temperature. At a low red heat it is converted into the carbonate. From the analysis of Dr. Wollaston, the crystals consist of one equivalent of potash, two of acid, and one of water. I have likewise analyzed this salt, and obtained a similar result.

Dr. Thomson, in his "First Principles," has described a sesqui-carbonate, which was discovered by Dr. Nimmo of Glasgow. Its crystals are composed of one equivalent of potash, an equivalent and a half of carbonic acid, and six equivalents of water.

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 and muriates of potash and soda, and on this account is of little service to the chemist. 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 lime 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.

Carbonate of soda crystallizes in octohedrons with a rhombic base, 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. According to Dr. Thomson the crystals are composed of 22 parts or one equivalent of carbonic acid, 32 parts or one equivalent of soda, and 90 parts or ten equivalents of water. The water of crystallization is apt to vary according to the temperature at which the crystals are formed.

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 processes as bicarbonate of potash, and is deposited in 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° F. for solution. It is decomposed partially at 212° F. and is converted into the carbonate by a red heat. It is composed, according to Thomson, of two equivalents of acid, one of the base, and one of water. This result I have confirmed by my own observation.

Sesqui-carbonate.—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 Mr. Phillips*, whose analysis corresponds with that of Klaproth. It consists of one equivalent of soda, an equivalent and a half of acid, and two equivalents of water.

Carbonate of Ammonia.—The only method of procuring this salt is by mixing dry carbonic acid over mercury, with twice its volume of ammoniacal gas. It is a dry white vola-

* Journal of Science, vol. vii.

tile powder of an ammoniacal odour, and alkaline reaction. From the proportion of its constituents by volume, it is easy to infer that it is composed, by weight, of 22 parts or one equivalent of carbonic acid, and 17 parts or one equivalent of ammonia.

Bicarbonate of Ammonia.—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 six-sided prisms, which have no smell, and very little taste: their primary form, according to Mr. Miller of Cambridge, is a right rhombic prism. Berthollet ascertained that it contains twice as much acid as the carbonate.

Sesqui-carbonate of Ammonia.—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 muriate of ammonia with one part and a half of carbonate of lime, carefully dried. Double decomposition ensues during the process; muriate of lime remains in the retort, and sesquicarbonate of ammonia is sublimed. The carbonic acid and ammonia are, indeed, in proper proportion in the mixture for forming the real carbonate; but from the heat employed in the sublimation, part of the ammonia is disengaged in a free state.

The salt thus formed consists, according to the analysis of Mr. Phillips, Dr. Ure, and Dr. Thomson, of 33 parts or an equivalent and a half of carbonic acid, of 17 parts or one equivalent of ammonia, and 9 parts or one equivalent of water. When recently prepared it is hard, compact, semi-transparent, of a crystalline texture, and pungent ammoniacal odour; but if exposed to the air, it loses weight rapidly, and is converted into an opaque brittle mass, which is the bicarbonate.

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 exceedingly insoluble in distilled water, requiring 4300 times its weight of water at 60° F., and 2300 of boiling water for solution; but when recently pre-

cipitated, 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 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 crystals. It may also be formed by precipitation. Though sparingly soluble in pure water, it is dissolved by carbonic acid in excess. On this account the spring water of limestone districts always contains carbonate of lime, which is deposited when the water is boiled.

Carbonate of Magnesia.—This salt is easily prepared by adding carbonate of potash in slight excess to a hot solution of sulphate of magnesia, and edulcorating the precipitated carbonate with warm water. It requires 2493 parts of cold, and 9000 of hot water for solution. It is so soluble in an excess of carbonic acid that sulphate of magnesia is not precipitated at all in the cold by alkaline bicarbonates, or by sesqui-carbonate of ammonia. On allowing a solution of carbonate of magnesia in carbonic acid to stand in an open vessel, minute crystals are deposited, which consist of 42 parts or one equivalent of the carbonate, and 27 parts or three equivalents of water. (Dr. Henry and Berzelius.)

Native carbonate of magnesia, according to the analysis of Dr. Henry and Stromeyer, is similar in composition to the precipitated carbonate.

Carbonate 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 rhomboids or hexagonal prisms. This protocarbonate of iron is contained 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 protosulphate 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.

Carbonate of Copper.—The beautiful green mineral, called *Malachite*, is a carbonate of the peroxide of copper; and a similar compound may be formed from the persulphate by double decomposition, or by exposing metallic copper to air and moisture. According to the analysis of malachite by Mr. Phillips, this mineral is composed of 80 parts or one equivalent of peroxide of copper, one equivalent of carbonic acid, and one equivalent of water. (Journal of Science, vol. iv.)

The blue pigment called *verditer*, said to be prepared by decomposing nitrate of copper by chalk, is an impure carbonate *.

Carbonate of Lead.—This salt, which is the *white lead* or *ceruse* of painters, occurs native, but may be obtained by double decomposition. It is prepared for the purposes of commerce by exposing coils of thin sheet lead to the vapour of vinegar, when, by the action of the acid fumes, the lead is both oxidized and converted into a carbonate.

Double Carbonates.—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 equivalents, yields uniform crystalline compounds, which have all the appearance of being definite. An equivalent of dolomite, double carbonate of lime and magnesia, fuses in like manner with four equivalents of carbonate of soda. Five parts of carbonate of potash and four of carbonate of soda, corresponding to an equivalent 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 equivalents; 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. 246.)

* On the composition and preparation of this pigment, the reader may consult the remarks of Mr. Phillips in the essay quoted in the text.

SECTION VI.

SALTS OF THE HYDRACIDS.

By the expression *salts of the hydracids* is meant those saline compounds, the acid of which contains hydrogen as one of its elements. These salts, owing to the peculiar constitution of their acid, have certain common properties, and may therefore be described advantageously in the same section. Many of the circumstances relative to them have already been mentioned in sufficient detail, partly in the remarks introductory to the study of the metals (page 416), and partly in the description of the individual metals themselves. It will hence suffice to describe the salts of the hydracids chiefly in a general manner, giving a particular description of those compounds only, which are possessed of some peculiar interest.

Most of the salts which are composed of a hydracid and a metallic oxide are so constituted, that the oxygen of the oxide contains a quantity of oxygen precisely sufficient for forming water with the hydrogen of the acid. This is true of all the neutral compounds containing a protoxide, without exception, and it likewise holds good in many other cases. Thus, in the soluble permuriate of iron, the oxide, which contains an equivalent and a half of oxygen, is united with an equivalent and a half of acid; and in the soluble permuriate of copper, the oxide, which contains two equivalents of oxygen, is united with two equivalents of acid.

The elements of the salts of the hydracids, as mentioned at page 416, are very prone to arrange themselves in a new order. All these salts are exposed to the action of two divellent and three quiescent affinities. In muriate of soda, for example, the forces which tend to prevent a change are the attraction of sodium for oxygen, of chlorine for hydrogen, and of muriatic acid for soda; while the opposite affinities are the attraction of chlorine for sodium and of hydrogen for oxygen. The latter always preponderate when heat is employed, because the volatility of water favours the production of that fluid; and in many instances the affinities appear so nicely balanced, that the co-

hesion of one of the compounds is sufficient to influence the result, as is exemplified by muriate of soda, which, in the act of crystallizing, is converted into chloride of sodium.

MURIATES OR HYDROCHLORATES.

Most of the salts of muriatic acid are soluble in water, and some of them exist only in a state of solution. They are distinguished from other salts by forming the white insoluble chloride of silver when mixed with the nitrate of that base, and by being decomposed with disengagement of muriatic acid fumes by strong sulphuric acid. The decomposition of the muriates, owing to the volatile nature of their acid, is effected by phosphoric and arsenic acids at the temperature of ebullition.

Muriate of Potash and Soda.—These salts exist only in a state of solution, and are frequently contained in mineral springs. Muriate of soda, as already mentioned in the section on sodium, is the chief constituent of sea water.

Muriate 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 method is to decompose sulphate of ammonia by the muriate either of soda or magnesia. Double decomposition ensues, giving rise in both cases to muriate of ammonia, and to sulphate of soda, when the muriate of that base is used, or to sulphate of magnesia when muriate of magnesia is employed. The sal-ammoniac is afterwards obtained in a pure state by sublimation. Sulphate of ammonia may be conveniently procured for this purpose, either by lixiviating the soot of coal, which contains that salt in considerable quantity; or by digesting impure carbonate of ammonia, procured by exposing bones and other animal matters to a red heat, with gypsum, so as to form an insoluble carbonate of lime, and a soluble sulphate of ammonia.

Muriate of ammonia has a pungent saline taste, and is soluble in three parts of water at 60° F., causing a considerable reduction of temperature during its solution. Boiling water dissolves about an equal weight, and the solution deposites crystals in cooling. At a temperature below redness,

it sublimes without fusing or undergoing any change in composition, and condenses on cool surfaces as an anhydrous salt, which attracts humidity in a moist atmosphere, but if pure is not deliquescent.

When muriatic acid gas is mixed with an equal volume of ammonia, both gases disappear entirely, and pure muriate of ammonia results. It hence follows that this salt is composed by weight of 37 parts or one equivalent of muriatic acid, and 17 parts or one equivalent of ammonia.

Muriate of Baryta.—This compound is best formed by dissolving carbonate of baryta, either native or artificial, in muriatic acid diluted with three parts of water. It may also be formed by the action of muriatic acid on hydro-sulphuret of baryta (page 440,) or by heating sulphate of baryta with an equal weight of muriate of lime until fusion takes place, and then dissolving the muriate of baryta which is generated, and separating it by means of a filter from the sulphate of lime.

Muriate of baryta, when its solution is gently evaporated, crystallizes readily in flat rectangular plates, bevelled at the edges, much resembling crystals of heavy spar. The crystals, according to Thomson, consist of 115 parts or one equivalent of muriate of baryta, and 9 parts or one equivalent of water. On heating the crystals to redness, two equivalents of water are expelled, and 106 parts or one equivalent of chloride of barium are left. The crystals, therefore, may be regarded as chloride of barium with two equivalents of water of crystallization. The fact, noticed by Mr. Graham, that the pulverized crystals lose two equivalents of water in a very dry atmosphere, and recover them again in a moist one, is very favourable to this opinion.

Crystallized muriate of baryta is insoluble in pure alcohol. It requires about two and a half times its weight of water at 60° F. for solution, and is much more soluble in boiling water. The crystals are permanent in the air.

This salt is much employed as a re-agent in chemistry.

Muriate of strontia is made in the same manner as muriate of baryta, from which it is distinguished by forming prismatic crystals, by its solubility in alcohol, and by imparting a red tint to flame. The crystals consist of one equivalent of muriate

of strontia, and eight equivalents of water; and when heated to redness, nine equivalents of water are expelled, and one equivalent of chloride of strontium remains.

The crystallized muriate attracts humidity from a moist atmosphere, but, if pure, it is permanent in a moderately dry air. The crystals are exceedingly soluble in boiling water, and require for solution about twice their weight of water at 60° F.

Muriate of lime is formed by neutralizing muriatic acid with pure marble. The salt is very soluble both in water and alcohol, and deliquesces with rapidity even in a dry atmosphere. It crystallizes, though with considerable difficulty, in prisms, which consist, according to Thomson, of one equivalent of muriate of lime, and six equivalents of water. When heated, seven equivalents of water are expelled and a chloride remains. It may of course be regarded as chloride of calcium with seven equivalents of water of crystallization.

The crystallized muriate is the compound which produces such an intense degree of cold when mixed with snow. It is prepared for this purpose by evaporating the solution until a drop of it on falling upon a cold saucer becomes solid.

Muriate of magnesia exists in many mineral springs, and is contained abundantly in sea-water. When muriate of soda is separated from sea-water by crystallization, an uncrystallizable liquid, called *bittern*, is left, which consists chiefly of muriate of magnesia, and is much employed in the manufacture of sal-ammoniac for decomposing sulphate of ammonia.

Muriate of magnesia has a bitter taste, is highly soluble in alcohol and water, and deliquesces with rapidity in the open air. When heated to redness it loses a portion of its acid as well as water.

Muriate of iron.—When iron is dissolved in dilute muriatic acid, a muriate of the protoxide is generated, which yields pale green coloured crystals when the solution is concentrated by evaporation. This salt is much more soluble in hot than in cold water, and is not deliquescent. It absorbs oxygen with rapidity from the air, forming an insoluble muriate of the peroxide. When boiled with a little nitric acid a soluble muriate of the peroxide is generated, which is of a red colour,

crystallizes with difficulty, deliquesces on exposure to the air, and is dissolved by alcohol. It is composed of one equivalent of the peroxide, and an equivalent and a half of muriatic acid, being a sesqui-muriate.

The black oxide is also dissolved by muriatic acid, forming a dark coloured solution, which may be regarded as a mixture of the muriates of the peroxide and protoxide of iron. (Page 485.)

Muriates of tin.—The protomuriate is conveniently prepared by digesting granulated tin in strong muriatic acid as long as hydrogen gas is disengaged, atmospheric air being excluded at the same time. On making a concentrated hot solution, the salt is deposited in the form of small white needles; but by slow evaporation it yields colourless, transparent, prismatic crystals, which consist of one equivalent of acid, one of protoxide of tin, and two of water. From the strong tendency of protoxide of tin to pass into its highest stage of oxidation, the protomuriate is much employed as a deoxidizing substance, especially for precipitating easily reducible metals from their solution; and owing to this tendency, it absorbs oxygen rapidly from the atmosphere. Its solution should be preserved in well stopped bottles, in contact with a few particles of metallic tin, which restores any peroxide that may be formed to its original condition.

The *permuriate*, so extensively employed as a base in dyeing, is generally prepared by dissolving tin in nitro-muriatic acid. The process is one of delicacy; for should the temperature be much raised by the heat disengaged by chemical action, as is sure to happen if strong acid is used, and much tin is 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 muriatic 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 oxidize the protomuriate either by chlorine or by gentle heat and nitric acid. The latter is the most convenient.

HYDRIODATES.

Hydriodic acid unites with the alkalies and alkaline earths, with magnesia, and with the oxides of manganese, zinc, and iron. With several of the metallic oxides it does not enter into combination. Thus, on mixing hydriodate of potash with a salt of mercury or silver, the iodides of these metals are deposited. With acetate of lead a yellow compound is thrown down, which is an iodide of lead.

The most direct method of forming the hydriodates of the alkalies and alkaline earths, all of which are soluble in water, is by neutralizing those bases with hydriodic acid. The hydriodates of iron and zinc may be made by digesting small fragments of those metals with water in which iodine is suspended.

All the hydriodates are decomposed by sulphuric and nitric acids, or by chlorine, the hydriodic acid being deprived of hydrogen, and the iodine set at liberty. (Page 319.) They are not decomposed by exposure to the air.

The only hydriodates which have hitherto been found native are those of potash and soda, the sources of which have already been mentioned in the section on iodine. Of these salts, hydriodate of potash is the most common.

Hydriodate of Potash.—This salt, which is the only hydriodate requiring particular description, exists only in solution; for it is converted in the act of crystallizing into iodide of potassium. It is exceedingly soluble in boiling water, and requires only two-thirds of its weight of water at 60° F. for solution. It is dissolved freely by alcohol; and when a saturated, hot, alcoholic solution is set aside to cool, iodide of potassium is deposited in cubic crystals. A solution of hydriodate of potash is capable of dissolving a large quantity of iodine, a property which is common to all the hydriodates.

Hydriodate of potash is easily made by neutralizing hydriodic acid with pure potash; but in preparing a considerable quantity of the salt, as for medical use, it is desirable to dispense with the preliminary step of making the acid. With this intention the following method, which I have described in the Edinburgh Medical and Surgical Journal for July 1825, may be employed

with advantage. The process consists in adding to a hot solution of pure potash as much iodine as it is capable of dissolving, by which means a deep brownish-red coloured fluid is formed, consisting of iodate and hydriodate of potash, together with a large excess of free iodine. Through this solution a current of sulphuretted hydrogen gas is transmitted until the free iodine and iodic acid are converted into hydriodic acid, changes which may be known to be accomplished by the liquid becoming quite limpid and colourless. The solution is then gently heated in order to expel any excess of sulphuretted hydrogen, and after being filtered, any free hydriodic acid is exactly neutralized by pure potash.

A still easier process has been proposed, which consists in adding iodine to a solution of hydrosulphate of potash, or the common *hepar-sulphuris* of the Pharmacopœia (page 413), until the potash is exactly neutralized. The hydriodate is then formed at once, without the necessity of a current of sulphuretted hydrogen gas; but when made with liver of sulphur, it contains a considerable quantity of sulphate of potash, and is therefore impure. Another mode of preparation is by decomposing hydriodate of zinc or iron by a quantity of carbonate of potash just sufficient to precipitate the oxide.

HYDROBROMATES.

The salts of hydrobromic acid have as yet been but partially examined, and the chief facts known respecting them have already been mentioned in the section on bromine.

HYDROFLUATES.

Hydrofluoric acid unites readily with the pure alkalies, yielding soluble hydrofluates, which are converted into metallic fluorides by the action of heat. The neutral hydrofluates of the alkalies, those namely that contain one equivalent of acid and one equivalent of base, have an alkaline reaction. It may be doubted if this acid can unite at all with the alkaline earths; for it yields with them insoluble compounds, which have all the characters of metallic fluorides. The same remark applies to the action of hydrofluoric acid on the earths, with

the exception of alumina and zirconia, which form soluble hydrofluates.

The salts of hydrofluoric acid are recognised by forming with muriate of lime a white gelatinous precipitate, which yields hydrofluoric acid when heated with concentrated sulphuric acid.

It is doubtful if any hydrofluate exists ready formed in the mineral kingdom. Four minerals may be enumerated as such; namely, *topaz* or the double hydrofluate of silica and alumina, hydrofluate of cerium, double the hydrofluate of cerium and yttria, and *cryolite* or the double hydrofluate of alumina and soda. It is probable, however, that these compounds, like fluor spar, are metallic fluorides.

Hydrofluate of Potash.—Potash unites with hydrofluoric acid in two proportions, forming a hydrofluate and bi-hydrofluate; the former of which consists of one, and the latter of two equivalents of acid, united with one equivalent of potash. The hydrofluate, which has an alkaline reaction, is best prepared by supersaturating carbonate of potash with hydrofluoric acid, evaporating the solution to dryness, and expelling the excess of acid by heat. The residue has a sharp saline taste; is deliquescent, and crystallizes with difficulty; but when evaporated at a temperature between 95° and 104°, it forms cubic crystals. These crystals, like the salt after being heated, are most probably fluoride of potassium.

The bi-hydrofluate is easily procured by adding to hydrofluoric acid a quantity of potash insufficient for neutralizing it completely, and concentrating the solution. By slow evaporation it yields rectangular tables, the lateral edges of which are bevelled. This salt has an acid reaction, is soluble in water, and decomposed by heat.

Hydrofluate of Soda.—The neutral and acid hydrofluate of soda may be formed in the same manner as the preceding salts. The acid hydrofluate consists of one equivalent of base and two of the acid, possesses a sharp and purely sour taste, is but sparingly soluble in cold water, and crystallizes in transparent rhombohedrons. The neutral hydrofluate is sparingly soluble in water, and its solubility is not increased by elevation of temperature. It is almost completely insoluble in alcohol. It commonly crystallizes in cubes like chloride of

sodium, but assumes the form of an octohedron when carbonate of soda is present.

The neutral and acid hydrofluate of lithia are sparingly soluble in water.

The neutral *hydrofluate of ammonia* may be prepared by mixing in a platinum crucible 1 part of sal-ammoniac and 2¼ parts of fluoride of sodium, both in fine powder and quite dry, and applying a gentle heat with a spirit lamp. The hydrofluate of ammonia sublimes, and condenses in small prisms on the lid of the crucible, if kept cool, without any admixture of muriate of ammonia. Chloride of sodium is generated at the same time.

This salt is permanent in the air, slightly soluble in alcohol, and copiously dissolved by water. It corrodes glass vessels, even in its dry state. In solution it gradually parts with ammonia, and is converted into a deliquescent bi-hydrofluate.

It is doubtful if the alkaline earths combine at all with hydrofluoric acid. On digesting recently precipitated carbonate of baryta in an excess of this acid, carbonic acid is gradually evolved, and a compound is formed, which appears to be a fluoride of barium. It is very slightly soluble in water and hydrofluoric acid; but it is dissolved freely by muriatic acid, and ammonia added to the solution causes a precipitate, which is a compound of fluoride and chloride of barium. A similar substance is formed on mixing a solution of muriate of baryta with an alkaline hydrofluate.

On digesting newly precipitated carbonate of lime in an excess of hydrofluoric acid, a granular fluoride of calcium is generated. It is insoluble in water and hydrofluoric acid, and is very slightly dissolved by muriatic acid. It may also be formed by double decomposition; but it then forms a translucid jelly, which fills up the pores of a filter, and is therefore washed with difficulty. This compound appears to be identical with the beautiful mineral commonly known by the name of *fluor* or *Derbyshire spar*. This mineral frequently accompanies metallic ores, especially those of lead and tin; and it often occurs crystallized either in cubes or some of its allied forms. 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

is employed in forming vases, as a flux to metallurgic processes, and in the preparation of hydrofluoric acid. The nature and composition of this substance were considered on a former occasion. (Page 335-7.)

For an account of the action of hydrofluoric acid on other metallic oxides, I may refer to an essay of Berzelius on this subject. (Annals of Philosophy, xxiv. 335.)

HYDROSULPHURETS OR HYDROSULPHATES.

Sulphuretted hydrogen forms soluble salts with the alkalies, alkaline earths, and magnesia, most of which are capable of crystallizing. With the alkalies, indeed, if not with other bases, this acid unites in two proportions, forming a hydrosulphate and a bi-hydrosulphate. It may be doubted if sulphuretted hydrogen is capable of uniting with any of the oxides of the common metals; for when their salts are mixed with hydrosulphate of potash, a precipitate takes place, which in most, if not in all cases, is the sulphuret of a metal, and not the hydrosulphate of its oxide. Thus, by the action of hydrosulphate of potash on the nitrates of lead, copper, bismuth, silver, or mercury, nitrate of potash is formed, water is generated, and a metallic sulphuret subsides. The precipitates occasioned by hydrosulphate of potash in a salt of iron, zinc, and manganese, may also be regarded as sulphurets; for though sulphuric acid decomposes these compounds with evolution of sulphuretted hydrogen, it does not follow that that acid had previously existed in them.

As sulphuretted hydrogen is a weak acid, and naturally gaseous, its salts are decomposed by most other acids, such as the sulphuric, muriatic, and acetic, with disengagement of sulphuretted hydrogen gas, a character by which all the hydrosulphates are easily recognised. They are decomposed, likewise, by chlorine and iodine, with separation of sulphur, and formation of a muriate or hydriodate. When recently prepared, they form solutions which are colourless, or nearly so; but on exposure to the air, oxygen gas is absorbed, a portion of its acid is deprived of its hydrogen, and a sulphuretted hydrosulphate of a yellow colour is generated. By continued exposure, the whole of the sulphuretted hydrogen is decomposed, water and hypo-sulphurous acid being produced.

The hydrosulphates of baryta and strontia, prepared by dissolving the sulphurets of barium and strontium in water, are sometimes used in preparing the salts of those bases. The hydrosulphates of potash and ammonia are employed as re-agents.

Hydrosulphate of Potash.—This salt is made by transmitting a current of sulphuretted hydrogen gas into a solution of pure potash, contained in Woulfe's apparatus, and continuing the operation as long as the gas is absorbed. When all the alkali is combined with sulphuretted hydrogen, it is no longer able to precipitate a salt of magnesia. If the alkali is completely saturated with the gas, the resulting compound, though it has still an alkaline reaction, is a by-hydrosulphate. This salt has an alkaline bitter taste, and crystallizes in six-sided prisms, which are deliquescent and soluble in alcohol as well as water.

Hydrosulphate of Ammonia.—This salt is obtained in the form of a volatile fluid, called *Fuming Liquor of Boyle*, by heating a mixture of one part of sulphur, two of sal-ammoniac, and two of unslaked lime. The changes which ensue have lately been examined by Gay-Lussac. The volatile products are ammonia and hydrosulphuret of ammonia; and the fixed residue consists of sulphate of lime with chloride and sulphuret of calcium. The sulphuretted hydrogen is formed from the hydrogen of muriatic 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 muriatic acid and sulphur. Hydrosulphuret 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 sulphuretted hydrogen gas.

Hydroseleniates.—These salts have been little examined, owing to the scarcity of selenium. The researches of Berzelius have demonstrated, however, that hydroselenic acid forms with the alkalies soluble compounds, which are very analogous in their chemical relations to the hydrosulphates, and which precipitate the salts of the common metals, giving rise in most, if not in all cases, to the formation of a metallic seleniuret.

HYDROCYANATES.

Hydrocyanic acid unites with alkalies and alkaline earths, and probably with several other bases; but these compounds have as yet been studied in a very imperfect manner. Hydrocyanate of potash is the best known. It is generated by decomposition of water when cyanuret of potassium is put into that fluid, and may be made directly by mixing hydrocyanic acid with a solution of potash. M. Robiquet recommends that it should be prepared by exposing ferrocyanate of potash to a long-continued red heat, by which means the ferrocyanic acid is decomposed, and a dark mass, consisting of cyanuret of potassium, mixed with charcoal and iron, remains in the crucible. This process succeeds well if carefully performed; but it is difficult to destroy the whole of the ferrocyanic acid, without decomposing at the same time the cyanuret of potassium. If the decomposition of the ferrocyanate is complete, the residue should form a colourless solution, which does not produce Prussian blue with a salt of the peroxide of iron.

Hydrocyanate of potash appears to exist only in solution; for when evaporated to dryness, it is converted into cyanuret of potassium, a compound which is far less liable to spontaneous decomposition than hydrocyanic acid, and is capable of supporting a very high temperature in close vessels without change. It is deliquescent, and highly soluble in water. The solution gives a green colour to violets, and has an alkaline taste, accompanied with the flavour and a faint odour of hydrocyanic acid. It is decomposed by nearly all the acids, even by the carbonic, and on this account should be preserved in well-closed vessels. It acts upon the animal system in the same manner as hydrocyanic acid, and MM. Robiquet and Villermé have proposed its employment in medical practice, as being more uniform in strength, and less prone to decomposition, than hydrocyanic acid. (Jour. de Physiologie, vol. iii.)

FERROCYANATES.

The neutral ferrocyanates, so far as is known, appear to be formed in the same manner as the salts of the hydracids

in general; namely, the hydrogen of the acid is in exact proportion for forming water with the oxygen of the salifiable base with which it is united. Thus, ferrocyanate of potash is composed of one equivalent of ferrocyanic acid, which contains two equivalents of hydrogen (page 392,) and two of potash. With the alkalies and alkaline earths this acid forms soluble compounds; but it precipitates nearly all the salts of the common metals, giving rise either to the ferrocyanate of an oxide or the ferrocyanuret of a metal.

Ferrocyanate of Potash.—This salt, sometimes called *triple prussiate of potash*, is prepared by digesting pure ferrocyanate of the peroxide of iron in potash until the alkali is neutralized, by which means the peroxide of iron is set free, and a yellow liquid is formed, which yields crystals of ferrocyanate of potash by evaporation. This salt is made on a large scale in the arts by igniting dried blood or other animal matters, such as hoofs and horns, with potash and iron. By the mutual reaction of these substances at a high temperature, ferrocyanuret of potassium, consisting of one equivalent of the radical of ferrocyanic acid (page 393), and two equivalents of potassium, is generated. Such at least is inferred to be the product; for on digesting the residue in water, a solution of ferrocyanate of potash is obtained.

Ferrocyanate of potash is a perfectly neutral salt, which is soluble in less than its own weight of water, and forms large transparent, four-sided tabular crystals, derived from an acute rhombic octohedron, the apices of which are deeply truncated. The colour of the salt is lemon-yellow; it is inodorous, has a slightly bitter taste, but quite different from that of hydrocyanic acid, and is permanent in the air. When heated to 212° F., or even below that temperature, each equivalent of the salt parts with three equivalents of water, leaving one equivalent of ferrocyanuret of potassium. The water, indeed, is disengaged with such facility, that Berzelius regards the crystals as consisting of ferrocyanuret of potassium combined with three equivalents of water of crystallization. (An. de Ch. et de Ph. vol. xv.) On heating the dry compound to full redness in close vessels, decomposition takes place, nitrogen gas is disengaged, and cyanuret of potassium mixed with carburet of iron remains in the retort.

Very great diversity of opinion prevails respecting the atomic constitution of this salt. There is good reason to believe from the experiments of Berzelius, Phillips, and others, that one equivalent of the crystallized salt contains the following substances:—

Cyanogen . .	78	or 3 equivalents.
Potassium . .	80	2 equivalents.
Iron . . .	28	1 equivalent.
Hydrogen . .	3	3 equivalents.
Oxygen . .	24	3 equivalents.
	213	

Its solution in water has all the properties that may be expected from the presence of ferrocyanic acid and potash, and I shall accordingly regard it, when in that state, as containing both these substances. In the form of crystals, it is perhaps more simple to consider it with Berzelius as a double cyanuret of iron and potassium with water of crystallization. The reader will find a discussion of this subject in the Philosophical Magazine and Annals, i. 110, by Mr. Phillips.

Ferrocyanate of potash is employed in the preparation of several compounds of cyanogen, and as a reagent for detecting the presence of iron and other substances.

Red Cyanuret of Iron and Potassium.—This compound, discovered by L. Gmelin, is generated by transmitting chlorine gas, freed by washing from muriatic acid, into a rather strong solution of ferrocyanate of potash, until it ceases to give a precipitate with persalts of iron. The liquid is then concentrated to two-thirds of its volume, and set aside in a moderately warm stove to crystallize. Tufts of slender, yellow, brilliant crystals are gradually deposited in the form of roses; and by a second crystallization very brilliant ruby-coloured crystals are obtained, the form of which appears to be an elongated octohedron. Chloride of potassium is generated at the same time; and the red crystals are quite anhydrous, and are composed of three equivalents of cyanogen, one and a half of potassium, and one of iron. They differ in composition from ferrocyanate of potash which has been dried at 212°, by containing half an equivalent less of potassium.

The solution of the red double cyanuret is remarkable for detecting protosalts of iron, causing a blue or green precipitate, according to the strength of the solution. According to M. Girardin it indicates the presence of protoxide of iron dissolved in 90,000 parts of water. The crystals require for solution twice their weight of cold, and less than their weight of boiling water; but are insoluble in alcohol. A dilute solution of the crystals has a greenish-red tint; but when concentrated, the colour is so deep that it appears almost black. A very small quantity renders a considerable portion of water green. (Phil. Mag. and An. v. 148.)

Ferrocyanate of Baryta is prepared by digesting purified Prussian blue with a solution of pure baryta. It is soluble in water, and forms yellow crystals by evaporation. It is used in the formation of ferrocyanic acid.

When ferrocyanate of potash is mixed in solution with a salt of lead, a white precipitate subsides, which Berzelius has proved to be similar in composition to ferrocyanuret of potassium, consisting of one equivalent of the radical of ferrocyanic acid, and two equivalents of lead. With salts of mercury and silver, analogous compounds, likewise of a white colour, are generated. With a persalt of copper, ferrocyanate of potash causes a brownish-red precipitate which appears to be ferrocyanate of the peroxide of copper.

Ferrocyanate of Peroxide of Iron, which is formed by mixing ferrocyanate of potash with a persalt of iron in slight excess, and washing the precipitate with water, is characterized by an intensely deep blue colour, and is the basis of the beautiful pigment called *Prussian blue*. It is insipid and inodorous, insoluble in water, and is not decomposed by dilute muriatic or sulphuric acids. Concentrated muriatic acid, by the aid of heat, separates the acid, and strong sulphuric acid renders it white—a change the nature of which has not been explained. The alkalies and alkaline earths decompose it readily, uniting with the ferrocyanic acid and separating the peroxide of iron. Peroxide of mercury, as already mentioned (page 559), effects the complete decomposition of the salt, forming cyanuret of mercury. Very complicated changes are produced by an elevated temperature. On heating the ferrocyanate to redness in a close vessel, a

considerable quantity of water and carbonate of ammonia, together with a small portion of hydrocyanate of ammonia, are generated, while a carburet of iron remains in the retort—phenomena which, in conjunction with the facts above stated, leave no doubt of this compound containing ferrocyanic acid and peroxide of iron. The precise proportion of its constituents has not been satisfactorily determined; but it most probably consists of one equivalent of the peroxide, and an equivalent and a half of the acid.

Prussian blue, the discovery of which was made in 1710, has been studied by several chemists, especially by Proust, (An. de Chimie, lx.) and by Berzelius, Porrett, and Robiquet, whose essays were referred to in the description of ferrocyanic acid. The colouring matter of this pigment is ferrocyanate of peroxide of iron, which is mixed with alumina and peroxide of iron, together with the subsulphates of one or both of those bases. It is prepared by heating to redness dried blood, or other animal matters, with an equal weight of pearlash, until the mixture has acquired a pasty consistence. The residue, which consists chiefly of cyanuret of potassium and carbonate of potash, is dissolved in water, and after being filtered, is mixed with a solution of two parts of alum and one part of protosulphate of iron. A dirty-greenish precipitate ensues, which absorbs oxygen from the atmosphere, and passes through different shades of green and blue, until at length it acquires the proper colour of the pigment.

The chemical changes which take place in this process are of a complicated nature. The precipitate, which is at first thrown down, is occasioned by the potash, and consists chiefly of alumina and protoxide of iron. Ferrocyanic acid is generated by the protoxide reacting upon some of the hydrocyanic acid, so as to form water and cyanuret of iron, which then unites with undecomposed hydrocyanic acid. The ferrocyanic acid, thus produced, combines with oxide of iron; and when the latter has attained its maximum of oxidation, the compound acquires its characteristic blue tint. Dr. Thomson, knowing the protoxide to be necessary to the success of the operation, concludes that this oxide enters into the composition of Prussian blue; but here this acute chemist is certainly in error. The only use of protoxide of iron is to convert hy-

drocyanic into ferrocyanic acid; a purpose for which its presence is essential, because peroxide of iron does not produce this effect, or at least in a very slow and imperfect manner. In every good specimen of Prussian blue which I have examined, the ferrocyanic acid was in combination with peroxide of iron only.

Sulphocyanates.—The salts of sulphocyanic acid have been chiefly studied by Mr. Porrett and Berzelius. Sulphocyanate of potash, which is the most interesting and the best known of these compounds, is prepared by heating ferrocyanate of potash with sulphur, a process first proposed by Grotthus, and since modified by M. Vogel and myself. The most convenient method of performing it is to mix the ferrocyanate, in fine powder, with an equal weight of sulphur, and to place the mixture, contained in a porcelain capsule, just above a pan of burning charcoal, so that it may be exposed to a very strong heat, but short of redness. The mixture is speedily fused, takes fire, and burns briskly for one or two minutes, during which it should be well stirred. The combustion then ceases spontaneously, and the dark-coloured residue, consisting of unburned sulphur, sulphocyanuret of potassium, and sulphuret of iron, on being dissolved in water and filtered, yields a very pure and neutral sulphocyanate of potash. To ensure the decomposition of all the ferrocyanate of potash, the mass may be allowed to remain in a fused condition for a few minutes after the combustion has ceased, previous to withdrawing it from the fire.

In this process the iron and cyanogen of the ferrocyanate combine with separate portions of sulphur, forming a sulphuret of iron and a sulphuret of cyanogen, the latter of which unites with potassium. On the addition of water, a portion of that liquid is decomposed, and sulphocyanate of potash is generated.

Sulphocyanate of potash (and most of the salts of this group have probably a similar constitution) contains one equivalent of the acid, and one equivalent of the oxide; so that the oxygen and hydrogen are in due proportion for the production of water. This salt, indeed, exists only in a liquid state; for the crystals which are deposited from a concentrated solution, when separated from adhering moisture by bibulous paper,

do not contain either water or its elements, but are a pure sulphocyanuret of potassium. The crystals are very deliquescent on exposure to the air, and dissolve freely in water, yielding a solution which is quite neutral. In form, taste, and fusibility, they are very analogous to nitre.

Sulphocyanate of potash is employed in preparing sulphocyanic acid, and as a test for detecting the presence of peroxide of iron.

SECTION VII.

ON HALOID SALTS AND SULPHO-SALTS.

With the salts properly so called Berzelius has of late associated two other series of compounds, which are closely analogous to salts either in appearance or composition; and as the high rank which Berzelius has so justly attained soon gives currency to his language and opinions, at least among continental chemists, a brief statement of his views cannot fail of being both useful and agreeable to the reader. Some notice of the sulpho-salts is even necessary; because, under this title, Berzelius has described several interesting compounds which were new to chemists, and which could not so conveniently be noticed in other parts of this treatise. For a full history of these compounds, the student may refer to the essay by Berzelius in the *Annales de Chimie et de Physique*, xxxii. 60, or to his *Lehrbuch der Chemie*.

Haloid salts.—This term comprehends all those compounds which consist of a metal on the one hand, and of chlorine, iodine, and the radicals of the hydracids in general, excepting sulphur, on the other. The word *haloid*, being derived from ἁλς, sea-salt, and εἶδος, appearance, is very appropriate, since the substances to which it is applied, such as the chlorides and iodides, cannot in many instances be distinguished by their aspect from real salts; but in point of composition they resemble oxides rather than salts, and in connexion with these they have already been described.

Berzelius has correctly remarked, that the number of haloid salts which a metal is capable of yielding with the same element, generally corresponds to the salifiable oxides which it

forms with oxygen. Thus, there are two chlorides and two iodides of mercury, proportional to the two oxides of mercury; and potassium, which has but one salifiable oxide, unites in one proportion only with chlorine and iodine. Besides simple haloid salts, Berzelius distinguishes three different combinations of them. The first of these is an acid haloid salt, formed of a simple haloid salt and the hydracid of its radical. A compound of the kind may be obtained by evaporating a muriatic solution of gold with excess of acid at a very moderate temperature, when crystals are obtained consisting of chloride of gold and muriatic acid. The compound of fluoride of potassium and hydrofluoric acid offers another example. These compounds may be called *hydro-haloid salts*. The second mode of combination, which is more frequent, gives rise to what may be termed *oxy-haloid salts*, being composed of a metallic oxide united with a haloid salt of the same metal. Thus, chloride of lead combines with oxide of lead; and submuriate of iron, obtained by evaporating permuriate of iron in an open vessel by a rather strong heat, is considered by Berzelius as a similar compound. The third kind of combination is productive of double haloid salts. They may consist, first, of two simple haloid salts which contain different metals, but the same non-metallic ingredient, as the double chloride of potassium and gold, or the double fluoride of potassium and silicium; secondly, of two haloid salts consisting of the same metal, but in which the other element is different, as the compound of chloride of lead with fluoride of lead; and, thirdly, of two simple haloid salts, of which both elements are entirely different. In some cases haloid salts unite with common salts; as, for example, when chloride of sodium is fused with carbonate of baryta, or carbonate of soda with chloride of barium. (Page 645.) A compound containing nitrate of oxide of silver and cyanuret of silver, observed by Wöhler, is an instance of the same description.

Sulpho-salts.—The substances comprised under this term are merely double sulphurets, in the constitution of which Berzelius has traced a close analogy to salts. The constituents of ordinary salts, in reference to the electro-chemical theory, are conceived to be oppositely electrical, the acid being negative, and the alkali positive; and the two sulphurets in a

sulpho-salt are believed by Berzelius to have in general a similar relation to each other. Metallic bodies are divided by this chemist into electro-positive and electro-negative metals. (Page 130.) To the former belong those metals, the protoxides of which are strong salifiable bases; and among the latter are those which are capable of yielding acids with oxygen. Now, in most of the sulpho-salts the negative ingredient is the sulphuret of an electro-negative metal, while the positive body is the sulphuret of an electro-positive metal. The negative sulphuret is proportional in composition to the acid of the same metal, and the positive sulphuret corresponds to the salifiable base of its metal; so that if each metal were combined with the same number of equivalents of oxygen as it possesses of sulphur, the negative metal would form an acid, and the positive metal an alkaline base; and a regular salt would be thus produced. Hence, the electro-negative sulphuret is thought to act the part of an acid, and the positive sulphuret of an alkali. Some of these compounds are insoluble; but many of them are soluble in water, and may be obtained in crystals by evaporation.

The electro-negative sulphurets, known to yield sulpho-salts, are those of arsenic, antimony, tungsten, molybdenum, tellurium, tin, and gold; and the sulphurets of several other substances not metallic are capable of acting as the negative ingredient. The compounds to which Berzelius attributes this property are sulphuret of selenium, sulphuretted hydrogen, sulphuret of carbon, and sulphocyanic acid. He adds, also, that in the same manner as positive oxides sometimes combine, so may sulpho-salts be formed 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.

Several methods for preparing sulpho-salts are enumerated by Berzelius. 1. A negative sulphuret is digested in an aqueous solution of sulphuret of potassium until it is saturated. The resulting sulpho-salt may be employed to prepare insoluble sulpho-salts by means of double decomposition. 2. A solution of hydrosulphuretted sulphuret of potassium, which is itself regarded as a sulpho-salt, is mixed with a negative sul-

phuret in powder; when the latter unites with sulphuret of potassium, and displaces the less negative sulphuretted hydrogen, which is disengaged with effervescence. 3. By dissolving a negative sulphuret in solution of potash. In this operation, some of the alkali exchanges elements with a portion of the electro-negative sulphuret, giving rise to sulphuret of potassium and an acid of the negative metal. This acid constitutes a salt with undecomposed potash, and the undecomposed negative sulphuret generates a sulpho-salt by uniting with sulphuret of potassium. For example, when orpiment is dissolved in solution of potash, the oxygen of a portion of potash unites with arsenic, and potassium with sulphur: arsenious acid and sulphuret of potassium result; and while the former attaches itself to the alkali, forming arsenite of potash, the latter combines with sulphuret of arsenic. Similar changes ensue when sulphuret of antimony, and other electro-negative sulphurets, are boiled with alkalies. A regular 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 sulpho-salt in solution. 4. The last method which requires mention, is by exposing a mixture of an electro-negative metal 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 sulphuret. The fused mass, accordingly, always contains a salt, the acid of which consists of oxygen and the negative metal, as well as a sulpho-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 double sulphuret of potassium and arsenic.

In this description, which will suffice for conveying a general knowledge of the subject, the opinions and explanations of Berzelius have been preserved; and to these the advantage of greater simplicity must, as I apprehend, be conceded. But the phenomena clearly admit of a different explanation. Instead of a double sulphuret being held in solution in the three first methods above mentioned, the liquid may contain

double salts of sulphuretted hydrogen, formed by decomposition of water. In like manner, the oxygen of the arsenious acid, which is generated in the example above adduced, may be derived from decomposed water, as well as from potash. If this view be taken—and there seems no decisive objection against it—the existence of a sulpho-salt in solution will no longer be admitted; and in that case the chief interest attached to the new opinions of Berzelius will be destroyed.

PART III.

ON ORGANIC CHEMISTRY.

The department of organic chemistry comprehends the history of those compounds which are solely of animal or vegetable origin, and which are hence called organic substances. These bodies, viewed collectively, form a remarkable contrast with those of the mineral kingdom. Such substances in general are characterized by containing some principle peculiar to each. Thus the presence of nitrogen in nitric, and of sulphur in sulphuric acid, establishes a wide distinction between these substances; and although in many instances two or more organic bodies consist of the same elements, as is exemplified by the compounds of sulphur and oxygen, or of nitrogen and oxygen, they are always few in number, and distinguished by a well-marked difference in the proportion in which they are united. The products of animal and vegetable life, on the contrary, consist essentially of the same elementary principles, the number of which is very limited. They are nearly all composed of carbon, hydrogen, and oxygen, in addition to which some of them contain nitrogen. Besides these, portions of phosphorus, sulphur, iron, silica, potash, lime, and other substances of a like nature, may sometimes be detected; but their quantity is exceedingly minute when compared with the principles above mentioned. In point of composition, therefore, most organic substances differ only in the proportion of their constituents, and on this account may not unfrequently be converted into one another.

The constitution of organic bodies is subject to the general laws of chemical union; but chemists are not agreed as to the mode in which they conceive the elements to be combined. Berzelius, for instance, is of opinion that the elements of

organic substances do not form binary compounds in the same manner as the constituents of inorganic bodies (page 587), but are united indiscriminately with each other.—Thus alcohol, which consists of three equivalents of hydrogen, one of oxygen, and two of carbon, is supposed by that chemist to consist of all these six equivalents, combined directly with each other, the oxygen belonging as much to the carbon as to the hydrogen. (Annals of Philosophy, vol. iv.) This opinion, however, is not universally adopted. Gay-Lussac, for instance, regards alcohol as a compound of olefiant gas and water, a view which is not only justified by the number of equivalents contained in that compound, but which, as I conceive, harmonizes with the constitution of other bodies better than that of Berzelius. It may therefore be admitted as probable, that the elements of organic substances are arranged in a similar manner.

When organic substances are heated to redness with pure potash or soda, they invariably yield alkaline carbonates; but at a temperature of about 400° or 450° F., many of them are decomposed with formation of oxalic acid. This fact has been noticed by Gay-Lussac, who observed it with cotton, sawdust, sugar, starch, gum, sugar of milk, and tartaric, citric, and mucic acids. The other products of course vary with the nature of the substance; but water and acetic acid are generally formed. (Quarterly Journal of Science, N. S. vi. 413.)

Organic substances, owing to the energetic affinities with which their elements are endowed, are very prone to spontaneous decomposition. The prevailing tendency of carbon and hydrogen is to appropriate to themselves so much oxygen as shall convert them into carbonic acid and water; and hence, in whatever manner these three elements may be mutually combined in a vegetable substance, they are always disposed to resolve themselves into the compounds just mentioned. If, at the time this change occurs, there is an insufficient supply of oxygen to oxidize the hydrogen and carbon completely, then, in addition to carbonic acid and water, carbonic oxide and carburetted hydrogen gases will probably be generated. One or both of these combustible products must in every case be formed, except when oxygen is freely supplied from extraneous sources; because organic bodies are so constituted that their oxygen is never in sufficient quantity for con-

verting the carbon into carbonic acid, and the hydrogen into water.

If substances composed of oxygen, hydrogen, and carbon, are liable to spontaneous decomposition, that tendency becomes much stronger when, in addition to these elements, nitrogen is annexed. Other and powerful affinities are then superadded to those above enumerated, and especially that of hydrogen for nitrogen. A body which contains these principles is peculiarly liable to change, and the usual products are water, carbonic acid, and ammonia; the two latter, having a strong attraction for each other, being always in combination.

Another circumstance which is characteristic of organic products is the impracticability of forming them artificially by direct union of their elements. Thus no chemist has hitherto succeeded in causing oxygen, hydrogen, and carbon to unite directly so as to form gum or sugar. When these principles are made to combine by chemical means, they always give rise to the production of water and carbonic acid.

Animal and vegetable substances are all decomposed by a red heat, and nearly all are partially affected by a temperature far below ignition. When heated in the open air, or with substances which yield oxygen freely, they burn, and are converted into water and carbonic acid; but if exposed to heat in vessels from which atmospheric air is excluded, very complicated products ensue. A compound consisting of carbon, hydrogen, and oxygen, yields water, carbonic acid, carbonic oxide, carburetted hydrogen of various kinds, and probably pure hydrogen. Besides these products, some acetic acid is commonly generated, together with a volatile oil which has a dark colour and burnt odour, and is hence called empyreumatic oil. An azotized substance, in addition to these, yields ammonia, cyanogen, and probably free nitrogen.

From the foregoing remarks, it appears that organic products are characterized by the following circumstances:—1st, by being composed of the same elements; 2d, by the facility with which they undergo spontaneous decomposition; 3d, by the impracticability of forming them by the direct union of their principles; and, 4th, by being decomposed at a red heat.

VEGETABLE CHEMISTRY.

All bodies which are of vegetable origin are termed vegetable substances. They are nearly all composed of oxygen, hydrogen, and carbon, and in a few of them nitrogen is likewise present. Every distinct compound which exists ready formed in plants, is called a *proximate* or *immediate principle* of vegetables. Thus sugar, starch, and gum, are proximate principles. Opium, though obtained from a plant, is not a proximate principle; but consists of several proximate principles mixed more or less intimately with each other.

The proximate principles of vegetables are sometimes distributed over the whole plant, while at others they are confined to a particular part. The methods by which they are procured are very variable. Thus gum exudes spontaneously, and the saccharine juice of the maple-tree is obtained by incisions made in the bark. In some cases a particular principle is mixed with such a variety of others, that a distinct process is required for its separation. Of such processes consists the *proximate analysis* of vegetables. Sometimes a substance is separated by mechanical means, as in the preparation of starch. On other occasions, advantage is taken of the volatility of a compound, or of its solubility in some particular menstruum. Whatever method is employed, it should be of such a nature as to occasion no change in the composition of the body to be prepared.

The reduction of the proximate principles into their simplest parts, constitutes their *ultimate analysis*. By this means chemists ascertain the quantity of oxygen, carbon, and hydrogen present in any compound. The former method of performing this operation was by what is termed *destructive distillation;* that is, by exposing the compounds to a red heat in close vessels, and collecting all the products. So many different substances, however, are procured in this way, such as water, carbonic acid, carbonic oxide, carburetted hydrogen, and the like, that it is almost impossible to arrive at a satisfactory conclusion. A more simple and effectual method was proposed by Gay-Lussac and Thenard in the second volume of their celebrated *Recherches Physico-Chimiques*. The object

of their process, which is applicable to the ultimate analysis of animal as well as vegetable substances, is to convert the whole of the carbon into carbonic acid, and the hydrogen into water, by means of some compound which contains oxygen in so loose a state of combination as to give it up to those elements at a red heat.

The agent first employed by these chemists was chlorate of potash. This substance, however, is liable to the objection, that it not only gives oxygen to the substance to be analyzed, but is itself decomposed by heat. On this account it is now very rarely employed in ultimate analysis, peroxide of copper, likewise proposed by Gay-Lussac and Thenard, having been substituted for it. This oxide, if alone, may be heated to whiteness without parting with oxygen; whereas it yields oxygen readily to any combustible substance with which it is ignited. It is easy, therefore, by weighing it before and after the analysis, to discover the precise quantity of oxygen which has entered into union with the carbon and hydrogen of the substance submitted to examination.

The ultimate analysis of organic bodies is one of the most delicate operations with which the analytical chemist can be engaged. The chief cause of uncertainty in the process arises from the presence of moisture, which is retained by some animal and vegetable substances with such force, that it can be expelled only by a temperature which endangers the decomposition of the compound itself. The best mode of drying organic matters for the purpose, is by confining them with sulphuric acid under the exhausted receiver of an air-pump, and exposing them at the same time to a temperature of 212° F.—a method adopted by Berzelius, and for which a neat apparatus has been described by Dr. Prout. (Annals of Philosophy, vol. vi. p. 272.) Another source of difficulty is occasioned by atmospheric air within the apparatus, owing to the presence of which nitrogen may be detected in the products, without having been contained in the substance analyzed.

But though the ultimate analysis of organic substances is difficult in practice, in theory it is exceedingly simple. It consists in mixing three or four grains of the body to be analyzed with about 200 grains of peroxide of copper, heating the mixture to redness in a glass tube, and collecting the gaseous

products in a graduated glass jar over mercury. From the quantity of carbonic acid procured by measure, its weight may readily be inferred (page 257); and from this, the quantity of carbonaceous matter may be calculated, by recollecting that every 22 grains of the acid contain 16 of oxygen and 6 of carbon.

In order to ascertain the quantity of hydrogen, the gaseous products are transmitted through a tube filled with fragments of fused chloride of calcium, which absorbs all the watery vapour; and by its increase in weight indicates the precise quantity of that fluid generated. Every nine grains of water thus collected correspond to one grain of hydrogen and eight of oxygen.

If the quantity of oxygen contained in the carbonic acid and water corresponds precisely to that lost by the oxide of copper, it follows that the organic substance itself was free from oxygen. But if, on the other hand, more oxygen exists in the products than was lost by the copper, it is obvious that the difference indicates the amount of oxygen contained in the subject of analysis.

If nitrogen enters into the constitution of the organic substance, it will pass over in the gaseous state, mixed with carbonic acid. Its quantity may be ascertained by removing the carbonic acid by means of a solution of pure potash.

It need scarcely be observed, that if the analysis has been successfully performed, the weight of the different products, added together, should make up the exact weight of the organic substance employed.

In analyzing an animal or vegetable fluid, the foregoing process will require slight modification. If the fluid is of a fixed nature, it may be made into a paste with oxide of copper, and heated in the usual manner. But if it is volatile, a given weight of its vapour is conducted over peroxide of copper heated to redness in a glass tube.

The constitution of vegetable substances is not yet sufficiently known to admit of their being classified in a purely scientific order. The chief data hitherto furnished towards forming a systematic arrangement are derived from a remarkable agreement between the composition and general properties of several vegetable compounds, first noticed by Gay-

Lussac and Thenard. (Recherches, vol. ii.) From the ultimate analysis of a considerable variety of proximate principles, these chemists draw the three following conclusions:—1st, A vegetable substance is always acid, when it contains more than a sufficient quantity of oxygen for converting all its hydrogen into water; 2dly, It is always resinous, oily, or alcoholic, &c. when it contains less than a sufficient quantity of oxygen for combining with the hydrogen; and, 3dly, it is neither acid nor resinous, but in a state analogous to sugar, gum, starch, or the woody fibre, when the oxygen and hydrogen, which it contains, are in the exact proportion for forming water. These laws, indeed, are not rigidly exact, nor do they include the vegetable products containing nitrogen; but for want of a better principle of classification, I shall follow M. Thenard in making them, to a certain extent, the basis of my arrangement. The proximate principles of plants will accordingly be arranged in five divisions. The first includes the vegetable acids; the second vegetable alkalies; the third comprises those substances which contain an excess of hydrogen; the fourth includes those, the oxygen and hydrogen of which are in proportion for forming water; and the fifth comprehends those bodies which, so far as is known, do not belong to either of the other divisions.

SECTION I.

VEGETABLE ACIDS.

Those compounds are regarded as vegetable acids which possess the properties of an acid, and are derived from the vegetable kingdom. These acids, like all organic principles, are decomposed by a red heat. They are in general less liable to spontaneous decomposition than other vegetable substances; a circumstance which probably arises from the large proportion of oxygen which they contain. They are nearly all decomposed by concentrated hot nitric acid, by which they are converted into carbonic acid and water.

ACETIC ACID.

Acetic acid exists ready formed in the sap of many plants, either free or combined with lime or potash; it is generated during the destructive distillation of vegetable matter, and is an abundant product of the acetous fermentation.

Common vinegar, the acidifying principle of which is acetic acid, is commonly prepared in this country by fermentation from an infusion of malt, and in France from the same process taking place in weak wine. Vinegar, thus obtained, is a very impure acetic acid, containing the saccharine, mucilaginous, glutinous, and other matters existing in the fluid from which it is prepared. It is separated from these impurities by distillation. Distilled vinegar was formerly called *acetous acid*, on the supposition of its differing chemically from strong acetic acid; but it is now admitted that distilled vinegar is real acetic acid merely diluted with water, and commonly containing a small portion of empyreumatic oil, formed during the distillation, and from which it receives a peculiar flavour. It may be rendered stronger by exposure to cold, when a considerable part of the water is frozen, while the acid remains liquid.

The distilled vinegar, which is now generally employed for chemical purposes, is prepared by the distillation of wood, and is sold under the name of *pyroligneous acid*. When first made it is very impure, and of a dark colour, holding in solution tar and volatile oil. In this state it is mixed with chalk, and obtained in the state of acetate of lime, which is decomposed by digestion with sulphate of soda: the resulting acetate of soda is then fused at a high temperature, insufficient to decompose the salt, but sufficient to expel or char the impurities. The acetate of soda is thus obtained pure and in crystals, and is decomposed by sulphuric acid.

Concentrated acetic acid is best obtained by decomposing the acetates either by sulphuric acid, or in some instances by heat. A convenient process is to distil acetate of potash with half its weight of concentrated sulphuric acid, the recipient being kept cool by the application of ice. The acid is at first contaminated with sulphurous acid; but by mixing it with a little peroxide of manganese, and redistilling, it is rendered

quite pure. A strong acid may likewise be procured from bin-acetate of copper by the sole action of heat. The acid when first collected has a greenish tint, owing to the presence of copper, from which it is freed by a second distillation. The density or the product varies from 1.056 to 1.08, the lightest acid being procured towards the end of the process. MM. Derosnes, indeed, have remarked that the liquid which passes over towards the end of the process is lighter than water, and contains very little acetic acid. On neutralizing the latter with pure solid potash, and distilling by a gentle heat, they procured an ethereal fluid, to which they applied the term of *pyro-acetic ether*.

Strong acetic acid is exceedingly pungent, and even raises a blister when kept for some time in contact with the skin. It has a very sour taste and an agreeable refreshing odour. Its acidity is well marked, as it reddens litmus paper powerfully, and forms neutral salts with the alkalies. It is exceedingly volatile, rising rapidly in vapour at a moderate temperature without undergoing any change. Its vapour is inflammable, and burns with a white light. In its most concentrated form it is a definite compound of one equivalent of water, and one equivalent of acid; and in this state it crystallizes when exposed to a low temperature, retaining its solidity until the thermometer rises to 50° F. It is decomposed by being passed through red-hot tubes; but owing to its volatility, a large quantity of it escapes decomposition.

Dr. Prout has established the singular fact, relative to the constitution of this acid, that its oxygen and hydrogen are in exact proportion to form water, and that it contains 47.05 per cent of carbon. (Phil. Trans. 1827, 355.) It may hence be inferred to consist of 24 parts or 4 equivalents of carbon, 24 parts or 3 equivalents of oxygen, and 3 of hydrogen. This would make the combining proportion of acetic acid 51, instead of 50 as stated by Dr. Thomson.

The only correct mode of estimating the strength of acetic acid is by its neutralizing power. Its specific gravity is no criterion, as will appear from the following table. (Thomson's First Principles, vol. ii. p. 135.)

Table exhibiting the density of acetic acid of different strengths.

Acid.		Water.	sp. gr. at 60 F.
1 atom	+	1 atom	1.06296
1	+	2	1.07060
1	+	3	1.07080
1	+	4	1.07132
1	+	5	1.06820
1	+	6	1.06708
1	+	7	1.06349
1	+	8	1.05974
1	+	9	1.05794
1	+	10	1.05439

The acetic is distinguished from all other acids by its flavour, odour, and volatility. Its salts, which are called *acetates*, are all soluble in hot and most of them in cold water, are destroyed by a high temperature, and are decomposed by sulphuric acid.

Acetate of Potash.—This salt is made by neutralizing carbonate of potash with acetic acid, or by decomposing acetate of lime with sulphate of potash. When cautiously evaporated it forms irregular crystals, which are obtained with difficulty owing to the deliquescent property of the salt. According to Dr. Thomson, the crystals are composed of one equivalent of neutral acetate of potash, and two equivalents of water. It is commonly prepared for pharmaceutic purposes by evaporating the solution to dryness, and heating the residue so as to cause the igneous fusion. On cooling it becomes a white crystalline foliated mass, which is generally alkaline.

This salt is highly soluble in water, and requires twice its weight of boiling alcohol for solution.

Dr. Thomson procured a bin-acetate by mixing acetic acid and carbonate of potash in the proportion of two equivalents of the former to one of the latter. On confining the solution along with sulphuric acid under the exhausted receiver of an air-pump, the bin-acetate was deposited in large transparent flat plates. The crystals contain six equivalents of water, and deliquesce rapidly on exposure to the air.

Acetate of soda is prepared in large quantity by manufacturers of pyroligneous acid by neutralizing the impure acid with chalk, and then decomposing the acetate of lime by sulphate of soda. It crystallizes readily by gentle evaporation, and its crystals, which are not deliquescent, are composed of

50 parts or one equivalent of acetic acid, 32 parts or one equivalent of soda, and 73 parts or six equivalents of water. (Berzelius and Thomson.) The form of its crystals is very complicated, and derived from an oblique rhombic prism. (Brooke.) When heated to 550° F. it is deprived of its water, and undergoes the igneous fusion without parting with any of its acid. At 600° F. decomposition takes place.

Acetate of soda is much employed for the preparation of concentrated acetic acid.

Acetate of ammonia is made by neutralizing carbonate of ammonia with acetic acid. It crystallizes with difficulty in consequence of being deliquescent and highly soluble. It has been long used in medicine as a febrifuge under the name of *spirit of Mindererus.*

The *Acetates of Baryta, Strontia, and Lime*, are of little importance. The former, which is occasionally employed as a re-agent, crystallizes in irregular six-sided prisms terminated by dihedral summits, the primary form of which is a right rhomboidal prism. The latter crystallizes in very slender acicular crystals of a silky lustre, and is chiefly employed in the preparation of acetate of soda.

Acetate of alumina is formed by adding acetate of lead to sulphate of alumina, when the sulphate of lead subsides and acetate of alumina remains in solution. It is used by dyers and calico printers as a basis or mordaunt.

Acetate of Lead.—This salt, long known by the names of sugar of lead (*saccharum saturni*) and *cerussa acetata*, is made by dissolving either carbonate of lead or litharge in distilled vinegar. The solution has a sweet, succeeded by an astringent taste, does not redden litmus paper, and deposits shining acicular crystals by evaporation. When more regularly crystallized it occurs in six-sided prismatic crystals, cleavable parallel to the lateral and terminal planes of a right rhombic prism, which may be regarded as its primary form. (Mr. Brooke.) The crystals effloresce slowly by exposure to the air, and require about four times their weight of water at 60° F. for solution. They are composed, according to Berzelius and Thomson, of fifty parts or one equivalent of the acid, 112 parts or one equivalent of protoxide of lead, and 27 parts or three equivalents of water.

Acetate of lead is partially decomposed, with formation of carbonate of lead, by water which contains carbonic acid, or by exposure to the air; but a slight addition of acetic acid renders the solution quite clear.

This salt is much used in the arts, in medical and surgical practice, as a sedative and astringent, and in chemistry as a re-agent.

Subacetate of lead, commonly called *extractum saturni*, is prepared by boiling one part of the neutral acetate, and two parts of litharge, deprived of carbonic acid by heat, with 25 parts of water.

This salt is less sweet and less soluble in water than the neutral acetate, has an alkaline re-action, and crystallizes in white plates by evaporation. It is decomposed by a current of carbonic acid, with production of pure carbonate of lead; and forms a turbid solution, owing to the formation of a carbonate, when it is mixed with water in which carbonic acid is present. It appears from the analysis of Berzelius to consist of one equivalent of acid and three equivalents of oxide of lead, and is therefore a *tris-acetate.*

A *di-acetate* may likewise be formed by boiling with water a mixture of litharge and acetate of lead in atomic proportion. (Thomson.)

Acetate of Copper.—The pigment called *verdigris*, which is an impure acetate of peroxide of copper, may be formed by exposing metallic copper to the vapour of vinegar, when the metal gradually absorbs oxygen from the atmosphere, and then unites with the acid. It is prepared in large quantity in the south of France by covering copper plates with the refuse of the grape after the juice has been extracted for making wine. The saccharine matter contained in the husks furnishes acetic acid by fermentation, and in four or six weeks the plates acquire a coating of the acetate.

Verdigris is commonly of a pale green, but sometimes of a blue colour. Its essential constituent is an acetate of copper, composed, according to Mr. Phillips*, of 80 parts or one equivalent of peroxide of copper, 50 parts or one equivalent of acetic acid, and six equivalents of water. This compound is decomposed by water, and is converted into an

* Annals of Philosophy, N. S. vol. i. ii. and iv.

insoluble green *di-acetate*, and into a soluble *bin-acetate* of copper. The former, as its name implies, consists of one equivalent of acid and two equivalents of the oxide. The bin-acetate crystallizes readily in rhombic octohedrons of a green colour, and is soluble in twenty times its weight of cold, and five of boiling water. It is conveniently prepared by dissolving verdigris in distilled vinegar, and evaporating the solution. The crystals consist of one equivalent of acid and two equivalents of peroxide of copper, combined, according to Mr. Phillips with three, and according to Berzelius and Dr. Ure with two equivalents of water.

Besides these compounds, Berzelius has described three other acetates of copper; but as they are of little importance, I refer the reader to the original paper on the subject. (Annals of Philosophy, N. S. vol. viii.)

Acetate of Zinc.—This salt may be prepared by way of double decomposition by mixing sulphate of zinc with acetate of lead in equivalent proportions. When made in this way it is very apt to retain some sulphate of lead in solution. The best mode of obtaining it quite pure, is by suspending metallic zinc in a dilute solution of acetate of lead, until all the lead is removed. (Page 550.) This is known to be accomplished by the addition of sulphuretted hydrogen, which then occasions a pure white precipitate. This salt is frequently employed as an astringent collyrium.

Acetate of Mercury.—The only interesting compound of mercury and acetic acid is the acetate of the protoxide, which is sometimes employed in the practice of medicine. It is prepared by mixing crystallized protonitrate of mercury with neutral acetate of potash in the ratio of one equivalent of each. If both salts are dissolved in a considerable quantity of hot water, the solutions retain their transparency after being mixed; but on cooling, the proto-acetate of mercury is deposited in white scales of a silky lustre. It is easily decomposed; and it should be dried by a very gentle heat, and washed with cold water slightly acidulated with acetic acid.

OXALIC ACID.

Oxalic acid exists ready formed in several plants, especially in the *rumex acetosa* or common sorrel, and in the *oxalis acetosella* or wood sorrel; but it almost always occurs in combination either with lime or potash. These plants contain binoxalate of potash; and the oxalate of lime has been found in large quantity by M. Braconnot in several species of lichen.

Oxalic acid is easily made artificially by digesting sugar in five or six times its weight of nitric acid, and expelling the excess of that acid by distillation, until a fluid of the consistence of syrup remains in the retort. The residue in cooling yields crystals of oxalic acid, the weight of which amounts to rather more than half the quantity of the sugar employed. They should be purified by repeated solution in pure water, and re-crystallization; for they are very apt to retain traces of nitric acid, the odour of which becomes obvious when the crystals are heated. In the conversion of sugar into oxalic acid, changes of a very complicated nature ensue, during which a portion of nitric acid is resolved, chiefly, into oxygen and deutoxide of nitrogen, while the sugar is converted, with formation of carbonic acid and water, into oxalic acid. A small quantity of malic and acetic acids are generated at the same time. As oxalic acid does not contain any hydrogen, and has a smaller proportional quantity of carbon than sugar, there can be no doubt that the production of this acid essentially depends upon the sugar being deprived of all its hydrogen and a portion of its carbon by oxygen derived from the nitric acid.

Many organic substances besides sugar, such as starch, gum, most of the vegetable acids, wool, hair, and silk, are converted into oxalic by the action of nitric acid;—a circumstance which is explicable on the fact that oxalic acid contains more oxygen than every other principle, whether of animal or vegetable origin. It is also generated by heating organic substances with potash. (Page 669.)

Oxalic acid crystallizes in slender, flattened, four and six sided prisms terminated by two-sided summits; but their primary form is an oblique rhombic prism. It has an exceedingly sour taste, reddens litmus paper strongly, and forms

neutral salts with alkalies. The crystals undergo no change in ordinary states of the air, but when the atmosphere is very dry, slight efflorescence ensues. They are soluble without limit in boiling water, and according to Christison in eleven times their weight of cold water; but the solubility is increased by the presence of nitric acid. They are dissolved also by alcohol, though less freely than in water. They contain rather more than 42 per cent of water of crystallization, part of which only, amounting to about 28 per cent, can be expelled by heat without decomposing the acid itself.

The atomic weight of oxalic acid, as determined by Dr. Thomson, is precisely 36; and the crystals consist of 36 parts or one equivalent of real acid, and 27 parts or three equivalents of water. (Berzelius and Prout.) It differs in composition from nearly all other vegetable acids in containing no hydrogen, the absence of which seems fully established by the analyses of Berzelius, Thomson, and Ure. From the researches of these chemists, oxalic acid is composed of one part of carbon and two parts of oxygen; and since its equivalent is 36, it must be regarded as a compound of

Carbon,	12	2 equiv.	or,	Carbonic oxide,	14 . 1 equiv.
Oxygen,	24	3 equiv.		Carbonic acid,	22 . 1 equiv.
	36				36

It is therefore intermediate between carbonic oxide and carbonic acid; and, as is obvious from the numbers above stated, it may be regarded as a compound of these gases. Consistently with this view, Döbereiner found that oxalic acid is converted into carbonic acid and carbonic oxide by the action of a very large excess of fuming sulphuric acid. (An. de Ch. et de Ph. xix.) The experiment succeeds so readily with common oil of vitriol, that I habitually prepare carbonic oxide by this process.

Oxalic acid is one of the most powerful and rapidly fatal poisons which we possess; and frequent accidents have occurred from its being sold and taken by mistake for Epsom salts, with the appearance of which its crystals have some resemblance. These substances may be easily distinguished, however, by the strong acidity of oxalic acid, which may be tasted without

danger, while sulphate of magnesia is quite neutral, and has a bitter saline taste. In cases of poisoning with this acid, chalk mixed with water should be administered as an antidote, an insoluble oxalate being formed, which is inert. Chalk was first suggested for this purpose by my colleague, Dr. A. T. Thomson, and his opinion has been since fully confirmed by the experiments of Drs. Christison and Coindet, who have recommended the use of magnesia with the same intention. (Christison on Poisons, 140.)

Oxalic acid is easily distinguished from all other acids by the form of its crystals, and by its solution giving with lime water a white precipitate, which is insoluble in an excess of the acid.

The salts of oxalic acid are termed *oxalates*. Most of these compounds are either insoluble or sparingly soluble in water; but they are all dissolved by the nitric, and also by muriatic acid, except when the latter precipitates the base of the salts. The only oxalates which are remarkable for solubility are those of potash, soda, lithia, ammonia, alumina, and iron.

A soluble oxalate is easily detected by adding to its solution a neutral salt of lime or lead, when a white oxalate of those bases will be thrown down. On digesting the precipitate in a little sulphuric acid, an insoluble sulphate is formed, and the solution yields crystals of oxalic acid on cooling. All insoluble oxalates, the bases of which form insoluble compounds with sulphuric acid, may be decomposed in a similar manner. All other insoluble oxalates may be decomposed by potash, by which means a soluble oxalate is procured.

The oxalates, like all salts which contain a vegetable acid, are decomposed by a red heat, a carbonate being left, provided the oxide can retain carbonic acid at the temperature which is employed. As oxalic acid is so highly oxidized, its salts leave no charcoal when heated in close vessels.

Several oxalates are reduced to the metallic state, with evolution of pure carbonic acid, when heated to redness in close vessels. (Pages 498 and 501.) The peculiar constitution of oxalic acid accounts for this change; for one equivalent of the acid, to be converted into carbonic acid, requires precisely one equivalent of oxygen, which is the exact quantity contained in the oxide of a neutral proto-oxalate.

Oxalates of Potash.—Oxalic acid forms with potash three compounds, of which the description was given, and the composition determined, in the year 1808 by Dr. Wollaston. (Philos. Trans. for 1808.) The first is the neutral oxalate which is formed by neutralizing carbonate of potash with oxalic acid. It crystallizes in oblique quadrangular prisms, which have a cooling bitter taste, require about twice their weight of water at 60° F. for solution, and contain 36 parts or one equivalent of oxalic acid, 48 parts or one equivalent of potash, and one equivalent of water. This salt is much employed as a re-agent for detecting lime. Binoxalate of potash is contained in sorrel, and may be procured from that plant by solution and crystallization. It crystallizes readily in small rhomboids, which are less soluble in water than the neutral oxalate. It is often sold under the name of *essential salt of lemons* for removing iron moulds from linen;—an effect which it produces by one equivalent of its acid uniting with the oxide of iron and forming a soluble oxalate. The third salt contains twice as much acid as the preceding compound, and has hence received the name of *quadroxalate* of potash. It is the least soluble of these salts, and is formed by digesting the binoxalate in nitric acid, by which it is deprived of one-half of its base. It is composed of four equivalents of acid, one of potash, and seven of water.

Oxalate of Soda, which may be made in the same manner as oxalate of potash, is very rarely employed, and is of little importance. It likewise forms a binoxalate, but no quadroxalate is known.

Oxalate of ammonia, prepared by neutralizing that alkali with oxalic acid, is much used as a re-agent. It is very soluble in hot water, and is deposited in acicular crystals when a saturated hot solution is allowed to cool. The crystals contain two equivalents of water. Dr. Thomson has likewise described a binoxalate of ammonia, which is less soluble than the preceding and contains three equivalents of water.

Oxalate of Lime.—This salt, like all the insoluble oxalates, is easily prepared by way of double decomposition. It is a white finely divided powder, which is remarkable for its extreme insolubility in pure water. On this account a soluble oxalate is an exceedingly delicate test for lime. It is soluble,

however, in muriatic and nitric acids. It is composed of 36 parts or one equivalent of the acid, and 28 parts or one equivalent of lime. It may be exposed to a temperature of 560° F. without decomposition, and is then quite anhydrous. No binoxalate of lime is known.

This salt is interesting in a pathological point of view, because it is a frequent ingredient of urinary concretions. It is the basis of what is called the *mulberry calculus*.

Oxalate of Magnesia.—This salt may be prepared by mixing oxalate of ammonia with a hot concentrated solution of sulphate of magnesia. It is a white powder, which is very sparingly soluble in water; but, nevertheless, when sulphate of magnesia is moderately diluted with cold water, oxalate of ammonia occasions no precipitate. On this fact is founded the best analytic process for separating lime from magnesia.

TARTARIC ACID.

This acid exists in the juice of several acidulous fruits, but it is almost always in combination with lime or potash. It is prepared by mixing intimately 198 parts or one equivalent of cream of tartar, in fine powder, with 50 parts or one equivalent of chalk, and throwing the mixture by small portions at a time into ten times its weight of boiling water. On each addition brisk effervescence ensues, owing to the escape of carbonic acid, and one equivalent of the insoluble tartrate of lime subsides; while one equivalent of neutral tartrate of potash is held in solution. On washing the former with water, and then digesting it, diffused through a moderate portion of water, with one equivalent of sulphuric acid, the tartaric acid is set free; and after being separated from the sulphate of lime by a filter, may be procured by evaporation in prismatic crystals, the primary form of which is a right rhombic prism.

Tartaric acid has a sour taste, which is very agreeable when diluted with water. It reddens litmus paper strongly, and forms with alkalies neutral salts, to which the name of *tartrates* is applied. It requires five or six times its weight of water at 60° for solution, and is much more soluble in boiling water. It is dissolved likewise, though less freely, in alcohol. The aqueous solution is gradually decomposed by keeping, and

a similar change is experienced under the same circumstances by most of the tartrates. The crystals may be exposed to the air without change. They are converted into the oxalic by digestion in nitric acid. When heated in close vessels, it fuses, froths up, and is decomposed, yielding, in addition to the usual products of destructive distillation, a distinct acid to which the name of *pyro-tartaric acid* is applied. A considerable quantity of charcoal remains.

The atomic weight of tartaric acid, inferred by Dr. Thomson from the tartrates of potash and lead, is 66; and the crystals, which cannot be deprived of their water by heat without decomposition, consist of 66 parts or one equivalent of acid, and one equivalent of water. According to the analysis of Dr. Prout and Dr. Thomson, which agrees pretty closely with that of Berzelius, the acid itself is composed of

Carbon	24	.	or 4 equivalents.
Oxygen	40	.	or 5 equivalents.
Hydrogen	2	.	or 2 equivalents.
	66		

Tartaric acid is distinguished from other acids by forming a white precipitate, bitartrate of potash, when mixed with any of the salts of that alkali. This acid, therefore, separates potash from every other acid. It occasions with lime water a white precipitate, which is very soluble in an excess of the acid.

Tartaric acid is remarkable for its tendency to form double salts, the properties of which are often more interesting than the simple salts. The most important of these double salts, and the only ones which have been much studied, are tartrate of potash and soda, and tartrate of antimony and potash. The neutral tartrates of the alkalies, of magnesia, and copper, are soluble in water; but most of the tartrates of the other bases, and especially those of lime, baryta, strontia, and lead, are insoluble. All these neutral tartrates, however, which are insoluble in pure water, are soluble in an excess of their acid. They are decomposed by digestion in carbonate of potash; and when an acid is added in excess, bitartrate of potash is precipitated. All the insoluble tartrates are easily procured from neutral tartrate of potash by way of double decomposition.

Tartrates of Potash.—The neutral tartrate, frequently called *soluble tartar*, is formed by neutralizing a solution of the bitartrate with carbonate of potash; and it is a product of the operation above described for making tartaric acid. Its primary form is a right rhomboidal prism; but it often occurs in irregular six-sided prisms with dihedral summits. Its crystals are very soluble in water, and attract moisture when exposed to the air. They consist of 114 parts or one equivalent of the neutral tartrate, and two of water. They are rendered quite anhydrous by a temperature not exceeding 248° Fahr.

Of the *bitartrate* an impure form, commonly known by the name of *tartar*, is found encrusted on the sides and bottom of wine-casks, a source from which all the tartar of commerce is derived. This salt exists in the juice of the grape, and, owing to its insolubility in alcohol, is gradually deposited during the vinous fermentation. In its crude state it is coloured by the wine from which it was procured; but when purified, it is quite white, and in this state constitutes the *cream of tartar* of the shops.

Bitartrate of potash is very sparingly soluble in water, requiring sixty parts of cold and fourteen of boiling water for solution, and is deposited from the latter on cooling in small crystalline grains. Its crystals are commonly irregular six-sided prisms, terminated at each extremity by six surfaces; and its primary form is either a right rectangular, or a right rhombic prism. It has a sour taste, and distinct acid reaction. It consists of one equivalent of potash and two of the acid, united according to Berzelius with one, and according to Dr. Thomson with two equivalents of water. Assuming the latter to be correct, the atomic weight of the bitartrate is 198. Its water of crystallization cannot be expelled without decomposing the salt itself.

Bitartrate of potash is employed in the formation of tartaric acid and all the tartrates. It is likewise used in preparing pure carbonate of potash. When exposed to a strong heat, it yields an acrid empyreumatic oil, some pyro-tartaric acid, together with water, carburetted hydrogen, carbonic oxide, and carbonic acid gases, the last of which combines with the potash. The fixed products are carbonate of potash and char-

coal, which may be separated from each other by solution and filtration. When deflagrated with half its weight of nitre, by which part of the charcoal is consumed, it forms *black-flux*; and when an equal weight of nitre is used, so as to oxidize all the carbon of the tartaric acid, a pure carbonate of potash, called *white-flux*, is procured.

Tartrate of Potash and Soda.—This double salt, which has been long employed in medicine under the name of *seignette* or *rochelle salt*, is prepared by neutralizing bitartrate of potash with carbonate of soda. By evaporation it yields prismatic crystals, the sides of which often amount to ten or twelve in number; but the primary form, as obtained by cleavage, is a right rhombic prism. (Mr. Brooke.) The crystals are soluble in five parts of cold and in a less quantity of boiling water, and are composed of 114 parts or one equivalent of tartrate of potash, 98 parts or one equivalent of tartrate of soda, and eight equivalents of water.

Tartrate of Soda is of little importance. It is frequently made extemporaneously by dissolving equal weights of tartaric acid and bicarbonate of soda in separate portions of water, and then mixing the solutions. A very agreeable effervescing draught is procured in this way. Soda is better adapted for this purpose than potash, because the former has little or no tendency to form an insoluble bitartrate.

Tartrate of Antimony and Potash.—This compound, long celebrated as a medicinal preparation under the name of *tartar emetic*, is made by boiling protoxide of antimony with a solution of bitartrate of potash. The oxide of antimony is furnished for this purpose in various ways. Sometimes the *glass* or *crocus* of that metal is employed. The Edinburgh college prepare an oxide by deflagrating sulphuret of antimony with an equal weight of nitre; and the college of Dublin employ the submuriate. Mr. Phillips recommends that 100 parts of metallic antimony in fine powder should be boiled to dryness in an iron vessel with 200 of sulphuric acid, and that the residual subsulphate be boiled with an equal weight of cream of tartar. The solution of the double salt, however made, should be concentrated by evaporation, and allowed to cool in order that crystals may form.

Tartrate of antimony and potash yields crystals, which are transparent when first formed, but become white and opaque by exposure to the air. Its primary form has been correctly described by Mr. Brooke as an octohedron with a rhombic base (An. of Phil. N. S. vi. 40.); but the edges of the base are frequently replaced by planes which communicate a prismatic form, and its summits are generally formed with an edge instead of a solid angle, which edge is frequently truncated, presenting a narrow rectangular surface. It frequently occurs in segments, having the outline of a triangular prism, a form which has deceived many into the belief, that the tetrahedron or regular octohedron is the primary form of tartar emetic. It has a styptic metallic taste, reddens litmus paper slightly, and is soluble in fifteen parts of water at 60°, and in three of boiling water. (Dr. Duncan, jun.) Its aqueous solution, like that of all the tartrates, undergoes spontaneous decomposition by keeping; and therefore, if kept in the liquid form, alcohol should be added in order to preserve it. According to the analysis of Dr. Thomson (First Principles, vol. ii. p. 441), it is composed of

Tartaric acid .	(66 × 2) .	132 or 2 equivalents.
Protoxide of antimony	(52 × 3) .	156 or 3 equivalents.
Potash . . .	.	48 or 1 equivalent.
Water . .	.	18 or 2 equivalents.
		354

With this result the analysis of Mr. Phillips accords, except that he found three instead of two equivalents of water. The atomic weight of the salt would, on this estimate, be 363.

Tartar emetic is decomposed by many reagents. Thus alkaline substances, from their superior attraction for tartaric acid, separate oxide of antimony. The pure alkalies, indeed, and especially potash and soda, precipitate it imperfectly, owing to their tendency to unite with and dissolve the oxide; but the alkaline carbonates throw down the oxide much more completely. Lime water occasions a white precipitate, which is a mixture of oxide or tartrate of antimony and tartrate of lime. The stronger acids, such as the sulphuric, nitric, and muriatic, cause a white precipitate, consisting of bitartrate of potash

and a subsalt of antimony. Decomposition is likewise effected by several metallic salts, the bases of which yield insoluble compounds with tartaric acid. Sulphuretted hydrogen throws down the orange sulphuret of antimony. It is precipitated by many vegetable substances, especially by an infusion of gall-nuts, and other similar astringent solutions, with which it forms a dirty white precipitate, which is regarded as a compound of tannin and oxide of antimony. This combination is inert, and therefore a decoction of cinchona bark is recommended as an antidote to tartar emetic.

CITRIC ACID.

This acid is contained in many of the acidulous fruits, but exists in large quantity in the juice of the lime and lemon, from which it is procured by a process very similar to that described for preparing tartaric acid. To any quantity of lime or lemon juice, finely powdered chalk is added as long as effervescence ensues; and the insoluble citrate of lime, after being well washed with water, is decomposed by digestion in dilute sulphuric acid. The insoluble sulphate of lime is separated by a filter, and the citric acid obtained in crystals by evaporation. They are rendered quite pure by being dissolved in water and recrystallized. The proportions required in this process are 86 parts or one equivalent of dry citrate of lime, and 49 parts or one equivalent of strong sulphuric acid, which should be diluted with about ten parts of water.

Citric acid crystallizes in rhomboidal prisms terminated by four plain surfaces. The crystals are large and transparent, undergo no change in the air, and if kept dry may be preserved for any length of time without decomposition. They have an intensely sour taste, redden litmus paper, and neutralize alkalies. Their flavour when diluted is very agreeable. They are soluble in an equal weight of cold and in half their weight of boiling water, and are also dissolved by alcohol. The aqueous solution is gradually decomposed by keeping. It is converted into oxalic by the action of nitric acid. Exposed to heat, the crystals undergo the watery fusion, and the acid itself is decomposed before all its water of crystallization is expelled. Besides the usual products of the decomposition

of vegetable matter, a peculiar acid sublimes, to which the name of *pyro-citric acid* is applied.

The atomic weight of citric acid, as deduced from the composition of citrate of lead by Thomson and Berzelius, is 58; and the crystals consist of 58 parts or one equivalent of the acid, and 18 parts or two equivalents of water. According to the analyses of the same chemists, this acid is inferred to consist of

Carbon	24	.	or 4 equivalents.
Oxygen	32	.	or 4 equivalents.
Hydrogen	2	.	or 2 equivalents.
	58		

The analysis of Gay-Lussac and Thenard, of Dr. Prout, and Dr. Ure *, would lead to a different statement; but the foregoing agrees better with the atomic weight of the acid.

Citric acid is characterized by its flavour, by the form of its crystals, and by forming an insoluble salt with lime and a deliquescent soluble compound with potash. It does not render lime water turbid, unless the latter is in excess, and fully saturated with lime in the cold.

Citric acid is chiefly employed as a substitute for lemon juice. On some occasions, as in making effervescing draughts or acidulous drinks, tartaric acid may be used with equal advantage.

The salts of citric acid are of little importance. The citrates of potash, soda, ammonia, magnesia, and iron are soluble in water. The first is often made extemporaneously as an effervescing draught. The citrates of lime, baryta, and strontia, lead, mercury, and silver, are very sparingly soluble. All of them are dissolved by an excess of their own acids, and are decomposed by sulphuric acid.

MALIC ACID.

This acid is contained in most of the acidulous fruits, being frequently associated with tartaric and citric acids. Grapes, currants, gooseberries, and oranges, contain it. Vauquelin found it in the tamarind mixed with tartaric and citric acids,

* Philosophical Transactions for 1812.

and in the house-leek (*sempervivum tectorum*), combined with lime. It is contained in considerable quantity in apples, a circumstance to which it owes its name. It is almost the sole acidifying principle of the berries of the service-tree (*sorbus aucuparia*), in which it was detected by Mr. Donovan, and described by him under the name of *sorbic acid* in the Philosophical Transactions for 1815; but it was afterwards identified with the malic acid by Braconnot and Houton-Labillardière. (An. de Ch. et de Ph. viii.)

Malic acid may be formed by digesting sugar with three times its weight of nitric acid; but the best mode of procuring it is from the berries of the service-tree. The juice of the unripe berries is diluted with three or four parts of water, filtered, and heated; and while boiling, a solution of acetate of lead is added as long as any turbidity appears. The colouring matter of the berry is thus precipitated, while malate of lead remains in solution. The liquid, while at a boiling temperature, is then filtered. At first a small quantity of dark-coloured salt subsides; but on decanting the hot solution into another vessel, the malate of lead is gradually deposited, in cooling, in groups of brilliant white crystals. This process—a modification of the common one—has lately been recommended by Wöhler. The malate is then decomposed by a quantity of dilute sulphuric acid, insufficient for combining with all the oxide of lead; by which means a solution is procured containing malic acid together with a little lead. The latter is afterwards precipitated by sulphuretted hydrogen.

Malic acid has a very pleasant acid taste. It crystallizes with great difficulty and in an imperfect manner, attracts moisture from the atmosphere, and is very soluble in water and alcohol. Its aqueous solution is gradually decomposed by keeping. Nitric acid converts it into oxalic acid. Heated in close vessels it is decomposed with formation of a new and volatile acid, which has hence received the name of *pyromalic acid*.

According to a recent analysis of the malates of lime, lead, and copper by Dr. Prout, 100 parts of anhydrous malic acid consist of 40.68 parts of carbon, 54.24 of oxygen, and 5.08 parts of hydrogen. This result differs considerably from that lately published by Liebig, according to whose analysis of

malate of zinc and malate of silver, the acid is composed of 4 equivalents of carbon, 4 of oxygen, and 1 of hydrogen; and the equivalent of the acid is 57. (An. de Ch. et Ph. xliii. 259.)

Most of the salts of malic acid are more or less soluble in water. The malates of soda and potash are deliquescent and very soluble. Those of lead and lime, the most insoluble of the malates, are sparingly soluble in cold water, but are freely dissolved by that liquid at a boiling temperature, a circumstance which distinguishes the malic from oxalic, tartaric, and citric acids.

BENZOIC ACID.

Benzoic acid exists in gum benzoin, in storax, in the balsams of Peru and Tolu, and in several other vegetable substances. M. Vogel has detected it in the flowers of the *trifolium melilotus officinalis*. It is found in considerable quantity in the urine of the cow and other herbivorous animals, and is perhaps derived from the grasses on which they feed. It has also been detected in the urine of children.

This acid is commonly extracted from gum benzoin. One method consists in heating the benzoin in an earthen pot, over which is placed a cone of paper to receive the acid as it sublimes; but since the product is always impure, owing to the presence of empyreumatic oil, it is better to extract the acid by means of an alkali. The usual process consists in boiling finely powdered gum benzoin in a large quantity of water along with lime or carbonate of potash, by which means a benzoate is formed. To the solution, after being filtered and concentrated by evaporation, muriatic acid is added, which unites with the base, and throws down the benzoic acid. It is then dried by a gentle heat, and purified by sublimation.

Benzoic acid has a sweet and aromatic rather than a sour taste; but it reddens litmus paper, and neutralizes alkalies. It fuses readily by heat, and at a temperature a little above its point of fusion, it is converted into vapour, emitting a peculiar, fragrant, and highly characteristic odour, and condensing on cool surfaces without change. When strongly heated, it takes fire, and burns with a clear yellow flame. It undergoes no change by exposure to the air, and is not de-

composed by the action even of nitric acid. It requires about 24 parts of boiling water for solution, and nearly the whole of it is deposited on cooling in the form of minute acicular crystals of a silky lustre. It is very soluble in alcohol, especially by the aid of heat.

Benzoic acid is easily distinguished by its odour and volatility. Its salts are all decomposed by muriatic acid, with deposition of benzoic acid if the solution is moderately concentrated.

The atomic weight of benzoic acid, as inferred from the analysis of benzoate of lead by Berzelius, and that of perbenzoate of iron by Dr. Thomson, is 120.

The ultimate analysis of this acid by Berzelius, together with the number representing the weight of its combining proportion, appears to justify the opinion that it is composed of

Carbon	90	or 15	equivalents.
Oxygen	24	or 3	equivalents.
Hydrogen	6	or 6	equivalents.
	120		

According to the analysis of Dr. Ure, it contains 13 instead of 15 equivalents of carbon. (Philos. Trans. for 1822.)

Most of the benzoates are soluble in water. Those of lead, mercury, and peroxide of iron are the most insoluble. The benzoate of soda and ammonia are sometimes employed for separating iron from manganese. If the solution is quite neutral, peroxide of iron is completely precipitated, while the manganese remains in solution.

GALLIC ACID.

This acid was discovered by Scheele in 1786, and exists ready formed in the bark of many trees, and in gall-nuts. It is always associated with tannin, a substance to which it is allied in a manner hitherto unexplained.

Several processes have been described for the preparation of gallic acid; but the most economical appears to be that of Scheele as modified by M. Braconnot. (An. de Ch. et de Ph. ix.) Any quantity of gall-nuts, reduced to powder, is infused for a few days in four times its weight of water; and the

infusion, after being strained through linen, is kept for two months in a moderately warm atmosphere. During this period, the surface of the liquid becomes mouldy, the tannin of the gall-nuts disappears more or less completely, and a yellowish crystalline matter is deposited. On evaporating the solution to the consistence of syrup, and allowing it to cool, an additional quantity of the same substance subsides. The gallic acid, thus procured, is impure, owing to the presence of colouring matter and a peculiar acid, to which M. Braconnot has applied the name of *ellagic acid*. The gallic acid is separated from the latter by boiling water, in which the ellagic acid is insoluble; and it is rendered white by digestion with animal charcoal deprived of its phosphate of lime by muriatic acid. When the colourless solution is concentrated by evaporation, the gallic acid is deposited in small white acicular crystals of a silky lustre. Some crystals prepared by Mr. Phillips, and examined by Mr. Brooke, were in the form of an oblique rhombic prism.

Pure gallic acid may easily be procured by sublimation. For this purpose the impure acid is exposed to a temperature of about 350° F., either in a wide-mouthed glass flask covered with a cone of paper, or in an earthern capsule covered with a capsule of the same kind, kept cool, for collecting the sublimate. If the process is conducted slowly and at a very gentle heat, the crystals are colourless and in delicate long scales; but they are soiled with dark oily matter, when the heat is too high.

Impure gallic acid has a weak sour taste, accompanied with slight astringency, and an acid reaction with test paper; but the pure sublimed acid barely reddens litmus, and has a faintly bitter and astringent taste without acidity. It fuses at 276°, and at a few degrees higher sublimes slowly, the fused mass being darkened at the same time. The odour of its vapour is faint, and somewhat resembles that of boracic acid. It is soluble in twenty-four parts of cold and in three of boiling water; and it is likewise dissolved by alcohol. The aqueous solution becomes mouldy by keeping. Nitric acid converts it into oxalic acid. When strongly heated in the open air, it takes fire; and at a high temperature in close vessels it is in part decomposed, and in part sublimes, apparently without change.

The composition and atomic weight of gallic acid has not been determined in a satisfactory manner. From an analysis of the gallate of lead by Berzelius, the equivalent of the acid is probably about 63 or 64; and according to the same chemist it is composed of (An. of Phil. v.)

Carbon . .	56.64
Oxygen . .	38.36
Hydrogen . .	5.00

With lime water gallic acid yields a brownish-green precipitate, which is redissolved by an excess of the solution, and acquires a reddish tint. It is distinguished from tannin by causing no precipitate in a solution of gelatine. With a salt of iron it forms a dark-blue coloured compound, which is the basis of ink. The finest colour is procured when the peroxide and protoxide of iron are mixed together. This character distinguishes gallic acid from every other substance excepting tannin.

The salts of gallic acid, called *gallates*, have been imperfectly examined. The gallates of potash, soda, and ammonia are soluble in water; but most of the other gallates are of sparing solubility. On this account many of the metallic solutions are precipitated by gallic acid.

Ellagic acid, so called by Braconnot from the word *galle* read backwards, is left in the process above described after the gallic acid is removed by hot water, in the form of a gray powder, the greater part of which is soluble in a dilute solution of potash. On exposure to the air, so that the alkali may absorb carbonic acid, small shining scales are deposited. These consist of ellagic acid and potash, and by washing them with dilute muriatic acid the former is left as a yellowish-gray powder, which is insoluble in water, alcohol, and ether, has no taste, and reddens litmus faintly. Its real nature is not yet determined.

SUCCINIC ACID.

This acid is procured by heating powdered amber in a retort by a regulated temperature, when the succinic acid,

which exists ready formed in amber, passes over and condenses in the receiver. As first obtained, it has a yellow colour and peculiar odour, owing to the presence of some empyreumatic oil; but it is rendered quite pure and white by being dissolved in nitric acid, and then evaporated to dryness. The oil is decomposed, and the succinic acid left unchanged.

Succinic acid has a sour taste, and reddens litmus paper. It is soluble both in water and alcohol, and crystallizes by evaporation in anhydrous prisms. When briskly heated, it fuses, undergoes decomposition, and in part sublimes, emitting a peculiar and very characteristic odour.

The salts of succinic acid have been little examined. The succinates of the alkalies are soluble in water. That of ammonia is frequently employed for separating iron from manganese, per-succinate of iron being quite insoluble in cold water, provided the solutions are neutral. Succinate of manganese, on the contrary, is soluble.

The atomic weight of succinic acid, deduced from the composition of succinate of iron and of lead by Thomson and Berzelius, is 50; and according to the analysis of succinate of lead by Berzelius, which has lately been confirmed by Liebig and Wöhler, this acid is inferred to consist of

Carbon	24	or 4 equivalents.
Oxygen	24	or 3 equivalents.
Hydrogen	2	or 2 equivalents.
	50	

It hence differs in composition from acetic acid only in containing one equivalent less of hydrogen.

Camphoric acid.—This compound has not hitherto been found in any plant, and is procured only by digesting camphor for a considerable time in a large excess of nitric acid. It is sparingly soluble in water. Its taste is rather bitter, and its odour somewhat similar to saffron. It reddens litmus paper, and combines with alkalies, forming salts which are called *camphorates*. This acid has not been applied to any useful purpose.

Mucic or *Saccholactic Acid* was discovered by Scheele in

1780. It is obtained by the action of nitric acid on certain substances, such as gum, manna, and sugar of milk. The readiest and cheapest mode of forming it is by digesting gum with three times its weight of nitric acid. On applying heat, effervescence ensues, and three acids—the oxalic, malic, and saccholactic—are the products. The latter, from its insolubility, subsides as a white powder, and may be separated from the others by washing with cold water. In this state Dr. Prout says it is very impure. To purify it he digests with a slight excess of ammonia, and dissolves the resulting salts in boiling water. It is filtered while hot, and the solution evaporated slowly almost to dryness. The saccholactate of ammonia is thus obtained in crystals, which are to be washed with cold distilled water, until they become quite white. They are then dissolved in boiling water, and the saturated hot solution dropped into cold dilute nitric acid.

The saccholactic is a weak acid, which is insoluble in alcohol, and requires sixty times its weight of boiling water for solution. When heated in a retort it is decomposed; and in addition to the usual products, yields a volatile white substance, to which the name of *pyro-mucic acid* has been applied. According to the analysis of Dr. Prout, saccholactic acid is composed of 33 parts of carbon, 61.5 of oxygen, and 4.9 of hydrogen.

Moroxylic acid.—This compound, which was discovered by Klaproth, is found in combination with lime on the bark of the *morus alba* or white mulberry, and has hence received the appellation of *moric* or *moroxylic acid.* It is obtained by decomposing moroxylate of lime by acetate of lead, and then separating the lead from the moroxylate of that base by means of sulphuric acid.

Hydrocyanic or *Prussic acid*, which is not an unfrequent production of plants, has already been described.

The *Sorbic*, as already mentioned, has been shown to be malic acid.

Rheumic acid.—This name was applied to the acid principle contained in the stem of the garden rhubarb; but M. Lassaigne has shown it to be oxalic acid.

Boletic acid was discovered by M. Braconnot, in the juice of the *Boletus pseudo-igniarius.* As it is a compound of no

importance, I refer the reader to the original paper for an account of it. (Annals of Phil. vol. ii.)

Igasuric acid.—M. Pelletier and Caventou have proposed this name for the acid which occurs in combination with strychnia in the nux vomica and St. Ignatius's bean; but its existence, as different from all other known acids, is doubtful.

Mellitic acid.—This acid is contained in the rare substance called *honey-stone*, which is occasionally met with at Thuringia in Germany. The honey-stone, according to Klaproth, is a mellitate of alumina, and on boiling it in a large quantity of water, the acid is dissolved, and the alumina subsides. On concentrating the solution, mellitic acid is deposited in minute acicular crystals. From its rarity it has been little studied, and is of little importance. According to a late analysis by Liebig and Wöhler, it consists solely of carbon and oxygen in the ratio of 4 equivalents of the former to 3 of the latter, giving an equivalent of 48 for the acid, which is the proportion in which it unites with alkalies. This is exactly the constitution of succinic acid without its hydrogen. (An. de Ch. et Ph. xliii. 200.)

Suberic acid is procured by the action of nitric acid on cork. Its acid properties are feeble. It is very soluble in boiling water, and the greater part of it is deposited from the solution in cooling in the form of a white powder. Its salts, which have been little examined, are known by the name of *suberates*.

Zumic acid.—This compound, procured by Braconnot from several vegetable substances which had undergone the acetous fermentation, appears from the observations of Vogel to be *lactic* (acetic) acid. (Annals of Philosophy, vol. xii.)

Kinic acid.—This acid exists in cinchona bark in combination with lime. On evaporating an infusion of bark to the consistence of an extract, and treating the residue with alcohol, a viscid matter remains, consisting of kinate of lime and mucilaginous matters. On dissolving it in water, and allowing the concentrated solution to evaporate spontaneously in a warm place, the kinate crystallizes in rhombic prisms with dihedral summits, and sometimes in rhomboidal plates. From a solution of this salt Vauquelin precipitated the lime by means of oxalic acid, and thus obtained kinic acid in a pure state. (An. de Ch. lix.)

Kinic acid has an acid taste like that of tartaric acid, reddens litmus, and neutralizes alkalies. Its specific gravity is 1.637. It is soluble in water and alcohol, requiring $2\frac{1}{2}$ times its weight of the former at 48° F. It forms soluble compounds with alkalies and alkaline earths, and is not precipitated by a salt of mercury, lead, or silver. Kinate of soda crystallizes in very fine six-sided prisms.

According to M. Henry, jun. and Plisson, kinic acid is composed of two equivalents of carbon, four of hydrogen, and three of oxygen, a constitution which would make its equivalent 40; but judging from the ratio in which it combines with alkalies, they found its equivalent to be 183. (An. de Ch. et Ph. xli. 325.)

Meconic acid, which is combined with morphia in opium, will be most conveniently described in the following section.

Pectic acid.—This substance, distinguished by its remarkable tendency to gelatinize, a property from which its name is derived (from πηκτις, coagulum), was originally described by Braconnot; and it has since been examined by the late celebrated Vauquelin. (An. de Ch. et Ph. xxviii. 173, and xli. 46.) Braconnot believed it to be present in all plants; but he extracted it chiefly from the carrot. For this purpose, carrot is made into a pulp, the juice is expressed, and the solid part well washed with distilled water. It is then boiled for about ten minutes with a very dilute solution of pure potash, or as Vauquelin advised, with bicarbonate of potash in the ratio of 5 parts to 100 of the washed pulp, and muriate of lime is added to the filtered liquor. The precipitate, consisting of pectic acid and lime, is well washed, and the lime removed by water acidulated with muriatic acid.

Pectic acid, as thus procured, is in the form of jelly. It is insoluble in cold water and acids, and nearly so in boiling water. It has a slight acid reaction, and a feeble neutralizing power with alkalies, with which it forms soluble compounds. The earthy pectates are very insoluble, and on this account, in preparing pectic acid, pure water must be used; for the process always fails, when water containing earthy salts is employed.

By digestion in a strong solution of potash, pectic acid disappears, the liquid becomes brown, and oxalate of potash

is obtained by evaporation. This fact excites some suspicion that pectic acid may be a compound of oxalic acid with a vegetable principle analogous to gum; but the conversion of organic substances in general into oxalic acid by the action of potash, as already noticed at page 669, diminishes the force of this objection.

Carbazotic acid.—This name has been applied by M. Liebig to a peculiar acid formed by the action of nitric acid on indigo. It was first noticed by Hausmann, and subsequently examined by Proust, Fourcroy and Vauquelin, Chevreul, and Liebig. It is made by dissolving small fragments of the best indigo in eight or ten times their weight of moderately strong nitric acid, and boiling as long as nitrous acid fumes are evolved. During the action, carbonic, prussic, and nitrous acids are evolved; and in the liquid, besides carbazotic acid, is found a resinous matter, artificial tannin, and a peculiar acid, mistaken for the benzoic by Fourcroy and Vauquelin, and recognised as a distinct compound under the name of *acid of indigo* by Chevreul. On cooling, carbazotic acid is freely deposited in transparent yellow crystals; and on evaporating the residual liquid, and adding cold water, an additional quantity of the acid is procured. To render it quite pure it should be dissolved in hot water, and neutralized by carbonate of potash. As the liquid cools, carbazotate of potash crystallizes, and may be purified by repeated crystallization. The acid may be precipitated from this salt by sulphuric acid.

Carbazotic acid is sparingly soluble in cold water; but it is dissolved much more freely by the aid of heat, and on cooling yields brilliant crystalline plates of a yellow colour. Ether and alcohol dissolve it readily. It is fused and volatilized by heat without decomposition; but when suddenly exposed to a strong heat, it inflames without explosion, and burns with a yellow flame, with a residue of charcoal. Its solution has a bright yellow colour, reddens litmus paper, is extremely bitter, acts like a strong acid on metallic oxides, and yields crystallizable salts. Its composition will be stated in the description of indigotic acid. (Journal of Science, ii. 210, and iii. 490.)

The bitter principle of Welter, formed by the action of nitric acid on silk, as also the bitter principle of aloes, which Bra-

connot prepared by heating aloes in nitric acid of 1.25 until reaction ceased, is carbazotic acid.

Indigotic acid.—The acid of indigo, above noticed, has lately been carefully studied by Dr. Buff. (An. de Ch. et Ph. xxxvii. 160, xxxix. 290, and xli. 174.) It is generated, with disengagement of carbonic acid and deutoxide of nitrogen in equal measures, but without the production of any carbazotic acid, by boiling indigo in rather dilute nitric acid, formed by mixing nitric acid of 1.2 with an equal weight of water. To the solution, kept boiling, indigo in coarse powder is gradually added, as long as effervescence continues; and hot water is occasionally added to supply loss by evaporation. The impure indigotic acid, deposited in cooling, is boiled with oxide of lead and filtered, in order to separate resin; and the clear yellow solution is decomposed by sulphuric acid, and again filtered at a boiling temperature. On cooling, the acid crystallizes in yellowish-white needles. In order to purify them completely, they were digested in water with carbonate of baryta; and the indigotate of baryta, deposited from the hot filtered solution in cooling, was dissolved in hot water, and decomposed by an acid. Indigotic acid was thus obtained in acicular crystals of snowy whiteness, which contracted greatly in drying, and lost their crystalline aspect; but the dry mass was dazzlingly white, and had a silky lustre.

Carbazotic acid decomposes carbonates, but is a feeble acid, and reddens litmus faintly. It requires 1000 times its weight of cold water for solution, but is soluble to any extent in hot water and alcohol. Heated in a tube it fuses, and sublimes without decomposition; and the fused mass, in cooling, crystallizes in six-sided plates. When heated in open vessels it is inflamed, and burns with much smoke. By digestion in nitric acid, it is converted into carbazotic acid, with evolution of carbonic acid and nitrous acid fumes, and production of a small quantity of oxalic acid. The change manifestly depends on the abstraction both of carbon and oxygen, as appears from the following view of the constitution of the two acids as given by Dr. Buff.

	Indigotic acid.		Carbazotic acid.
Carbon	15		10 equivalents.
Oxygen	10		10 equivalents.
Nitrogen	2		4 equivalents.

The substances called resin and artificial tannin, formed during the preceding processes, consist of a brown friable matter united or mixed with different proportions of indigotic and nitric acid. It is insoluble in water and alcohol; but it is dissolved by pure alkalies and their carbonates, and is precipitated from the solution by acids. It is best procured by boiling one part of indigo with 2 of nitric acid diluted with 15 or 20 of water, being purified from indigotic acid by the action of hot water. In order to separate it from unchanged indigo, it is dissolved by carbonate of potash, and precipitated by an acid.

SECTION II.

VEGETABLE ALKALIES.

Under this title are comprehended those proximate vegetable principles which are possessed of alkaline properties. The honour of discovering the existence of this class of bodies is due to Sertuerner, a German apothecary, who published an account of morphia so long ago as the year 1803; but the subject excited no notice until the publication of his second essay in 1816. The chemists who have since cultivated this department with most success are M. Robiquet, and MM. Pelletier and Caventou.

All the vegetable alkalies, according to the researches of Pelletier and Dumas, consist of carbon, hydrogen, oxygen, and nitrogen. (An. de Ch. et de Ph. xxiv.) They are decomposed with facility by nitric acid and by heat, and ammonia is always one of the products of the destructive distillation. They never exist in an insulated state in the plants which contain them; but are apparently in every case combined with an acid, with which they form a salt more or less soluble in water. These alkalies are for the most part very insoluble in water, and of sparing solubility in cold alcohol; but they are all readily dissolved by that fluid at a boiling temperature,

being deposited from the solution, commonly in the form of crystals, on cooling. Most of the salts are far more soluble in water than the alkalies themselves, and several of them are remarkable for their solubility.

As the vegetable alkalies agree in several of their leading chemical properties, the mode of preparing one of them admits of being applied with slight variation to all. The general outline of the method is as follows.—The substance containing the alkaline principle is digested, or more commonly macerated, in a large quantity of water, which dissolves the salt, the base of which is the vegetable alkali. On adding some more powerful salifiable base, such as potash or ammonia, or boiling the solution for a few minutes with lime or pure magnesia, the vegetable alkali is separated from its acid, and being in that state insoluble in water, may be collected on a filter and washed. As thus procured, however, it is impure, retaining some of the other principles, such as the oleaginous, resinous, or colouring matters with which it is associated in the plant. To purify it from these substances, it should be mixed with a little animal charcoal, and dissolved in boiling alcohol. The alcoholic solution, which is to be filtered while hot, yields the pure alkali, either on cooling or by evaporation; and if not quite colourless, it should again be subjected to the action of alcohol and animal charcoal. In order to avoid the necessity of employing a large quantity of alcohol, the following modification of the process may be adopted. The vegetable alkali, after being precipitated and collected on a filter, is made to unite with some acid, such as the acetic, sulphuric, or muriatic, and the solution boiled with animal charcoal until the colouring matter is removed. The alkali is then precipitated by ammonia or some other salifiable base.

MORPHIA.

Opium contains a great diversity of different principles, among which the following may in particular be enumerated:—morphia, meconic acid, narcotine, gummy, resinous, and extractive colouring matters, lignin, fixed oil, and a small quantity of caoutchouc. On infusing opium in water, several of these principles are dissolved, and especially meconate of

morphia, together with narcotine, which is likewise rendered soluble by an acid.

One of the best processes for preparing pure morphia is that recommended by M. Robiquet. (An. de Ch. et de Ph. v.) The concentrated infusion of a pound of opium is boiled for a quarter of an hour with about 150 grains of pure magnesia, and the grayish crystalline precipitate, which consists of meconate of magnesia, morphia, narcotine, colouring matter, and the excess of magnesia, is collected on a filter and edulcorated with cold water. This powder is then digested at a temperature of 120° or 130° F. in dilute alcohol, which removes the narcotine and the greater part of the colouring matter. The morphia is then taken up by concentrated boiling alcohol, and is deposited in crystals on cooling. Dr. Christison informs me that by this process, conducted in the laboratory of M. Robiquet, he procured three drachms and a half of morphia from half a pound of a very pure specimen of the best Turkey opium.

Dr. Thomson proposes to precipitate the morphia by ammonia, and to purify it by solution in acetic acid and digestion with animal charcoal. (Annals of Phil. vol. xv.) This process is very convenient; but it does not give so large a product as the foregoing, as some of the morphia is retained in solution. The animal charcoal should be deprived of phosphate of lime by muriatic acid before being used.

Pure morphia crystallizes readily when its alcoholic solution is evaporated, and yields colourless crystals of a brilliant lustre. They mostly occur in irregular six-sided prisms with dihedral summits; but their primary form is a right rhombic prism, of which the lateral planes only appear in the crystals. (Brooke.) It is almost wholly insoluble in cold, and to very small extent in hot water. It is soluble in strong alcohol, especially by the aid of heat. In its pure state it has scarcely any taste; but when rendered soluble by combining with an acid or by solution in alcohol, it is intensely bitter. It has an alkaline reaction, and combines with acids, forming neutral salts, which are far more soluble in water than morphia itself, and for the most part are capable of crystallizing.

Strong nitric acid decomposes morphia, forming a red solution, which by the continued action of the acid acquires a yel-

low colour, and is ultimately converted into oxalic acid. This circumstance was first noticed by Pelletier and Caventou; but it is not peculiar to morphia, since nitric acid has a similar effect on strychnia.

Morphia is the narcotic principle of opium. When pure, owing to its insolubility, it is almost inert; for M. Orfila gave twelve grains of it to a dog without its being followed by any sensible effect. In a state of solution, on the contrary, it acts on the animal system with great energy, Sertuerner having noticed alarming symptoms from so small a quantity as half a grain. From this it appears to follow that the effects of an overdose of a salt of morphia may be prevented by giving a dilute solution of ammonia, or an alkaline carbonate, so as to precipitate the vegetable alkali. When carefully administered morphia may be employed very advantageously in the practice of medicine; since, according to Magendie, it produces the soothing effects of opium, without causing the feverish excitement, heat, and headach which so frequently accompany the employment of that drug. The best mode of exhibiting it is in the form of acetate of morphia, a salt which is very soluble in water, and crystallizes in divergent prisms by evaporation. The basis of Battley's sedative liquor is supposed to be acetate of morphia. This compound, from being inodorous, and therefore less easily detected than opium, has been employed for criminal purposes, and M. Lassaigne has described the following method for discovering its presence. (An. de Ch. et de Ph. xxv. 102.) The suspected solution is evaporated by a temperature of 212°, and the residue treated with alcohol, by which the acetate of morphia, together with osmazome and some salts, is dissolved. The alcohol is next evaporated, and water added to separate some fatty matter. The aqueous solution is then set aside for spontaneous evaporation, during which the acetate of morphia, if present, crystallizes in divergent prisms of a yellowish colour. The salt is recognised by its bitter taste, by yielding a precipitate with ammonia, by disengagement of acetic acid on the addition of concentrated sulphuric acid, and by the orange-red colour developed by nitric acid.

Morphia may be distinguished from other vegetable alkalies by decomposing iodic acid. A grain of morphia dissolved

in 7,000 grains of water may be detected by this means, the iodine, which is set free, forming the characteristic blue tint with starch. (Serullas.)

The composition of morphia, as will appear from the following numbers, has been stated differently by different chemists. The specimen analyzed by Dr. Thomson must surely have been impure.

	Pelletier and Dumas.	Bussy.	Brande.	Thomson.
Carbon .	72.02	69.0	72.0	44.71
Oxygen .	14.84	20.0	17.0	49.69
Hydrogen .	7.61	6.5	5.5	5.59
Nitrogen .	5.53	4.5	5.5	0.00
	100	100	100	100

Meconic Acid.—This acid, so named from Μηκων poppy, was procured by M. Robiquet from the magnesian precipitate above mentioned, after the morphia had been separated from it. The meconate of magnesia is dissolved in dilute sulphuric acid, and muriate of baryta is then added, which throws down the sulphate and meconate of that base. By acting on this precipitate with dilute sulphuric acid, the meconic acid is set free, and crystallizes when its solution is evaporated. As it retains colouring matter very obstinately, it should be purified by sublimation. Meconic acid may easily be prepared, as recommended by Dr. Hare, by precipitating the acid from an aqueous infusion of opium with acetate of lead, and decomposing the insoluble meconate of lead, while diffused through water, by a current of sulphuretted hydrogén gas. The filtered solution yields crystals of meconic acid by evaporation.

Meconic acid has a sour, followed by a bitter taste, reddens litmus paper, and is very soluble both in water and alcohol. It is characterized by giving a red colour to a salt of the peroxide of iron, and communicates an emerald-green tint to sulphate of copper. These tests, especially the former, are very delicate, and afford a means of inferring the presence of opium, when the morphia cannot be detected. (Ure in Journal of Science, N.S. vii. 56.) It exerts no action on the animal system. Its presence even in a dilute solution of opium may

be detected by acetate of lead. The insoluble meconate of lead, which subsides, is decomposed by sulphuric acid; and on adding a persalt of iron, the red colour caused by the free meconic acid makes its appearance.

Narcotine.—This substance, though not regarded as a vegetable alkali, may be conveniently noticed in connexion with morphia. It was particularly described in 1803 by Derosne, and was long known by the name of *the salt of Derosne.* Sertuerner supposed it to be meconate of morphia; but Robiquet proved that it is an independent principle, and applied to it the name of *narcotine.* It is easily prepared by evaporating an aqueous infusion of opium to the consistence of an extract, and digesting it in sulphuric ether. This solvent, which does not act on meconate of morphia, takes up all the narcotine, and deposits it in acicular crystals by evaporation; and the extract of opium, thus deprived of narcotine, may be advantageously employed in medical practice. Morphia may be purified from narcotine in the same manner.

Pure narcotine is insoluble in cold and very slightly soluble in hot water. It dissolves in oil, ether, and alcohol, the latter, though diluted, acting as a solvent for it by the aid of heat. It does not possess alkaline properties, though it is rendered soluble in water by means of an acid. Its presence in an aqueous solution of opium seems owing to a free acid, which M. Robiquet imagines to be different from the meconic. Like the vegetable alkalies, nitrogen enters into its constitution.

The unpleasant stimulating properties of opium are attributed by Magendie to the presence of narcotine, the ill effects of which, according to the experiments of the same physiologist, are in a great degree counteracted by acetic acid. These results, though they require confirmation, render it probable that the superiority assigned to the *black drop* over the common tincture of opium of the Pharmacopœia is owing to the vegetable acids which enter into its composition.

CINCHONIA AND QUINA.

The existence of a distinct vegetable principle in cinchona bark was inferred by Dr. Duncan, junior, in the year 1803, who ascribed to it the febrifuge virtues of the plant, and pro-

posed for it the name of *cinchonin**. Dr. Gomez of Lisbon, whose attention was directed to the subject by the researches of Dr. Duncan, succeeded in procuring cinchonin in a separate state; but its alkaline nature was first discovered in 1820 by Pelletier and Caventou. It has been fully established by the labours of those chemists that the febrifuge property of bark is possessed by two alkalies, the *cinchonia* or cinchonin of Dr. Duncan, and quina, both of which are combined with kinic acid. These principles, though very analogous, are distinctly different, standing in the same relation to each other as potash and soda. The former exists in *Cinchona condaminea*, or pale bark; the latter is present in *C. cordifolia*, or yellow bark; and they are both contained in *C. oblongifolia*, or red bark. They were procured by Pelletier and Caventou by a process similar to that of Robiquet for preparing morphia†; and slight modifications of the method have been proposed by Badollier and Voreton‡. From one pound of yellow bark Voreton procured 80 grains of quina, which is nearly 1.4 per cent.

Pure cinchonia is white and crystalline, requires 2500 times its weight of boiling water for solution, and is insoluble in cold water. Its proper menstruum is boiling alcohol; but it is dissolved in small quantity by oils and ether. Its taste is bitter, though slow in being perceived, on account of its insolubility; but when the alkali is dissolved by alcohol or an acid, the bitterness is very powerful, and accompanied by the flavour of cinchona bark. Its alkaline properties are exceedingly well marked, since it neutralizes the strongest acids. The sulphate, muriate, nitrate, and acetate of cinchona are soluble in water, and the sulphate crystallizes in very short six-sided prisms derived from an oblique rhomboidal prism. It commonly occurs in twin crystals. The neutral tartrate, oxalate, and gallate of cinchonia, are insoluble in cold, but may be dissolved by hot water, or by alcohol.

Quina, or *Quinine*, which was discovered by Pelletier and Caventou, does not crystallize like cinchonia when precipitated

* Edinburgh New Dispensatory, 11th edit. p. 299, or Nicholson's Journal for 1803. † Ann. de Ch. et de Ph. vol. xv. ‡ Ibid. vol. xvii.

from its solutions; but it has a white, porous, and rather flocculent aspect. It is very soluble in alcohol, forming a solution which is intensely bitter, and possesses a distinct alkaline reaction.—Ether likewise dissolves it, but it is almost insoluble in water. Its febrifuge virtues are more powerful than those of cinchonia, and it is now extensively employed in the practice of medicine. It is most commonly exhibited in the form of sulphate, a salt of such activity that three grains have been known to cure an intermittent fever. This salt, which consists of 90 parts of the alkali and 10 of the acid, crystallizes in delicate white needles, having the appearance of amianthus. It is less soluble in water than sulphate of cinchonia, but is very bitter. It dissolves readily in strong alcohol by the aid of heat, a character which affords a useful test of its purity.

The analyses of different chemists, relative to the composition of cinchonia and quina, do not correspond better than those of morphia, as appears by the following results:—

	Pelletier and Dumas.		Brande.	
	Cinchonia.	Quina.	Cinchonia.	Quina.
Carbon	76.97	74.14	79.30	73.80
Oxygen	7.97	6.77	0.00	5.55
Hydrogen	6.22	8.80	7.17	7.65
Nitrogen	9.02	10.76	13.72	13.00
	100.18	100.47	100.19	100.00

The neutral gallate, tartrate, and oxalate of quina, like the analogous salts of cinchonia, are insoluble in cold water.

From the new facts which have been ascertained relative to the constituents of bark, the action of chemical tests on a decoction of this substance is now explicable. According to the analysis of Pelletier and Caventou, the different kinds of Peruvian bark, besides the kinate of cinchonia or quina, contain the following substances:—a greenish fatty matter; a red insoluble matter; a red soluble principle, which is a variety of tannin; a yellow colouring matter; kinate of lime; gum, starch, and lignin. It is hence apparent that a decoction of bark, owing to the tannin which it contains, may precipitate

a solution of tartar emetic, of gelatine, or a salt of iron, without containing a trace of the vegetable alkali, and consequently without possessing any febrifuge virtues. An infusion of gall-nuts, on the contrary, causes a precipitate only by its gallic acid uniting with cinchonia or quina, and therefore affords a test for distinguishing a good from an inert variety of bark.

Sulphate of quina, from its commercial value, is frequently adulterated. The substances commonly employed for the purpose are water, sugar, gum, starch, ammoniacal salts, and earthy salts, such as sulphate of lime and magnesia, or acetate of lime. When moderately dried, so as to expel its water of crystallization, pure sulphate of quina should lose only from 8 to 10 per cent of water. Sugar may be detected by dissolving the suspected salt in water, and adding precisely so much carbonate of potash as will precipitate the quina. The taste of the sugar, no longer obscured by the intense bitter of quina, will generally be perceived; and it may be separated from the sulphate of potash, by evaporating gently to dryness, and dissolving the sugar by boiling alcohol. Gum and starch are left when the impure sulphate of quina is digested in strong alcohol. Ammoniacal salts are discovered by the strong odour of ammonia, which may be observed when the sulphate is put into a warm solution of potash. Earthy salts may be detected by burning a portion of the sulphate. Several of the preceding directions are taken from a paper on the subject by Mr. Phillips. (Phil. Mag. and Ann. iii. 111.)

Sertuerner states, cinchona bark contains other alkalies besides cinchonia and quina, and which are to be considered as modifications of these alkalies. One in particular he has called *Chinoidea*. The observations, however, appear to be erroneous; the mistake was occasioned by the properties of the well-known alkalies being obscured by adhering impurity. (Journal of Science, vii. 422.)

STRYCHNIA.—BRUCIA.

Strychnia.—Strychnia was discovered in 1818 by Pelletier and Caventou in the fruit of the *Strychnos ignatia* and *Strychnos nux vomica*, and has since been extracted by the

same chemists from the Upas. (An. de Ch. et de Ph. x. and xxvi.)

The most economical process for preparing this alkali is that recommended by M. Corriol. (Journal de Pharmacie for October 1825, p. 492.) It consists in treating *nux vomica* with successive portions of cold water, evaporating the solution to the consistence of syrup, and precipitating the gum, which is present, by alcohol. The alcoholic solution is then evaporated to the consistence of an extract by the heat of a water-bath. The extract, which consists almost entirely of igasurate of strychnia, is dissolved by cold water, and by this means deprived of a little fatty matter, which had originally been dissolved, probably through the medium of the gum. The solution is next heated, and the strychnia precipitated by a slight excess of lime water, and then dissolved by boiling alcohol. On evaporating the spirit, the alkali is obtained pure except in containing a little brucia and colouring matter, both of which are effectually removed by maceration in dilute alcohol.

Strychnia is very soluble in boiling alcohol, and is procured in minute four-sided prisms by allowing the solution to evaporate spontaneously. It is almost insoluble in water, requiring more than 6000 parts of cold and 2500 of boiling water for solution; but notwithstanding its sparing solubility, it excites an insupportable bitterness in the mouth.—Water containing only 1-600,000th of its weight of strychnia has a bitter taste. It has a distinct alkaline reaction, and neutralizes acids, forming salts, most of which are soluble in water. It is united in the *nux vomica* and St. Ignatius's bean with igasuric acid. (Page 699.) By the action of strong nitric acid it yields a red colour; but it appears from some recent observations of Pelletier and Caventou, that the red tint is owing to the presence of some impurity, which is probably brucia.

Strychnia is one of the most virulent poisons hitherto discovered, and is the poisonous principle of the substance in which it is contained. Its energy is so great, that half a grain blown into the throat of a rabbit occasioned death in the course of five minutes. Its operation is always accompanied with symptoms of locked jaw and other tetanic affections.

Strychnia, according to the analysis of Pelletier and Dumas, is composed of 78.22 of carbon, 6.38 of oxygen, 6.54 of hydrogen, and 8.92 of nitrogen.

Brucia.—This alkali was discovered in the *Brucea antidysenterica* by Pelletier and Caventou soon after their discovery of strychnia (An. de Ch. et de Ph. vol. xii.); and it likewise exists in small quantity in the St. Ignatius's bean and *nux vomica*. In its bitter taste and poisonous qualities, it is very similar to strychnia, but is twelve or sixteen times less energetic than that alkali. It is soluble both in hot and cold alcohol, especially in the former; and it crystallizes when its solution is evaporated. Even dilute alcohol by aid of heat dissolves it, and on this property is founded the method of separating it from strychnia. It is more soluble in water than most of the other vegetable alkalies, requiring only 850 times its weight of cold, and 500 of boiling water for solution. It is composed of 75.04 of carbon, 11.21 of oxygen, 6.52 of hydrogen, and 7.22 of nitrogen. With nitric acid it acquires a deep blood-red colour, which afterwards passes into yellow; and when either of these changes has taken place, the addition of protomuriate of tin produces a pretty violet tint, and a precipitate of the same colour subsides.

VERATRIA, EMETIA, PICROTOXIA, SOLANIA, DELPHIA, &c.

Veratria.—The medicinal properties of the seeds of the *Veratrum sabadilla*, and the root of the *Veratrum album* or white hellebore, and *Colchicum autumnale* or meadow saffron, are owing to the peculiar alkaline principle *veratria*, which was discovered by Pelletier and Caventou in 1819, and may be extracted by the usual process. (Journal de Pharmacie, vol. vi.) This alkali, which appears to exist in those plants in combination with gallic acid, is white and pulverulent, inodorous, and of an acrid taste. It requires 1000 times its weight of boiling, and still more of cold water for solution. It is very soluble in alcohol, and may also be dissolved, though less readily, by means of ether. It has an alkaline reaction, and neutralizes acids; but it is a weaker base than morphia, quina, or strychnia. It acts with singular energy on

the membrane of the nose, exciting violent sneezings though in very minute quantity. When taken internally in very small doses, it produces excessive irritation of the mucous coat of the stomach and intestines; and a few grains were found to be fatal to the lower animals.

Veratria, according to the analysis of Pelletier and Dumas, consists of 66.75 of carbon, 19.6 of oxygen, 8.54 of hydrogen, and 5.04 of nitrogen.

Emetia.—Ipecacuanha consists of an oily matter, gum, starch, lignin, and a peculiar principle, which was discovered in 1817 by M. Pelletier, and to which he has applied the name of *emetine.* (Journal de Pharmacie, iii.) This substance, of which ipecacuanha contains 16 per cent, appears to be the sole cause of the emetic properties of that root, and is procured by a process similar to that for preparing the other vegetable alkalies.

Emetia is a white pulverulent substance, of a rather bitter and disagreeable taste, sparingly soluble in cold but more freely in hot water, and insoluble in ether. It is readily dissolved by alcohol. At 122° it fuses. It has a distinct alkaline reaction, and neutralizes acids; but its salts are little disposed to crystallize. (An. de Ch. et de Ph. xxiv. 181.) According to Pelletier and Dumas, it consists of carbon 64.57, oxygen 22.95, hydrogen 7.77, and nitrogen 4.

Picrotoxia.—The bitter poisonous principle of *Cocculus indicus* was discovered in 1819 by M. Boullay, who gave it the name of *picrotoxine.* Its claim to the title of a vegetable alkali, among which class of bodies it was placed by its discoverer, has been called in question by M. Casaseca, from whose remarks it seems that picrotoxia has no alkaline reaction, and does not neutralize acidity. It combines, however, with acids, and with the acetic and nitric acids forms crystallizable compounds. It appears, also, that the menispermic acid, supposed by M. Boullay to be united in *cocculus indicus* with picrotoxia, is merely a mixture of sulphuric and malic acids. (Edinburgh Journal of Science, v.)

Corydalin.—This alkali, discovered by Dr. Wackenroder, is contained in the root of the fumitory, (not the common fumitory, *fumaria officinalis*, but) *fumaria cava* and *cory-*

dalis tuberosa of Decandolle. It exists in the plant as a soluble malate, and is precipitated from its aqueous solution in the usual manner, and purified by alcohol.

It is soluble in alcohol, and the hot saturated solution in cooling yields colourless prismatic crystals of a line in length. By spontaneous evaporation fine laminæ are formed. It is likewise soluble in ether, but very sparingly in water. It is insipid and inodorous; but when dissolved by acids or alcohol it is very bitter. Its solution has an alkaline reaction, and it neutralizes acids. Cold dilute nitric acid dissolves it and yields a colourless solution; but when heated it acquires a red tint, and becomes blood-red when concentrated. Its salts are precipitated by potash, pure or carbonated, and by infusion of gall-nuts. The precipitate is white when the solution is dilute, and grayish yellow if concentrated. (Phil. Mag. and An. iv. 153.)

Solania.—The active principle of the *Solanum dulcamara*, or woody nightshade, was procured in a pure state by Desfosses; and the same alkali exists in other species of *solanum*. Solania is combined in the plant with malic acid, and is thrown down of a gray colour by ammonia from the expressed and filtered juice of the ripe berries. After being well washed and dried, it is purified by solution in hot alcohol, from which by slow evaporation it is deposited as a white powder with a pearly lustre. It is insoluble in cold water, and requires 8000 times its weight of hot water for solution. Alcohol is its proper menstruum: it is sparingly dissolved by ether, and is insoluble in oil. It has a distinct alkaline reaction, and with acids forms neutral salts, which have a bitter taste. (Journ. de Pharm. vi. and vii.)

Cynopia.—Professor Ficinus of Dresden has discovered a new alkali in the *Æthusa Cynapium*, or lesser hemlock, to which he has given the name of *Cynopia*. It is crystallizable, and soluble in water and alcohol, but not in ether. The crystals are in the form of a rhombic prism, which is also that of the crystals of the sulphate.

Delphia.—This substance was discovered about the same time by Feneuille and Lassaigne in France, and Brandes in Germany, in the seeds of the *Delphinium Staphysagria* or

Stavesacre. It is easily prepared by digesting the seeds in water acidulated with sulphuric acid, and precipitating by magnesia or other alkaline substance. It is then purified in the usual manner by solution in alcohol and digestion with animal charcoal. It is left by evaporation as a white crystalline powder, which is almost insoluble in water, but is dissolved by alcohol, ether, and the oils. It has a feeble alkaline reaction, and yields neutral salts of a bitter taste, but which rarely crystallize. (An. de Ch. et Ph. xii.)

Althea was announced by M. Bacon of Caen as a new vegetable alkali, said to be procured from the root of the marsh-mallow. (Althæa Officinalis.) According to M. Plisson this alkali has no existence, and what was thought to be supermalate of althea is asparagin.

Sanguinaria is a vegetable alkali, obtained by M. Dana from the *Sanguinaria Canadensis*, called *blood-root* in America, from the red colour of its juice. The powdered root is digested in pure alcohol, and the red solution mixed with a little ammonia is poured into water, when a brown matter subsides. After washing carefully, and removing colouring matter by animal charcoal, the alkali is removed by hot alcohol, and obtained by evaporation as a pearly white matter of an acrid taste and alkaline reaction. By exposure to air it becomes yellow. It is insoluble in water, but dissolved by alcohol and ether. Its salts have a red colour. (Phil. Mag. and An. V. 151.)

Besides the vegetable alkalies, already described, it has been rendered highly probable, chiefly by the researches of M. Brandes, that several other plants, such as the *Atropa belladonna*, *Conium maculatum*, *Hyoscyamus niger*, *Datura stramonium*, and *Digitalis*, owe their activity to the presence of an alkali. Vauquelin rendered it probable that an alkali is contained in the *Daphne mezereum*, to which, if it exist, the name of Daphnia may be applied. A vegetable alkali is said also by MM. Posselt and Reimann to be obtained from tobacco. It is described as being volatile, and a liquid at 21° F., characters so different from those of other vegetable alkalies, that the remarks of these chemists require confirmation before they can be admitted as exact.

SECTION III.

SUBSTANCES WHICH, IN RELATION TO OXYGEN, CONTAIN AN EXCESS OF HYDROGEN.

OILS.

Oils are characterized by a peculiar unctuous feel, by inflammability, and by insolubility in water. They are divided into the fixed and volatile oils, the former of which are comparatively fixed in the fire, and therefore give a permanently greasy stain to paper; while the latter, owing to their volatility, produce a stain which disappears by gentle heat.

Fixed Oils.—The fixed oils are usually contained in the seeds of plants, as for example in the almond, linseed, rape-seed and poppy-seed; but olive oil is extracted from the pulp which surrounds the stone. They are procured by bruising the seed, and subjecting the pulpy matter to pressure in hempen bags, a gentle heat being generally employed at the same time to render the oil more limpid.

Fixed oils, the palm oil excepted, are fluid at common temperatures, are nearly inodorous, and have little taste. They are lighter than water, their density in general varying from 0.9 to 0.96. They are commonly of a yellow colour, but may be rendered nearly or quite colourless by the action of animal charcoal. At or near the temperature of 600° F., they begin to boil, but suffer partial decomposition at the same time, an inflammable vapour being disengaged even below 500°. When heated to redness in close vessels a large quantity of the combustible compounds of carbon and hydrogen are formed, together with the other products of the destructive distillation of vegetable substances; and in the open air they burn with a clear white light, and formation of water and carbonic acid. They may hence be employed for the purposes of artificial illumination, as well in lamps, as for the manufacture of gas.

Fixed oils undergo considerable change by exposure to the air. The rancidity which then takes place is occasioned by the mucilaginous matters which they contain becoming acid.

From the operation of the same cause, they gradually lose their limpidity, and some of them, which are hence called *drying* oils, become so dry that they no longer feel unctuous to the touch nor give a stain to paper. This property, for which linseed oil is remarkable, may be communicated quickly by heating the oil in an open vessel. Drying oils are employed for making oil paint, and mixed with lamp-black constitute printer's ink. During the process of drying, oxygen is absorbed in considerable quantity.

The absorption of oxygen by fixed, and especially by drying oils, is under some circumstances so abundant and rapid, and accompanied with such free disengagement of caloric, that light porous combustible materials, such as lamp-black, hemp, or cotton-wool, may be kindled by it. Substances of this kind, moistened with linseed-oil, have been known to take fire during the space of 24 hours, a circumstance which has repeatedly been the cause of extensive fires in warehouses and in cotton manufactories.

Fixed oils do not unite with water, but they may be permanently suspended in that fluid by means of mucilage or sugar, so as to constitute an *emulsion*. They are for the most part very sparingly soluble in alcohol and ether. Strong sulphuric acid thickens the fixed oils, and forms with them a tenacious matter like soap; and they are likewise rendered thick and viscid by the action of chlorine. Concentrated nitric acid acts upon them with great energy, giving rise in some instances to the production of flame.

Fixed oils unite with the common metallic oxides. Of these compounds, the most interesting is that with oxide of lead. When linseed oil is heated with a small quantity of litharge, a liquid results which is powerfully drying, and is employed as oil varnish. Olive oil combined with half its weight of litharge forms diachylon plaster.

The fixed oils are readily attacked by alkalies. With ammonia, oil forms a soapy liquid to which the name of *volatile liniment* is applied. The fixed alkalies, boiled with oil or fat, give rise to the soap employed for washing, the soft inferior kind being made with potash, and the hard with soda. The chemical nature of soap has of late years been elucidated by the labours of M. Chevreul. This chemist has found that

fixed oils and fats are not pure proximate principles, but consist of two substances, one of which is solid at common temperatures, while the other is fluid. To the former he has applied the name of *stearine* from στεαρ, suet, and to the latter *eläine* from ελαιον, oil. Stearine is the chief ingredient of suet, butter, and lard, and is the cause of their solidity; whereas oils contain a greater proportional quantity of eläine, and are consequently fluid. These principles may be separated from one another by exposing fixed oil to a low temperature, and pressing it, when congealed, between folds of bibulous paper. The stearine is thus obtained in a separate form; and by pressing the bibulous paper under water, an oily matter is procured, which is eläine in a state of purity. This principle is peculiarly fitted for greasing the wheels of watches, or other delicate machinery, since it does not thicken or become rancid by exposure to the air, and requires a cold of about 20° F. for congelation. In the formation of soap the stearine and eläine disappear entirely, being converted by a change in the arrangement of their elements into three compounds, to which Chevreul * has applied the names of *margaric* and *oleic* acids, and *glycerine*. The two acids enter into combination with the alkali employed, and the resulting compound is soap. A similar change appears to be effected by the action not only of the alkaline earths, but of several of the other metallic oxides.

Soap is decomposed by acids, and by earthy and most metallic salts. On mixing muriate of lime with a solution of soap, a muriate of the alkali is produced, and the lime forms an insoluble compound with the margaric and oleic acids. A similar change ensues when a salt of lead is employed.

According to the analysis of Gay-Lussac and Thenard, 100 parts of olive oil consist of carbon 77.213, oxygen 9.427, and hydrogen 13.36. From these proportions it is inferred that olive oil contains ten equivalents of carbon, one of oxygen, and eleven of hydrogen.

Volatile Oil.—Aromatic plants owe their flavour to the presence of a *volatile* or *essential* oil, which may be obtained by distillation, water being put into the still along with the plant, in order to prevent the latter from being burned. The oil

* Recherches sur les Corps gras.

and water pass over into the recipient, and the oil collects at the bottom or the surface of the water according to its density.

Essential oils have a penetrating odour and acrid taste, which are often pleasant when sufficiently diluted. They are soluble in alcohol, though in different proportions. They are not appreciably dissolved by water; but that fluid acquires the odour of the oil with which it is distilled. With the fixed oils they unite in every proportion, and are sometimes adulterated with them, an imposition easily detected by the mixed oil causing on paper a greasy stain which is not removed by heat.

Volatile oils burn in the open air with a clear white light, and the sole products of the combustion are water and carbonic acid. On exposure to the atmosphere, they gradually absorb a large quantity of oxygen, in consequence of which they become thick, and are at length converted into a substance resembling resin. This change is rendered more rapid by the agency of light.

Of the acids, the action of strong nitric acid on volatile oils is the most energetic, being often attended with vivid combustion,—an effect which is rendered more certain by previously adding to the nitre a few drops of sulphuric acid.

Volatile oils do not unite readily with metallic oxides, and are attacked with difficulty even by the alkalies. The substance called Starkey's soap is made by triturating oil of turpentine with an alkali.

Volatile oils dissolve sulphur in large quantity, forming a deep brown coloured liquid, called *balsam of sulphur*. The solution is best made by boiling flowers of sulphur in spirit of turpentine. Phosphorus may likewise be dissolved by the same menstruum.

The most interesting of the essential oils are those of turpentine, caraway, cloves, peppermint, nutmeg, anise, lavender, cinnamon, citron, and chamomile. Of these the most important is the first, which is much employed in the preparation of varnishes, and for some medical and chemical purposes. It is procured by distilling common turpentine; and when purified by a second distillation, it is *spirit* or *essence* of turpentine. In this state it is limpid and colourless, may be distilled without residue, and yields a dense white light in

burning. Its boiling point is 324° F.: it boils indeed slightly at 280°, but the thermometer is not stationary until it reaches 324°.

Common oil of turpentine is inferred by Dr. Ure to consist of 14 equivalents of carbon, 1 of oxygen, and 10 of hydrogen *. According to M. Houton Labillardière, the purified oil contains no oxygen, but is composed of carbon and hydrogen in such proportions, that one volume of its vapour contains four volumes of olefiant gas, and two volumes of the vapour of carbon †.

Camphor.—This inflammable substance, which in several respects is closely allied to the essential oils, exists ready formed in the *Laurus camphora* of Japan, and is obtained from its trunk, root, and branches by sublimation.

Camphor has a bitterish, aromatic, pungent taste, accompanied with a sense of coolness. It is unctuous to the touch, and rather brittle, though possessing a degree of toughness which prevents it from being pulverized with facility; but it is easily reduced to powder by trituration with a few drops of alcohol. Its specific gravity is 0.988. It is exceedingly volatile, being gradually dissipated in vapour if kept in open vessels. At 288° F. it enters into fusion, and boils at 400° F.

Camphor is insoluble in water; but when triturated with sugar, and then mixed with that fluid, a portion is dissolved sufficient for communicating its flavour. It is dissolved freely by alcohol, and is thrown down by the addition of water. It is likewise soluble in the fixed and volatile oils, and in strong acetic acid. Sulphuric acid decomposes camphor, converting it into a substance like artificial tannin. (Mr. Hatchett.) With the nitric it yields camphoric acid.

Camphor, according to the analysis of Dr. Ure, appears to consist of ten equivalents of carbon, one equivalent of oxygen, and nine equivalents of hydrogen.

On transmitting a current of dry muriatic acid gas through the purified oil of turpentine, surrounded by a mixture of snow and salt, a quantity of gas is absorbed equal to one-third of the weight of the oil; the liquid acquires a deep brown colour; and a white crystalline substance, very similar to camphor, is

* Philosophical Transactions for 1822. † Journal de Pharmacie, vol. iv.

slowly generated. This matter was discovered by Kind, and has since been studied by Trommsdorf, Gehlen, and Thenard. The last chemist maintains that this peculiar substance is a compound of turpentine and muriatic acid, a view which is supported by the researches of M. Houton Labillardière.

Coumarin.—This name was first applied to the odoriferous principle of the Tonka bean by M. Guibourt, and has since been adopted by MM. Boullay and Boutron-Charlard. (Journal de Pharmacie for October, 1825.) It is derived from the term *Coumarouna odorata*, given by Stublet to the plant which yields the bean.

Coumarin is white, of a hot pungent taste, and distinct aromatic odour. It crystallizes sometimes in square needles, and at other times in short prisms. It is moderately hard, fracture clean, lustre considerable, and density greater than that of water. It fuses at a moderate temperature into a transparent fluid, which yields an opaque crystalline mass on cooling. Heated in close vessels, it is sublimed without change. It is sparingly soluble in water; but is readily dissolved by ether and alcohol, and the solutions crystallize by spontaneous evaporation. It is very soluble in fixed and volatile oils.

M. Vogel mistook coumarin for benzoic acid; but MM. Boullay and Boutron-Charlard maintain, that it has neither an acid nor alkaline reaction, and that it is a peculiar independent principle, nearly allied to the essential oils. These chemists did not find any benzoic acid in the Tonka bean, and consider coumarin as the sole cause of its odour.

RESINS.

Resins are the inspissated juices of plants, and commonly occur either pure or in combination with an essential oil. They are solid at common temperatures, brittle, inodorous, and insipid. They are non-conductors of electricity, and when rubbed become negatively electric. They are generally of a yellow colour, and semi-transparent.

Resins are fused by the application of heat, and by a still higher temperature are decomposed. In close vessels they yield empyreumatic oil, and a large quantity of carburetted hydrogen, a small residue of charcoal remaining. In the open

air they burn with a yellow flame and much smoke, being resolved into carbonic acid and water.

Resins are dissolved by alcohol, ether, and the essential oils, and the alcoholic and ethereal solutions are precipitated by water, a fluid in which they are quite insoluble. Their best solvent is pure potash and soda, and they are also soluble in the alkaline carbonates by the aid of heat. The product is in each case a soapy compound, which is decomposed by an acid.

Concentrated sulphuric acid dissolves resins; but the acid and the resin mutually decompose each other, with disengagement of sulphurous acid, and deposition of charcoal. Nitric acid acts upon them with violence, converting them into a species of tannin, which was discovered by Mr. Hatchett. No oxalic acid is formed during the action.

The uses of resin are various. Melted with wax and oil resins constitute ointments and plasters. Combined with oil or alcohol, they form different kinds of oil and spirit varnish. Sealing wax is composed of lac, Venice turpentine, and common resin. The composition is coloured black by means of lamp-black, or red by cinnabar or red lead. Lamp-black is the soot of imperfectly burned resin.

Of the different resins the most important are common resin, copal, lac, sandarach, mastich, elemi, and dragon's blood. The first is procured by heating turpentine, which consists of oil of turpentine and resin, so as to expel the volatile oil. The common turpentine, obtained by incisions made in the trunk of the Scotch fir-tree (*Pinus sylvestris*) is employed for this purpose; but the other kinds of turpentine, such as Venice turpentine, that from the larch (*Pinus larix*), Canadian turpentine from the *Pinus balsamea*, or the Strasburgh turpentine from the *Pinus picea*, yield resin by a similar treatment.

When turpentine is extracted from the wood of the fir-tree by heat, partial decomposition ensues, and a dark substance, consisting of resin, empyreumatic oil, and acetic acid is the product. This constitutes tar; and when inspissated by boiling, it forms pitch. Common resin fuses at 276° F., is completely liquid at 306°, and at about 316° bubbles of gaseous matter escape, giving rise to the appearance of ebullition. By

distillation it yields empyreumatic oils: in the first part of the process a limpid oil passes over, which rises in vapour at 300° F., and boils at 360°; but subsequently the product becomes less and less limpid, till towards the close it is very thick. This matter becomes limpid when heat is applied, and boils at about 500° F. At a red heat resin is entirely decomposed, yielding a large quantity of combustible gas, which is employed for the purpose of artificial illumination. (Page 363.)

Considerable uncertainty prevails as to the composition of common resin, as will appear by the following statement:—

	Gay-Lussac and Thenard.	Thomson.	Ure.
Carbon,	75.944	63.15	75.00
Oxygen,	13.337	25.26	12.50
Hydrogen,	10.719	11.59	12.50
	100	100	100

Amber.—This substance is brought chiefly from the southern coast of the Baltic, occurring sometimes in beds of bituminous wood, and at others on the shore, being doubtless washed out from strata of brown coal by the action of water. Its vegetable origin is amply attested by the substances with which it is associated, by its resinous nature, and by the vegetable matters which it frequently envelops. It is commonly met with in translucent pieces of various shades of yellow and brown; but it is sometimes transparent. Its specific gravity varies from 1.065 to 1.07. It may be regarded as a mixture of several substances; namely, a volatile oil, succinic acid, separable like the former by heat, two different modifications of resin both soluble in alcohol and ether, and a peculiar bituminous matter, which is insoluble in both, and is the most abundant principle in amber. (Berzelius.)

Balsams.—The balsams are native compounds of resin and benzoic acid, and issue from incisions made in the trees which contain them, in the same manner as turpentine from the fir. Some of them, such as storax and benzoin, are solid; while others, of which the balsams of Tolu and Peru are examples, are viscid fluids.

Gum Resins.—The substances to which this name is applied are the concrete juices of certain plants, and consist of resin,

essential oil, gum, and extractive vegetable matter. The two former principles are soluble in alcohol, and the two latter in water. Their proper solvent, therefore, is proof spirit. Under the class of gum resins are comprehended several valuable medicines, such as aloes, ammoniacum, assafœtida, euphorbium, galbanum, gamboge, myrrh, scammony, and guaiacum.

Caoutchouc, commonly called elastic gum or Indian rubber, is the concrete juice of the *Hævea caoutchouc* and *Iatropa elastica*, natives of South America, and of the *Ficus Indica* and *Artocarpus integrifolia*, which grow in the East Indies. It is a soft yielding solid, of a whitish colour when not blackened by smoke, possesses considerable tenacity, and is particularly remarkable for its elasticity. It is inflammable, and burns with a bright flame. When cautiously heated, it fuses without decomposition. It is insoluble in water and alcohol; but it dissolves, though with some difficulty, in pure ether. It is very sparingly dissolved by the alkalies, but its elasticity is destroyed by their action. By the sulphuric and nitric acids it is decomposed, the former causing deposition of charcoal, and the latter formation of oxalic acid.

Caoutchouc is soluble in the essential oils, in petroleum, and in cajeput oil; and may be procured by evaporation from the two latter without loss of its elasticity. The purified naphtha from coal tar dissolves it readily, and as the solvent is cheap, and the properties of the caoutchouc are unaltered by the process, the solution may be conveniently employed for forming elastic tubes, or other apparatus of a similar kind. It is used by Mr. Mackintosh of Glasgow for covering cloth with a thin stratum of caoutchouc, so as to render it impermeable to moisture. This property of coal naphtha was discovered by Mr. James Syme, Lecturer on Surgery in Edinburgh. (Annals of Philosophy, xii.)

The composition of caoutchouc has not been satisfactorily determined. According to the analysis of Dr. Ure, 100 parts of it consist of carbon 90, oxygen 0.88, and hydrogen 9.12. But caoutchouc yields ammonia when heated in close vessels, and therefore must contain nitrogen as one of its constituents, a principle which was not detected by Dr. Ure.

Wax.—This substance, which partakes of the nature of a

fixed oil, is an abundant vegetable production, entering into the composition of the pollen of flowers, covering the envelope of the plum and other fruit, especially the berries of the *Myrica cerifera*, and in many instances forming a kind of varnish to the surface of leaves. From this circumstance it was long supposed that wax is solely of vegetable origin, and that the wax of the honey-comb is derived from flowers only; but it appears from the observations of Huber that it must likewise be regarded as an animal product, since he found bees to deposit wax though fed on nothing but sugar.

Common wax is always more or less coloured, and has a distinct peculiar odour, of both which it may be deprived by exposure in thin slices to light, air, and moisture, or more speedily by the action of chlorine. At ordinary temperatures it is solid, and somewhat brittle; but it may easily be cut with a knife, and the fresh surface presents a characteristic appearance, to which the name of waxy lustre is applied. Its specific gravity is 0.96. At about 150° F. it enters into fusion, and boils at a high temperature. Heated to redness in close vessels it suffers complete decomposition, yielding products very similar to those which are procured under the same circumstances from oil. As it burns with a clear white light, it is employed for forming candles.

Wax is insoluble in water, and is only sparingly dissolved by boiling alcohol or ether, from which the greater part is deposited on cooling. It is readily attacked by the fixed alkalies, being converted into a soap which is soluble in hot water; and according to Pfaff, the action is attended, as in oils, with the formation of an acid, to which the name of *ceric acid* is applied. It unites by the aid of heat in every proportion with the fixed and volatile oils, and with resin. With different quantities of oil it constitutes the simple liniment, ointment, and cerate of the pharmacopœia.

Wax, according to the observations of John, consists of two different principles, one of which is soluble, and the other insoluble in alcohol. To the former he has given the name of *cerin*, and to the latter of *myricin*. From the ultimate analysis of Dr. Ure, whose result corresponds closely with that of Gay-Lussac and Thenard, 100 parts of wax are composed of carbon

80.4, oxygen 8.3, and hydrogen 11.3; from which it is probable that it consists of 13 equivalents of the first element, 1 equivalent of the second, and 11 equivalents of the third.

ALCOHOL.

Alcohol is the intoxicating ingredient of all spirituous and vinous liquors. It does not exist ready formed in plants, but is a product of the vinous fermentation, the theory of which will be stated in a subsequent section.

Common alcohol or spirit of wine is prepared by distilling whisky or some ardent spirit, and the rectified spirit of wine is procured by a second distillation. The former has a specific gravity of about 0.867, and the latter of 0.835 or 0.84 In this state it contains a quantity of water, from which it may be freed by the action of substances which have a strong affinity for that liquid. Thus, when carbonate of potash, heated to about 300° F. is mixed with spirit of wine, the alkali unites with the water, forming a dense solution, which, on standing, separates from the alcohol, so that the latter may be removed by decantation. To the alcohol, thus deprived of part of its water, fresh portions of the dry carbonate are successively added, until it falls through the spirit without being moistened. Other substances, which have a powerful attraction for water, may be substituted for carbonate of potash. Gay-Lussac recommends the use of pure lime or baryta; (An. de Ch. lxxxvi.) and dry alumina may also be employed with advantage. A very convenient process is to mix the alcohol with chloride of calcium in powder, or with quicklime, and draw off the stronger portions by distillation. Another process which has been recommended for depriving alcohol of water is to put it into the bladder of an ox, and suspend it over a sand bath. The water gradually passes through the coats of the bladder, while the pure alcohol is retained; but though this method answers well for strengthening weak spirit, its power of purifying strong alcohol is very questionable. (Journal of Science, xviii.) The strongest alcohol which can be procured by any of these processes has a specific gravity of 0.796 at 60° F. This is called *absolute* alcohol, on the supposition of its being quite free from water.

An elegant and easy process for procuring absolute alcohol has lately been proposed by Mr. Graham. (Edinburgh Philos. Trans. for 1828.) A large shallow basin is covered to a small depth with quicklime in coarse powder, and a smaller one containing three or four ounces of commercial alcohol is supported just above it. The whole is placed upon the plate of an air pump, covered by a low receiver, and the air withdrawn until the alcohol evinces signs of ebullition. Of the mingled vapours of water and alcohol which fill the receiver, the former alone is absorbed by the quicklime, while the latter is unaffected. Now it is found that water cannot remain in alcohol, unless covered by an atmosphere of its own vapour; and consequently the water continues to evaporate without interruption, while the evaporation of the alcohol is entirely arrested by the pressure of the vapour of alcohol on its surface. Common alcohol is in this way entirely deprived of water in the course of about five days. The temperature should be preserved as uniform as possible during the process. Sulphuric acid cannot be substituted for quicklime, since both vapours are absorbed by this liquid.

Alcohol is a colourless elastic fluid, of a penetrating odour, and burning taste. It is highly volatile, boiling, when its density is 0.820, at the temperature of 176° F. The specific gravity of its vapour, according to Gay-Lussac, is 1.613. Like volatile liquids in general, it produces a considerable degree of cold during evaporation. It has hitherto retained its fluidity under every degree of cold to which it has been exposed. Mr. Hutton, indeed, announced in the 34th volume of Nicholson's Journal, that he had succeeded in freezing alcohol; but the fact itself is regarded as doubtful, since no description of the method has hitherto been published. In the experiments of Mr. Walker, alcohol was found to retain its fluidity at —91° F.

Alcohol is highly inflammable, and burns with a lambent yellowish-blue flame. Its colour varies considerably with the strength of the alcohol, the blue tint predominating when it is strong, and the yellow when it is diluted. Its combustion is not attended with the least degree of smoke, and the sole products are water and carbonic acid. When transmitted through a red-hot tube of porcelain, it is resolved into car-

buretted hydrogen, carbonic oxide, and water, and the tube is lined with a small quantity of charcoal.

Alcohol unites with water in every proportion. The act of combining is usually attended with diminution of volume, so that a mixture of 50 measures of alcohol and 50 of water occupies less than 100 measures. Owing to this circumstance, the action is accompanied with increase of temperature. Since the density of the mixture increases as the water predominates, the strength of the spirit may be estimated by its specific gravity. Equal weights of absolute alcohol and water constitute *proof spirit*, the density of which is 0.917; but the proof spirit employed by the colleges for tinctures has a specific gravity of 0.930, or 0.935.

Of the salifiable bases alcohol can alone dissolve potash, soda, lithia, ammonia, and the vegetable alkalies. None of the earths, or other metallic oxides, are dissolved by it. Most of the acids attack it by the aid of heat, giving rise to a class of bodies to which the name of *ether* is applied. All the salts which are either insoluble, or sparingly soluble in water, are insoluble in alcohol. The efflorescent salts are, likewise, for the most part insoluble in this menstruum; but, on the contrary, it is capable of dissolving all the deliquescent salts, except carbonate of potash. Many of the vegetable principles, such as sugar, manna, camphor, resins, balsams, and the essential oils, are soluble in alcohol.

The solubility of certain substances in alcohol appears owing to the formation of definite compounds, which are soluble in that liquid. This has been proved of the chlorides of calcium, manganese, and zinc, and of the nitrates of lime and magnesia, by Mr. Graham in the essay above cited. It appears from his experiments that all these bodies unite with alcohol in definite proportion, and yield crystalline compounds, which are deliquescent and soluble both in water and alcohol. From their analogy to hydrates, Mr. Graham has applied to them the name of *alcoates*. These are formed by dissolving the substances in absolute alcohol by means of heat, when on cooling a group of crystals more or less irregular is deposited. The salt and alcohol employed for the purpose should be quite anhydrous; for the crystallization is prevented by a very small quantity of water. Estimating the combining proportion of

alcohol at 23, the alcoate of chloride of calcium is composed of one equivalent of chloride of calcium, and three equivalents and a half of alcohol. Nitrate of magnesia crystallizes with nine equivalents of alcohol; nitrate of lime with 2½ equivalents; proto-chloride of manganese with three equivalents; and chloride of zinc with half an equivalent of alcohol.

The constitution of alcohol has been ably investigated by M. Saussure, jun. (An. de Ch. lxxxix.) According to his analysis, which was made by transmitting the vapour of absolute alcohol through a red-hot porcelain tube, and examining the products, this fluid is composed of carbon 51.98, oxygen 34.32, and hydrogen 13.70. From these data, alcohol is inferred to consist of

Carbon, . . .	12	2 equivalents .	52.17
Oxygen, . . .	8	1 equivalent .	34.79
Hydrogen, . . .	3	3 equivalents .	13.04
	23		100.00

These numbers, it is obvious, are in such proportion that alcohol may be regarded as a compound of 14 parts or one equivalent of olefiant gas, and 9 parts or one equivalent of water. Hence the equivalent of alcohol is 23.

Knowing the composition of alcohol by weight, it is easy to calculate the proportion of its constituents by measure. For this purpose it is only necessary to divide 14 by 0.972, (the sp. gr. of olefiant gas) and 9 by 0.625, (the sp. gr. of aqueous vapour;) and as the quotients are very nearly equal, it follows that alcohol must consist of equal measures of aqueous vapour and olefiant gas. It is inferred, also, that these two gaseous bodies, in uniting to form the vapour of alcohol, occupy half the space which they possessed separately; because the density of the vapour of alcohol, as calculated on this supposition, ($0.9722 + 0.625 = 1.5972$) corresponds closely with 1.613, the number which was ascertained experimentally by Gay-Lussac.

Considerable uncertainty prevailed a few years ago as to the state in which alcohol exists in wine. Some chemists were of opinion that it is generated by the heat employed in the distillation; while others thought that the alcohol is merely sepa-

rated during the process. This question was finally determined by Mr. Brande, who made it the subject of two essays which were published in the Philosophical Transactions for 1811 and 1813. That wine contains alcohol ready formed he demonstrated, by separating it without the aid of heat. His method consists in precipitating the acid and extractive colouring matters of the wine by subacetate of lead, and then depriving the alcohol of water by dry carbonate of potash, in the way already mentioned. The pure alcohol, which rises to the surface, is then measured by means of a narrow graduated glass tube. The same fact has since been established by the experiments of Gay-Lussac, who procured alcohol from wine by distilling it *in vacuo* at the temperature of 60° F. He also succeeded in separating the alcohol by the method of Mr. Brande; but he suggests the employment of litharge in fine powder, instead of subacetate of lead, for precipitating the colouring matter. (Mem. d'Arcueil, vol. iii.)

The preceding researches of Mr. Brande led him to examine the quantity of alcohol contained in spirituous and fermented liquors. According to his experiments, brandy, rum, gin, and whisky, contain from 51 to 54 per cent of alcohol, of specific gravity 0.825. The stronger wines, such as Lissa, Raisin wine, Marsala, Port, Madeira, Sherry, Teneriffe, Constantia, Malaga, Bucellas, Calcavella, and Vidonia, contain from between 18 or 19 to 25 per cent of alcohol. In Claret, Sauterne, Burgundy, Hock, Champagne, Hermitage, and Gooseberry wine, the quantity is from 12 to 17 per cent. In cider, sherry, ale, and porter, the quantity varies from 4 to near 10 per cent. In all spirits, such as brandy or whisky, the alcohol is simply combined with water; whereas in wine it is in combination with mucilaginous, saccharine, and other vegetable principles, a condition which tends to diminish the action of the alcohol upon the system. This may, perhaps, account for the fact that brandy, which contains little more than twice as much real alcohol as good port wine, has an intoxicating power which is considerably more than double.

ETHER.

The name *ether* was formerly employed to designate the volatile inflammable liquid which is formed by heating a mix-

ture of alcohol and sulphuric acid; but the same term has since been extended to several other compounds produced by the action of acids on alcohol, and which, from their volatility and inflammability, were supposed to be identical or nearly so with sulphuric ether. It appears, however, from the researches of several chemists, but especially of Thenard, that ethers, though analogous in their leading properties, frequently differ both in composition and in their mode of formation. (Mémoires d'Arcueil, vol. i. and ii.)

Sulphuric ether.—In forming this compound, strong sulphuric acid is gently poured upon an equal weight of rectified spirit of wine contained in a thin glass retort, and after mixing the fluids together by agitation, which occasions a free disengagement of caloric, the mixture is heated as rapidly as possible until ebullition commences. At the beginning of the process nothing but alcohol passes over; but as soon as the liquid boils, ether is generated, and condenses in the recipient, which is purposely kept cool by the application of ice or moist cloths. When a quantity of ether is collected, equal in general to about half of the alcohol employed, white fumes begin to appear in the retort. At this period, the process should be discontinued, or the receiver changed; for although ether does not cease to be generated, its quantity is less considerable, and several other products make their appearance. Thus on continuing the operation, sulphurous acid is disengaged, and a yellowish liquid, commonly called *ethereal oil* or *oil of wine*, passes over into the receiver. If the heat be still continued, a large quantity of olefiant gas is disengaged, and all the phenomena ensue which were mentioned in the description of that compound. (Page 350.)

Ether, thus formed, is always mixed with alcohol, and generally with some sulphurous acid. To separate these impurities the ether should be agitated with a strong solution of potash, which neutralizes the acid, while the water unites with the alcohol. The ether is then distilled by a very gentle heat, and may be rendered still stronger by distillation from chloride of calcium.

To comprehend the theory of the formation of ether, it is necessary to compare the composition of this substance with that of alcohol. Ether was analyzed by Saussure in the same

manner as alcohol; and from the data furnished by his analysis, corrected by Gay-Lussac, (An. de Ch. xcv. 314), ether is inferred to consist of 28 parts or two equivalents of olefiant gas, and 9 parts or one equivalent of water. But alcohol is composed of one equivalent of olefiant gas and one equivalent of water; so that, if from two equivalents of alcohol one of water be withdrawn, the remaining elements are in exact proportion for constituting ether. This is the precise mode in which sulphuric acid is supposed to operate in generating ether, an effect which it is well calculated to produce, owing to its strong affinity for moisture. (Page 268.) This view was first proposed by Fourcroy and Vauquelin, and accounts for the phenomena in a very satifactory manner. These chemists, it is true, erred in thinking that the sulphuric acid occasions no other change; since subsequent observation has proved that sulpho-vinic acid, to the constitution of which sulphuric acid is essential, is formed even at the very commencement of the process. Notwithstanding this error, however, the production of ether may be justly ascribed to the sulphuric acid abstracting water or its elements from the alcohol, an opinion which is supported by various circumstances. Thus it accounts for the disengagement of sulphurous acid and olefiant gas towards the middle and close of the process; for since the elements of the alcohol alone contribute to the formation of ether, while all the sulphuric acid remains in the retort, and most of it in a free state, it is apparent that the relative quantities of alcohol and acid must be continually changing during the operation, until at length the latter predominates so greatly as to be able to deprive the former of all its water, and thus give rise to the disengagement of olefiant gas. (Page 350.) Accordingly it is well known, that if fresh alcohol be added as soon as the production of pure ether ceases, an additional quantity of that substance will be produced. It follows, also, from the same doctrine, that the power of the same portion of acid in forming ether must be limited, because it gradually becomes so diluted with water that it is at last unable to disunite the elements of the alcohol. Consistently with the same view, it is found that ether, precisely analogous to that from sulphuric acid, may be prepared by digesting alcohol with

other acids which have a strong affinity for water, as for example with phosphoric, arsenic, and fluoboric acids.

The production of a peculiar acid in the preceding process was first noticed by M. Dabit, about the year 1800. This substance, to which the name of *sulpho-vinic* acid is applied, has since been examined by Sertuerner, Vogel, and Gay-Lussac, and the two last mentioned philosophers regarded it as a compound of hyposulphuric acid and a peculiar vegetable matter. Mr. Hennel, however, has lately given a different, and to all appearance a more correct view of its nature. According to this chemist, sulphuric acid and oil of wine are both composed of sulpho-vinic acid and carburet of hydrogen. Oil of wine, which has no acid reaction when pure, consists of 2 equivalents of sulphuric acid, 8 of carbon, and 8 of hydrogen. When heated, it parts with half of its carbon and hydrogen, and sulpho-vinic acid remains, consisting of 2 equivalents of sulphuric acid, 4 of carbon, and 4 of hydrogen. Oil of wine is a perfectly neutral compound, in which carburet of hydrogen acts the part of an alkali in neutralizing sulphuric acid. In sulpho-vinic acid half the sulphuric acid appears to be neutralized by carburet of hydrogen. (Philos. Trans. for 1826, p. 247, or Journal of Science, xxi. 331.)

Additional researches by Mr. Hennel have rendered it probable, that sulpho-vinic acid is in reality a stage in the formation of sulphuric ether. That acid is present in greatest quantity when the ingredients are first mixed, and prior to the application of artificial heat, one-half of the sulphuric acid being then in combination with carburet of hydrogen; but on distilling the mixture, sulpho-vinic acid diminishes as the quantity of ether increases, until towards the close of the process sulpho-vinic acid entirely disappears, and the sulphuric acid, which was previously in combination, is set free. In support of this view Mr. Hennel remarks, that however the operation may be conducted, the formation of ether is always accompanied or preceded with that of sulpho-vinic acid; and he has added the additional fact, that on distilling sulpho-vinate of potash with concentrated sulphuric acid, no alcohol being present, ether is generated. It appears, then, that ether may be directly developed from sulpho-vinic acid; that, in the

ordinary process, the formation of the latter always precedes that of the former; and that during the period of ether being generated, sulpho-vinic acid is decomposed. These facts give great plausibility to the opinion of Mr. Hennel; but it does not follow, nor does Mr. Hennel maintain, that ether cannot be generated but through the medium of sulpho-vinic acid. The nature of the difference in the constitution of alcohol and ether, and the production of ether from alcohol and phosphoric acid, incline to an opposite inference. (Phil. Trans. 1828.)

Mr. Hennel has succeeded in obtaining alcohol through the medium of ether. For, when ether and sulphuric acid are heated together, oil of wine and sulpho-vinic acid are among the products; and on distilling sulpho-vinate of potash with sulphuric acid, not concentrated as above, but previously diluted with half its weight of water, alcohol is generated. It hence appears that carburet of hydrogen, at the moment of separation from sulphuric acid, is in a state peculiarly favourable for combining with water; and that, in doing so, it gives rise to alcohol or ether, according to the condition in which it is placed.

Sulphuric ether is a colourless fluid, of a hot pungent taste, and fragrant odour. Its specific gravity in its purest form is about 0.700, or according to Lovitz 0.632; but that of the shops is 0.74 or even lower, owing to the presence of alcohol. Its volatility is exceedingly great:—Under the atmospheric pressure, ether of density 0.720 boils at 96° or 98° F., and at about —40° F. in a vacuum. (Black's Lectures, i. 151.) Its evaporation, from the rapidity with which it takes place, occasions intense cold, sufficient under favourable circumstances for freezing mercury. Its vapour has a density of 2.586. At 46 degrees below zero of Fahr. it is congealed.

Ether combines with alcohol in every proportion, but is very sparingly soluble in water. When agitated with that fluid, the greater part separates on standing, a small quantity being retained, which imparts an ethereal odour to the water. The ether so washed is very pure, because the water retains the alcohol with which it is mixed.

Ether is highly inflammable, burning with a blue flame, and

formation of water and carbonic acid. With oxygen gas its vapour forms a mixture which explodes violently on the approach of flame, or by the electric spark. On being transmitted through a red-hot porcelain tube it undergoes decomposition, and yields the same products as alcohol.

When a coil of platinum wire is heated to redness, and then suspended above the surface of ether contained in an open vessel, the wire instantly begins to glow, and continues in that state until all the ether is consumed. (Davy.) During this slow combustion, pungent acrid fumes are emitted, which, if received in a separate vessel, condense into a colourless liquid possessed of acid properties. Mr. Daniell, who prepared a large quantity of it, was at first inclined to regard it as a new acid, and described it under the name of *lampic acid;* but he has since ascertained that its acidity is owing to the acetic acid, which is combined with some compound of carbon and hydrogen different both from ether and alcohol. (Journal of Science, vi. and xii.) Alcohol, when similarly burned, likewise yields acetic acid.

If ether is exposed to light in a vessel partially filled, and which is frequently opened, it gradually absorbs oxygen, and a portion of acetic acid is generated. This change was first noticed by M. Planche, and has been confirmed by Gay-Lussac. (An. de Ch. et de Ph. ii. 98 and 213.) M. Henry of Paris attributes its developement to acetic ether, which he believes to be always contained in sulphuric ether.

The composition of ether by volume may be inferred in the same manner as in the case of alcohol; (page 730) namely, by dividing 28 by 0.972, and 9 by 0.625. Ether is thus found to consist of two measures of olefiant gas and one measure of watery vapour; and supposing these three measures, in combining, to contract to one third of their volume, the specific gravity of the vapour of ether will be $0.972 \times 2 + 0.625 = 2.569$. Now this is so near 2,586, the specific gravity which Gay-Lussac found by actual trial, that the preceding supposition may fairly be admitted.

The solvent properties of ether are less extensive than those of alcohol. It dissolves the essential oils and resins, and some of the vegetable alkalies are soluble in it. It unites also

with ammonia; but the fixed alkalies are insoluble in this menstruum.

Nitrous ether.—This compound is prepared by distilling a mixture of concentrated nitric acid with an equal weight of alcohol; but as the reaction is apt to be exceedingly violent, the process should be conducted with extreme care. The safest method is to add the acid to the alcohol by small quantities at a time, allowing the mixture to cool after each addition before more acid is added. The distillation is then conducted at a very gentle temperature, and the ether collected in Woulfe's apparatus. The theory of the process is in some respects obscure; but as the formation of ether is attended with the disengagement of protoxide and deutoxide of nitrogen, together with free nitrogen and carbonic acid, it follows that the alcohol and acid mutually decompose each other. Thenard inferred from his experiments, that ether is a compound of alcohol and nitrous acid; and, consequently, that the essential change during its formation consists in the conversion of nitric into nitrous acid at the expense of one part of the alcohol, while the remainder of that fluid combines with the nitrous acid. Consistently with this view, nitrous ether may be made directly by the action of anhydrous nitrous acid on pure alcohol.

In an essay lately published by MM. Dumas and Boullay, a different opinion has been suggested. According to a careful analysis of nitrous ether, they find it to consist of 4 equivalents of carbon, 5 of hydrogen, 1 of nitrogen, and 4 of oxygen. These elements are in proportion to constitute 2 equivalents of olefiant gas, 1 of water, and 1 of hyponitrous acid. (An. de Ch. et Physique, xxxvii. 26.)

The nitrous agrees with sulphuric ether in its leading properties; but it is still more volatile. When recently distilled from quicklime by a gentle heat, it is quite neutral; but it soon becomes acid by keeping. The products of its spontaneous decomposition are alcohol, nitrous acid, and a little acetic acid. A similar change is instantly effected by mixing the ether with water, or distilling it at a high temperature. It is also decomposed by potash, and, on evaporation, crystals of the nitrite or hyponitrite of that alkali are deposited. (Mémoires d'Arcueil, vol. i.)

Acetic ether.—This ether is analogous in composition to the preceding, and is formed by distilling acetic acid with an equal weight of alcohol. When set on fire, it burns with disengagement of acetic acid; and when mixed with a strong solution of potash, and subjected to distillation, pure alcohol passes over, and acetate of potash remains in the retort. It is hence inferred by Thenard to consist of acetic acid and alcohol. When pure it is quite neutral.

According to Thenard, the acetic is the only vegetable acid which forms ether by being heated alone with alcohol. Ether may also be generated by treating tartaric, oxalic, malic, citric, or benzoic acid with a mixture of alcohol and sulphuric acid, and Thenard regards these ethers as compounds of a vegetable acid with alcohol. But Dumas and Boullay, in the essay above referred to, declare that the elements of all these ethers are in such proportion as to constitute one equivalent of acid, one of water, and two of olefiant gas. They believe them, as also nitrous acid, to be hydrated salts, in which carburet of hydrogen acts the part of an alkali. This view is certainly supported by the observations of Mr. Hennel relative to oil of wine, and by the constitution of muriatic ether. The employment of sulphuric acid in their formation is likewise favourable to this opinion. The alcohol obtained by distillation with potash, is supposed by Dumas and Boullay to be generated during the process.

Muriatic ether.—This compound, which is prepared by distilling a mixture of concentrated muriatic acid and pure alcohol, was supposed by Thenard to be analogous in composition to nitrous ether. It appears, however, from the experiments of Robiquet and Colin, that it consists of muriatic acid and the elements of olefiant gas, and is therefore quite free from oxygen. (An. de Ch. et de Ph. ii.) It does not affect the colour of litmus paper, is denser than water, volatilizes still more rapidly than sulphuric ether, and is highly inflammable. Its combustion is attended with the disengagement of a large quantity of muriatic acid gas.

Hydriodic ether, first prepared by Gay-Lussac, appears to be similar in composition to muriatic ether. Serullas recommends that it should be formed by introducing into a retort

40 parts of iodine and 100 of alcohol of 0.827, and then gradually adding 2.5 parts of phosphorus in small fragments. The mixture is kept in ebullition till it is nearly exhausted, and then 25 or 30 parts of alcohol are added and distilled off from the remainder. The ether is purified by washing with water; after which it is dried by distillation from chloride of calcium. (An. de Ch. et Ph. xlii. 119.)

Hydro-bromic ether may be prepared by a process similar to the foregoing.

Liebig has prepared *sulpho-cyanic ether*, which he believes to be a compound of sulphuret of cyanogen and carburet of hydrogen, by distilling a mixture of 1 part of sulpho-cyanuret of potassium, 2 of sulphuric acid, and 3 of strong alcohol. (An. de Ch. et Ph. xli. 202.)

BITUMINOUS SUBSTANCES.

Under this title are included several inflammable substances which, though of vegetable origin, are found in the earth, or issue from its surface. They may be conveniently arranged under the two heads of bitumen and pit-coal. The first comprehends naphtha, petroleum, mineral tar, mineral pitch, asphaltum, and retinasphaltum, of which the three first mentioned are liquid, and the others solid. The second comprises brown coal, the different varieties of *common* or *black coal*, and *glance coal*.

Bitumen.—Naphtha is a volatile limpid liquid, of a strong peculiar odour, and generally of a light yellow colour; but it may be rendered colourless by careful distillation. Its specific gravity, when highly rectified, is 0.758. It is very inflammable, and burns with a white flame mixed with much smoke. At 186° F. it enters into ebullition, and its vapour has a density of 2.833. (Saussure.) It retains its liquid form at zero of Fahrenheit. It is insoluble in water, and very soluble in alcohol; but it unites in every proportion with sulphuric ether, petroleum, and oils. It appears from the observations of Saussure to undergo no change by keeping, even in contact with air.

Naphtha contains no oxygen, and is hence employed for

protecting the more oxidable metals, such as potassium and sodium, from oxidation. According to the analysis of Saussure, it is composed of carbon and hydrogen in the proportion of six equivalents of the former to five of the latter. Dr. Thomson states the composition of naphtha from coal tar, which seems identical with mineral naphtha, to consist of six equivalents of carbon and six of hydrogen. (Page 358.)

Naphtha occurs in some parts of Italy, and on the banks of the Caspian Sea. It may be procured also by distillation from petroleum.

Petroleum is much less limpid than naphtha, has a reddish-brown colour, and is unctuous to the touch. It is found in several parts of Britain and the continent of Europe, in the West Indies, and in Persia. It occurs particularly in coal districts. *Mineral tar* is very similar to petroleum, but is more viscid and of a deeper colour. Both these species become thick by exposure to the atmosphere, and in the opinion of Mr. Hatchett pass into solid bitumen.

Asphaltum is a solid brittle bitumen, of a black colour, vitreous lustre, and conchoidal fracture. It melts easily, and is very inflammable. It emits a bituminous odour when rubbed, and by distillation yields a fluid like naphtha. It is soluble in about five times its weight of naphtha, and the solution forms a good varnish. It is rather denser than water.

Asphaltum is found on the surface and on the banks of the Dead Sea, and occurs in large quantity in Barbadoes and Trinidad. It was employed by the ancients in building, and is said to have been used by the Egyptians in embalming.

Mineral Pitch or *Maltha* is likewise a solid bitumen, but is much softer than asphaltum. Elastic bitumen, or *mineral caoutchouc*, is a rare variety of mineral pitch, found only in the Odin mine, near Castleton in Derbyshire.

Retinasphaltum is a peculiar bituminous substance, found associated with the brown coal of Bovey in Devonshire, and described by Mr. Hatchett in the Philosophical Transactions for 1804. It consists partly of bitumen, and partly of resin, a composition which led Mr. Hatchett to the opinion that bitumens are chiefly formed from the resinous principle of plants.

Pit Coal.—Brown coal is characterized by burning with a

peculiar bituminous odour, like that of peat. It is sometimes earthy, but the fibrous structure of the wood from which it is derived is generally more or less distinct, and hence this variety is called *bituminous wood*. *Pitch coal* or jet, which is employed for forming ear-rings and other trinkets, is intermediate between brown and black coal, but is perhaps more closely allied to the former than the latter.

Brown coal is found at Bovey in Devonshire, (Bovey coal) in Iceland, where it is called *surturbrand*, and in several parts of the continent, especially at the Meissner in Hessia, in Saxony, Prussia, and Styria.

Of the *black or common coal* there are several varieties, which differ from each other, not only in the quantity of foreign matters, such as sulphuret of iron and earthy substances, which they contain, but also in the proportion of what may be regarded as essential constituents. Thus some kinds of coal consist almost entirely of carbonaceous matters, and therefore form little flame in burning; while others, of which cannel coal is an example, yield a large quantity of inflammable gases by heat, and consequently burn with a large flame. Dr. Thomson has arranged the different kinds of coal which are met with in Britain into four subdivisions. (An. of Phil. xiv.) The first is *caking coal*, because its particles are softened by heat and adhere together, forming a compact mass. The coal found at Newcastle, around Manchester, and in many other parts of England, is of this kind. The second is termed *splint coal*, from the splintery appearance of its fracture. The *cherry coal* occurs in Staffordshire, and in the neighbourhood of Glasgow. Its structure is slaty, and it is more easily broken than splint coal, which is much harder. It easily takes fire, and is consumed rapidly, burning with a clear yellow flame. The fourth kind is *cannel coal*, which is found of peculiar purity at Wigan in Lancashire. In Scotland it is known by the name of *parrot coal*. From the brilliancy of the light which it emits while burning, it is sometimes used as a substitute for candles, a practice which is said to have led to the name of *cannel* coal. It has a very compact structure, does not soil the fingers when handled, and admits of being polished. Snuff-boxes and other ornaments are made with this coal; and it is peculiarly

well fitted for forming coal gas. According to the experiments of Dr. Thomson, these varieties of coal are thus constituted:

	Caking Coal.	Splint Coal.	Cherry Coal.	Cannel Coal.
Carbon,	75.28	75.00	74.45	64.72
Hydrogen,	4.18	6.25	12.40	21.56
Nitrogen,	15.96	6.25	10.22	13.72
Oxygen,	4.58	12.50	2.93	0.00
	100.00	100.00	100.00	100.00

Judging from the quantity of oxidized products (water, carbonic acid, and carbonic oxide) which are procured during the distillation of coal, Dr. Henry infers that coal contains more oxygen than was found by Thomson. (Elements, 11th Edit. ii. p. 348.) This opinion is supported by the analysis of Dr. Ure, who found 26.66 per cent of oxygen in splint, and 21.9 in cannel coal. When coal is heated to redness in close vessels, a great quantity of volatile matter is dissipated, and a carbonaceous residue, called *coke*, remains in the retort. The volatile substances are coal tar, acetic acid, water, sulphuretted hydrogen, and hydrosulphuret and carbonate of ammonia, together with the several gases formerly enumerated. (Page 361.) The greater part of these substances are real products, that is, are generated during the distillation. The bituminous matters probably exist ready formed in coal; but Dr. Thomson is of opinion that these are also products, and that coals are atomic compounds of carbon, hydrogen, nitrogen, and oxygen.

Glance coal.—Glance coal, or *anthracite*, differs from common coal, which it frequently accompanies, in containing no bituminous substances, and in not yielding inflammable gases by distillation. Its sole combustible ingredient is carbon, and consequently it burns without flame. It commonly occurs in the immediate vicinity of basalt, under circumstances which lead to the suspicion that it is coal from which the volatile ingredients have been expelled by subterranean heat. At the Meissner, in Hessia, it is found between a bed of brown coal and basalt. Kilkenny coal appears to be a variety of glance coal. (Thomson, An. of Phy. vol. xv.)

SECTION IV.

SUBSTANCES, THE OXYGEN AND HYDROGEN OF WHICH ARE IN EXACT PROPORTION FOR FORMING WATER.

SUGAR.

Sugar is an abundant vegetable product, existing in a great many ripe fruits, though few of them contain it in sufficient quantity for being collected. The juice which flows from incisions made in the trunk of the American maple tree, is so powerfully saccharine that it may be applied to useful purposes. Sugar was prepared in France and Germany during the late war from the beet-root; and this manufacture is at present carried on in France on a scale of considerable magnitude. Proust extracted it in Spain from grapes. But nearly all the sugar at present used in Europe is obtained from the sugar-cane (*Arundo saccharifera*), which contains it in greater quantity than any other plant. The process, as practised in our West India Islands, consists in evaporating the juice of the ripe cane by a moderate and cautious ebullition, until it has attained a proper degree of consistence for crystallizing. During this operation lime water is added, partly for the purpose of neutralizing free acid, and partly to facilitate the separation of extractive and other vegetable matters, which unite with the lime and rise as a scum to the surface. When the syrup is sufficiently concentrated, it is drawn off into shallow wooden coolers, where it becomes a soft solid composed of loose crystalline grains. It is then put into barrels with holes in the bottom, through which a black ropy juice, called molasses or treacle, gradually drops, leaving the crystallized sugar comparatively white and dry. In this state it constitutes raw or muscovado sugar.

Raw sugar is further purified by boiling a solution of it with white of eggs, or the serum of bullock's blood, lime water being generally employed at the same time. When properly concentrated, the clarified juice is received in conical earthen vessels, the apex of which is undermost, in order that the

fluid parts may collect there, and be afterwards drawn off by the removal of a plug. In this state it is loaf or refined sugar. In the process of refining sugar, it is important to concentrate the syrup at a low temperature; and on this account a very great improvement was introduced some years ago by conducting the evaporation *in vacuo*.

Pure sugar is solid, white, inodorous, and of a very agreeable taste. It is hard and brittle, and when two pieces are rubbed against each other in the dark, phosphorescence is observed. It crystallizes in the form of four or six-sided prisms bevelled at the extremities. The crystals are best made by fixing threads in syrup, which is allowed to evaporate spontaneously in a warm room; and the crystallization is promoted by adding spirit of wine. In this state it is known by the name of *sugarcandy*.

Sugar undergoes no change on exposure to the air; for the deliquescent property of raw sugar is owing to impurities. It is soluble in an equal weight of cold, and to almost any extent in hot water. It is soluble in about four times its weight of boiling alcohol, and the saturated solution, by cooling and spontaneous evaporation, deposits large crystals. When the aqueous solution of sugar is mixed with yeast, it undergoes the vinous fermentation, the theory of which will be explained in a subsequent section.

Sugar unites with the alkalies and alkaline earths, forming compounds in which the taste of the sugar is greatly injured; but it may be obtained again unchanged by neutralizing with sulphuric acid, and dissolving the sugar in alcohol. When boiled with oxide of lead, it forms an insoluble compound, which consists of 58.26 parts of oxide of lead, and 41.74 parts of sugar (Berzelius); but it is not precipitated by acetate or subacetate of lead.

Sulphuric acid decomposes sugar with deposition of charcoal; and nitric acid causes the production of oxalic acid, as already described in a former section. The vegetable acids diminish the tendency of sugar to crystallize.

Sugar is very easily affected by heat, acquiring a dark colour and burned flavour. At a high temperature it yields the usual products of the destructive distillation of vegetable matter, together with a considerable quantity of pyromucic acid.

The analyses of sugar by different chemists are considerably discordant. This is accounted for not only by errors of manipulation, and impurity in the materials; but in part arises, according to Dr. Prout, from difference in composition. In his Essay on Alimentary Substances, published in the Philosophical Transactions for 1827, page 355, he states that pure cane sugar as exemplified in sugarcandy and the best loaf sugar, well dried at 212° F., consists of 42.85 parts of carbon, and 57.15 of oxygen and hydrogen in the proportion for forming water; while sugar from honey contains only 36.36 per cent of carbon. He considers the sugar from starch, diabetic urine, and grapes, to be nearly the same as that from honey. The sugar from the maple tree and beet root corresponds with that from the cane; but the quantity of carbon in these kinds of sugar appears to vary from 40 to 42.85 per cent. The atomic constitution of sugar is unknown; but from a former analysis of Dr. Prout, it is thought that its elements are in the ratio of 6 parts or one equivalent of carbon to 9 parts or one equivalent of water, or by volume of one measure of the vapour of carbon to one measure of aqueous vapour. This estimate is admitted by most chemists.

Molasses.—The saccharine principle of treacle has been supposed to be different from crystallizable sugar; but it chiefly consists of common sugar, which is prevented from crystallizing by the presence of foreign substances, such as saline, acid, and other vegetable matters.

Sugar of Grapes.—The sugar procured from the grape has the essential properties of common sugar. Its taste, however, is not so sweet as that of common sugar, and according to Saussure and Prout it differs slightly in composition, containing a smaller quantity of carbon. The saccharine principle of the acidulous fruits has not been particularly examined. It is obtained with difficulty in a pure state, owing to the presence of vegetable acids, which prevent it from crystallizing.

A saccharine substance similar to that from grapes may be procured from several vegetable principles, such as starch and the ligneous fibre, by the action of sulphuric acid.

Honey.—According to Proust honey consists of two kinds of saccharine matter, one of which crystallizes readily and is analogous to common sugar, while the other is uncrystallizable.

They may be separated by mixing honey with alcohol, and pressing the solution through a piece of linen. The liquid sugar is removed, and the crystallizable portion is left in a solid state. Besides sugar it contains mucilaginous, colouring, and odoriferous matter, and probably a vegetable acid. Diluted with water honey is susceptible of the vinous fermentation without the addition of yeast.

The natural history of honey is as yet imperfect. It is uncertain whether honey is merely collected by the bee from the nectaries of flowers, and then deposited in the hive unchanged, or whether the saccharine matter of the flower does not undergo some change in the body of the animal.

Manna.—This saccharine matter is the concrete juice of several species of ash, and is procured in particular from the *Fraxinus ornus*. The sweetness of manna is owing, not to sugar, but to a distinct principle called *mannite*, which is mixed with a peculiar vegetable extractive matter. Manna is soluble both in water and boiling alcohol, and the latter, on cooling, deposits pure mannite in the form of minute acicular crystals, which are often arranged in concentrical groups. Mannite differs from sugar, in not fermenting when mixed with water and yeast. According to Dr. Prout it contains 38.7 per cent of carbon, and 61.3 of oxygen and hydrogen in the proportion to form water.

Sugar of Liquorice.—The root of the *Glycirrhiza glabra*, as also the black extract of the root well known under the name of *liquorice*, contains a saccharine principle; but it is quite distinct from sugar. It may be prepared by infusing the root in boiling water, filtering when cold, and gradually adding sulphuric acid as long as a precipitate, which is a compound of the acid and saccharine matter, is formed. It is first washed with water acidulated with sulphuric acid, and then with pure water; and it is subsequently dissolved in alcohol, which leaves a little vegetable albumen and mucilage. Solution of carbonate of potash is then added very gradually, so as exactly to neutralize the acid; and after the sulphate of potash has subsided, the alcoholic solution is decanted and evaporated. It may also be obtained in a similar manner from the extract, except that the solution, when first made, must be purified by white of egg.

Sugar of liquorice is thus procured in the form of a yellow transparent mass, which is unchangeable in the air, and soluble in water and alcohol. It is characterized by its tendency to form sparingly soluble compounds with acids, which accordingly precipitate it from its solution in cold water. It unites also readily with alkaline bases; and when digested in water containing carbonate of potash, baryta, or lime, carbonic acid is slowly evolved, and a soluble compound of the base with the saccharine matter is generated. (Berzelius.)

STARCH OR FECULA.—AMIDINE.

Starch exists abundantly in the vegetable kingdom, being one of the chief ingredients of most varieties of grain, of some roots, such as the potato, and of the kernels of leguminous plants. It is easily procured by letting a small current of water fall upon the dough of wheat flour enclosed in a piece of linen, and subjecting it at the same time to pressure between the fingers, until the liquid passes off quite clear. The gluten of the flour is left in a pure state, the saccharine and mucilaginous matters are dissolved, and the starch is washed away mechanically, being deposited from the water on standing in the form of a white powder. An analogous process is practised on a large scale in the preparation of the starch of commerce; and very pure starch may also be obtained in a similar manner from the potato.

Starch is insipid and inodorous, of a white colour, and insoluble in alcohol, ether, and cold water. It does not crystallize; but is commonly found in the shops in six-sided columns of considerable regularity, a form occasioned by the contraction which it suffers in drying. Boiling water acts upon it readily, converting it into a tenacious bulky jelly, which is employed for stiffening linen. In a large quantity of hot water, it is dissolved completely, and is not deposited on cooling. The aqueous solution is precipitated by sub-acetate of lead; but the best test of starch, by which it is distinguished from all other substances, is iodine. This principle forms a blue compound with starch, whether in a solid state or when dissolved in cold water.

Starch unites with the alkalies, forming a compound which

is soluble in water, and from which the starch is thrown down by acids. Strong sulphuric acid decomposes it. Nitric acid in the cold dissolves starch; but converts it by the aid of heat into oxalic and malic acid.

The effects of heat on starch are peculiar, and have lately been examined by M. Caventou. (An. de Chem. et de Ph. xxxi.) On exposing dry starch to a temperature a little above 212° F. it acquires a slightly red tint, emits an odour of baked bread, and is rendered soluble in cold water; and a similar modification is effected by the action of hot water. Gelatinous starch is generally supposed to be a hydrate of starch; but M. Caventou maintains that the jelly cannot by any method be restored to its original state. He regards this modified starch as identical with the substance described by Saussure under the name of *amidine*. Saussure thought it was generated by exposing a paste made with starch and water for a long time to the air; but according to Caventou, the amidine was formed by the action of the hot water on starch in making the paste. Its essential character is to yield a blue colour with iodine, and to be soluble in cold water. On gently evaporating the solution to dryness, it becomes a transparent mass like horn, which retains its solubility in cold water.—To torrefied starch, that is, to starch thus modified by heat, whether in the dry way or by boiling water, the term *amidine* may be applied.

When starch is exposed to a still higher temperature than is sufficient for its conversion into amidine, a more complete change is effected. It then assumes a reddish-brown colour, swells up and softens, dissolves with much greater facility in cold water, and gives with iodine either a purple colour or none at all. In this state it is very analogous to gum, and is employed by calico-printers under the name of *British gum*; but it differs from real gum in not yielding mucic acid by digestion with nitric acid. A similar change may be produced by long-continued ebullition.

The starch from wheat, according to the analysis of Gay-Lussac and Thenard, is composed, in 100 parts, of carbon 43.55, oxygen 49.68, and hydrogen 6.77; and this result agrees with the analysis of potato starch made by Berzelius. The results of Prout and Marcet correspond closely with the

foregoing. The proportion of the constituents of starch is therefore very analogous to that of sugar, a circumstance which will account for the conversion of the former into the latter. This change is effected in seeds at the period of germination, and is particularly exemplified in the process of malting barley, during which the starch of that grain is converted into sugar. Proust* finds that barley contains a peculiar principle which he calls *hordein*, and which he conceived to be converted in malting partly into starch and partly into sugar. Dr. Thomson is of opinion that hordein should rather be regarded as a modification of starch than as a distinct proximate principle†. A similar conversion of starch into sugar appears in some instances to be the effect of frost, as in the potato, apple, aud parsnip.

If starch is boiled for a considerable time in water acidulated with 1-12th of its weight of sulphuric acid, it is wholly converted into a saccharine matter similar to that of the grape; and this change takes place much more rapidly if the temperature is a few degrees above 212° F. This fact was first observed by Kirchoff, and has since been particularly examined by Vogel, De la Rive, and Saussure. It has been established by Saussure that the oxygen of the air exerts no influence over the process, that no gas is disengaged, that the quantity of acid suffers no diminution, and that 100 parts of starch yield 110.14 of sugar. By careful analysis, he found that the only difference in the composition of starch and sugar is, that the latter contains more of the elements of water than the former. He hence inferred that, in Kirchoff's process, the starch is converted into sugar by its elements combining with a certain quantity of oxygen and hydrogen in the proportion to form water; and that the acid acts only by increasing the fluidity of the mass. (An. of Philosophy, vi.) M. Saussure also found that a large quantity of saccharine matter is produced, when gelatinous starch or amidine is kept for a long time either with or without the access of air. (An. de Ch. et de Ph. vol. xi.)

The recent researches of M. Caventou, already referred to, have thrown considerable light on the chemical nature of

* An. de Ch. et de Ph. vol. v. † Annals of Philosophy, vol. x.

several of the amylaceous principles of commerce. The *Indian arrow root*, which is prepared from the root of the *Maranta arundinacea*, has all the characters of pure starch. Sago, obtained from the pith of an East Indian palm tree, (*Cycas circinalis*) and tapioca and cassava, from the root of the *Iatropha Manihot*, are chemically the same substance. They both exist in the plants from which they are extracted in the form of starch; but as heat is employed in their preparation, the starch is more or less completely converted into amidine. It hence follows that pure potato starch may be used instead of arrow root; and that the same material, modified by heat, would afford a good substitute for sago and tapioca. Salep, which is obtained from the *Orchis mascula*, consists almost entirely of the substance called *bassorin*, together with a small quantity of gum and starch.

When starch moistened with water is digested with an equal weight of peroxide of manganese, a volatile acid, possessed of an odour similar to prussic acid, passes over. Its discoverer, M. Tünnermann, who has given it the name of *amylic acid*, considers it a compound of 3 equivalents of oxygen and 2.5 of carbon; but it requires further examination before being enumerated as a distinct acid. (Journal of Science, N. S. iv. 444.)

GUM.

Gum is a common proximate principle of vegetables, and is not confined to any particular part of plants. The purest variety is gum arabic, the concrete juice of several species of the *Mimosa* or *Acacia*, natives of Africa and Arabia.

Gum arabic occurs in small rounded, transparent, friable grains, commonly of a pale yellow colour, inodorous, and nearly tasteless. It softens when put into water, and then dissolves, forming a viscid solution called *mucilage*. It is insoluble in alcohol and ether, and the former precipitates gum from its solution in water in the form of opaque white flakes. It is soluble both in alkaline solutions and in lime water, and is precipitated unchanged by acids. The dilute acids dissolve, and the concentrated acids decompose gum. Sulphuric acid causes the formation of water and acetic acid, and deposition of charcoal. Digested with strong nitric acid,

it yields saccholactic acid, a property which forms a good character for gum. Malic and oxalic acids are generated at the same time.

The aqueous solution of gum may be preserved a considerable time without alteration; but at length it becomes sour, and exhales an odour of acetic acid; a change which takes place without exposure to the air, and must therefore be owing to a new arrangement of its own elements.

Gum is precipitated from its solution in water by several metallic salts, and especially by sub-acetate of lead, which occasions a curdy precipitate, consisting of 38.25 parts of oxide of lead and 61.75 parts of gum. (Berzelius.)

When gum is heated to redness in close vessels, it yields, in addition to the usual products, a small quantity of ammonia, which is probably derived from some impurity. It affords a large residue of ash, when burned, which amounts to three per cent, and consists chiefly of the carbonate, together with some phosphate of lime, and a little iron.

From the analysis of Gay-Lussac and Thenard, it appears that 100 parts of gum arabic consist of carbon 42.23, oxygen 50.84, and hydrogen 6.93. This result corresponds very closely with that of Berzelius.

Besides gum arabic there are several well-marked kinds of this principle, especially gum tragacanth, cherry-tree gum, and the mucilage from linseed. All these varieties, though distinguishable from one another by some peculiarity, have the common character of yielding the saccholactic by the action of nitric acid. (Dr. Bostock in Nicholson's Journal, vol. xviii.) The substance called *vegetable jelly*, such as is derived from the currant, appears to be mucilage or some modification of gum combined with vegetable acid.

LIGNIN.

Lignin or *woody fibre* constitutes the fibrous structure of vegetable substances, and is the most abundant principle in plants. The different kinds of wood contain about 96 per cent of lignin. It is prepared by digesting the sawings of any kind of wood successively in alcohol, water, and dilute mu-

riatic acid, until all the substances soluble in these menstrua are removed.

Lignin has neither taste nor odour, undergoes no change by keeping, and is insoluble in alcohol, water, and the dilute acids. By digestion in a concentrated solution of pure potash, it is converted, according to M. Braconnot, into a substance similar to ulmin. Mixed with strong sulphuric acid it suffers decomposition, and is changed into a matter resembling gum; and on boiling the liquid for some time the mucilage disappears, and a saccharine principle like the sugar of grapes is generated. M. Braconnot finds that several other substances which consist chiefly of woody fibre, such as straw, bark, or linen, yield sugar by a similar treatment. (An. de Ch. et de Ph. vol. xii.) Digested in nitric acid, lignin is converted into the oxalic, malic, and acetic acids.

When the woody fibre is heated in close vessels, it yields a large quantity of impure acetic acid, (pyroligneous acid) and charcoal of great purity remains in the retort. During this process a peculiar spirituous liquid is formed, which was discovered in 1812 by Mr. P. Taylor *, and has been examined by MM. Macaire and Marcet †, who proposed for it the name of *pyroxylic spirit*. This liquid is similar to alcohol in several of its properties, but differs from it essentially in not yielding ether by the action of sulphuric acid. It has a strong, pungent, ethereal odour, with a flavour like the oil of peppermint. It boils at 150° F., and its density is 0.828. It burns with a blue flame, and without residue. The pyro-acetic spirit, obtained by Mr. Chenevix by distilling the acetates of manganese, zinc, and lead, differs from pyroxylic spirit, not only in composition, but in burning with a yellow flame, and in being miscible in all proportions with oil of turpentine. Pyroxylic spirit, according to the analysis of Macaire and Marcet, consists of carbon, oxygen, and hydrogen, very nearly in the proportion of 6 equivalents of the first, 4 of the second, and 7 of the third; and pyro-acetic spirit, of 4 equivalents of carbon, 2 of oxygen, and 3 of hydrogen. Pyro-acetic spirit appears very similar, if not identical with the pyro-

* Quarterly Journal, vol. xiv. p. 436.

† Annals of Philosophy, N. S. vol. viii. p. 69.

acetic ether of Derosne; and, like pyroxylic spirit, differs essentially from alcohol in not yielding ether by the action of sulphuric acid. (Page 732.)

The ligneous fibre was found by Gay-Lussac and Thenard to consist of carbon 51.43, oxygen 42.73, and hydrogen 5.82. According to Dr. Prout it contains 50 per cent of carbon.

SECTION V.

SUBSTANCES WHICH SO FAR AS IS KNOWN DO NOT BELONG TO EITHER OF THE PRECEDING SECTIONS.

COLOURING MATTER.

INFINITE diversity exists in the colour of vegetable substances; but the prevailing tints are red, yellow, blue, and green, or mixtures of these colours. The colouring matter rarely or never occurs in an insulated state, but is always attached to some other proximate principle, such as mucilaginous, extractive, farinaceous, or resinous substances, by which some of its properties, and in particular that of solubility, is greatly influenced. Nearly all kinds of vegetable colouring matter are decomposed by the combined agency of the sun's rays and a moist atmosphere; and they are all, without exception, destroyed by chlorine. (Page 293.) Heat, likewise, has a similar effect, even without being very intense; for a temperature between 300° or 400° F., aided by moist air, destroys the colouring ingredient. Acids and alkalies commonly change the tint of vegetable colours, entering into combination with them, so as to form new compounds.

Several of the metallic oxides, and especially alumina and the oxides of ironand tin, form with colouring matter insoluble compounds, to which the name of *lakes* is applied. Lakes are commonly obtained by mixing alum or pure muriate of tin with a coloured solution, and then by means of an alkali precipitating the oxide which unites with the colour at the moment of separation. On this property are founded many of the processes in dyeing and calico-printing. The art of the dyer consists in giving an uniform and permanent colour to

cloth. This is sometimes effected merely by immersing the cloth in the coloured solution; whereas in other instances the affinity between the colour and the fibre of the cloth is so slight, that it only receives a stain which is removed by washing with water. In this case some third substance is requisite, which has an affinity both for the cloth and colouring matter, and which, by combining at the same time with each, may cause the dye to be permanent. A substance of this kind was formerly called a *mordaunt;* but the term *basis*, introduced by the late Mr. Henry of Manchester, is now more generally employed. The most important bases, and indeed the only ones in common use, are alumina, oxide of iron, and oxide of tin. The two former are exhibited in combination either with the sulphuric or acetic acid, and the latter most commonly as the muriate. Those colouring substances that adhere to the cloth without a basis are called *substantive* colours, and those which require a basis, *adjective* colours.

Various as are the tints observable in dyed stuffs, they may all be produced by the four simple ones, blue, red, yellow, and black; and hence it will be convenient to treat of colouring matters in that order.

Blue Dyes.—Indigo is chiefly obtained from an American and Asiatic plant, the *indigofera*, several species of which are cultivated for the purpose. It is likewise extracted from the *Nerium tinctorium;* and an inferior sort is prepared from the *Isatis tinctoria* or *woad*, a native of Europe. Two different methods are employed for its extraction. In one, the recent plant, cut a short time before its flowering, is placed in bundles in a steeping vat, where it is kept down with cross bars of wood, and covered to the depth of an inch or two with water. In a short time fermentation sets in, carbonic acid gas is freely disengaged, and a yellow solution is formed. In the course of ten or twelve hours, when its surface begins to look green from the mixture of blue indigo with the yellow solution, it is drawn off into the beating vat, where it is agitated with paddles, until all the colouring matter is oxidized by absorbing oxygen from the atmosphere, and is deposited in the form of blue insoluble indigo. The other method consists in drying the leaves like hay, removing the leaf from its stalk by threshing, and grinding the former into powder, in which state it is pre-

served for use. The dye is then extracted either by maceration in water at the temperature of the air, and fermentation; or by digestion in water at 150° or 180° F., without being fermented. In either case it is beaten with paddles as before. (Ure in Journ. of Science, N. S. vi. 259.) The process of fermentation, by some thought essential, may be dispensed with. According to Mr. Weston, however, the dye, as contained in the plant, is insoluble in cold water; but by exposure to the air it undergoes a change, in which oxygen acts a part, and by which it is rendered soluble in water. (Journ. of Science, N. S. v. 296.)

The indigo of commerce, which occurs in cakes of a deep blue colour, and earthy aspect, is a mixed substance, containing, in addition to salts of magnesia and lime, the four following ingredients:—1. a glutinous matter; 2. indigo-brown; 3. indigo-red; 4. indigo-blue. (Berzelius in Lehrbuch, iii. 679.)

1. The gluten is obtained by digesting finely pulverized indigo in dilute sulphuric acid, neutralizing with chalk, and evaporating the filtered solution to dryness. The gluten is then taken up by alcohol, and on evaporation is left with the appearance of a yellow or yellowish-brown, transparent, shining varnish. Its odour is similar to that of broth, and it contains nitrogen as one of its elements. It differs, however, from common gluten in its free solubility both in alcohol and water.

2. Indigo-brown has not been obtained in a perfectly pure state, owing to its tendency to unite both with acids and alkalies. With the former it yields in general sparingly soluble, and with the latter very soluble compounds, which have a deep brown colour. From indigo, freed from gluten by dilute acid, it is separated by a strong solution of potash aided by gentle heat; and after dilution with water, without which it passes with difficulty through paper, the liquid is filtered. The solution has a green tint, owing to some indigo-blue being dissolved, and with sulphuric acid yields a bulky semi-gelatinous precipitate of a blackish colour. By dissolving it in solution of carbonate of ammonia, evaporating to dryness, and removing the soluble parts by a small quantity of water, the brown matter is freed from indigo-blue and sulphuric acid. It still, however, contains ammonia, and though this alkali may

be expelled by means of hydrated lime or baryta, the indigo-brown retains some of the earth in combination. Like indigo-gluten it contains a considerable quantity of nitrogen as one of its elements. The *indigo-green* of Chevreul is probably a mixture of this substance with indigo-blue.

3. Indigo-red is obtained by boiling indigo, previously purified by potash, in successive portions of strong alcohol as long as a red solution is obtained. The alcoholic solutions are then concentrated by evaporation, during which the indigo-red is deposited as a blackish-brown powder. The concentrated solution, of a deep red colour, yields by evaporation a compound of indigo-red and indigo-brown with alkali, which is soluble in water.

Indigo-red is insoluble in water, and alkalies; but it is soluble, though sparingly, in hot alcohol, and rather more freely in ether. It dissolves in strong sulphuric acid, and forms a dark yellow liquid; and with nitric acid it yields a beautiful purple solution, which speedily becomes yellow by decomposition. When heated *in vacuo* it yields a gray crystalline sublimate, which, when purified by a second sublimation, is obtained in minute transparent needles, shining, and white. This substance, in its relation to reagents, resembles indigo-red; and especially by yielding with nitric acid a similar purple-red solution, which subsequently becomes yellow.

4. *Indigo-blue.*—This term is applied to the real colouring matter of indigo, and is left, though not quite pure, after acting on common indigo with dilute acid, potash, and alcohol. It is conveniently prepared from the greenish-yellow solution, which dyers make by mixing indigo with green vitriol, hydrate of lime, and water; when the indigo is deoxidized by the protoxide of iron, and yields a soluble compound with lime. On pouring this solution into an excess of muriatic acid, while freely exposed to the air, oxygen gas is absorbed, and the indigo is obtained in the form of a blue powder. It may also be procured in a state of great purity by sublimation; but this process is one of delicacy, from the circumstance that the subliming and decomposing points of indigo are very near each other; and minute directions have been given by Mr. Crum for conducting it with success. (An. of Phil. N. S. v.) To be sure of obtaining it quite pure by either process, the indigo

should first be purified by the action of dilute acid, potash, and alcohol.

Pure indigo sublimes at 550° F., forming a violet vapour with a tint of red, and condensing into long flat acicular crystals which appear red by reflected, and blue by transmitted light. It has neither taste nor odour, and it is insoluble in water, alkalies, and ether. Boiling alcohol takes up a trace of it, and acquires a blue tint; but it is generally deposited again on standing. Nitric acid produces a change which has already been described (Page 701). Concentrated sulphuric acid, especially that of Nordhausen, dissolves it readily, forming an intensely deep blue solution, commonly termed *sulphate of indigo*, which is employed by dyers for giving the *Saxon blue*. The indigo during solution undergoes a change, and in this modified state it has received the name of *Cerulin* from Mr. Crum, who regards it as a compound of one equivalent of indigo and four of water. According to Berzelius the solution is of a more complicated nature, and contains the three following substances: 1. *indigo-purple;* 2. sulphate of indigo; 3. hyposulphate of indigo.

Indigo-purple is chiefly formed when indigo is dissolved in English oil of vitriol, and subsides when the solution is diluted with from 30 to 50 times its weight of water. It was first described under the name of *phenecin*, from φοῖνιξ, purple, by Mr. Crum, who considers it a hydrate of indigo with two equivalents of water. Into the dilute solution, after phenecin is separated, Berzelius inserts fragments of carefully washed flannel, until all the colour is withdrawn from the liquid. The dyed flannel, after the adhering acid is entirely removed, is digested in water with a little carbonate of ammonia, by which means a blue solution is obtained, consisting of ammonia in combination with sulphate and hyposulphate of indigo. The solution is evaporated to dryness at 140° F., and to the residue is added alcohol of 0.833, which dissolves only the hyposulphate.

The compounds of indigo with sulphuric and hyposulphuric acid are considered by Berzelius, not as salts in which indigo acts as a base, but as distinct acids of which indigo is an essential ingredient. *Indigo-sulphuric acid*, as sulphate of indigo may therefore be called, is prepared by mixing indigo-

sulphate of ammonia with acetate of lead, when indigo-sulphate of lead subsides. This salt is suspended in water, and decomposed by sulphuretted hydrogen: the sulphuret of lead is collected on a filter; and the filtered solution, at first colourless or nearly so, owing to deoxidation of indigo by sulphuretted hydrogen, but which soon becomes blue by the action of the air, is evaporated at a temperature not exceeding 122° F. The acid is left as a dark blue solid, of a sour astringent taste, soluble in water and alcohol, and capable of forming a distinct group of salts with alkalies. *Indigo-hyposulphuric acid* may be prepared by a similar process.

One of the most remarkable characters of indigo-blue is its susceptibility of being deoxidized, and thus returning to the state in which it appears to exist in the plant, and of again recovering its blue tint by subsequent oxidation. The change is effected by various deoxidizing agents, such as sulphuretted hydrogen, hydrosulphuret of ammonia, hydrated protoxide of iron, or solution of orpiment in potash. In the deoxidized state it readily unites with alkaline substances, such as potash or lime, and forms compounds which are very soluble in water. The method by which dyers prepare their blue vat is founded on these properties. A portion of indigo is put into a tub with about three times its weight of green vitriol and an equal quantity of slaked lime, and water is added. The protoxide of iron, precipitated by lime, gradually deoxidizes the indigo, and in the course of a day or two a yellow solution is obtained. When cotton cloth is moistened with this liquid and exposed to the air, it speedily becomes green from the mixture of colours, and then blue; and as the blue indigo is insoluble, and unites chemically with the fibre of the cloth, the dye is permanent.

Deoxidized indigo has been obtained in a separate state by Liebig. A mixture is made with 1.5 parts of indigo, 2 of green vitriol, 2.5 of hydrate of lime, and 50 or 60 of water; and after an interval of 24 hours the yellow solution is carefully drawn off by a syphon, and mixed with dilute muriatic acid. A thick white precipitate falls, which remains without change if carefully excluded from oxygen, and may even be exposed to the air when quite dry; but it rapidly becomes blue by exposure to the atmosphere while moist, or by being covered with

aerated water. To this substance Liebig has applied the name of *indigogene*; and he has ascertained that, in passing into blue indigo, it absorbs 11.5 per cent of oxygen. The necessity for perfectly excluding every source of oxygen, renders the preparation of indigogene difficult. All the vessels employed in the process should be filled with hydrogen gas, the water be freed from air by boiling, and as a further protection a little sulphite of ammonia is added both to the acid by which the precipitate is made, and to the water with which it is washed.

From the analytical researches of Mr. Crum, it appears that indigo is composed of nitrogen, oxygen, hydrogen, and carbon, in the proportion of 1 equivalent of the first element, 2 of the second, 4 of the third, and 16 of the fourth. This would make its atomic weight 130; but it admits of doubt whether the indigo analyzed by Mr. Crum was absolutely pure.

Red Dyes.—The chief substances which are employed for the red dye are cochineal, lac, archil, madder, Brazil wood, logwood, and safflower, all of which are adjective colours. The cochineal is obtained from an insect which feeds upon the leaves of several species of the *cactus*, and which is supposed to derive this colouring matter from its food. It is very soluble in water, and is fixed on cloth by means of alumina or oxide of tin. Its natural colour is crimson; but when bitartrate of potash is added to the solution, it yields a rich scarlet dye. The beautiful pigment called *carmine* is a lake made of cochineal and alumina, or oxide of tin.

The dye called *archil* is obtained from a peculiar kind of lichen, (*Lichen roccella,*) which grows chiefly in the Canary Islands, and is employed by the Dutch in forming the blue pigment called *litmus* or *turnsol.* The colouring ingredient of litmus is a compound of the red colouring matter of the lichen and an alkali; and hence, on the addition of an acid, the colouring matter is set free, and the red tint of the plant is restored. Litmus is not only used as a dye, but is employed by chemists for detecting the presence of a free acid.

The colouring principle of logwood has been procured in a separate state by M. Chevreul, who has applied to it the name of *hematin.* (An. de Ch. vol. lxxxi.) It is obtained in crystals by digesting the aqueous extract of logwood in alcohol, and allowing the alcoholic solution to evaporate spontaneously.

Safflower is the dried flowers of the *carthamus tinctorius*, which is cultivated in Egypt, Spain, and in some parts of the Levant. The pigment called *rouge* is prepared from this dye.

Madder, extensively employed in dyeing the *Turkey red*, is the root of the *Rubia tinctorum*. A red substance, supposed to be the chief colouring principle of the plant, has been obtained in an insulated state by Robiquet and Colin, who have termed it *Alizarine*, from *Ali-zari*, the commercial name by which madder is known in the Levant. Their process has received the following modification by Zenneck. Ten parts of madder are digested in four of sulphuric ether, the solution is evaporated to the consistence of syrup, and then allowed to become dry by spontaneous evaporation. The residue is pulverized, and sublimed by a gentle heat from a watch glass. The sublimate, which is collected by covering the watch glass with a cone of paper, is deposited in the form of yellowish red, brilliant, diaphanous, acicular crystals, which are soft, flexible, and heavier than water. They soften when heated, and sublime at a temperature between 500 and 600° F., causing an aromatic odour. They are nearly insoluble in cold and very sparingly soluble in hot water. They require for solution 210 times their weight of alcohol, and 160 of ether at 60° F. According to Zenneck the acidity of alizarine is very decisive, both in its sour taste, and its power of neutralizing alkalies. It consists, in 100 parts, of 18 of carbon, 20 of hydrogen, and 62 of oxygen. (Journal of Science, N. S. v. 198.)

Yellow Dyes.—The chief yellow dyes are quercitron bark, turmeric, wild American hiccory, fustic, and saffron; all of which are adjective colours. Quercitron bark, which is one of the most important of the yellow dyes, was introduced into notice by Dr. Bancroft. With a basis of alumina, the decoction of this bark gives a bright yellow dye. With oxide of tin it communicates a variety of tints, which may be made to vary from a pale lemon colour to deep orange. With oxide of iron it gives a drab colour.

Turmeric is the root of the *Curcuma longa*, a native of the East Indies. Paper stained with a decoction of this substance constitutes the *turmeric* or *curcuma* paper employed by che-

mists as a test of free alkali, by the action of which it receives a brown stain.

The colouring ingredient of saffron *(Crocus sativus)* is soluble in water and alcohol, has a bright yellow colour, is rendered blue and then lilac by sulphuric acid, and receives a green tint on the addition of nitric acid. From the great diversity of colours which it is capable of assuming under different circumstances, MM. Bouillon Lagrange and Vogel have proposed for it the name of *Polychroite.* (An. de Ch. vol. lxxx.)

Black Dyes.—The black dye is made of the same ingredients as writing ink, and therefore consists essentially of a compound of oxide of iron with gallic acid and tannin. From the addition of logwood and acetate of copper, the black receives a shade of blue.

By the dexterous combination of the four leading colours, blue, red, yellow, and black, all other shades of colour may be procured. Thus green is communicated by forming a blue ground with indigo, and then adding a yellow by means of quercitron bark.

The reader who is desirous of studying the details of dyeing and calico-printing, a subject which does not fall within the plan of this work, may consult Berthollet's *Elemens de l'Art de la Teinture;* the treatise of Dr. Bancroft on Permanent Colours; a paper by Mr. Henry in the third volume of the Manchester Memoirs; and the Essay of Thenard and Roard in the 74th volume of the *Annales de Chimie.*

TANNIN.

Tannin exists in large quantity in the excrescences of several species of the oak, called *gall-nuts;* in the bark of most trees; in some inspissated juices, such as kino and catechu; in the leaves of the tea-plant, sumach, and whortleberry, *(uva ursi;)* and in all astringent plants, being the chief cause of the astringency of vegetable matter. It is frequently associated with gallic acid, as for example in gall-nuts, most kinds of bark, and in tea; but in kino, catechu, and cinchona bark, no gallic acid is present. In some instances tannin appears to be converted into gallic acid. Thus on exposing an infusion of gall-nuts for some time to the air, nearly all the tannin disappears, and a quantity of gallic acid is found in the

liquid much greater than that which it had originally contained. (Page 695.)

Several methods have been proposed for preparing tannin; but the following process of Berzelius, modified in the first part by my assistant Mr. Warrington, is the most convenient. Gall-nuts, in coarse powder, are digested in water so as to form a rather concentrated solution, and the decanted liquid is treated with a little white of eggs until the colour changes from a brown to a pale yellow, when it is filtered. When cold, concentrated sulphuric acid is added as long as a precipitate falls; and by preserving the solution for a few days an additional quantity is obtained. The precipitate, of a yellowish white colour, consisting of sulphuric acid and tannin, is then washed with dilute sulphuric acid, pressed in folds of bibulous paper, dissolved in pure water, and macerated with carbonate of lead in fine powder. Sulphate of lead is thus formed, and is separated by filtration from the pale yellow solution of tannin, which should be evaporated *in vacuo* with a vessel of sulphuric acid. A hard yellowish brown extract remains; and on dissolving the soluble portions in ether, and evaporating spontaneously, pure tannin is left.

Another process, recommended by Berzelius, is to precipitate tannin with a concentrated solution of carbonate of potash, avoiding an excess of the alkali which would redissolve the precipitate. The white compound of tannin and potash is washed with ice-cold water, dissolved in dilute acetic acid, filtered, and mixed with acetate of lead. The precipitate, which consists of oxide of lead and tannin, is carefully washed, suspended in water, and decomposed by sulphuretted hydrogen. The filtered solution of tannin is then evaporated and purified by ether, as already mentioned.

Pure tannin is colourless and inodorous, has an astringent taste, is unchangeable in the air, and may be rubbed into powder. It is soluble in water, and the solution reddens litmus. It is dissolved also by ether, and with the aid of heat by absolute alcohol. By exposure to the air it becomes yellow, yellowish brown, and dark brown; and when evaporated to the consistence of an extract, a portion of it is rendered insoluble. The infusion of gall-nuts owes its colour chiefly to this cause; and the foregoing directions to evaporate *in vacuo* are given with the view of avoiding the agency of air. With

acids, it forms compounds of sparing solubility, which, when saturated, are purely astringent in taste without any acidity. Alkaline bases have a similar effect. Tannin is precipitated, for example, by the carbonates of potash and ammonia, by the alkaline earths, by alumina, and many of the oxides of the common metals. Nitric acid and chlorine decompose tannin, producing a change, the nature of which is not well understood.

The most characteristic property of tannin is its action on a salt of iron and a solution of gelatine. With peroxide of iron, or still better with the protoxide and peroxide mixed, tannin forms a black-coloured compound, which, together with gallate of iron, constitutes the basis of writing ink and the black dyes. (Page 696.) Mixed with a solution of gelatine, a yellowish flocculent precipitate subsides, which is insoluble in water, resists putrefaction powerfully, and on drying becomes hard and tough. This substance, to which the name of *tanno-gelatine* has been applied, is the essential basis of leather, being always formed when skins are macerated in an infusion of bark. The composition of tanno-gelatine is not always uniform, having been found by Dr. Duncan, jun., and Dr. Bostock, to vary with the proportions employed. If the gelatine is added in slight excess only, the resulting compound consists, according to Sir H. Davy, of 54 parts of gelatine and 46 of tannin; so that the quantity of tannin contained in any fluid may in this way be determined with tolerable precision. Tanno-gelatine is soluble to a considerable extent in an excess of gelatine.

From an analysis of the compound of tannin and oxide of lead Berzelius states that 100 parts of tannin are composed of carbon 52.69, oxygen 43.45, and hydrogen 3.86.

From the experiments of Sir H. Davy, it appears that the inner cortical layers of barks are the richest in tannin. The quantity is greatest in the beginning of spring, at the time the buds begin to open, and smallest during winter. Of all the varieties of bark which he examined, that of the oak contains the greatest quantity of tannin.

By processes similar to those above described tannin may be obtained from cinchona bark, catechu, kino, and other sources. These various kinds of tannin correspond in most

respects, but in some points a difference is observable. This may be traced in their action on the salts of iron, with which, instead of striking a black or bluish-black tint, as solution of gall-nuts or oak-bark does, some varieties of tannin give a green colour.

Artificial tannin.—This interesting substance was discovered twenty years ago by Mr. Hatchett, who gave a full description of it in the Philosophical Transactions for 1805 and 1806. The best method of preparing it is by the action of nitric acid on charcoal. For this purpose 100 grains of charcoal in fine powder are digested in nitric acid, of density 1.4, diluted with two ounces of water. The mixture is exposed to a gentle heat, which is to be continued until all the charcoal is dissolved. The reddish-brown solution is then evaporated to dryness, in order to expel the pure acid, the temperature being carefully regulated towards the close of the process, so that the product may not be decomposed.

Artificial tannin is a brown fusible substance, of a resinous fracture, and astringent taste. It is soluble even in cold water and in alcohol. It reddens litmus paper, probably from adhering nitric acid. With a salt of iron and solution of gelatine it acts precisely in the same manner as natural tannin. It differs, however, from that substance in not being decomposed by the action of strong nitric acid.

Artificial tannin may be prepared in several ways. Thus it is generated by the action of nitric acid, both on animal or vegetable charcoal, and on pit-coal, asphaltum, jet, indigo, common resin, and several other resinous substances. It is also procured by treating common resin, elemi, asafœtida, camphor, balsams, &c. first with sulphuric acid, and then with alcohol.

VEGETABLE ALBUMEN. GLUTEN. YEAST.

Vegetable Albumen.—Under this name is distinguished a vegetable principle which has a close resemblance to animal albumen, especially in the characteristic property of being coagulable by heat. This substance was found by Vogel in the bitter almond, and in the sweet almond by Boullay; it appears to be an ingredient of emulsive seeds generally; and it exists in the sap of many plants. Einhof detected it in

wheat, rye, barley, peas, and beans. Vegetable albumen is soluble in cold water, but by a boiling temperature it is coagulated, and thus completely deprived of its solubility. It is insoluble in alcohol, and very sparingly soluble in acids. Alkalies dissolve it readily, and it may be precipitated from them by acids; but the albumen falls in combination with a portion of the acid. Ferrocyanate of potash and corrosive sublimate act upon it as on solutions of animal albumen.

Vegetable albumen contains nitrogen as one of its elements, and is very prone, when kept in the moist state, to undergo the putrefactive fermentation, emitting an offensive odour, with disengagement of ammonia and formation of acetate of ammonia. During a certain period of putrefaction it has the odour of old cheese. (Berzelius.)

Gluten.—In the separation of starch from wheat flour, as already described (page 747), a gray viscid substance remains, fibrous in its texture, and elastic. Beccaria, who first carefully examined its properties, was struck with its analogy to glue, both in its viscidity as well as its tendency to putrefy like animal matter, and gave it the name of *vegetable gluten.* Einhof has since shown that this gluten is a mixed substance, containing gluten and vegetable albumen.

Pure gluten is obtained by washing dough in water until the starch and soluble parts are removed, and treating the residue with boiling alcohol. On mixing the alcoholic solution with water, and distilling off the spirit, the gluten is deposited in large coherent flakes. As thus obtained it has a pale yellow colour, and a peculiar odour, but no taste; adheres tenaciously to the fingers when handled, and has considerable elasticity. It is insoluble in water and ether, but dissolves readily in hot alcohol, apparently without any change of property; but if the alcoholic solution is evaporated to dryness, the gluten is left as a transparent varnish. It swells up and softens with acetic acid, forming a compound which is soluble in water. It unites also with the mineral acids; and these compounds, excepting that with sulphuric acid, dissolve readily in pure water, but are insoluble when there is an excess of acid. It is dissolved by dilute solution of potash, apparently without being decomposed; for the gluten, after being thrown down by the mineral acids, retains its viscidity.

In this state, however, it is combined with some of the acid. (Berzelius.)

When gluten is kept in a warm moist situation it ferments, and an acid is formed; but in a few days putrefaction ensues, and an offensive odour, like that of putrefying animal matter, is emitted. According to Proust, who made these spontaneous changes a particular object of study, the process is divisible into two distinct periods. In the first, carbonic acid and hydrogen gases are evolved; and in the second, besides acetic and phosphoric acids and ammonia, two new compounds are generated, for which he proposed the names of *caseic acid* and *caseous oxide*. These are the same principles which are generated during the fermentation of the curd of milk, and their real nature will be considered in the section on milk. It is apparent from these circumstances that gluten contains nitrogen as one of its elements, and that it approaches closely to the nature of animal substances. It has hence been called a vegeto-animal principle.

If gluten is dried by a gentle heat, it contracts in volume, becomes hard and brittle, and may in this state be preserved without change. Exposed to a strong heat, it yields, in addition to the usual inflammable gases, a thick fetid oil, and carbonate of ammonia.

Gluten is present in most kinds of grain, such as wheat, barley, rye, oats, peas, and beans; but the first contains it in by far the largest proportion. This is the reason that wheaten bread is more nutritious than that made with other kinds of flour; for of all vegetable substances gluten appears to be the most nutritive. It is to the presence of gluten that wheat flour owes its property of forming a tenacious paste with water. To the same cause is owing the formation of light spongy bread; the carbonic acid which is disengaged during the fermentation of dough, being detained by the viscid gluten, distends the whole mass, and thus produces the *rising* of the dough. From the experiments of Sir H. Davy, it appears that good wheat flour contains from 19 to 24 per cent of gluten. The wheat grown in the south of Europe is richer in gluten than that of colder climates.

M. Taddey, an Italian chemist, has given an account of two principles separable from the gluten of Beccaria by means

of boiling alcohol. To the substance soluble in alcohol he has applied the name of *gliadine*, from γλία, *gluten*; and to the other that of *zymome*, from ζυμὴ, a ferment. (An. of Phil. xv.) For the latter he has discovered a delicate test in the powder of guaiacum, which when rubbed in a mortar with moist zymome, instantly strikes a beautiful blue colour; and the same tint appears, though less rapidly, when it is kneaded with gluten or dough made with good wheat flour. But with bad flour, the gluten of which has suffered spontaneous decomposition, the blue tint is scarcely visible; and accordingly M. Taddey conceives that useful inferences as to the quality of flour may be drawn from the action of guaiacum.

These views have been lately criticised by Berzelius, who declares that the substances described by Taddey are nothing else than the gluten and vegetable albumen already described; and the habitual accuracy of Berzelius leaves little chance of error in his statement. The blue tint, above alluded to, must have arisen from the action of guaiacum either on vegetable albumen itself, or on some substance by which it is accompanied in wheat. (An. of Phil. iv. 69, or Lehrbuch, iii. 362.)

Yeast.—This substance is always generated during the vinous fermentation of vegetable juices and decoctions, rising to the surface in the form of a frothy, flocculent, somewhat viscid matter, the nature and composition of which are unknown. It is insoluble in water and alcohol, and in a warm, moist atmosphere gradually putrefies, a sufficient proof that ammonia is one of its elements. Submitted to a moderate heat, it becomes dry and hard, and may in this state be preserved without change. Heated to redness in close vessels, it yields products similar to those procured under the same circumstances from gluten. To this substance, indeed, yeast is supposed by some chemists to be very closely allied.

The most remarkable property of yeast is that of exciting fermentation. By exposure for a few minutes to the heat of boiling water, it loses this property, but after some time again acquires it. Nothing conclusive is known concerning either the nature of these changes, or the mode in which yeast operates in establishing the fermentative process.

ASPARAGIN, BASSORIN, CAFFEIN, CATHARTIN, FUNGIN, SUBERIN, ULMIN, LUPULIN, INULIN, MEDULLIN, POLLENIN, PIPERIN, OLIVILE, SARCOCOLL, EXTRACTIVE MATTER, BITTER PRINCIPLE, &c.

Asparagin.—This principle was discovered by MM. Vauquelin and Robiquet in the juice of the asparagus, from which it is deposited in crystals by evaporation. The form of its crystals is a rectangular octahedron, six sided prism, or right rhombic prism. Its taste is cool and slightly nauseous, it is soluble in water, and has neither an acid nor alkaline reaction. (Ann. de Ch. lvii. 88.)

Asparagin is contained also in the root of marsh-mallow and liquorice. Robiquet, who first obtained it from the juice of the recent liquorice root, doubted its identity with asparagin, and gave it the name of *agedoite;* but the mistake has been corrected by M. Plisson.

Plisson has noticed that when asparagin is boiled for some time with hydrate of lead or magnesia, it is resolved into ammonia and a new acid called the *aspartic.* On decomposing aspartate of lead by sulphuretted hydrogen, and evaporating the filtered solution, the acid is obtained as a colourless powder composed of minute prismatic crystals. It has little taste, is sparingly soluble in cold water, and still less so in alcohol. Its aqueous solution is not precipitated by the soluble salts of baryta, lime, lead, magnesia, copper, mercury, or silver. The aspartates, when the taste of the base does not interfere, have the taste of the juice of meat. It yields ammonia when decomposed by heat. (An. de Ch. et Ph. xxxv. 175, and xl. 309.)

Bassorin was first noticed in gum *Bassora* by Vauquelin. According to Gehlen and Bucholz, it is contained, together with common gum, in gum tragacanth; and John found it in the gum of the cherry-tree. Salep, from the experiments of Caventou, appears to consist almost totally of bassorin.

Bassorin is characterized by forming with cold water a bulky jelly which is insoluble in that menstruum, as well as in alcohol and ether. Boiling water does not dissolve it except by long-continued ebullition, when the bassorin at length dis-

appears, and is converted into a substance similar to gum-arabic.

Caffein was discovered in coffee by Robiquet in the year 1821, and was soon after obtained from the same source by Pelletier and Caventou, without a knowledge of the discovery of Robiquet. It is a white crystalline volatile matter, which is soluble in boiling water and alcohol, and is deposited on cooling in the form of silky filaments like amianthus. Pelletier, contrary to the opinion of Robiquet, at first regarded it as an alkaline base; but he now admits that it does not affect the vegetable blue colours, nor combine with acids. (Journal de Pharmacie for May 1826.)

Hitherto the properties of Caffein have not been fully described. From the analysis of Pelletier and Dumas, 100 parts of it consist of carbon 46.51, nitrogen 21.54, hydrogen 4.81, and oxygen 27.14. Though it contains more nitrogen than most animal substances, it does not, under any circumstances, undergo the putrefactive fermentation.

Cathartin.—This name has been applied by MM. Lassaigne and Feneulle to the active principle of senna. (An. de Ch. et de Ph. vol. xvi.)

Fungin.—This name is applied by M. Braconnot to the fleshy substance of the mushroom, and is procured in a pure state by digestion in hot water, to which a little alkali is added. Fungin is nutritious in a high degree, and in composition is very analogous to animal substances. Like flesh, it yields nitrogen gas when digested in dilute nitric acid.

Suberin.—This name has been applied by Chevreul to the cellular tissue of the common cork, the outer bark of the cork-oak, *(quercus suber)*, after the astringent, oily, resinous, and other soluble matters have been removed by the action of water and alcohol. Suberin differs from all other vegetable principles by yielding the suberic when treated by nitric acid.

Ulmin, discovered by Klaproth, is a substance which exudes spontaneously from the elm, oak, chestnut, and other trees; and according to Berzelius is a constituent of most kinds of bark. It may be prepared by acting upon elm-bark by hot alcohol and cold water, and then digesting the residue in water, which contains an alkaline carbonate in solution. On neutralizing the alkali with an acid, the ulmin is precipitated.

Ulmin is a dark brown, nearly black substance, is insipid and inodorous, and is very sparingly soluble in water and alcohol. It dissolves freely, on the contrary, in the solution of an alkaline carbonate, and is thrown down by an acid. Ulmin is regarded as an acid by M. P. Boullay, who has proposed for it the name of *ulmic* acid. He found that 100 parts of it contain 56.7 of carbon, and 43.3 of oxygen and hydrogen in the proportion to form water. According to him it is an ingredient of vegetable mould and turf, and contributes much to the growth of plants. The black matter deposited during the decomposition of prussic acid, supposed by Gay-Lussac to be a carburet of nitrogen, is an acid very similar to the ulmic, and to which he has given the name of *azulmic* acid. (An. de Ch. Ph. xliii. 273.)

Lupulin is the name applied by Dr. Ives to the active principle of the hop, but which has not yet been obtained in a state of purity.

Inulin is a white powder like starch, which is spontaneously deposited from a decoction of the roots of the *Inula helenium* or *Elecampane*. This substance is insoluble in cold, and soluble in hot water, and is deposited from the latter as it cools, a character which distinguishes it from starch. With iodine it forms a greenish-yellow compound of a perishable nature. Its solution is somewhat mucilaginous; but inulin is distinguished from gum by insolubility in cold water, and in not yielding the saccholactic when digested in nitric acid.

Medullin.—This name was applied by John to the pith of the sun-flower, but its existence as an independent principle is somewhat dubious. The term *pollenin* has been given by the same chemist to the pollen of tulips.

Piperin is the name which is applied to a white crystalline substance extracted from black pepper. It is tasteless, and is quite free from pungency, the stimulating property of the pepper being found to reside in a fixed oil. (Pelletier, in An. de Ch. et de Ph. vol. xvi.)

A process lately recommended for its preparation by Vogel consists in digesting for two days 16 ounces of black pepper in coarse powder in twice its weight of water, five times in succession; and digesting the insoluble parts, previously well pressed and dried, for three days in 24 ounces of alcohol.

The solution is pressed through linen cloth, filtered, and evaporated to the consistence of syrup; and the impure crystals of piperin, deposited by cooling, are freed from adhering resinous matter by ether, and purified by animal charcoal and a second crystallization from alcohol.

Piperin crystallizes in four-sided prisms, which have commonly a yellow colour, owing to adhering oil or resin. It is insoluble in cold, and sparingly soluble in hot water; but it is very soluble in alcohol, and less so in ether. Acetic acid also dissolves it, and leaves it by evaporation in feathery crystals. It fuses at 212°, and consists of carbon, oxygen, and hydrogen.

Olivile.—When the gum of the olive tree is dissolved in alcohol, and the solution is allowed to evaporate spontaneously, a peculiar substance, apparently different from the other proximate principles hitherto examined, is deposited either in flattened needles or as a brilliant amylaceous powder. To this M. Pelletier, its discoverer, has given the name of *Olivile.* (An. of Phil. vol. xii.)

Sarcocoll is the concrete juice of the *Penæa sarcocolla*, a plant which grows in the northern parts of Africa. It is imported in the form of small grains of a yellowish or reddish colour like gum arabic, to which its properties are similar. It has a sweetish taste, dissolves in the mouth like gum, and forms a mucilage with water. It is distinguished from gum, however, by its solubility in alcohol, and by its aqueous solution being precipitated by tannin. Dr. Thomson, who has given a full account of sarcocoll in his System of Chemistry, considers it closely allied to the saccharine matter of liquorice.

Rhubarbarin is the name employed by Pfaff to designate the principle in which the purgative property of the rhubarb resides. M. Nani of Milan regards the active principle of this plant as a vegetable alkali; but he has not given any proof of its alkaline nature. (Journal of Science, xvi. 172.)

Rhéin.—M. Vaudin has applied this name to a substance which he obtained by gently heating rhubarb in powder with eight times its weight of nitric acid of 1.375, evaporating to the consistence of syrup, and diluting with cold water. Rhéin, which is then deposited, is inodorous, has a slightly bitter taste, and an orange colour. It is sparingly soluble in cold

water; but it dissolves in alcohol, ether, and hot water, and its solutions are rendered pale yellow by acids, and rose-red by alkalies. It may be extracted from rhubarb by ether, a fact which proves that it exists ready formed in the plant; and its mode of preparation shows that it possesses unusual permanence, powerfully resisting the action of nitric acid.

Colocyntin.—This name was applied by Vauquelin to a bitter resinous matter extracted from colocynth by the action of alcohol, and left by evaporation as a brittle substance of a golden-yellow colour. It is slightly soluble in water, is freely dissolved by alcohol and alkalies, and possesses the purgative properties of colocynth. (Journ. of Science, xviii. 400.)

Bitter Principle.—This name was formerly applied to a substance supposed to be common to bitter plants, and to be the cause of their peculiar taste. The recent discoveries in vegetable chemistry, however, have shown that it can no longer be regarded as an uniform unvarying principle. The bitterness of the *nux vomica*, for example, is owing to strychnia, that of opium to morphia, that of cinchona bark to cinchonia and quina, &c. The cause of the bitter taste in the root of the squill is different from that of the hop or of gentian. The term bitter principle, when applied to any one principle common to bitter plants, conveys an erroneous idea, and should therefore be abandoned.

Extractive Matter.—This expression, if applied to one determinate principle supposed to be the same in different plants, is not less vague than the foregoing. It is indeed true that most plants yield to water a substance which differs from gum, sugar, or any proximate principle of vegetables, which therefore constitutes a part of what is called an *extract* in pharmacy, and which, for want of a more precise term, may be expressed by the name of *extractive*. It must be remembered, however, that this matter is always mixed with other proximate principles, and that there is no proof whatever of its being identical in different plants. The solution of saffron in hot water, said to afford pure extractive matter by evaporation, contains the colouring matter of the plant, together with all the other vegetable principles of saffron, which happen to be soluble in the menstruum employed.

Plumbagin, extracted by Dulong from the root of the

Plumbago Europæa, is soluble in water, alcohol, and ether, and crystallizes from its solutions in acicular crystals of a yellow colour. Its aqueous solution is made cherry-red by alkalies, sub-acetate of lead, and per-muriate of iron; but acids restore the yellow tint, and the plumbagin is found unaltered. Its taste is at first sweet, but is subsequently sharp and acrid, extending to the throat. (Journal of Science, N. S. vi. 191.)

Chlorophyle.—This name has been applied by Pelletier and Caventou to the green colouring matter of leaves. It is prepared by bruising green leaves into a pulp with water, pressing out all the liquid, and boiling the pulp in alcohol. The solution is mixed with water, and the spirit driven off by distillation, when the chlorophyle is left floating on the surface of the water. As thus obtained, it appears to be wax stained with the green colour of the leaves; and from some late observations of M. Macaire Prinsep, the wax may be removed by ether, and the colouring matter left in a pure state. The red autumnal tint of the leaves, according to the same observer, is the effect of an acid generated in the leaf. The green tint may be restored by the action of an alkali.

SECTION VI.

ON THE SPONTANEOUS CHANGES OF VEGETABLE MATTER.

Vegetable substances, for reasons already explained in the remarks introductory to the study of organic chemistry, are very liable to spontaneous decomposition. So long, indeed, as they remain in connexion with the living plant by which they were produced, the tendency of their elements to form new combinations is controlled; but as soon as the vital principle is extinct, of whose agency no satisfactory explanation can at present be afforded, they become subject to the unrestrained influence of chemical affinity. To the spontaneous changes which they then experience from the operation of this power, the term *fermentation* is applied.

As might be expected from the difference in the constitution of different vegetable compounds, they are not all equally prone to fermentation; nor is the nature of the change the

same in all. Thus alcohol, oxalic, acetic, and benzoic acids, probably the vegetable alkalies, and pure naphtha, may be kept for years without change, and some of them appear unalterable; while others, such as gluten, sugar, starch, and mucilaginous substances, are very liable to decomposition. In like manner, the spontaneous change sometimes terminates in the formation of sugar, at another time in that of alcohol, at a third in that of acetic acid, and at a fourth in the total dissolution of the substance. This has led to the division of the fermentative processes into four distinct kinds, namely, the *saccharine*, *vinous*, *acetous*, and *putrefactive* fermentation.

SACCHARINE FERMENTATION.

The only substance known to be subject to the first kind of fermentation is starch. When gelatinous starch, or amidine, is kept in a moist state for a considerable length of time, a change gradually ensues, and a quantity of sugar, equal to about half the weight of the starch employed, is generated. Exposure to the atmosphere is not necessary to this change, but the quantity of sugar is increased by access of air.

The germination of seeds, as exemplified in the malting of barley, is likewise an instance of the saccharine fermentation; but as it differs in some respects from the process above mentioned, being probably modified by the vitality of the germ, it may with greater propriety be discussed in the following section.

The ripening of fruit has also been regarded as an example of the saccharine fermentation, especially since some fruits, such as the pear and apple, if gathered before their maturity, become sweeter by keeping. I cannot, however, adopt this opinion. The process of ripening appears to consist in the conversion, not of starch, but of acid into sugar. Such at least is the view deducible from the experiments of Proust, who examined the unripe grape in its different stages towards maturity. He found that the green fruit contains a large quantity of free acid, chiefly the citric, which gradually disappears as the grape ripens, while its place is occupied by sugar. It is hence probable that the elements of the acid itself, as the result of a vital process, are made to enter into a new

arrangement, by which sugar is generated. The formation of an acid may be regarded as one step towards the production of saccharine matter, a view which will account for the strong acidity of many fruits, such as the gooseberry and currant, just before they begin to ripen.

VINOUS FERMENTATION.

The conditions which are required for establishing the vinous fermentation are four in number, namely, the presence of sugar, water, yeast or some ferment, and a certain temperature. The best mode of studying this process, so as to observe the phenomena and determine the nature of the change, is to place five parts of sugar with about twenty of water in a glass flask furnished with a bent tube, the extremity of which opens under an inverted jar full of water or mercury; and after adding a little yeast, to expose the mixture to a temperature of about 60° or 70° Fahr. In a short time bubbles of gas begin to collect in the vicinity of the yeast, and the liquid is soon put into brisk motion, in consequence of the formation and disengagement of a large quantity of gaseous matter; the solution becomes turbid, its temperature rises, and froth collects upon its surface. After continuing for a few days, the evolution of gas begins to abate, and at length ceases altogether; the impurities gradually subside, and leave the liquor clear and transparent.

The only appreciable changes which are found to have occurred during the process are the disappearance of the sugar, and the formation of alcohol, which remains in the flask, and of carbonic acid gas, which is collected in the pneumatic apparatus. A small portion of yeast is indeed decomposed; but the quantity is so minute that it may without inconvenience be left out of consideration. The yeast indeed appears to operate only in exciting the fermentation, without further contributing to the products. The atmospheric air, it is obvious, has no share in the phenomena, since it may be altogether excluded without affecting the result. The theory of the process is founded on the fact that the sugar, which disappears, is almost precisely equal to the united weights of the alcohol

and carbonic acid; and hence the former is supposed to be resolved into the two latter. The mode in which this change is conceived to take place has been ably explained by Gay-Lussac, an explanation which will easily be understood by comparing the composition of sugar with that of alcohol. The elements of sugar, which consist of carbon, hydrogen, and oxygen, in the ratio of one equivalent of each, (page 745.) are multiplied by three, in order to equalize the quantity of hydrogen contained in the two compounds. (An. de Ch. xcv. 317.)

	By weight.		By volume.		
	Sugar.	Alcohol.		Sugar.	Alcohol.
Carbon,	18 or 3 equiv.	12 or 2 equiv.	Vapour of Carbon,	3	2
Hydrogen,	3 or 3 equiv.	3 or 3 equiv.	Hydrogen, .	3	3
Oxygen,	24 or 3 equiv.	8 or 1 equiv.	Oxygen, .	$\frac{3}{2}$	$\frac{1}{2}$
	45	23			

Now on inspecting this table, and remembering that carbonic acid consists of one equivalent of carbon, or one volume of its vapour, and two equivalents or one volume of oxygen, it will be apparent that the elements of sugar are in such proportion as to form one equivalent of alcohol, or one volume of its vapour, and one equivalent or one volume of carbonic acid. Therefore forty-five parts of sugar are capable of furnishing twenty-three parts of alcohol and twenty-two of carbonic acid.

It admits of doubt whether any substance besides sugar is capable of undergoing the vinous fermentation. The only other principle which is supposed to possess this property is starch, and this opinion chiefly rests on the two following facts. First, It is well known that potatoes, which contain but little sugar, yield a large quantity of alcohol by fermentation, during which the starch disappears. And, secondly, M. Clement procured the same quantity of alcohol from equal weights of malted and unmalted barley. (An. de Ch. et Ph. v. 422.) Nothing conclusive can be inferred, however, from these data; for, from the facility with which starch is converted into sugar it is probable that the saccharine may precede the vinous fermentation. This view is, indeed, justified by the practice of dis-

tillers, who do not ferment with unmalted barley only, but are obliged to mix with it a certain proportion of malt, which appears to act as a ferment to the unmalted grain.

Though a solution of pure sugar is not susceptible of the vinous fermentation without being mixed with yeast, or some such ferment, yet the saccharine juices of plants do not require the addition of that substance, or in other words, they contain some principle which, like yeast, excites the fermentative process. Thus, must or the juice of the grape ferments spontaneously; but Gay-Lussac has observed that these juices cannot begin to ferment unless they are exposed to the air. By heating must to 212° F., and then corking it carefully, the juice may be preserved without change; but if it be exposed to the air for a few seconds only, it absorbs oxygen, and fermentation takes place. From this it would appear that the must contains a principle which is convertible into yeast, or at least acquires the characteristic property of that substance, by absorbing oxygen.

It appears from the experiments of M. Colin, that various substances are capable of acting as a ferment. This property is possessed by gluten and vegetable albumen, caseous matter, albumen, fibrin, gelatine, blood, and urine. In general they act most efficaciously after the commencement of putrefaction; and indeed exposure to oxygen gas seems equally necessary for enabling these substances to act as ferments, as to the principle contained in the juice of fruit.

The various kinds of stimulating fluids, prepared by means of the vinous fermentation, are divisible into wines which are formed from the juices of saccharine fruits, and the various kinds of ale and beer produced from a decoction of the nutritive grains previously malted.

The juice of the grape is superior, for the purpose of making wine, to that of all other fruits, not merely in containing a larger proportion of saccharine matter, since this deficiency may be supplied artificially, but in the nature of its acid. The chief or only acidulous principle of the mature grape, ripened in a warm climate, such as Spain, Portugal, or Madeira, is bitartrate of potash. As this salt is insoluble in alcohol, the greater part of it is deposited during the vinous fermentation; and an additional quantity subsides, constituting the *crust*,

during the progress of wine towards its point of highest perfection. The juices of other fruits, on the contrary, such as the gooseberry or currant, contain malic and citric acids, which are soluble both in water and alcohol, and of which therefore they can never be deprived. Consequently these wines are only rendered palatable by the presence of free sugar, which conceals the taste of the acid; and hence it is necessary to arrest the progress of fermentation long before the whole of the saccharine matter is consumed. For the same reason, these wines, unless made very sweet, do not admit of being long kept; for as soon as the free sugar is converted into alcohol by the slow fermentative process, which may be retarded by the addition of brandy, but cannot be prevented, the wine acquires a strong sour taste.

Ale and beer differ from wine in containing a large quantity of mucilaginous and extractive matters derived from the malt with which they are made. From the presence of these substances they always contain a free acid, and are greatly disposed to pass into the acetous fermentation. The sour taste is concealed partly by free sugar, and partly by the bitter flavour of the hop, the presence of which diminishes the tendency to the formation of an acid.

The fermentative process which takes place in dough mixed with yeast, and on which depends the formation of good bread, has been supposed to be of a peculiar kind, and is sometimes designated by the name of *panary fermentation.* The late ingenious researches of Dr. Colquhoun, however, leave little or no doubt that the phenomena are to be ascribed to the saccharine matter of the flour undergoing the vinous fermentation, by which it is resolved into alcohol and carbonic acid. (Brewster's Journal, vi.) Indeed Mr. Graham has actually procured alcohol by distillation from fermented dough.

ACETOUS FERMENTATION.

When any liquid which has undergone the vinous fermentation, or even pure alcohol diluted with water, is mixed with yeast, and exposed in a warm place to the open air, an intestine movement speedily commences, heat is developed, the fluid becomes turbid from the deposition of a peculiar filamentous

matter, oxygen is absorbed from the atmosphere, and carbonic acid is disengaged. These changes, after continuing a certain time, cease spontaneously; the liquor becomes clear, and instead of alcohol, it is now found to contain acetic acid. This process is called the *acetous fermentation.*

The vinous may easily be made to terminate in the acetous fermentation; nay, the transition takes place so easily, that in many instances, in which it is important to prevent it, this is with difficulty effected. It is the uniform result if the fermenting liquid be exposed to a warm temperature and to the open air; and the means by which it is avoided is by excluding the atmosphere, or by exposure to cold.

For the acetous fermentation a certain degree of warmth is indispensable. It takes place tardily below 60° F.; at 50° it is very sluggish; and at 32°, or not quite so low, it is wholly arrested. It proceeds with vigour, on the contrary, when the thermometer ranges between 60° and 80°, and is even promoted by a temperature somewhat higher. The presence of water is likewise essential; and a portion of yeast, or some analogous substance, by which the process may be established, must also be present.

The information contained in chemical works relative to the substances susceptible of the acetous fermentation is somewhat confused, a circumstance which appears to have arisen from phenomena of a totally different nature being included under the same name. It seems necessary to distinguish between the mere formation of acetic acid, and the acetous fermentation. Several or perhaps most vegetable substances yield acetic acid when they undergo spontaneous decomposition. Mucilaginous substances in particular, though excluded from the air, gradually become sour; and consistently with this fact, inferior kinds of ale and beer are known to acquire acidity in a short time, even when confined in well-corked bottles. In like manner, a solution of sugar, mixed with water in which the gluten of wheat has fermented, and kept in close vessels, was found by Fourcroy and Vauquelin to yield acetic acid. All these processes, however, appear essentially different from the proper acetous fermentation above described, being unattended with visible movement in the liquid, with absorption of oxygen, or disengagement of carbonic acid.

The acetous fermentation, in this limited sense, consists in the conversion of alcohol into acetic acid. That this change does really take place is inferred, not only from the disappearance of alcohol and the simultaneous production of acetic acid, but also from the quantity of the latter being precisely proportional to that of the former. The nature of the chemical action, however, is at present exceedingly obscure. Indeed the only probable explanation which has been offered is the following. Since alcohol contains a greater proportional quantity of carbon and hydrogen than acetic acid, it has been supposed that the oxygen of the atmosphere, the presence of which is indispensable, abstracts so much of those elements by giving rise to the formation of carbonic acid and water, as to leave the remaining carbon, hydrogen, and oxygen of the alcohol in the precise ratio for forming acetic acid. The experiments of Saussure, however, are incompatible with this view. According to his researches, the quantity of carbonic acid generated during the acetous fermentation is precisely equal in volume to the oxygen which is absorbed; and hence it is inferred, that this gas unites exclusively with the carbon of the alcohol. This result is different from what might have been anticipated, and requires confirmation.

The acetous fermentation is conducted on a large scale for yielding the common vinegar of commerce. In France it is prepared by exposing weak wines to the air during warm weather; and in this country it is made from a solution of brown sugar or molasses, or an infusion of malt. The vinegar thus obtained always contains a large quantity of mucilaginous and other vegetable matters, the presence of which renders it liable to several ulterior changes.

PUTREFACTIVE FERMENTATION.

By this term is implied a process which is not attended with the phenomena of the saccharine, vinous, or acetous fermentation, but during which the vegetable matter is completely decomposed. All proximate principles are not equally liable to this kind of dissolution. Those in which charcoal and hydrogen prevail, such as the oils, resins, and alcohol, do not undergo the putrefactive fermentation; nor do acids, which

contain a considerable excess of oxygen, manifest a tendency to suffer this change. Those substances alone are disposed to putrefy, the oxygen and hydrogen of which are in proportion to form water; and such, in particular, as contain nitrogen. Among these, however, a singular difference is observable. Caffein evinces no tendency to spontaneous decomposition; while gluten, which certainly must contain a less proportional quantity of nitrogen, putrefies with great facility. It is difficult to assign the precise cause of this difference; but it most probably depends partly upon the mode in which the ultimate elements of bodies are arranged, and partly on their cohesive power;—those substances, the texture of which is the most loose and soft, being, *cæteris paribus*, the most liable to spontaneous decomposition.

The conditions which are required for enabling the putrefactive process to take place, are moisture, air, and a certain temperature.

The presence of a certain degree of moisture is absolutely necessary; and hence vegetable substances, which are disposed to putrefy under favourable circumstances, may be preserved for an indefinite period if carefully dried, and protected from humidity. Water acts apparently by softening the texture, and thus counteracting the agency of cohesion; and a part of the effect may also be owing to its affinity for some of the products of putrefaction. It is not likely that this liquid is actually decomposed, since water appears to be an uniform product.

The air cannot be regarded as absolutely necessary, since putrefaction is found to be produced by the concurrence of the two other conditions only; but the process is without doubt materially promoted by free exposure to the atmosphere. Its operation is of course attributable to the oxygen combining with the carbon and hydrogen of the decaying substance.

The temperature most favourable to the putrefactive process is between 60° and 100° Fahr. A strong heat is unfavourable, by expelling moisture; and a cold of 32° F., at which water congeals, arrests its progress altogether. The mode in which caloric acts is the same as in all similar cases, namely, by

tending to separate elements from one another which are already combined.

The products of the putrefactive fermentation may be divided into the solid, liquid, and gaseous. The liquid are chiefly water, together with a little acetic acid, and probably oil. The gaseous products are light carburetted hydrogen, carbonic acid, and, when nitrogen is present, ammonia. Pure hydrogen, and probably nitrogen, are sometimes disengaged. Thus hydrogen and carbonic acid, according to Proust, are evolved from putrefying gluten; and Saussure obtained the same gases from the putrefaction of wood in close vessels. Under ordinary circumstances, however, the chief gaseous product of decaying plants is light carburetted hydrogen, which is generated in great quantity at the bottom of stagnant pools during summer and autumn. (Page 346.) Another elastic principle, supposed to arise from putrefying vegetable remains, is the noxious miasm of marshes. The origin of these miasms, however, is exceedingly obscure. Every attempt to obtain them in an insulated state has hitherto proved abortive; and, therefore, if they are really a distinct species of matter, they must be regarded, like the effluvia of contagious fevers, as of too subtile a nature for being subjected to chemical analysis.

When the decay of leaves or other parts of plants has proceeded so far that all trace of organization is effaced, a dark pulverulent substance remains, consisting of charcoal combined with a little oxygen and hydrogen. This compound is vegetable mould, which, when mixed with a proper quantity of earth, constitutes the soil necessary to the growth of plants. Saussure, in his excellent *Recherches Chimique sur la Vegetation*, has described vegetable mould as a substance of uniform composition; and on heating it to redness in close vessels, he procured carburetted hydrogen and carbonic acid gases, water holding acetate or carbonate of ammonia in solution, a minute quantity of empyreumatic oil, and a large residue of charcoal mixed with saline and earthy ingredients. On exposing vegetable mould to the action of light, air, and moisture, a chemical change ensues, the effect of which is to render a portion of it soluble in water, and thus applicable to the nutrition and growth of plants.

SECTION VII.

ON THE CHEMICAL PHENOMENA OF GERMINATION AND VEGETATION.

GERMINATION.

GERMINATION is the process by which a new plant originates from seed. A seed consists essentially of two parts, the *Germ* of the future plant, endowed with a principle of vitality, and the *Cotyledons* or *Seed-lobes*, both of which are enveloped in a common covering of cuticle. In the germ two parts, the *radicle* and *plumula*, may be distinguished, the former of which is destined to descend into the earth and constitute the root, the latter to rise into the air and form the stem of the plant. The office of the seed-lobes is to afford nourishment to the young plant until its organization is so far advanced, that it may draw materials for its growth from extraneous sources. For this reason seeds are composed of highly nutritious ingredients. The chief constituent of most of them is starch, in addition to which they frequently contain gluten, gum, vegetable albumen or curd, and sugar.

The conditions necessary to germination are three-fold; namely, moisture, a certain temperature, and the presence of oxygen gas. The necessity of moisture to this process has been proved by extensive observation. It is well known that the concurrence of other conditions cannot enable seeds to germinate provided they are kept quite dry.

A certain degree of warmth is not less essential than moisture. Germination cannot take place at 32° F.; and a strong heat, such as that of boiling water, prevents it altogether by depriving the germ of the vital principle. The most favourable temperature ranges from 60° to 80°, the precise degree varying with the nature of the plant, a circumstance that accounts for the difference in the season of the year at which different seeds begin to germinate.

That the presence of air is necessary to germination was demonstrated by several philosophers, such as Ray, Boyle,

Muschenbroeck and Boerhaave, before the chemical nature of the atmosphere was discovered; and Scheele, soon after the discovery of oxygen, proved that beans do not germinate without exposure to that gas. Achard afterwards demonstrated the same fact with respect to seeds in general, and his experiments have been fully confirmed by subsequent observers. It has even been shown by Humboldt, that a dilute solution of chlorine, owing to the tendency of that gas to decompose water and set oxygen at liberty, promotes the germination of seeds. These circumstances account for the fact that seeds, when buried deep in the earth, are unable to germinate.

It is remarkable that the influence of light, which is so favourable to all the subsequent stages of vegetation, is injurious to the process of germination. Ingenhousz and Sennebier have proved that a seed germinates more rapidly in the shade than in light, and in diffused daylight quicker than when exposed to the direct solar rays.

From the preceding remarks it is apparent that when a seed is placed an inch or two under the surface of the ground in spring, and is loosely covered with earth, it is in a state every way conducive to germination. The ground is warmed by absorbing the solar rays, and is moistened by occasional showers; the earth at the same time protects the seed from light, but by its porosity gives free access to the air.

The operation of malting barley, in which the grain is made to germinate by exposure to warmth, air, and humidity, affords the best means of studying the phenomena of germination. In preparing malt, the grain passes through four distinct stages, called *steeping*, *couching*, *flooring*, and *kiln-drying*. In the first it is steeped in water for about two days, when it absorbs moisture, softens, and swells considerably. It is then removed to the *couch-frame*, where it is laid in heaps 30 inches in depth for from 26 to 30 hours. In this situation the grain becomes warm and acquires a disposition to germinate; but as the temperature, in such large heaps, would rise very unequally, and germination consequently be rapid in some portions and slow in others, the process of *flooring* is employed. This consists in laying the grain in strata a few inches thick on large airy but shaded floors, where it remains for about 12 or 14 days until germination has advanced to the extent desired by the

maltster. During this interval the grain is frequently turned, in order that the temperature of the whole mass should be uniform, that each grain should be duly exposed to the air, and that the radicles of contiguous grains should not become entangled with each other. As soon as saccharine matter is freely developed, germination must be arrested; since otherwise, being taken up as nutriment by the young plant, it would speedily disappear. Accordingly, the grain is removed to the kiln, where it is exposed to a temperature gradually rising from 100° to 160°, or rather higher; the object being, first, to dry the grain completely, and then to provide against any recurrence of germination by destroying the vitality of the plant. The most convenient mode of applying the heat is to place the grain on a metallic net-work, through which passes hot air issuing from a fire made with good coke. The process of malting is not conducted during summer, because in hot weather the grain is apt to become mouldy.

The difference between malted and unmalted barley is readily perceived by the taste; but it will be more correctly appreciated by inspecting the result of Proust's comparative analysis of malted and unmalted barley. (An. de Ch. et de Ph. v.)

	In 100 parts of Barley.	In 100 parts of Malt.
Resin,	1	1
Gum,	4	15
Sugar,	5	15
Gluten,	3	1
Starch,	32	56
Hordein,	55	12

It is hence apparent that during germination the hordein is converted into starch, gum, and sugar; so that from an insoluble material, which could not in that state be applied to the uses of the young plant, two soluble and highly nutritive principles result, which by being dissolved in water are readily absorbed by the radicle.

The chemical changes which take place during germination have been ably investigated by Saussure, whose experiments are detailed in the work to which I have already referred. The leading facts which he determined are the following;—that oxygen gas is consumed, that carbonic acid is evolved, and that

the volume of the latter is precisely equal to that of the former. Now since carbonic acid gas contains its own volume of oxygen, it follows that this gas must have united exclusively with carbon. It is likewise obvious that the grain must weigh less after than before germination, provided it is brought to the same state of dryness in both instances. Saussure indeed found that the loss is greater than can be accounted for by the carbon of the carbonic acid which is evolved, and hence he concluded that a portion of water, generated at the expense of the grain itself, is dissipated in drying. According to Proust, the diminution in weight is about a third; but Dr. Thomson affirms that in 50 processes, conducted on a large scale under his inspection, the average loss did not exceed one-fifth.

ON THE GROWTH OF PLANTS.

While a plant differs from an animal in exhibiting no signs of perception or voluntary motion, and in possessing no stomach to serve as a receptacle for its food, there exists between them a close analogy both of parts and functions, which, though not discerned at first, becomes striking on a near examination. The stem and branches act as a frame-work or skeleton for the support and protection of the parts necessary to the life of the individual. The root serves the purpose of a stomach by imbibing nutritious juices from the soil, and thus supplying the plant with materials for its growth. The sap or circulating fluid, composed of water holding in solution saline, extractive, mucilaginous, saccharine, and other soluble substances, rises upwards through the wood in a distinct system of tubes called the *common vessels*, which correspond in their office to the lacteals and pulmonary arteries of animals, and are distributed in minute ramifications over the surface of the leaves. In its passage through this organ, which may be termed the lungs of a plant, the sap is fully exposed to the agency of light and air, experiences a change by which it is more completely adapted to the wants of the vegetable economy, and then descends through the inner layer of the bark in another system of tubes called the *proper vessels*, yielding in its course all the juices and principles peculiar to the plant.

The chemical changes which take place during the circula-

tion of the sap are in general of such a complicated nature, and so much under the control of the vital principle, as to elude the sagacity of the chemist. One part of the subject, however, namely, the reciprocal agency of the atmosphere and growing vegetables on each other, falls within the reach of chemical inquiry, and has accordingly been investigated by several philosophers.

For the leading facts relative to what is called the *respiration* of plants, or the chemical changes which the leaves of growing vegetables produce on the atmosphere, we are indebted to Priestley and Ingenhousz, the former of whom discovered that plants absorb carbonic acid from the air under certain circumstances, and emit oxygen in return; and the latter ascertained that this change occurs only during exposure to the direct rays of the sun. When a healthy plant, the roots of which are supplied with proper nourishment, is exposed to the direct solar beams in a given quantity of atmospheric air, the carbonic acid after a certain interval is removed, and an equal volume of oxygen is substituted for it. If a fresh portion of carbonic acid is supplied, the same result will ensue. In like manner, Sennebier and Woodhouse observed, that when the leaves of a plant are immersed in water, and exposed to the rays of the sun, oxygen gas is disengaged. That the evolution of oxygen in this experiment is accompanied with a proportional absorption of carbonic acid, is proved by employing water deprived of carbonic acid by boiling, in which case no oxygen is procured.

Such are the changes induced by plants when exposed to sunshine: but in the dark an opposite effect ensues. Carbonic acid gas is not absorbed under these circumstances, nor is oxygen gas evolved; but, on the contrary, oxygen disappears, and carbonic acid gas is disengaged. In the dark, therefore, vegetables deteriorate rather than purify the air, producing the same effect as the respiration of animals.

From several of the preceding facts, it is supposed that the oxygen emitted by plants while under the influence of light is derived from the carbonic acid which they absorb, and that the carbon of that gas is applied to the purposes of nutrition. Consistently with this view it has been observed that plants do not thrive when kept in an atmosphere of pure oxygen; and it

was found by Dr. Percival and Mr. Henry, that the presence of a little carbonic acid is even favourable to their growth. Saussure, who examined this subject minutely, ascertained that plants grow better in an atmosphere which contains about one-twelfth of carbonic acid than in common air, provided they are exposed to sunshine. But if that gas be present in a greater proportion, its influence is prejudicial:—in an atmosphere consisting of one-half of its volume of carbonic acid, the plants perished in seven days; and they did not vegetate at all when that gas was in the proportion of two-thirds. In the shade, the presence of carbonic acid is always detrimental. He likewise observed that the presence of oxygen is necessary, in order that a plant should derive benefit from admixture with carbonic acid.

Saussure is of opinion that plants derive a large quantity of their carbon from the carbonic acid of the atmosphere, an opinion which receives great weight from the two following comparative experiments. On causing a plant to vegetate in pure water, supplied with common air and exposed to light, the carbon of the plant increased in quantity; but when supplied with common air, in a dark situation, it even lost a portion of the carbon which it had previously possessed.

Light is necessary to the colour of plants. The experiments of Sennebier and Mr. Gough have shown that the green colour of the leaves is not developed, except when they are in a situation to absorb oxygen and give out carbonic acid.

Though the experiments of different philosophers agree as to the influence of vegetation on the air in sunshine and during the night, considerable uncertainty prevails both as to the phenomena occasioned by diffused daylight, and concerning the total effect produced by plants on the constitution of the atmosphere. Priestley found that air, vitiated by combustion or the respiration of animals, and left in contact for several days and nights with a sprig of mint, was gradually restored to its original purity; and hence he inferred that the oxygen gas, consumed during these and various other processes, is restored to the mass of the atmosphere by the agency of growing vegetables.

This doctrine receives confirmation from the researches of Ingenhousz and Saussure, who were led to adopt the opinion

that the quantity of oxygen gas evolved from plants by day, exceeds that of carbonic acid emitted during the night. The conclusions of Mr. Ellis, on the contrary, are precisely the reverse. From an extensive series of experiments, contrived with much sagacity, Mr. Ellis inferred that growing plants give out oxygen only in direct sunshine, while at all other times they absorb it; that when exposed to the ordinary vicissitudes of sunshine and shade, light and darkness, they form more carbonic acid in the period of a day and night, than they destroy; and, consequently, that the general effect of vegetation on the atmosphere is the same as that produced by animals. (Ellis's Researches and Farther Inquiries on Vegetation, &c.)

This question has been ably discussed by Sir H. Davy in his Elements of Agricultural Chemistry. Sir H. Davy was of opinion that the experiments of Mr. Ellis cannot be regarded as decisive, having been conducted under circumstances unfavourable to accuracy of result. He considers the original experiments of Priestley as unexceptionable, and adduces others made by himself in support of the same doctrine.

ON THE FOOD OF PLANTS.

The chief source from which plants derive the materials for their growth is the soil. However various the composition of the soil, it consists essentially of two parts, so far as its solid constituents are concerned. One is a certain quantity of earthy matters, such as siliceous earth, clay, lime, and sometimes magnesia; and the other is formed from the remains of animal and vegetable substances, which, when mixed with the former, constitute common mould. A mixture of this kind, moistened by rain, affords the proper nourishment of plants. The water, percolating through the mould, dissolves the soluble salts with which it comes in contact, together with the gaseous, extractive, and other matters which are formed during the decomposition of the animal and vegetable remains. In this state it is readily absorbed by the roots, and conveyed as sap to the leaves, where it undergoes a process of assimilation.

But though this is the natural process by which plants obtain the greater part of their nourishment, and without which

they do not arrive at perfect maturity, they may live, grow, and even increase in weight, when wholly deprived of nutrition from this source. Thus in the experiment of Saussure, already described, sprigs of peppermint were found to vegetate in distilled water; and it is well known that many plants grow when merely suspended in the air. In the hot-houses of the botanical garden of Edinburgh, for example, there are two plants, species of the fig-tree, the *ficus australis* and *ficus elastica*, the latter of which, as Dr. Graham informs me, has been suspended for six, and the former for nearly twelve years, during which time they have continued to send out shoots and leaves.

Before scientific men had learned to appreciate the influence of atmospheric air on vegetation, the increase of carbonaceous matter, which occurs in some of these instances, was supposed to be derived from water, an opinion naturally suggested by the important offices performed by this fluid in the vegetable economy. Without water, plants speedily wither and die. It gives the soft parts that degree of succulence necessary for the performance of their functions;—it affords two elements, oxygen and hydrogen, which either as water, or under some other form, are contained in all vegetable products;—and, lastly, the roots absorb from the soil those substances only, which are dissolved or suspended in water. So carefully, indeed, has nature provided against the chance of deficient moisture, that the leaves are endowed with a property both of absorbing aqueous vapour directly from the atmosphere, and of lowering their temperature during the night by radiation, so as to cause a deposition of dew upon their surface, in consequence of which, during the driest seasons and in the warmest climates, they frequently continue to convey this fluid to the plant, when it can no longer be obtained in sufficient quantity from the soil. But necessary as is this fluid to vegetable life, it cannot yield to plants a principle which it does not possess. The carbonaceous matter which accumulates in plants, under the circumstances above mentioned, may, with every appearance of justice, be referred to the atmosphere; since we know that carbonic acid exists there, and that growing vegetables have the property of taking carbon from that gas.

When plants are incinerated, their ashes are found to con-

tain saline and earthy matters, the elements of which, if not the compounds themselves, are supposed to be derived from the soil. Such at least is the view deducible from the researches of Saussure, and which might have been anticipated by reasoning on chemical principles. The experiments of M. Schrader, however, lead to a different conclusion. He sowed several kinds of grain, such as barley, wheat, rye, and oats, in pure flowers of sulphur, and supplied the shoots as they grew with nothing but air, light, and distilled water. On incinerating the plants, thus treated, they yielded a greater quantity of saline and earthy matters than were originally present in the seeds.

These results, supposing them accurate, may be accounted for in two ways. It may be supposed, in the first place, that the foreign matters were introduced accidentally from extraneous sources, as by fine particles of dust floating in the atmosphere; or, secondly, it may be conceived, that they were derived from the sulphur, air, and water, with which the plants were supplied. If the latter opinion be adopted, we must infer either that the vital principle, which certainly controls chemical affinity in a surprising manner, and directs this power in the production of new compounds from elementary bodies, may likewise convert one element into another; or that some of the substances, supposed by chemists to be simple, such as oxygen and hydrogen, are compounds, not of two, but of a variety of different principles. As these conjectures are without foundation, and are utterly at variance with the facts and principles of the science, I do not hesitate in adopting the more probable opinion, that the experiments of M. Schrader were influenced by some source of error which escaped detection.

ANIMAL CHEMISTRY.

All distinct compounds, which are derived from the bodies of animals, are called *proximate animal principles.* They are distinguished from inorganic matter by the characters stated in the introduction to inorganic chemistry. The circumstances which serve to distinguish them from vegetable matter are, the presence of nitrogen, their strong tendency to putrefy, and the highly offensive products to which their spontaneous decomposition gives rise. It should be remembered, however, that nitrogen is likewise a constituent of many vegetable substances; though few of these, the vegeto-animal principles excepted, (page 766.) are prone to suffer the putrefactive fermentation. It is likewise remarkable that some compounds of animal origin, such as cholesterine and the oils, do not contain nitrogen as one of their elements, and are not disposed to putrefy.

The essential constituents of animal compounds are carbon, hydrogen, oxygen, and nitrogen, besides which some of them contain phosphorus, sulphur, iron, and earthy and saline matters in small quantity. Owing to the presence of sulphur and phosphorus, the process of putrefaction, which will be particularly described hereafter, is frequently attended with the disengagement of sulphuretted and phosphuretted hydrogen gases. When heated in close vessels, they yield water, carbonic oxide, carburetted hydrogen, probably free nitrogen and hydrogen, carbonate and hydrocyanate of ammonia, and a peculiarly fetid thick oil. The carbonaceous matter left in the retort is less easily burned, and is more effectual as a decolorizing agent, than charcoal derived from vegetable matter.

The principle of the method of analyzing animal substances has already been mentioned. (Page 671.)

In describing the proximate animal principles, the number

of which is far less considerable than vegetable compounds, the arrangement suggested by Gay-Lussac and Thenard in their *Recherches Physico-Chimiques*, and followed by Thenard in his System of Chemistry, has been adopted. The animal compounds are accordingly arranged in three sections. The first contains substances which are neither acid nor oleaginous; the second comprehends the vegetable acids; and the third includes the animal fats. Several of the principles belonging to the first division, such as fibrin, albumen, gelatine, caseous matter, and urea, were shown by Gay-Lussac and Thenard to have several points of similarity in their composition. They all contain, for example, a large quantity of carbon, and their hydrogen is in such proportion as to convert all their oxygen into water, and their nitrogen into ammonia. No general laws have been established relative to the constitution of the compounds comprised in the other sections.

SECTION I.

SUBSTANCES WHICH ARE NEITHER ACID NOR OLEAGINOUS.

FIBRIN.

Fibrin enters largely into the composition of the blood, and is the basis of the muscles; it may be regarded, therefore, as one of the most abundant of the animal principles. It is most conveniently procured by stirring recently drawn blood with a stick during its coagulation, and then washing the adhering fibres with water until they are perfectly white. It may also be obtained from lean beef cut into small slices, the soluble parts being removed by digestion in several successive portions of water.

Fibrin is solid, white, insipid, and inodorous. When moist it is somewhat elastic, but on drying it becomes hard, brittle, and semi-transparent. In a moist warm situation it readily putrefies. It is insoluble in water at common temperatures, and is dissolved in very minute quantity by the continued action of boiling water. Alcohol, of specific gravity 0.81, converts it into a fatty adipocirous matter, which is soluble in alcohol and ether, but is precipitated by water.

The action of acids on fibrin has been particularly described

by Berzelius*. Digested in concentrated acetic acid, fibrin swells and becomes a bulky tremulous jelly, which dissolves completely, with disengagement of a little nitrogen, in a considerable quantity of hot water.

By the action of nitric acid, of specific gravity 1.25, aided by heat on fibrin, a yellow solution is formed with disengagement of a large quantity of nearly pure nitrogen, in which Berzelius could not detect the least trace of the deutoxide of nitrogen. After digestion for twenty-four hours, a pale yellow pulverulent substance is deposited, which Fourcroy and Vauquelin described as a new acid under the name of *yellow acid*. According to Berzelius, however, it is a compound of modified fibrin and nitric acid, together with some malic and nitrous acids. It likewise contains some fatty matter, which may be removed by alcohol. The origin of the nitrogen which is disengaged in the beginning of the process is somewhat obscure. From the total absence of deutoxide of nitrogen, it is probable that in the early stages very little, if any, of the nitric acid is decomposed, and that the nitrogen gas is solely or chiefly derived from the fibrin.

Dilute muriatic acid hardens without dissolving fibrin, and the strong acid decomposes it. The action of sulphuric acid, according to Braconnot, is very peculiar. When fibrin is mixed with its own weight of concentrated sulphuric acid, a perfect solution ensues, without change of colour, or disengagement of sulphuric acid. On diluting with water, boiling for nine hours, and separating the acid by means of chalk, the filtered solution was found to contain a peculiar white matter, to which Braconnot has applied the name of *leucine*. (An. de Ch. et de Ph. xiii.) Digested in strong sulphuric acid, a dark reddish-brown, nearly black, solution is formed, and the fibrin is carbonized and decomposed.

Fibrin is dissolved by pure potash, and is thrown down when the solution is neutralized. The fibrin thus precipitated, however, is partially changed, since it is no longer soluble in acetic acid. It is soluble likewise in ammonia.

According to the analysis of Gay-Lussac and Thenard, 100 parts of fibrin are composed of carbon 53.36, hydrogen 7.021,

* Medico-Chirurgical Transactions, vol. iii. p. 201, et seq.

oxygen 19.685, and nitrogen 19.934. From these numbers fibrin may be regarded as an atomic compound of 18 equivalents of carbon, 14 of hydrogen, 5 of oxygen, and 3 of nitrogen.

ALBUMEN.

Albumen enters largely into the composition both of animal fluids and solids. Dissolved in water it forms an essential constituent of the serum of the blood, the liquor of the serous cavities, and the fluid of dropsy; and in a solid state it is contained in several of the textures of the body, such as the cellular membrane, the skin, glands, and vessels. From this it appears that albumen exists under two forms, liquid and solid.

Liquid albumen is best procured from the white of eggs, which consists almost solely of this principle, united with water and free soda, and mixed with a small quantity of saline matter. In this state it is a thick glairy fluid, insipid, inodorous, and easily miscible with cold water, in a sufficient quantity of which it is completely dissolved. When exposed in thin layers to a current of air it dries, and becomes a solid and transparent substance, which retains its solubility in water, and may be preserved for any length of time without change; but if kept in its fluid condition it readily putrefies. From the free soda which they contain, albuminous liquids have always an alkaline reaction.

Liquid albumen is coagulated by heat, alcohol, and the stronger acids. Undiluted albumen is coagulated by a temperature of 160°, and when diluted with water at 212° F. Water which contains only 1-1000th of its weight of albumen is rendered opaque by boiling. (Bostock.) On this property is founded the method of clarifying by means of albuminous solutions; for the albumen being coagulated by heat, entangles in its substance all the foreign particles which are not actually dissolved, and carries them with it to the surface of the liquid. The character of being coagulated by hot water distinguishes albumen from all other animal fluids.

The acids differ in their action on albumen. The sulphuric, muriatic, and nitric acids coagulate it; and in each case, according to Thenard, some of the acid is retained by the albumen. It is precipitated also by pyrophosphoric acid, but not

by the phosphoric, a character, as already mentioned, by which these acids may be distinguished from each other. (Page 278.) The solution of albumen is not precipitated at all by acetic acid. By maceration in dilute nitric acid for a month, it is converted, according to Mr. Hatchett, into a substance soluble in hot water, and possessed of the leading properties of gelatine. Digested in strong sulphuric acid, the coagulum is dissolved, and a dark solution is formed similar to that produced by the same acid on fibrin; but if the heat be applied very cautiously, the liquid assumes a beautiful red colour. This property was discovered some years ago by Dr. Hope, who informs me that the experiment does not always succeed, the result being influenced by very slight causes.

Albumen is precipitated by several re-agents, especially by metallic salts. This effect is produced by muriate of tin, subacetate of lead, muriate of gold, and solution of tannin. Corrosive sublimate is a very delicate test of the presence of albumen, causing a milkiness when the albumen is diluted with 2000 parts of water. The nature of the precipitate has already been explained. (Page 557.) Ferrocyanate of potash is equally if not still more delicate, provided a little acetic acid is previously added to neutralize the free soda.

When an albuminous liquid is exposed to the agency of galvanism, pure soda makes its appearance at the negative wire, and the albumen coagulates around that which is in connexion with the positive pole of the battery. Mr. Brande*, who first observed this phenomenon, ascribes it to the separation of free soda, upon which he supposes the solubility of albumen in water to depend; but M. Lassaigne† attributes it to the decomposition of muriate of soda, the acid of which coagulates the albumen. However this may be, galvanism is one of the most elegant and delicate tests which we possess of the presence of albumen in animal fluids.

Chemists are not agreed as to the cause of the coagulation of albumen. When it is coagulated by different chemical agents, such as tannin and metallic salts, the albumen is thrown down in consequence of forming an insoluble compound with the substance employed; and perhaps this is also the mode by

* Philosophical Transactions for 1809. † An. de Ch. et de Ph. vol. xx.

which acids coagulate it. With respect to the agency of heat, alcohol, and probably of acids, a different view must be adopted. The explanation usually given is that proposed by Dr. Thomson, who ascribes the solubility of albumen to the presence of free soda, and its coagulation to the removal of the alkali. To this hypothesis Dr. Bostock objects, and with every appearance of justice, that albuminous liquids do not contain a sufficient quantity of free alkali for the purpose. (Medico-Chir. Trans. vol. ii. p. 175.) Were I to hazard an opinion on this subject, it would be the following:—that albumen combines directly with water at the moment of being secreted, at a time when its particles are in a state of minute division; but as its affinity for that liquid is very feeble, the compound is decomposed by slight causes, and for the same reason the albumen becomes quite insoluble, as soon as it is rendered solid by coagulation. Silica affords an instance of a similar phenomenon. (Page 464.)

Albumen coagulates without appearing to undergo any change of composition, but it is quite insoluble in water, and is less liable to putrefy than in its liquid state. It is dissolved by alkalies with disengagement of ammonia, and is precipitated from its solution by acids. In the coagulated state it bears a very close resemblance to fibrin, and is with difficulty distinguished from it. Alcohol, ether, acids, and alkalies, according to Berzelius, act upon each in the same manner. He observes, however, that acetic acid and ammonia dissolve fibrin more easily than coagulated albumen. According to Thenard, they are readily distinguished by means of deutoxide of hydrogen, from which fibrin causes evolution of oxygen, while albumen has no action upon it.

Albumen has been analyzed by Gay-Lussac and Thenard, and Dr. Prout, with the following results:—

	Gay-Lussac and Thenard.		Dr. Prout.	
Carbon,	52.883,	17 equivalents.	50,	15 equivalents.
Hydrogen,	7.540,	13 equivalents.	7.78,	14 equivalents.
Oxygen,	23.872,	6 equivalents.	26.67,	6 equivalents.
Nitrogen,	15.705,	2 equivalents.	15.55,	2 equivalents.
	100.000		100.00	

GELATINE.

Gelatine exists abundantly in many of the solid parts of the body, especially in the skin, cartilages, tendons, membranes, and bones. According to Berzelius, it is not contained in any of the healthy animal fluids; and Dr. Bostock, with respect to the blood, has demonstrated the accuracy of this statement. (Medico-Chir. Trans. vol. i. and ii.)

Gelatine is distinguished from all animal principles by its ready solubility in boiling water, and by the solution forming a bulky, semi-transparent, tremulous jelly as it cools. Its tendency to gelatinize is such, that one part of gelatine, dissolved in 100 parts of water, becomes solid in cooling. This jelly is a hydrate of gelatine, and contains so much water, that it readily liquefies when warmed. On expelling the water by a gentle heat, a brittle mass is left, which retains its solubility in hot water, and may be preserved for any length of time without change. Jelly, on the contrary, soon becomes acid by keeping, and then putrefies.

The common gelatine of commerce is the well-known cement called *glue*, which is prepared by boiling cuttings of parchment, or the skins, ears, and hoofs of animals, and evaporating the solution. Isinglass, which is the purest variety of gelatine, is prepared from the sounds of fish of the genus *acipenser*, especially from the sturgeon. The animal jelly of the confectioners is made from the feet of calves, the tendinous and ligamentous parts of which yield a large quantity of gelatine.

Gelatine is insoluble in alcohol, but is dissolved readily by most of the diluted acids, which form an excellent solvent for it. Mixed with twice its weight of concentrated sulphuric acid, it dissolves without being charred; and on diluting the solution with water, boiling for several hours, separating the acid by means of chalk, and evaporating the filtered liquid, a peculiar saccharine principle is deposited in crystals. This substance has a sweet taste, somewhat like that of the sugar of grapes, is soluble in water, though less so than common sugar, and is insoluble in alcohol. When heated to redness, it yields ammonia as one of the products, a circumstance

which shows that it contains nitrogen. Mixed with yeast, its solution does not undergo the vinous fermentation; and it combines directly with nitric acid. It is hence apparent that, though possessed of a sweet taste, it differs entirely from sugar. This substance was discovered by M. Braconnot. (An. de Ch. et de Ph. vol. xiii.)

Gelatine is dissolved by the liquid alkalies, and the solution is not precipitated by acids.

Gelatine manifests little tendency to unite with metallic oxides. Corrosive sublimate and subacetate of lead do not occasion any precipitate in a solution of gelatine, and the salts of tin and silver affect it very slightly. The best precipitant for it is tannin. By means of an infusion of gall-nuts, Dr. Bostock detected the presence of gelatine when mixed with 5000 times its weight of water; and its quantity may even be estimated approximately by this re-agent. (Page 763.) But since other animal substances, as for example albumen, are precipitated by tannin, it cannot be relied on as a test of gelatine. The best character for this substance is that of solubility in hot water, and of forming a jelly as it cools.

According to the analysis of gelatine by Gay-Lussac and Thenard, 100 parts of this substance consist of carbon 47.881, hydrogen 7.914, oxygen 27.207, and nitrogen 16.998.—From these numbers it appears that its composition, as to the relative quantity of its elements, is identical with that of albumen as determined by Dr. Prout.

UREA.

Pure urea is procured by evaporating fresh urine to the consistence of a syrup, and then gradually adding to it, when quite cold, pure concentrated nitric acid, which should be free from nitrous acid, till the whole becomes a dark-coloured crystallized mass, which is to be repeatedly washed with ice-cold water, and then dried by pressure between folds of bibulous paper. To the nitrate of urea, thus procured, a pretty strong solution of carbonate of potash or soda is added, until the acid is neutralized; and the solution is afterwards concentrated by evaporation, and set aside, in order that the nitre may separate in crystals. Dr. Prout recommends that the residual liquid,

which is an impure solution of urea, should be made up into a thin paste with animal charcoal, and be allowed to remain in that state for a few hours. The paste is then mixed with cold water, which takes up the urea, while the colouring matter is retained by the charcoal; and the colourless solution is evaporated to dryness at a low temperature. The residue is then boiled in pure alcohol, by which the urea is dissolved, and from which it is deposited in crystals on cooling. (Medico-Chir. Trans. viii. 529.) In order to obtain them quite colourless, it is necessary to redissolve in alcohol, and crystallize a second or even a third time.

The crystals of pure urea are transparent and colourless, of a slight pearly lustre, and have commonly the form of a four-sided prism.—It leaves a sensation of coldness on the tongue like nitre, and its smell is faint and peculiar, but not urinous. Its specific gravity is about 1.35. It does not affect the colour of litmus or turmeric paper. In a moist atmosphere it deliquesces slightly; but otherwise undergoes no change on exposure to the air. (Prout.) It is fused at 248° F., and at a rather higher temperature it is decomposed, being resolved chiefly into carbonate of ammonia and cyanic acid, the latter of which, if the heat be not incautiously raised, is left in the retort. (Wöhler).

Water at 60° dissolves more than its own weight of urea, and boiling water takes up an unlimited quantity. It requires for solution about five times its weight of alcohol of specific gravity 0.816 at 60° F., and rather less than its own weight at a boiling temperature. The aqueous solution of pure urea may be exposed to the atmosphere for several months, or be heated to the boiling point, without change; but, on the contrary, if the other constituents of urine are present, it putrefies with rapidity, and is decomposed by a temperature of 212° F., being almost entirely resolved into carbonate of ammonia by continued ebullition.

The pure fixed alkalies and alkaline earths decompose urea, especially by the aid of heat, carbonate of ammonia being the chief product.

Though urea has not any distinct alkaline properties, it unites with the nitric and oxalic acids, forming sparingly soluble compounds, which crystallize in scales of a pearly lustre.

This property affords an excellent test of the presence of urea. Both compounds have an acid reaction, and the nitrate consists of 54 parts or one equivalent of nitric acid, and 60 parts or two equivalents of urea.

The constituents of urea, according to the analysis of Dr. Prout, are in the proportion of one equivalent of carbon, two of hydrogen, one of oxygen, and one of nitrogen. Its atomic weight, therefore, is 30.

A singular instance of the artificial production of urea has been noticed by Wöhler. It is formed by the action of ammonia on cyanogen, as also by direct contact of cyanous acid and ammonia; but the best mode of preparing it is by decomposing cyanite of silver with muriate of ammonia, or acting on cyanite of lead with ammonia. In the last case, oxide of lead is set free, and the only other product appears in colourless, transparent, four-sided, rectangular crystals. These crystals, judging by the mode of preparation, must be cyanite of ammonia; but yet no ammonia is evolved from them by the action of potash; the stronger acids do not, as with other cyanites, cause an evolution of carbonic and cyanous acids; nor do they yield precipitates with salts of lead and silver. In fact, though procured by the mutual action of cyanous acid and ammonia, the characters above mentioned do not indicate the presence of either; but on the contrary the crystals agree with urea obtained from urine in composition and in all their chemical properties. (Journal of Science, N. S. iii. 491.) The cyanous acid above referred to is that discovered by Wöhler. (Page 384.)

SUGAR OF MILK AND SUGAR OF DIABETES.

Sugar of Milk.—The saccharine principle of milk is obtained from whey by evaporating that liquid to the consistence of syrup, and allowing it to cool. It is afterwards purified by means of albumen and a second crystallization.

The sugar of milk has a sweet taste, though less so than the sugar of the cane, from which it differs essentially in several other respects. Thus it requires seven parts of cold and four of boiling water for solution, and is insoluble in alcohol. It is not susceptible of undergoing the vinous fermentation; and when digested with nitric acid it yields saccholactic acid, a property first noticed by Scheele, and which distinguishes the

saccharine principle of milk from every other species of sugar. Like starch, it is convertible into real sugar by being boiled in water acidulated with sulphuric acid.

Sugar of milk contains no nitrogen, and according to the analysis of Gay-Lussac and Thenard, is very analogous to common sugar in the proportion of its elements.

Sugar of Diabetes.—In the disease called *Diabetes* the urine contains a peculiar saccharine matter, which, when properly purified, appears identical both in properties and composition to vegetable sugar, approaching nearer to the sugar of grapes than that from the sugar-cane. This kind of sugar is obtained in an irregularly crystalline mass by evaporating diabetic urine to the consistence of syrup, and keeping it in a warm place for several days. It is purified by washing the mass with alcohol, either cold or at most gently heated, till that liquid comes off colourless, and then dissolving it in hot alcohol. By repeated crystallization it is thus rendered quite pure. (Prout.)

A few other principles yet remain to be considered, such as the colouring principle of the blood, caseous matter, and mucus; but these will be more conveniently studied in subsequent sections.

SECTION II.

ANIMAL ACIDS.

In animal bodies several acids are found, such as the sulphuric, muriatic, phosphoric, acetic, &c., which belong equally to the mineral or vegetable kingdom, and which have consequently been described in other parts of the work. In this section are included those acids only which are believed to be peculiar to animal bodies.

URIC, PURPURIC, ROSACIC, FORMIC, AND LACTIC ACIDS, &c.

Uric or Lithic Acid.—This acid is a common constituent of urinary and gouty concretions, and is always present in healthy urine, combined with ammonia or some other alkali.

The urine of birds of prey, such as the eagle, and of the *boa constrictor* and other serpents, consists almost solely of urate of ammonia, from which pure uric acid may be procured by a very simple process. For this purpose the solid urine of the *boa constrictor* is reduced to a fine powder, and digested in a solution of pure potash, in which it is readily dissolved with disengagement of ammonia. The urate of potash is then decomposed by adding acetic, muriatic, or sulphuric acid in slight excess, when the uric acid is thrown down, and, after being washed, is collected on a filter. On its first separation from the alkali it is in the form of a gelatinous hydrate, but in a short time this compound is decomposed spontaneously, and the uric acid subsides in small crystals.

Pure uric acid is white, tasteless, and inodorous. It is insoluble in alcohol, and is dissolved very sparingly by cold or hot water, requiring about 10,000 times its weight of that fluid at 60° F. for solution. (Prout.) It reddens litmus paper, and unites with alkalies, forming salts which are called *urates* or *lithates*. The uric acid does not effervesce with alkaline carbonates; but Dr. Thomson affirms that when boiled for some time with carbonate of soda, the whole of the carbonic acid is expelled. A current of carbonic acid, on the contrary, throws down the uric acid when dissolved by potash. This acid undergoes no change by exposure to the air.

Of the acids none exert any peculiar action on the uric excepting nitric acid. When a few drops of nitric acid, slightly diluted, are mixed on a watch-glass with uric acid, and the liquid is evaporated to dryness, a beautiful purple colour comes into view, the tint of which is improved by the addition of water. This character affords an unequivocal test of the presence of uric acid. The nature of the change will be considered immediately.

Uric acid is decomposed by chlorine. Liebig has observed, that when dry uric acid is heated with dry chlorine, an enormous quantity of cyanic and muriatic acid is generated. If the uric acid is moist, chlorine then gives rise to the disengagement of carbonic and cyanous acids; while in solution there remain muriatic acid, ammonia, and much oxalic acid.

Uric acid has been repeatedly analyzed by Dr. Prout, and

its constituents, according to his latest analysis, (Medico-Chir. Trans. vol. ix.) are in the following proportions:—

Carbon,	36	or	6 equivalents.
Hydrogen,	2	.	2
Oxygen,	24	.	3
Nitrogen,	28	.	2
	90		

The crystallized acid, as analyzed by Prout, is supposed by most chemists to be anhydrous; but Dr. Thomson maintains that on exposing 90 parts of it to a temperature of 400° F. it loses 18 parts, or two equivalents of water, and that the residue is anhydrous uric acid, composed of 6 equivalents of carbon, 1 of oxygen, and 2 of nitrogen. On this view the atomic weight of uric acid is 72, a number which Dr. Thomson has deduced from his analysis of urate of soda.

The salts of uric acid have been described by Dr. Henry. (Manchester Memoirs, vol. ii. N.S.) The only ones of importance are the urates of ammonia, potash, and soda. Urate of ammonia is soluble to a considerable extent in boiling, but more sparingly in cold water. The urates of soda and potash, if neutral, are of very sparing solubility; but an excess of either alkali takes up a large quantity of the acid. The former was found by Dr. Wollaston to be the chief constituent of gouty concretions.

When uric acid is heated in a retort, carbonate and hydrocyanate of ammonia are generated, and a volatile acid sublimes, called *pyro-uric acid*, which was formerly described by Dr. Henry, and has since been studied by Chevallier and Lassaigne, Liebig, and Wöhler. The two latter chemists have noticed, that pyro-uric is identical with cyanic acid (page 383); and Wöhler finds that urea, as well as cyanic acid, is an essential product of the destructive distillation of uric acid.

Purpuric acid.—This compound was first recognised as a distinct acid by Dr. Prout, and was described by him in the Philosophical Transactions for 1818. Though colourless itself, it has a remarkable tendency to form red or purple coloured salts with alkaline bases, a character by which it is distinguished

from all other substances, and to which it owes the name of *purpuric acid*, suggested by Dr. Wollaston. Thus the purple residue above mentioned, as indicative of the presence of uric acid, is purpurate of ammonia, which is always generated when the uric is decomposed by nitric acid.

Purpuric acid may be prepared by the following process, for the outline of which I am indebted to directions kindly given me by Dr. Prout. Let 200 grains of uric acid, prepared from the urine of the *boa constrictor*, be dissolved in 300 grains of pure nitric acid diluted with an equal weight of water, the uric acid being added gradually in order that the heat may not be excessive. Effervescence ensues after each addition, nitrous acid fumes appear, heat is evolved, and a colourless solution is formed, which, on standing in a cool place for some hours, yields colourless crystals, which have the outline of an oblique rhomboidal prism. By gentle evaporation an additional quantity may be obtained. They contain nitric and purpuric acid and ammonia, should be dissolved in water, and be exactly neutralized by pure ammonia; and the liquid is then digested in a solution of potash until the ammonia is wholly expelled. On pouring this solution into dilute sulphuric acid, purpuric acid is set free, and, being insoluble in water, subsides as a granular powder, of a white colour if pure, but commonly of a yellowish white tint.

Considerable uncertainty prevails as to the nature of purpuric acid. Vauquelin denied that its salts have a purple colour, attributing that tint to some impurity, and Lassaigne is inclined to the same opinion (An. de Ch. et Ph. xxii. 334.); but from the intense colour given even by a very minute quantity of purpuric acid, the opinion of Dr. Prout appears to me the more probable. The composition of the acid is, likewise, unsettled; for Dr. Prout has expressed a doubt of the accuracy of the analysis which he formerly published.

The name of *erythric acid* (from ἐρυθραίνειν, *to redden*) was applied by Brugnatelli to a substance which he procured by the action of nitric on uric acid. It obviously contains purpuric acid, and Dr. Prout thinks it probable that it is a super-salt, consisting of purpuric and nitric acids, and ammonia, being probably identical with the crystals above mentioned.

Rosacic acid.—This name was applied by Proust to a

peculiar acid supposed to exist in the red matter, commonly called by medical practitioners the *lateritious sediment*, which is deposited from the urine in some stages of fever. From the experiments of Vogel it appears to be uric acid, either combined with an alkali, or modified by the presence of animal matter. Dr. Prout is of opinion that it contains some purpurate of ammonia; and, as he has detected the presence of nitric acid in the urine from which such sediments were deposited, he thinks it probable that the purpurate may be generated by the reaction of the uric and nitric acids on each other in the urinary passages.

Hippuric acid.—Under this name, derived from ἱππος a horse and ὑρη urine, Liebig has lately described a peculiar compound, which is deposited from the urine of the horse when it is mixed with muriatic acid in excess. The deposite, which is crystalline and of a yellowish-brown tint, is boiled with milk of lime, to which small quantities of chloride of lime are added, until the urinous odour ceases. It is then digested with animal charcoal; and on mixing the hot filtered solution with a large excess of muriatic acid, hippuric acid is deposited in cooling in rather large prisms, two or three inches in length, and beautifully white.

The claim of hippuric acid to be regarded as a proximate principle is doubtful, since it is closely allied to benzoic acid. Liebig, indeed, conceives that Fourcroy and Vauquelin, who report benzoic acid to exist in the urine of the cow and some other animals, were deceived by hippuric acid; and he considers that the latter is clearly distinguished from the former by its form, by the character of its salts, in being less soluble in water, and in containing nitrogen. But when hippuric acid is heated, partial decomposition takes place, and benzoic acid is sublimed; and a similar conversion is effected by the action of sulphuric and nitric acid. These facts render it probable that hippuric acid is a compound of benzoic acid with some animal matter, by which its properties are modified. (An. de Ch. et Ph. xliii. 188.)

Formic acid.—The acid extracted from ants was for some time suspected, chiefly on the authority of Fourcroy and Vauquelin, to be a mixture of acetic and malic acids; but the experiments of Suersen, Gehlen, Berzelius, and Döbereiner leave

no doubt of its being a distinct compound. In volatility and odour it does, indeed, resemble the acetic acid; but in composition it is entirely different. According to the analysis of formate of lead by Berzelius, the atomic weight of formic acid is inferred to be 37; and it is composed of carbon 12 parts or two equivalents, hydrogen 1 or one equivalent, and 24 parts or three equivalents of oxygen. It hence differs from oxalic acid only in containing one equivalent of hydrogen. According to Döbereiner it is resolved into carbonic oxide and water by the action of strong sulphuric acid. The same ingenious chemisth as succeeded in preparing formic acid artificially, by applying a gentle heat to a mixture of tartaric acid, water, and peroxide of manganese. The tartaric acid is converted into water, carbonic acid, and formic acid. (An. of Phil. vol. iv. N.S. 311.)

Liebig and Gmelin have found that several other substances, such as sugar, starch, sugar of milk, and ligneous fibre, may be substituted for tartaric acid; but the formic acid is then accompanied by some foreign matter, which may be removed by neutralizing with an alkali, and decomposing the formate by sulphuric acid. Even alcohol may be used; but it must be employed in a dilute state, in order to prevent the production of sulphuric or formic ether.

Lactic acid.—The existence of this acid, though described by Berzelius, and found by him in sour milk and in many animal fluids, was never demonstrated in a satisfactory manner. Berzelius himself now admits it to be acetic acid disguised by animal matter, an opinion which is confirmed by Tiedemann and Gmelin in their experimental Essay on Digestion. (Die Verdauung nach Versuche. Heidelberg, 1826.)

The *Amniotic* is a weak acid which was discovered by Buniva and Vauquelin in the liquor of the Amnios of the cow, from which it is deposited by gentle evaporation in the form of white acicular crystals. It is very sparingly soluble in water, but yields with the alkalies soluble compounds which are decomposed by most of the acids.

Several other animal acids, such as the stearic, oleic, margaric, and others, should also be mentioned here; but as they are closely allied to the fatty principles from which they are

derived, they will be more conveniently described in the following section.

SECTION III.

OLEAGINOUS SUBSTANCES.

ANIMAL OILS AND FATS.

The fatty principles derived from the bodies of animals are very analogous in composition and properties to the vegetable fixed oils; and in Britain, where the latter are comparatively expensive, the former are employed, both for the purpose of giving light, and for the manufacture of soap. Their ultimate elements are carbon, hydrogen, and oxygen; and most of them, like the fixed oils, consist of stearine and elaïne.

From a curious experiment of Bérard it appears that a substance very analogous to fat may be made artificially.—On mixing together one measure of carbonic acid, ten measures of carburetted hydrogen, and twenty of hydrogen, and transmitting the mixture through a red-hot tube, several white crystals were obtained, which were insoluble in water, soluble in alcohol, and fusible by heat into an oily fluid.—(An. of Ph. xii. 41.) Döbereiner prepared an analogous substance from a mixture of coal gas and aqueous vapour.

Train oil.—Train oil is obtained by means of heat from the blubber of the whale, and is employed extensively in making oil gas, and for burning in common lamps. It is generally of a reddish or yellow colour, emits a strong unpleasant odour, and has a considerable degree of viscidity, properties which render it unfit for being burned in argand lamps, and which are owing partly to the heat employed in its extraction, and partly to the presence of impurities. By purification, indeed, it may be rendered more limpid, and its odour less offensive; but it is always inferior to spermaceti oil.

Spermaceti oil is obtained from an oily matter lodged in a bony cavity in the head of the *Physeter macrocephalus*, or spermaceti whale. On subjecting this substance to pressure

in bags, a quantity of pure limpid oil is expressed; and the residue, after being melted, strained, and washed with a weak solution of potash, is sold under the name of *spermaceti.*

Animal oil of Dippel.—This name is applied to a limpid volatile oil, which is entirely different from the oils above mentioned, and is a product of the destructive distillation of animal matter, especially of albuminous and gelatinous substances. When purified by distillation, it is clear and transparent. It was formerly much used in medicine, but is now no longer employed.

Hogslard and suet.—The most common kinds of fat are hogslard and suet, which differ from each other chiefly in consistence. The latter, when separated by fusion from the membrane in which it occurs, is called tallow, which is extensively employed in the manufacture of soap and candles. Both these varieties of fat, as well as train and spermaceti oil, consist almost entirely of stearine and elaïne; and when converted into soap, undergo the same change as the fixed oils, yielding margaric and oleic acids, and the mild principle of oils called *glycerine.* Stearic acid is also a constituent of soap made from these animal fats.

The method of preparing stearine and elaïne from the vegetable oils has already been detailed; (page 719) and the same process, which originated with M. Braconnot, is also applicable to hogslard. The mode by which M. Chevreul obtains these principles is by treating hogslard in successive portions of hot alcohol. The spirit in cooling deposites the stearine in the form of white crystalline needles, which are brittle, and have the aspect of wax, fuse readily when heated, and are insoluble in water. The alcoholic solution, when evaporated, leaves an oily fluid which is elaïne. They may be then rendered quite pure by re-solution in boiling alcohol.

For a full account of the acids generated during the formation of soap by the action of alkaline substances on oil or fat, I refer to the treatise of M. Chevreul *Sur Les Corps Gras.* Margaric and oleic acids are best prepared from soap made with potash and fluid vegetable oil. This soap, after being dried as much as possible, is treated by successive portions of cold alcohol of specific gravity 0.821, in which the oleate of

potash is soluble, and the margarate insoluble. The two salts being thus separated, are decomposed by means of an acid.

Margaric acid, so named from its pearly lustre (from *μαργαριτης a pearl*) is insoluble in water, and is hence precipitated in acids from the solution of its salts. It is abundantly dissolved by hot alcohol, and is deposited from the saturated solution, in cooling, in a crystalline mass of a pearly lustre. At 140° F. it is fused, and shoots into brilliant white acicular crystals as it cools. It has an acid reaction, and its salts, those of the alkalies excepted, are very sparingly soluble in water. The crystallized acid contains 3.4 per cent of water, and the acid itself consists of 79 parts of carbon, 12 of hydrogen, and 9 of oxygen.

Oleic acid is best prepared from soap made with linseed oil and potash, since the greater part of it consists of oleate of potash. This salt is first separated from margarate of potash by cold alcohol, and the oleic acid then precipitated from an aqueous solution of the oleate by means of an acid. At the mean temperature oleic acid is a colourless oily fluid, which congeals when it is cooled to near zero. It has a slightly rancid odour and taste, and reddens litmus paper. Its specific gravity is 0.898. It is insoluble in water, but is dissolved in every proportion by alcohol. Of the neutral oleates hitherto examined, that of soda and potash are alone soluble in water. In its pure state it contains 3.8 per cent of water, and consists, the water abstracted, of 80.97 parts of carbon, 11.36 of hydrogen, and 7.7 of oxygen.

Stearic Acid.—This acid is best prepared from soap made with potash and suet or hogslard, and exists in this soap, together with margaric and oleic acids. The soap is dissolved in six times its weight of warm water, then mixed with 40 or 50 parts of cold water, and the mixture set aside in a place the temperature of which is about 56°. A precipitate of a pearly lustre gradually collects, consisting of the bi-margarate and bi-stearate of potash, which are to be collected and well washed upon a filter. The two salts are then separated by repeated solution in about 20 times their weight of boiling alcohol, from which on cooling the whole of the bi-stearate is deposited, while part of the bi-margarate on each occasion is

retained in solution. The former is considered pure when the stearic acid, separated from the potash by means of another acid, requires a temperature of 158° F. for fusion.

Stearic acid is very similar in its appearance and properties to margaric acid, and the chief ground of distinction between them is in the latter being rather more fusible, and containing rather more oxygen than the former.

Sebacic Acid.—Thenard has applied this name to an acid which is obtained by the distillation of hogslard or suet, and is found in the recipient mixed with acetic acid and fat, partially decomposed. It is separated from the latter by means of boiling water, and from the former by acetate of lead. The sebate of lead, which subsides, is subsequently decomposed by sulphuric acid.

Sebacic acid reddens litmus paper, dissolves freely in alcohol, and is more soluble in hot than in cold water. It melts like fat when heated, and crystallizes in small white needles in cooling. It is not applied to any use.

Butyrine.—Butter differs from the common animal fats in containing a peculiar oleaginous matter, which is quite fluid at 70° F, and to which Chevreul has applied the name of *butyrine.* When converted into soap, it yields, in addition to the usual products, three volatile odoriferous compounds, namely, the *butyric*, *caproic*, and *capric* acids.

Phocenine is a peculiar fatty substance contained in the oil of the porpoise *(Delphinum phocæna)* mixed with elaïne. When converted into soap it yields a volatile odoriferous acid, called the *phocenic acid.* (Chevreul.)

Hircine is contained in the fat of the goat and sheep, and yields the *hircic acid* when converted into soap. (Chevreul.)

Other acids more or less analogous to those above described are formed during the conversion of other oleaginous substances into soap. Thus, castor oil yields three acids, to which M.M. Bussy and Lecanu have applied the names of *margaritic*, *ricinic*, and *elaiodic* acid. The *Cevadic* acid was prepared in a similar manner by Pelletier and Caventou from oil derived from the seeds of the Veratrum Sabadilla; and the same chemist has given the name of *jatrophic* acid (more pro-

perly *crotonic*) to the acid of the soap made from croton oil. This oil is derived from the seeds of the *Croton Tiglium*.

The sweet principle of oils, *glycerine* of Chevreul, was discovered by Scheele. It was originally obtained in the formation of common plaster by boiling oil with oxide of lead and a little water; and Chevreul found that it is produced during the saponification of fatty substances in general. In preparing soap by means of potash, the glycerine is left in the mother liquor; and on neutralizing the free alkali with sulphuric acid, evaporating to the consistence of syrup, and treating the residue with alcohol, it is dissolved. The alcoholic solution, when evaporated, yields glycerine in the form of an uncrystallizable syrup. It is soluble in water and alcohol, and has a sweet taste, but is not susceptible either of the vinous or acetous fermentation. According to the analysis of Chevreul, glycerine, of the specific gravity of 1.27, contains 40.071 parts of carbon, 8.925 of hydrogen, and 51.004 of oxygen.

Spermaceti.—This inflammable substance, which is prepared from the spermaceti whale as above mentioned, commonly occurs in crystalline plates of a white colour and silvery lustre. It is brittle, and feels soft and slightly unctuous to the touch. It has no taste, and scarcely any odour. It is insoluble in water, but dissolves in about thirteen times its weight of boiling alcohol, from which the greater part is deposited on cooling in the form of brilliant scales. It is still more soluble in ether. It is exceedingly fusible, liquefying at a temperature which is distinctly below 212° F. Digested with pure potash it is converted into soap, and the acid then generated has received from Chevreul the name of *cetic acid*.

The spermaceti of commerce always contains some fluid oil, from which it may be purified by solution in boiling alcohol. To the white crystalline scales deposited from the spirit as it cools, and which is spermaceti in a state of perfect purity, Chevreul has given the name of *cetine*.

Adipocire.—When a piece of fresh muscle is exposed for some time to the action of water, or is kept in moist earth, the fibrin entirely disappears, and a fatty matter called *adipocire* remains, which has some resemblance to spermaceti. The

fibrin was formerly thought to be really converted into adipocire; but Gay-Lussac* and Chevreul maintain that this substance proceeds entirely from the fat originally present in the muscle, and that the fibrin is merely destroyed by putrefaction. Dr. Thomson maintains, however, that the conversion of fibrin into fat does occur in some instances, and has related a remarkable case in proof of his opinion. (Ann. of Phil. vol. xii. p. 41.) According to M. Chevreul, the adipocire is not a pure fatty principle, but a species of soap, chiefly consisting of margaric acid in combination with ammonia generated during the decomposition of the fibrin.

Cholesterine†. This name is applied by Chevreul to the crystalline matter which constitutes the basis of most of the biliary concretions formed in the human subject. Fourcroy, regarding it as identical with spermaceti and the fatty matter just described, comprehended all these substances under the general appellation of adipocire; but Chevreul has shown that it is an independent principle, wholly different from spermaceti.

Cholesterine is a white brittle solid of a crystalline lamellated structure and brilliant lustre, very much resembling spermaceti; but it is distinguished from that substance by requiring a temperature of 278° F. for fusion, and by not being convertible into soap when digested in a solution of potash. It is free from taste and odour, and is insoluble in water. It dissolves freely in boiling alcohol, from which it is deposited on cooling in white pearly scales. According to the analysis of Chevreul it is composed of 85.095 parts of carbon, 11.88 of hydrogen, and 3.025 of oxygen.

When heated with its own weight of concentrated nitric acid, cholesterine is dissolved with disengagement of nitric oxide gas; and in cooling a yellow matter subsides, an additional quantity of which may be obtained by dilution with water. This substance possesses the properties of acidity, and is called *cholesteric* acid. It is insoluble in water, but dissolves freely in alcohol, especially with the aid of heat. Its taste is slightly styptic, and its odour somewhat like that of butter; it is lighter than water, and fusible at 136½ F. In

* An. de Ch. et de Ph. vol. iv.

† From χολη *bile* and στιρεος *solid*.

mass it is of an orange-yellow tint; but when the alcoholic solution is evaporated spontaneously, it is deposited in acicular crystals of a white colour. It reddens litmus paper, and neutralizes alkaline bases. The cholesterates of potash and soda are deliquescent and very soluble in water, but insoluble in alcohol and ether. The cholesterates of the earths and other metallic oxides are either sparingly dissolved by water or altogether insoluble. Its salts are precipitated by the mineral and most of the vegetable acids; but are not decomposed by carbonic acid.—For these facts respecting the formation and properties of cholesteric acid, we are indebted to the experiments of Pelletier and Caventou. (Journal de Pharmacie, III. 292.)

Cholesterine has been detected in the bile of man, and of several of the lower animals, such as the ox, dog, pig, and bear. This interesting discovery was made about the same time by Chevreul in Paris, and by Tiedemann and Gmelin in Heidelberg. Lassaigne has likewise found it in the biliary calculus of a pig. (An. de Ch. et de Ph. xxxi.) It is frequently formed in parts of the body quite unconnected with the hepatic circulation, and appears to be a common product of deranged vascular action. Caventou, in the Journal de Pharmacie for October 1825, states that the contents of an abscess, formed under the jaw apparently in consequence of a carious tooth, was found by him to consist almost entirely of cholesterine. In the article *calcul* of the *Nouveau* Dictionnaire de Médecine, M. Breschet observes that cholesterine has been found in cancer of the intestines, and in the fluid of hydrocele and ascites in the human subject; and adds that M. Barruel procured it in large quantity from an ovarian cyst in a mare, and in the fluid drawn off from the ovary of a woman, and scrotum of a man. Breschet has found it also in a tumour under the tongue. Dr. Christison found it in the fluid of hydrocele, taken from a patient in the Royal Infirmary of Edinburgh by the late Dr. William Cullen, in an osseous cyst into which the kidneys of another patient was converted, and in the membranes of the brain of an epileptic patient.

The best method of preparing pure cholesterine is to treat human biliary concretions, reduced to powder, with boiling alcohol, and to filter the hot solution as rapidly as possible.

As the liquid cools, the greater part of the cholesterine subsides. In this way it is freed from the colouring matter with which it is commonly associated in the gall-stone.

Ambergris.—This substance is found floating on the surface of the sea near the coasts of India, Africa, and Brazil, and is supposed to be a concretion formed in the stomach of the spermaceti whale. It has commonly been regarded as a resinous principle; but its chief constituent is a substance very analogous to cholesterine, and to which Pelletier and Caventou have given the name of *ambreine*. By digestion in nitric acid ambreine is converted into a peculiar acid called the *ambreic acid*. (An. of Phil. vol. xvi.)

ON THE MORE COMPLEX ANIMAL SUBSTANCES, AND SOME FUNCTIONS OF ANIMAL BODIES.

SECTION I.

ON THE BLOOD.—RESPIRATION AND ANIMAL HEAT.

The blood, while circulating in the vessels of living animals, is fluid, and of a florid-red colour in the arteries, and of a dark purple colour in the veins. Its taste is slightly saline, its odour peculiar, and to the touch it seems somewhat unctuous. Its specific gravity is variable, but most commonly is near 1.05; and in man its temperature is about 98° or 100° Fahr. When recently drawn, it appears to the naked eye as a uniform homogeneous fluid; but if examined with a microscope of sufficient power, numerous red particles of a globular form are seen floating in a colourless fluid. The compound nature of the blood is rendered still more apparent by the process of coagulation, during which it separates spontaneously into two distinct portions, a yellowish liquid called the *serum* of the blood, and a red solid, known by the name of the *clot*, *cruor*, or *crassamentum*. The proportion of these parts is variable, the latter being more abundant in healthy vigorous animals than in those which have been debilitated by depletion, low living, or disease.

The serum is somewhat unctuous to the touch, of a saline taste, and of slightly alkaline reaction, owing to the presence of a little free soda. Its average specific gravity is about 1.029. Like other albuminous liquids, it is coagulated by heat, acids, alcohol, and all other substances which coagulate albumen. On subjecting the coagulum prepared by heat to gentle pressure, a small quantity of a colourless limpid fluid, called the *serosity*, oozes out, which contains according to Dr. Bostock about 1-50th of its weight of animal matter, together with a little muriate of soda. Of this animal matter a portion is albumen, which may easily be coagulated by means of galvanism; but a small quantity of some other principle is present, which differs both from albumen and gelatine. (Med. Chir. Trans. ii. 166.)

From the analysis of the late Dr. Marcet, 1000 parts of the serum of human blood are composed of water 900 parts, albumen 86.8, muriate of potash and soda 6.6, muco-extractive matter 4, carbonate of soda 1.65, sulphate of potash 0.35, and of earthy phosphates 0.60. This result agrees very nearly with that obtained by Berzelius, who states that the *extractive matter* of Marcet is lactate (acetate) of soda united with animal matter. (Med. Chir. Trans. iii. 231.)

The serum, instead of being transparent as it commonly is, has sometimes a cloudy appearance like whey, and in some more rare instances is perfectly opaque and white, as if it had been mixed with milk. The cause of the opacity has been experimentally examined by Drs. Traill and Christison, who have traced it to the presence of oleaginous matter, which the latter has shown to contain both stearine and elaïne, and to be very similar to human fat. The milkiness may therefore be ascribed to fat being mechanically diffused through the serum like oil in an emulsion. It may be easily separated by agitating the serum in a tube with half its bulk of sulphuric ether, when the adipose matter is instantly dissolved, the opacity in consequence disappears, and on evaporating the clear ethereal solution, which rises to the surface of the mixture, the fat is obtained in a separate state. By this means he procured on one occasion five per cent of fat from milky serum, and one per cent from serum which had the aspect of whey. Dr. Christison has detected traces of fat in perfectly transparent

serum, so that adipose matter in small quantity appears to be frequently contained in the blood. (Edin. Med. and Surg. Journal, April, 1830.)

The crassamentum or clot of the blood consists of two parts, the fibrin and colouring principle. The latter resides in distinct particles which, according to Prevost and Dumas, are elliptical in birds and cold-blooded animals, and assume the globular form in mammiferous animals. These globules are insoluble in serum; but their colour is dissolved by pure water, acids, alkalies, and alcohol. Much uncertainty prevails among chemists relative to the cause of the colour of the red globules. As soon as the blood was known to contain iron, the peroxide of which has a red tint, the colour of the red globules was ascribed to the presence of that metal, and some chemists supposed it to be in the form of subphosphate of iron. This opinion was adopted by Fourcroy and Vauquelin, who affirmed that phosphate of iron may be dissolved in serum by means of an alkali, and that the colour of the solution is exactly similar to that of the blood.

This subject was investigated in the year 1806 by Berzelius, who showed that subphosphate of iron cannot be dissolved in serum, in the way supposed by Fourcroy and Vauquelin, except in very minute quantity; and that this salt, even when rendered soluble by phosphoric acid, communicates a tint quite different from that of the red globules. On comparing together the composition of the three principal ingredients of the blood, viz. fibrin, albumen, and colouring matter, he found that the ashes of the last always yielded oxide of iron in the proportion of 1.200th of the original mass, while the oxide was entirely wanting in the two former. From this it was a probable inference that iron is somehow or other concerned in the production of the red colour; but the experiments of Berzelius did not make known the state in which that metal exists in the blood. He could not detect its presence by any of the liquid tests. (Med. Chir. Trans. iii. 213.)

In a series of experiments published in 1812, (Philos. Trans.) Mr. Brande obtained results quite contrary to those of Berzelius. He detected iron in the ashes of the serum and fibrin as well as those of the red globules; and in each it was present in such minute quantity, that no effect as a colouring

agent could be expected from it. Mr. Brande supposed that the tint of the red globules is produced by a peculiar animal colouring principle, capable, like other substances of a similar nature, of combining with metallic oxides. He succeeded in obtaining a compound of the colouring matter of the blood with oxide of tin; but its best precipitants are nitrate of mercury and corrosive sublimate. Woollen cloths impregnated with either of these compounds, on being dipped into an aqueous solution of the colouring matter, acquired a permanent red dye, unchangeable by washing with soap.

The conclusions of Brande, relative to the presence of iron in the albumen and fibrin of the blood, received additional support from the researches of Vauquelin; (An. de Ch. et de Ph. i.) but the question has been finally decided by Dr. Engelhart, a young German chemist of great promise, who gained the prize offered in the year 1825 by the Medical Faculty of Göttingen for the best Essay on the nature of the colouring matter of the blood. (Edinb. Med. and Surg. Journ. for January, 1827.) He demonstrated that the fibrin and albumen of the blood, when carefully separated from colouring particles, do not contain a trace of iron; and, on the contrary, he procured iron from the red globules by incineration. But he has likewise succeeded in proving the existence of iron in the colouring matter of the blood by the liquid tests; for, on transmitting a current of chlorine gas through a solution of the red globules, the colour entirely disappeared, white flocks were thrown down, and a transparent solution remained, in which peroxide of iron was discovered by all the usual reagents. The results obtained by Dr. Engelhart relative to the quantity of the iron, correspond with those of Berzelius. These facts have been since confirmed by Rose, who has accounted in a satisfactory manner for the failure of former chemists in detecting iron in the blood while in a fluid state. He finds that oxide of iron cannot be precipitated by the alkalies, hydrosulphuret of ammonia, or infusion of galls, if it is dissolved in a solution which contains albumen or other soluble organic principles.

From the presence of iron in the red globules, and its total absence in the other principles of the blood, it is probable that this metal, though its quantity does not exceed one-half

per cent, is essential to the production of the red colour. The experiments of Dr. Engelhart, however, have not determined the manner in which it acts, nor in what state it exists in the blood, though it is most probably in the form of an oxide. It is a singular coincidence that sulpho-cyanic acid, which forms with peroxide of iron a colour exactly like that of venous blood, has been detected in the saliva. The existence of this acid in the blood itself is, therefore, a circumstance by no means improbable.

Dr. Engelhart is likewise the first chemist who has procured the colouring matter of blood in a state of perfect purity. The method formerly recommended is that of Berzelius, whose process consists in allowing the clot cut into thin slices to drain as much as possible on bibulous paper, triturating it with water, and then evaporating the solution at a temperature not exceeding 122° F. As thus prepared, the colouring matter retains all its properties, but is mixed with a little serum. The method of Dr. Engelhart is founded on the fact, that serum, when much diluted, does not coagulate by heat, while the red particles are coagulated, and fall down in the form of brown flocks. Serum diluted with ten parts of water does not coagulate at 160° F.; but the colouring matter, dissolved in fifty parts of water, begins to coagulate at 149° F.

The colouring particles, when prepared in this way, are no longer of a bright-red colour, and their nature is somewhat modified, in consequence of which they are insoluble in water. When half dried, they form a brownish-red, granular, friable mass; and when completely dried at a temperature between 167° and 190°, the mass is tough, hard, brilliant, black with reflected, and garnet-red with transmitted light. Except in their insolubility, they have all the properties of the red particles obtained by the method of Berzelius. The caustic alkalies with the aid of heat dissolve them entirely, and the solution acquires a dark blood-red colour.

The fibrin of the blood may easily be obtained in a pure state by washing the clot in cold water until the colouring matter is entirely removed. While circulating in the animal body it is either in a fluid state, or suspended in the serum in the form of minute colourless globules; but when removed

from the vessels, and set at rest, it becomes solid in the course of a few minutes, giving rise to what is called the *coagulation* of the blood. The time required for coagulation is influenced by temperature, being promoted by heat, and retarded by cold. Dr. Scudamore finds that blood which begins to coagulate in four minutes and a half in an atmosphere of 53° F., undergoes the same change in two minutes and a half at 98°; and that which coagulates in four minutes at 98° will become solid in one minute at 120°. On the contrary, blood which coagulates firmly in five minutes at 60° will remain quite fluid for twenty minutes at the temperature of 40°, and requires upwards of an hour for complete coagulation. (Scudamore on the Blood.)

The process of coagulation is influenced by exposure to the air. If atmospheric air be excluded, as by filling a bottle completely with recently drawn blood, and closing the orifice with a good stopper, coagulation is retarded. It is singular, however, that if blood be confined within the exhausted receiver of an air-pump, the coagulation is accelerated. (Scudamore.)

Recently drawn blood, owing doubtless to its temperature, is known to give off a portion of aqueous vapour, which has a peculiar odour, indicative of the presence of some peculiar principle, but in which nothing but water can be detected. Physiologists are not agreed upon the question whether the act of coagulation is or is not accompanied with disengagement of gaseous matter. In the experiments of Vogel, Brande, and Scudamore, blood coagulating in the vacuum of an air-pump was found to emit carbonic acid, and Dr. Scudamore even inferred that the evolution of this gas constitutes an essential part of the process. Other experimentalists, however, have obtained a different result. Dr. John Davy and Dr. Duncan, jun., failed in their attempts to procure carbonic acid from blood during coagulation; and Dr. Christison, in an experiment performed four years ago in my laboratory, was not more successful. These facts appear conclusive against the opinion of Dr. Scudamore, and they receive additional weight from the consideration that the appearance of carbonic acid in the experiments above mentioned might easily have been occasioned by casual

exposure to the atmosphere previous to the blood being placed under the receiver.

Coagulation is influenced by the rapidity with which the blood is removed from the body. Dr. Scudamore observed, that blood slowly drawn from a vein coagulates more rapidly than when taken in a full stream.

Experiments are still wanting to show the influence of different gases on coagulation. Oxygen gas accelerates coagulation, and carbonic acid retards, but cannot prevent it.

Caloric is evolved during the coagulation of the blood. The late Dr. Gordon estimated the rise of the thermometer at six degrees; and Dr. Davy, on the other hand, regards the increase of temperature from this cause as very slight. Dr. Scudamore finds that the rate at which blood cools is distinctly slower than it would be were no caloric disengaged, and he observed the thermometer to rise one degree at the commencement of coagulation.

Some substances prevent the coagulation of the blood. This effect is produced by a saturated solution of muriate of soda, muriate of ammonia or nitre, and a solution of potash. The coagulation, on the contrary, is promoted by alum and the sulphates of zinc and copper. The blood of persons who have died a sudden violent death, by some kinds of poison, or from mental emotion, is usually found in a fluid state. Lightning is said to have a similar effect; but Dr. Scudamore declares this to be an error. Blood, through which electric discharges were transmitted, coagulated as quickly as that which was not electrified; and in animals killed by the discharge of a powerful galvanic battery, the blood in the veins was always found in a solid state.

The cause of the coagulation of the blood has been the subject of much speculation to physiologists. The tendency of this fluid to preserve the liquid form while contained in a living animal, cannot be ascribed to the motion to which it is continually subject within the vessels. It is a familiar fact that blood, though continually stirred out of the body, is not prevented from coagulating; and it has been noticed, that the coagulation of blood, which is set at rest within its proper vessels by the application of ligatures, or which has been accidentally extravasated within the body, is materially retarded.

It has, indeed, been hitherto found impossible to account in a satisfactory manner for the blood retaining its fluidity from the influence of motion, temperature, or the operation of any physical or chemical laws; and, consequently, it is generally ascribed to the agency of the vital principle. The blood is supposed either to be endowed with a principle of vitality, or to receive from the living parts with which it is in contact a certain vital impression, which, together with constant motion, counteracts its tendency to coagulate.

The clot of blood drawn from an individual in a state of health is red throughout its whole substance, because the fibrin coagulates before the red globules have had time to subside. In inflammatory diseases, on the contrary, the blood undergoes a peculiar change, in consequence of which the red globules sink to the bottom before the fibrin has become solid, and thus leave the upper surface of the latter of its natural pale colour. This appearance is familiarly known by the name of *buffy coat*. Its formation must obviously depend either on the coagulation being unusually slow, so that the red globules have full leisure to subside; or on the coagulation taking place in the ordinary period, while the red globules subside with unusual rapidity. The nature of the change which gives rise to the buffy coat is altogether unknown.

In addition to the constituents of the blood already enumerated, M. Barruel declares that this fluid contains a volatile principle, peculiar to each species of animal. This principle has an odour resembling that of the cutaneous or pulmonary exhalation of the animal, and serves as a distinctive character by which the blood of different animals may be recognized. It is dissolved in the blood, and its odour may be perceived when the blood or its serum is mixed with strong sulphuric acid. The odour is commonly stronger in the male than in the female. In man it resembles the human perspiration; in the ox, it smells like oxen or a cow-house; and the odour from horses' blood is similar to that of its perspiration. (Journ. of Science, vi. N. S. 187.) Should the accuracy of these observations be confirmed, they may be advantageously applied in some cases of legal medicine.

RESPIRATION.

When venous blood is brought into contact with atmospheric air, its surface passes from a dark-purple to a florid-red colour, oxygen disappears, and carbonic acid gas is emitted. These changes take place more speedily when air is agitated with blood; they are still more rapid when pure oxygen is substituted for atmospheric air; and they do not occur at all when oxygen is entirely excluded. It is hence inferred that the process of *arterialization*, as it is called, or the conversion of venous into arterial blood, depends entirely on the presence of oxygen. It is also presumed that the alternating shades of colour are caused by the red particles undergoing certain chemical changes, the nature of which, however, is at present quite inexplicable.

The same changes that occur out of the body are continually taking place within it. During respiration, venous blood is exposed in the lungs to the agency of the air and is arterialized, oxygen gas disappears, and carbonic acid is evolved; and it is remarkable that these phenomena ensue not only during life, but even after death, provided the respiratory process be preserved artificially. Since, therefore, the essential phenomena of arterialization, according to the best data we possess, are the same in a living and in a dead animal, and whether the blood is or is not contained in the body, it seems legitimate to infer, that this process is not necessarily dependent on the vital principle, but is solely determined by the laws of chemical action.

In studying the subject of respiration the first object is to determine the precise change produced in the constitution of the air which is inhaled. Dr. Black was the first to notice that the air exhaled from the lungs contains a considerable quantity of carbonic acid, which may be detected by transmission through lime water. Priestley, some years after, observed that air is rendered unfit for supporting flame or animal life by the process of respiration, from which it was probable that oxygen is consumed; and Lavoisier subsequently established the fact, that during respiration oxygen gas disappears, and carbonic acid is disengaged. The chief experimentalists

who have since cultivated this department of chemical physiology are Priestley, Scheele, Lavoisier, Seguin, Crawford, Goodwin, Davy, Ellis, Allen and Pepys, Edwards and Despretz. Of these the results obtained by Messrs. Allen and Pepys*, and Dr. Edwards†, are the most conclusive and satisfactory, their researches having been conducted with great care, and aided by all the resources of modern chemistry.

One of the chief objects of Messrs. Allen and Pepys, in their experiments, was to ascertain if any uniform relation exists between the oxygen consumed and the carbonic acid evolved. They found in general that the quantity of the former exceeds that of the latter; but as the difference was very trifling, they inferred that the carbonic acid of the expired air is exactly equal to the oxygen which disappears. The experiments of Dr. Edwards were attended with a remarkable result, which accounts very happily for some of the discordant statements of preceding inquirers. He found the ratio between the gases to vary with the animal. In some animals it might be regarded as nearly equal; while in others the loss of oxygen considerably exceeded the gain of carbonic acid, so that the respired air suffered a material diminution in volume. With respect to the human subject, the statement of Allen and Pepys seems very near the truth.

The quantity of oxygen withdrawn from the atmosphere, and of carbonic acid disengaged, is variable in different individuals, and in the same individual at different times. It is estimated by Allen and Pepys, that in every minute during the calm respiration of a healthy man of ordinary stature, 26.6 cubic inches of carbonic acid of the temperature of 50° F. are emitted, and an equal volume of oxygen withdrawn from the atmosphere. From these data it has been calculated, that in an interval of twenty-four hours not less than eleven ounces of carbon are given off from the lungs alone,—an estimate which must surely be inaccurate, the quantity being so great as sometimes to exceed the weight of carbon contained in the food. The same observers have lately found the production of carbonic acid in a pigeon, breathing freely in atmospheric

* Philosophical Transactions for 1808.

† De l'Influence des Agens Physiques sur la Vie, 1824.

air, to be such that, supposing the same rate to continue, the bird must have thrown off 96 grains of carbon in the space of 24 hours. From the observations of Dr. Prout, it appears that the quantity of carbonic acid emitted from the lungs is variable at particular periods of the day, and in particular states of the system. It is more abundant during the day than the night; about daybreak it begins to increase, continues to do so till about noon, and then decreases until sunset. During the night it seems to remain uniformly at a minimum; and the maximum quantity given off at noon, exceeds the minimum by about one-fifth of the whole. The quantity of carbonic acid is diminished by any debilitating causes, such as low diet, depressing passions, and the like. (An. of Phil. xiii. 269.) The experiments of Dr. Fyfe, published in his Inaugural Dissertation, are confirmatory of those above mentioned.

Messrs. Allen and Pepys have shown that atmospheric air, when drawn into the lungs, returns charged in the succeeding expiration with from 8 to 6 per cent of carbonic acid gas. They found also, that when an animal is confined in the same quantity of air, death ensues before all the oxygen is consumed; that when the same portion of air is repeatedly respired until it can no longer support life, it then contains only 10 per cent of carbonic acid.

Although in respiration the arterialization of the blood by means of free oxygen is the essential change, without the due performance of which the life of warm-blooded animals cannot be preserved beyond a few minutes, and which is likewise necessary to the lowest of the insect tribe, it is important to determine whether the nitrogen of the atmosphere has any influence in the function. The results of different inquirers differ considerably. In the experiments of Priestley, Davy, Humboldt, Henderson, and Pfaff, there appeared to be absorption of nitrogen, a less quantity of that gas being exhaled than was inspired. Nysten, Berthollet, and Despretz, on the contrary, remarked an increase in the bulk of the nitrogen; and from the researches of Seguin and Lavoisier, Vauquelin, Ellis, Dalton, and Spallanzani, it was inferred that there is neither absorption nor exhalation of nitrogen, the quantity of that gas undergoing no change during its passage through

the air-cells of the lungs. Messrs. Allen and Pepys arrived at a similar conclusion; and since the appearance of their Essay, the opinion has prevailed very generally among physiologists, that in respiration the nitrogen of the air is altogether passive.

The facts ascertained by Dr. Edwards relative to this subject are novel and of peculiar interest. This acute physiologist has reconciled the discordant results of preceding experimenters by showing that, during the respiration even of the same animal, the quantity of nitrogen may one while be increased, at another time diminished, and at a third wholly unchanged. He has traced these phenomena to the influence of the seasons; and he suspects, as indeed is most probable, that other causes, independently of season, have a share in their production. In nearly all the lower animals which were made the subjects of experiment, an augmentation of nitrogen was observable during summer. Sometimes, indeed, it was so slight that it might be disregarded. But in many other instances it was so great as to place the fact beyond the possibility of doubt; and on some occasions it almost equalled the whole bulk of the animal. Such continued to be the result of his inquiries until the close of October, when he observed a sensible diminution of nitrogen, and the same continued throughout the whole of winter and the beginning of spring.

There are two modes of accounting for these phenomena. According to one view, the nitrogen which disappears is ascribed to the absorption of what was inhaled, and its increase to direct exhalation, the opposite processes of absorption and exhalation being supposed not to occur at the same moment. According to the other view, both these processes are always going on at the same time, and the result depends on the preponderance of one over the other. When absorption prevails, a smaller quantity of nitrogen is exhaled than was inspired; when exhalation exceeds absorption, increase of nitrogen takes place; but when absorption and exhalation are equal, the bulk of the inspired air, so far as concerns nitrogen, is unchanged. The latter opinion, which is adopted by Dr. Edwards, is supported by two decisive experiments performed by Messrs. Allen and Pepys, in one of which a guinea-pig was confined in a vessel of oxygen gas, and in the other in an

atmosphere composed of 21 measures of oxygen and 79 of hydrogen. In both cases the residual air contained a quantity of nitrogen greater than the bulk of the animal itself; and in the latter a portion of hydrogen had disappeared. Hence it follows that nitrogen may be exhaled from the lungs, and that hydrogen may be absorbed.

An account of some interesting researches on the respiration of birds, bearing directly on this subject, was published last year by Messrs. Allen and Pepys (Phil. Trans. 1829). The subject of inquiry was the pigeon, and the phenomena attending its respiration were observed under three different circumstances, namely, in atmospheric air, in oxygen gas, and in a mixture of oxygen and hydrogen, in which the former amounted, as in the atmosphere, to 20 per cent. In each case the bulk of the gaseous mixture remained without change. In the experiments with atmospheric air, the oxygen which disappeared was equal to the carbonic acid evolved; the nitrogen was unaffected, except on one occasion when the bird appeared uneasy, and then there was a slight loss of nitrogen. In oxygen gas the production of carbonic acid was about half the quantity emitted when the pigeon breathed common air; and the decrease in oxygen was exactly equal to the united volumes of the carbonic acid and nitrogen which were disengaged. When the pigeon was placed in mixed oxygen and hydrogen gases, the production of carbonic acid was rather more abundant than in atmospheric air, and its volume equalled exactly the loss in oxygen; nitrogen, as before, was given out with considerable freedom, and its bulk precisely corresponded to the decrease in hydrogen. In the two latter series of experiments, especially in the last, the respiration of the pigeon was at times laborious. The experiments, however, are decisive of the fact, that carbonic acid and nitrogen gases may be thrown off from the lungs, and that oxygen and hydrogen gases may be absorbed.

Two theories have been proposed to explain the phenomena of respiration. According to one theory, the carbonic acid found in the respired air is actually generated in the lungs themselves; while, according to the other, this gas is thought to exist ready formed in the blood, and to be merely thrown off from that liquid during its distribution through the lungs.

The former theory, which appears to have originated with Priestley, has received several modifications. Priestley imagined that the phenomena of respiration are owing to the disengagement of phlogiston from the blood, and its combination with the air. Dr. Crawford modified this doctrine in the following manner. (Crawford on Animal Heat.) He was of opinion that venous blood contains a peculiar compound of carbon and hydrogen, termed *hydro-carbon*, the elements of which unite in the lungs with the oxygen of the air, forming water with the one, and carbonic acid with the other; and that the blood, thus purified, regains its florid hue, and becomes fit for the purposes of the animal economy.

The hypothesis of Crawford, however, is not merely liable to the objection that the supposed hydro-carbon, as respects the blood, is quite imaginary; but it was found at variance with the leading facts established by Messrs. Allen and Pepys. By the elaborate researches of these chemists it was established, that carbonic acid gas contains its own volume of oxygen; and they also concluded that air, inhaled into the lungs, returns charged with a quantity of carbonic acid, almost exactly equal in bulk to the oxygen which disappears—an inference which, as applied to man and some of the lower animals, seems very near the truth. A review of these circumstances induced them to adopt the opinion, that the oxygen of the air combines in the lungs exclusively with carbon; and that the watery vapour, which is always contained in the breath, is an exhalation from minute pulmonary vessels. They conceived that the fine animal membrane interposed between the blood and the air does not prevent chemical action from taking place between them.

This view has been further modified by Mr. Ellis, who supposes that the carbon is separated from the venous blood by a process of secretion, and that then, coming into direct contact with oxygen, it is converted into carbonic acid. (Inquiry, &c. Parts I. and II.)

The circumstance which led Mr. Ellis to this opinion, was a disbelief in the possibility of oxygen acting upon the blood through the animal membrane in which it is confined. The experiments adduced in proof of the impermeability of membranous substances are not, however, quite satisfactory; while,

on the contrary, the facts noticed by several accurate observers appear to leave no doubt that moist animal membranes, even in the living body, are in some way or other permeable to substances in a gaseous form*.

According to the second theory, which was supported by La Grange and Hassenfratz, and has lately been adopted by Dr. Edwards, carbonic acid generated during the course of the circulation is given off from venous blood in the lungs, and oxygen gas is absorbed. This doctrine, though generally regarded hitherto as less probable than the preceding, is supported by very powerful arguments. The experiments and observations of Dr. Edwards seem to leave no doubt that the blood, while circulating through the lungs, is capable of absorbing hydrogen, nitrogen, and oxygen gases, and of emitting nitrogen; and he has gone very far towards proving that the carbonic acid is derived from the same source. On confining frogs and snails for some time in an atmosphere of hydrogen, the residual air was found to contain a quantity of carbonic acid, which was in some instances even greater than the bulk of the animal; and a similar result was obtained with young kittens.

The confined limits of the present work do not admit of an examination into the respective advantages and disadvantages of these two theories. It will therefore suffice to observe that, in the present stage of the inquiry, the deficiency of precise data prevents the establishment of one of them in preference to the other; but that the arguments preponderate in favour of the last.

The conversion of venous into arterial blood appears not to be confined to the lungs. The disengagement of carbonic acid from the surface of the skin, and the corresponding disappearance of oxygen gas, was demonstrated by the experiments of Jurine and Abernethy; and although the accuracy of their results has been doubted by some persons, it has been confirmed by others. However this may be in the human subject, the fact with respect to many of the lower animals is unquestionable. Spallanzani proved that some animals pos-

* See some judicious remarks on this subject in the Essay on Respiration and Animal Heat, by Dr. Williams, in the Med. Chir. Trans. of Edinburgh, vol. ii.

sessed of lungs, such as serpents, lizards, and frogs, produce the same changes on the air by means of their skin, as by their proper respiratory organs; and Dr. Edwards, in a series of masterly experiments, has shown that this function compensates so fully for the want of respiration by the lungs, as to enable these animals, in the winter season, to live for an almost unlimited period under the surface of water.

ON ANIMAL HEAT.

The striking analogy between the processes of combustion and respiration, in both of which oxygen gas disappears, and an oxidized body is substituted for it, led Dr. Black to infer that the caloric generated in the animal system, by means of which the more perfect animals preserve their temperature above that of the surrounding medium, is derived from the changes going forward in the lungs. But this opinion is not founded on analogy alone; many circumstances conspire to show that the development of animal heat is dependent on the function of respiration, although the mode by which the effect is produced has not hitherto been satisfactorily determined. Thus, in all animals whose respiratory organs are small and imperfect, and which therefore consume but a comparatively minute quantity of oxygen, and generate little carbonic acid, the temperature of the blood varies with that of the medium in which they live. In warm-blooded animals, on the contrary, in which the respiratory apparatus is larger, and the chemical changes more complicated, the temperature is almost uniform; and those have the highest temperature whose lungs, in proportion to the size of their bodies, are largest, and which consume the greatest quantity of oxygen. The temperature of the same animal at different times is connected with the state of the respiration. When the blood circulates sluggishly, and the temperature is low, the quantity of oxygen consumed is comparatively small; but, on the contrary, a large quantity of that gas disappears when the circulation is brisk, and the power of generating heat energetic. It has also been observed, especially by Crawford and De Laroche, that when an animal is placed in a very warm atmosphere, so as to require little heat to be generated within his own body, the

consumption of oxygen is unusually small, and the blood within the veins retains the arterial character.

The connexion between the power of generating heat and respiration has been illustrated in a very pointed manner by Dr. Edwards. Some young animals, such as puppies and kittens, require so small a quantity of oxygen for supporting life, that they may be deprived of that gas altogether for twenty minutes without material injury; and it is remarkable that so long as they possess this property, the temperature of their bodies sinks rapidly by free exposure to the air. But as they grow older they become able to maintain their own temperature, and at the same time their power to endure the privation of oxygen ceases. The same observation applies to young sparrows, and other birds which are naked when hatched; while young partridges, which are both fledged and able to retain their own temperature at the period of quitting the shell, die when deprived of oxygen as rapidly as an adult bird.

The first consistent theory of the production of animal heat was proposed by Dr. Crawford. This theory was founded on the assumption that the carbonic acid contained in the breath is generated in the lungs, and that its formation is accompanied with disengagement of caloric. But since the temperature of the lungs is not higher than that of other internal organs, and arterial very little if at all warmer than venous blood, it follows that the greater part of the caloric, instead of becoming free, must in some way or other be rendered insensible. Accordingly, on comparing the specific caloric of arterial and venous blood, Dr. Crawford found the capacity of the former to exceed that of the latter in the ratio of 1030 to 892. He therefore inferred that the dark blood within the veins, at the moment of being arterialized, acquires an increase of insensible caloric; and that while circulating through the body, and gradually resuming the venous character, it suffers a diminution of capacity, and evolves a proportional degree of heat.

Unfortunately for the hypothesis of Crawford, one of the leading facts on which it is founded has been called in question, Dr. Davy maintaining, on the authority of his own experiments, that there is little or no difference between the capa-

city of venous and arterial blood. (Philos. Trans. for 1814.) If this be true, the hypothesis itself necessarily falls to the ground. One part of the doctrine of Crawford may, however, in a modified form, be applied to the theory of respiration advocated by Dr. Edwards. For if oxygen be absorbed by the blood in its passage through the lungs, and carbonic acid, ready formed, be emitted in return, it follows that this gas must be generated during the course of the circulation; and it may be inferred that the heat developed in consequence of this chemical change is at once communicated to the adjacent organs. In this way the question concerning the capacity of the blood for caloric may be entirely disregarded.

While some physiologists have been disposed to refer the source of animal heat entirely to the alternate changes of venous to arterial, and of arterial to venous blood, others have denied its agency altogether, ascribing the evolution of caloric solely to the influence of the nervous system. The chief foundation for this opinion is in the experiments of Mr. Brodie, who inflated the lungs of animals recently killed by narcotic poisons or division of spinal marrow. (Phil. Trans. for 1811 and 1812.) In an animal so treated, the blood continued to circulate, the phenomena of arterialization took place with regularity, oxygen gas disappeared, and carbonic acid was evolved; but notwithstanding the concurrence of all these circumstances, the temperature fell with equal if not greater rapidity than in another animal killed at the same time, but in which artificial respiration was not performed.

Were these experiments rigidly exact, they would lead to the opinion that no caloric is evolved by the mere process of arterialization. This inference, however, cannot be admitted for two reasons:—first, because other physiologists, in repeating the experiments of Brodie, have found that the process of cooling is retarded by artificial respiration; and, secondly, because it is difficult to conceive why the formation of carbonic acid, which uniformly gives rise to increase of temperature in other cases, should not be attended within the animal body with a similar effect. It may hence be inferred, that this is one of the sources of animal heat. It is certain, however, that the heat of animals cannot be maintained by the sole process of arterialization. Consistently with this fact, the researches

of Dulong and Despretz agree in proving, in opposition to the results obtained by Lavoisier and Crawford, that a healthy animal imparts to surrounding bodies a quantity of heat considerably greater than can be accounted for by the combustion of the carbon thrown off during the same interval from the lungs in the form of carbonic acid. (An. de Ch. et Ph. xxvi.)

Though the influence of the nervous system over the development of animal heat is no longer doubtful, physiologists are not agreed as to the mode by which it operates. Its action may either be direct or indirect; that is, the nerves may possess some specific power of generating heat, or they may excite certain operations by which the same effect is occasioned. It is far from improbable, that the nerves act more by the latter than the former mode; that the infinite number of chemical phenomena going on in the minute arterial branches during the processes of secretion and nutrition, processes which are entirely dependent on the nervous system, are attended with disengagement of caloric. This view has, at least, been ably defended by Dr. Williams in the essay to which I have already referred.

SECTION II.

ON THE SECRETED FLUIDS SUBSERVIENT TO DIGESTION.

SALIVA, PANCREATIC AND GASTRIC JUICES.

Saliva.—The saliva is a slightly viscid liquor, secreted by the salivary glands. When mixed with distilled water, a flaky matter subsides which is mucus, derived apparently from the lining membrane of the mouth. The clear solution, when exposed to the agency of galvanism, yields a coagulum, and is hence inferred by Mr. Brande to contain albumen; but the quantity of this principle is so very small that its presence cannot be demonstrated by any other reagent. The greater part of the animal matter remaining in the liquid is peculiar to the saliva, and may be termed *salivary matter*. It is soluble in water, insoluble in alcohol, and, when freed from the accompanying salts, is not precipitated by subacetate of lead, corrosive sublimate, or infusion of gall-nuts. The saliva likewise con-

tains a small quantity of animal matter, which is soluble both in alcohol and water, and which is supposed by Tiedemann and Gmelin to be osmazome.

The solid contents of the saliva, according to Berzelius, do not exceed seven in 1000 parts, the rest being water. From the recent analysis of Tiedemann and Gmelin, the chief saline constituent is muriate of potash; but several other salts, such as the sulphate, phosphate, acetate, carbonate, and sulpho-cyanate of potash, are likewise present in small quantity. The saliva of the human subject, according to the same authority, contains very little soda. The property which the saliva possesses of striking a red colour with a per-salt of iron is owing to sulpho-cyanate of potash. This acid exists also in the saliva of the sheep; but it has not been found in that of the dog. The saliva of the sheep contains so much carbonate of soda, that it effervesces with acids.

The only known use of the saliva is to form a soft pulpy mass with the food during mastication, so as to reduce it into a state fit for being swallowed with facility, and for being more readily acted on by the juices of the stomach.

Concretions are sometimes found in the salivary glands and ducts. A stone contained in the salivary gland of an ass was found by M. Caventou to contain 91.6 parts of carbonate of lime, 4.8 of phosphate of lime, and 3.6 of animal matter. A salivary concretion of a horse was found by M. Henry, jun. to consist of carbonate of lime 85.52, carbonate of magnesia 7.56, phosphate of lime 4.40, and 2.48 of animal matter.—Carbonate of lime is the chief ingredient of salivary concretions.

Pancreatic juice.—This fluid is commonly supposed to be analogous to the saliva, but it appears from the analysis of Tiedemann and Gmelin that it is essentially different. The chief animal matters are albumen, and a substance like curd; but it also contains a small quantity of salivary matter and osmazome. It reddens litmus paper, owing to the presence of free acid, which is supposed to be the acetic. Its salts are nearly the same as those contained in the saliva, except that sulpho-cyanic acid is wanting. The uses of this fluid are entirely unknown.

Gastric juice.—The gastric juice, collected from the stomach of an animal killed while fasting, is a transparent fluid which

has a saline taste, and has neither an acid nor alkaline reaction. During the process of digestion, on the contrary, it is found to be distinctly acid. Thus free muriatic acid was detected under these circumstances by Dr. Prout* in the stomach of the rabbit, hare, horse, calf, and dog; and he has discovered the same acid in the sour matter ejected from the stomach of persons labouring under indigestion, a fact which has since been confirmed by Mr. Children. Messrs. Tiedemann and Gmelin have observed that the secretion of acid commences as soon as the stomach receives the stimulus of food or any foreign body. This effect is occasioned, for example, by the presence of flint stones or other indigestible matters; but it is produced in a still greater degree by substances of a stimulating nature. According to their observation the acidity is owing to the secretion of free muriatic and acetic acids.

The gastric juice coagulates milk, and it is generally supposed to produce this effect quite independently of the presence of an acid. According to the experiments of Spallanzani and Stevens it is highly antiseptic, not only preventing putrefaction, but rendering meat fresh after it is tainted. But of all the properties of the gastric juice, its solvent virtues is the most remarkable, being that on which depends the first stage of the process of digestion. When the food is introduced into the stomach, it is there intimately mixed with the gastric juice, by the agency of which it is dissolved, and converted into a semi-fluid matter called *chyme*. That this change is really owing to the solvent power of the gastric juice fully appears from the researches of Spallanzani, Reaumur, and Stevens. In the experiments of Dr. Stevens, described in his Inaugural Dissertation, the common articles of food were enclosed in hollow silver spheres perforated with holes, and after remaining for some time within the stomach, completely protected from pressure and trituration, the alimentary substances were found to have been entirely dissolved. A similar effect takes place when nutritious matters, out of the body, are mixed with the gastric fluid, and the mixture is exposed to a temperature of 100° Fahr. So great, indeed, is the solvent power of this fluid, that it has been known to dissolve the coats of the

* Philosophical Transactions for 1824.

stomach itself; at least the corrosions of this organ sometimes witnessed in persons who have died suddenly while fasting, and in good health, were ascribed by the celebrated physiologist, John Hunter, to this cause.

No department of chemical physiology is more obscure than that of digestion. There appears so little connexion between the properties and composition of the gastric juice, that physiologists are quite at a loss in what way to account for its solvent power. An attempt has lately been made by Tiedemann and Gmelin to explain the phenomena on chemical principles. They ascribe its solvent action to the dilute muriatic and acetic acids, which they maintain to be always secreted during the digestive process, and which, according to their observation, are capable of dissolving most or all of the substances employed as food. They have not shown, however, that the gastric juice in its neutral state, or when neutralized by an alkali, is devoid of solvent properties, a circumstance which requires investigation before a decisive opinion can be formed of the accuracy of their views.

BILE AND BILIARY CONCRETIONS.

The bile is a yellow or greenish-yellow coloured fluid, of a peculiar sickening odour, and of a taste at first sweet and then bitter, but exceedingly nauseous. Its consistence is variable, being sometimes limpid, but more commonly viscid and ropy. It is rather denser than water, and may be mixed with that liquid in every proportion. It contains a minute quantity of free soda, and is therefore slightly alkaline; but owing to the colour of the bile itself, its action on test paper is scarcely visible.

Of the chemists who have of late years investigated the composition of the bile, Thenard, Berzelius, Tiedemann, and Gmelin deserve particular mention. In an elaborate essay published in the *Memoires d'Arcueil*, vol. i. Thenard endeavoured to show that the bile of the ox consists of three distinct animal principles, a yellow colouring matter, a species of resin, and a peculiar substance, to which, from its sweetish bitter taste, he applied the name of *picromel*. According to his analysis, 800 parts of bile consist of water 700 parts, resin

15, picromel 69, yellow matter about 4, soda 4, phosphate of soda 2, muriates of soda and potash 3.5, sulphate of soda 0.8, phosphate of lime and perhaps magnesia 1.2, and a trace of oxide of iron. He supposed the resin to be combined with the picromel and soda, and ascribes its solubility in water to this cause.

Berzelius takes a totally different view of the constitution of the bile. He denies that this fluid contains any resinous principle, and regards the yellow matter, resin, and picromel of Thenard, as one and the same substance, to which he applies the name of *biliary matter*. (Med. Chir. Trans. vol. iii.) Tiedemann and Gmelin, however, in their recent work on Digestion, admit the existence of picromel and resin as the chief constituents of bile; although it appears from their experiments that the substance described by Thenard as picromel was not pure, but contained a portion of resin. According to the analysis of these chemists, the bile of the ox is a very complex fluid, consisting of the following ingredients:— water to the extent of 91.5 per cent; a volatile odoriferous principle; cholesterine; resin; asparagin; picromel; yellow colouring matter; a peculiar azotized substance soluble in water and alcohol; a substance which is soluble in hot alcohol, but insoluble in water, supposed to be gluten; osmazome; a principle which emits an urinous odour when heated; a substance analogous to albumen or caseous matter; and mucus. The salts of the bile are the margarate, oleate, acetate, *cholate*, bicarbonate, phosphate, sulphate, and muriate of soda, together with a little phosphate of lime. The *cholic* is a peculiar animal acid, which crystallizes in needles, reddens litmus paper, and is distinguished from analogous compounds by having a sweet taste.

The flaky precipitate which is occasioned by adding acids to bile from the ox, consists of several substances. At first the caseous and colouring matters, along with mucus, are thrown down; and, afterwards, the margaric acid, and a compound of picromel and resin with the acid employed, are precipitated. When acetate of lead is mixed with this fluid, a white precipitate falls, which consists of oxide of lead combined with the phosphoric, sulphuric, and several other acids, together with a small quantity of the compound of picromel and resin. On

adding subacetate of lead to the clear liquid, a copious precipitate ensues, consisting chiefly of picromel, resin, and oxide of lead. If this compound be suspended in water, through which a current of sulphuretted hydrogen gas is transmitted, sulphuret of lead and the resin subside, while the picromel remains in solution. By collecting and drying the precipitate, and digesting it in alcohol, the resin is dissolved, and may be obtained by evaporation. The aqueous solution, when evaporated, yields the picromel of Thenard; but according to Tiedemann and Gmelin, it still contains a portion of resin. The chief difficulty, indeed, of preparing pure picromel arises from its tendency to dissolve the resin; and the only mode of separation is by throwing them down repeatedly by means of subacetate of lead. By this process the affinity of the picromel and resin for each other is gradually lessened, until at length the separation is rendered complete.

Pure picromel occurs in opaque rounded crystalline particles, is soluble in water and alcohol, but is insoluble in ether. Its taste is sweet without any bitterness; but it cannot be regarded as a species of sugar, because a large quantity of nitrogen enters into its composition. Its aqueous solution is not precipitated by acids, nor by acetate and sub-acetate of lead. When digested with the resin of bile, a portion of the latter is dissolved, and a solution is obtained, which has both a bitter and sweet taste, and yields a precipitate with subacetate of lead and the stronger acids. This is the compound which causes the peculiar taste of the bile.

The bile of the human subject has not been studied so minutely as that of the ox. According to Thenard it consists, besides salts, of water, colouring matter, albumen, and a species of resin. Chevallier has since detected picromel, and Chevreul cholesterine, in human bile; and both these discoveries have been confirmed by the observations of Tiedemann and Gmelin.

The derangement which takes place in the system when the secretion of bile or its passage into the intestines is arrested, is a sufficient indication of the importance of this fluid. It acts as a stimulus to the intestinal canal generally, and produces on the chyme some peculiar change, which is essential to its conversion into chyle.

Biliary Calculi.—The concretions which are sometimes formed in the human gall-bladder have been particularly examined by Fourcroy, Thenard, and Chevreul. Fourcroy found that they consist chiefly of a peculiar fatty matter, resembling spermaceti, which he included under the name of *adipocire*, (page 812); and the experiments of Thenard tended to confirm this view. According to Chevreul, however, biliary concretions in general are composed of the yellow colouring matter of the bile and cholesterine, the latter predominating, and being sometimes in a state of purity; and I have had frequent opportunities of satisfying myself of the accuracy of this observation. These substances may easily be separated from each other by boiling alcohol, which dissolves the cholesterine, and leaves the colouring matter; or by digestion in dilute potash, in which the colouring matter is dissolved, while the cholesterine is insoluble.

Gall-stones sometimes contain a portion of inspissated bile; and in some rare instances the cholesterine is entirely wanting.

The concretions found in the gall-bladder of the ox consist almost entirely of the yellow biliary colouring matter, which, from the beauty and permanence of its tint, is much valued by painters. This substance is readily distinguished by its yellow or brown colour, by insolubility in water and alcohol, and by being readily dissolved by a solution of potash. The solution has at first a yellowish-brown colour, which gradually acquires a green tint, and is precipitated in green flocks by muriatic acid. According to the observation of Tiedemann and Gmelin the colouring matter is influenced by the presence of oxygen gas. The yellowish precipitate, occasioned by adding muriatic acid to bile, absorbs oxygen by exposure to the air, and its colour changes to green. The action of nitric acid is still more remarkable. By successive additions of this acid, the tint of the colouring matter may be converted into green, blue, violet, and red, in the course of a few seconds.

Erythrogen.—This substance was discovered in 1821 by M. Bizio of Venice in a peculiar fluid, quite different from bile, which was found in the gall-bladder of a person who had died of jaundice. It is of a green colour, transparent, tasteless, and of the odour of putrid fish. It is unctuous to the

touch, may be scratched or cut with facility, and has a specific gravity of 1.57. It does not affect the colour of litmus or turmeric paper. At 110° F. it fuses, having the appearance of oil, and crystallizes when slowly cooled; and at 122° F. it rises in the form of vapour. It is insoluble in water and ether, but is dissolved readily by hot alcohol; and the solution, by partial evaporation and cooling, yields crystals in the form of rhomboidal parallelopipedons.

When erythrogen is put into nitric acid of the temperature of about 120° or 140° Fahr. its green tint disappears, effervescence, owing to the escape of oxygen gas, ensues, and the solution acquires a deep purple colour. A similar phenomenon takes place, with disengagement of hydrogen gas, when erythrogen is digested in a solution of ammonia; and when volatilized in the open air, it yields a purple-coloured vapour. M. Bizio is of opinion that the erythrogen, under all these circumstances, unites with nitrogen, and that the product is identical with the colouring matter of the blood. The production of the red compound is characteristic of erythrogen, and suggested the name by which this substance is designated. (Ερυθρος, *ruber*.) (Journal of Science, vol. xvi.)

Erythrogen has not been discovered either in bile or in any of the animal fluids.

SECTION III.

CHYLE.—MILK.—EGGS.

Chyle.—The fluid absorbed by the lacteal vessels from the small intestines during the process of digestion is known by the name of *chyle*. Its appearance varies in different animals; but as collected from the thoracic duct of a mammiferous animal three or four hours after a meal, it is a white opaque fluid like milk, having a sweetish and slightly saline taste. In a few minutes after removal from the duct it becomes solid, and in the course of twenty-four hours separates into a firm coagulum, and a limpid liquid, which may be called the serum of the chyle. The coagulum is an opaque white substance, of a

slightly pink hue, insoluble in water, but soluble easily in the alkalies and alkaline carbonates. Vauquelin* regards it as fibrin in an imperfect state, or as intermediate between that principle and albumen; but Mr. Brande† considers it more closely allied to the caseous matter of milk than to fibrin.

The serum of chyle is rendered turbid by heat, and a few flakes of albumen are deposited; but when boiled after being mixed with acetic acid, a copious precipitation ensues. To this substance, which thus differs slightly from albumen, Dr. Prout has applied the name of *incipient albumen*. The same chemist has made a comparative analysis of the chyle of two dogs, one of which was fed on animal and the other on vegetable substances, and the result of his inquiry is as follows:—(Annals of Philos. vol. xiii. p. 25.)

	Vegetable Food.	Animal Food.
Water, ...	93.6	89.2
Fibrin, ...	0.6	0 8
Incipient albumen? . . .	4.6	4.7
Albumen with a little red colouring matter,	0.4	4.6
Sugar of milk? . . .	a trace	—
Oily matter, ...	a trace	a trace
Saline matters, ...	0.8	0.7
	100.0	100.0

Milk.—This well-known fluid, secreted by the females of the class *mammalia* for the nourishment of their young, consists of three distinct parts, the cream, curd, and whey, into which by repose it spontaneously separates. The cream, which collects upon its surface, is an unctuous yellowish-white opaque fluid, of an agreeable flavour. According to Berzelius 100 parts of cream, of specific gravity 1.0244, consists of butter 4.5, caseous matter 3.5, and whey 92. By agitation, as in the process of churning, the butter assumes the solid form, and is thus obtained in a separate state. During the operation there is an increase of temperature amounting

* An. de Ch. vol. xxxi. † Philos. Trans. for 1812.

to about three or four degrees, oxygen gas is absorbed, and an acid is generated; but the absorption of oxygen cannot be an essential part of the process, since butter may be obtained by churning, even when atmospheric air is entirely excluded.

After the cream has separated spontaneously, the milk soon becomes sour, and gradually separates into a solid coagulum called curd, and a limpid fluid which is whey. This coagulation is occasioned by free acetic acid, and it may be produced at pleasure either by adding a free acid, or by means of the fluid known by the name of *rennet*, which is made by infusing the inner coat of a calf's stomach in hot water. When an acid is employed, the curd is found to contain some of it in combination, and may therefore be regarded as an insoluble compound of an acid with the caseous matter of milk, but nothing certain is known respecting the mode by which the gastric fluid, the active principle of rennet, produces its effect.

The curd of skim milk, made by means of rennet, and separated from the whey by washing with water, is generally considered to be *caseous matter*, or the basis of cheese in a state of purity. In this state, it is a white, insipid, inodorous substance, insoluble in water, but readily soluble in the alkalies, especially in ammonia. By alcohol it is converted, like albumen and fibrin, into an adipocirous substance of a fetid odour; and, like the same substances, it may be dissolved by a sufficient quantity of acetic acid.

In a recent essay Braconnot maintains that caseum, in its coagulated state, is always combined with some foreign substance, generally an earthy salt or an acid, on which its insolubility depends; and that when pure, it is soluble both in hot and cold water, is not coagulated either by heat or air, and when concentrated becomes viscid like mucilage, being so highly adhesive that it may be usefully employed as a cement. Soluble caseum may be obtained from curd, spontaneously formed in milk as it becomes sour, in which state it is combined with acetic acid, by washing the curd, and digesting it with water, to which so much carbonate of potash is added, as is sufficient to unite with the acetic acid. Acetate of potash is generated with disengagement of carbonic acid, and the caseum is dissolved. In order to separate it from the accompanying acetate, the solution, after separating the cream which

collects on its surface by repose, is mixed with a little sulphuric acid, and the precipitated *sulphate* of caseum, carefully washed, is dissolved in water by means of the smallest possible quantity of carbonate of potash. If alcohol is then freely employed, the caseum itself is thrown down; but if the solution is mixed with about its own volume of alcohol, a deposite of sulphate of potash with some curd and cream takes place, and the filtered liquor contains caseum in a state of great purity.

Caseum, as thus prepared, still contains a little potash; but Braconnot considers its solubility as not dependent on the presence of the alkali. When evaporated to dryness it forms a diaphanous mass which strongly resembles gum arabic, may be long preserved without change, and still retains its solubility in water. It has an acid reaction, and combines readily with the alkalies, forming very soluble compounds. With other metallic oxides, as well as with their salts, it forms sparingly soluble compounds. Its affinity for acids is equally marked, and it is precipitated by all the mineral acids, except the phosphoric. Braconnot conceives that soluble caseum may be advantageously employed in a commercial point of view. Its adhesiveness fits it as a cement for glass, porcelain, wood, and paper. Its solution, flavoured with sugar and aromatics, may be serviceable to convalescents as an article of food. It may be taken in its dry state in long voyages, forming together with water, butter, and sugar, an excellent substitute for milk. (An. de Ch. et Ph. xliii. 337.)

Caseum is commonly considered to have a close resemblance to animal albumen, and the analogy is supported by its being coagulated by acids. In other respects, if the remarks of Braconnot prove correct, it resembles gum rather than albumen. It differs from both, however, in the nature of the spontaneous changes to which it is subject; for when kept in a moist state, it undergoes a species of fermentation precisely analogous to that experienced by gluten under the same circumstances. (Page 766.) The accuracy of the remarks made by Proust on this subject has been questioned by Braconnot. (Brewster's Journal, viii. 369.) The latter states that in his experiments the curd from spontaneously coagulated skim milk, covered with water, and kept at a temperature of about 75° F, underwent complete putrefaction in the space of a month. The

soluble parts were then filtered, and by evaporation yielded a product of a very fetid odour, acetate of ammonia, and acetic acid. The residue, after being reduced to the consistence of syrup, concreted on cooling into a granulated reddish mass like honey, but of a saline bitter taste, and was separated by the action of alcohol into two parts, one soluble and the other insoluble. The former is the caseate of ammonia of Proust, and the latter is his caseous oxide.

In order to obtain caseous oxide quite pure, it must be washed carefully with alcohol, treated with animal charcoal, and dissolved repeatedly in boiling water, from which it is separated by evaporation. In this state it is a beautiful white powder, inodorous, and of a slight bitter taste. It is heavier than water, and soluble in 14 parts of that fluid at 72° F. On allowing the solution to evaporate spontaneously, it crystallizes either in the form of elegant dendritic ramifications, or in rings composed of delicate acicular crystals of a silky lustre.

Caseous oxide is almost entirely insoluble even in boiling alcohol. Its aqueous solution yields a white flaky precipitate with infusion of gall-nuts, soluble in excess of the precipitant; and sub-acetate of lead likewise throws down a white precipitate. The crystals, if suddenly heated, volatilize without change; but if the heat is gradually raised, decomposition ensues, and a large quantity of carbonate and hydrosulphate of ammonia is generated. When strongly heated in open vessels it takes fire, and burns with flame without residue.

The composition of caseous oxide has not been determined, but from the facility with which its aqueous solution putrefies, Braconnot regards it as a highly azotized animal principle. It contains sulphur also. He believes it to be a product of the putrefaction of all animal substances, and proposes for it the name of *aposepedine*, from απο and σηπεδων, result of putrefaction, as more appropriate than caseous oxide.

Braconnot denies the existence of caseic acid. Proust's caseate of ammonia consists of various substances, such as free acetic acid, aposepedine, animal matter, resin, several salts, and a yellow pungent oil, which is the chief cause of the pungency of old cheese.

From 750 parts of curd completely putrefied were obtained 36 of dry matter insoluble in water. These consisted of 14.92

parts of margarate of lime, 2.57 of margaric acid, and 18.51 of oleic acid, retaining margaric acid and a brown animal matter.

According to the analysis of Gay-Lussac and Thenard, 100 parts of the caseous matter are composed of carbon 59.781, hydrogen 7.429, oxygen 11.409, and nitrogen 21.381. It yields by incineration a white ash amounting to 6.5 per cent of its weight, the greater part of which is phosphate of lime, a circumstance which renders caseous matter an article of food peculiarly proper for young animals.

Milk carefully deprived of its cream has a specific gravity of about 1.033; and 1000 parts of it, according to Berzelius, are thus constituted:—water 928.75, caseous matter with a trace of butter 28; sugar of milk 35; muriate and phosphate of potash 1.95; lactic (acetic) acid, acetate of potash, and a trace of lactate of iron 6.00; and earthy phosphates 0.30. Subtracting the caseous matter, the remaining substances constitute whey.

Eggs.—The composition of the recent egg and the changes which it undergoes during the process of incubation, have been ably investigated by Dr. Prout. (Phil. Trans. for 1822.) New-laid eggs are rather heavier than water; but they become lighter after a time, in consequence of water evaporating through the pores of the shell, and air being substituted for it. An egg of ordinary size yields to boiling water about three-tenths of a grain of saline matter, consisting of the sulphates, carbonates, and phosphates of lime and magnesia, together with animal matter and a little free alkali.

Of an egg which weighs 1000 grains, the shell constitutes 106.9, the white 604.2, and the yelk 288.9 grains. The shell contains about two per cent of animal matter, one per cent of the phosphates of lime and magnesia, and the residue is carbonate of lime with a little carbonate of magnesia.

When the yelk of a hard boiled egg is repeatedly digested in alcohol of specific gravity 0.807, until that fluid comes off colourless, there remains a white pulverulent residuum, possessed of many of the properties of albumen, but distinguished from that principle by containing a large quantity of phosphorus in some unknown state of combination. The alcoholic solution is of a deep yellow colour, and on cooling deposits crystals of a sebaceous matter, and a portion of yellow semi-

fluid oil. On distilling off the alcohol, the oil is left in a separate state. When the yelk is dried and burned, the phosphorus is converted into phosphoric acid, which, melting into a glass upon the surface of the charcoal, protects it from complete combustion. In the white of the egg, which consists chiefly of albumen, sulphur is present.

The obvious use of the phosphorus contained in the yelk is to supply phosphoric acid for forming the bones of the chick; but Dr. Prout was unable to discover any source of the lime with which that acid unites to form the earthy part of bone. It cannot be discovered in the soft parts of the egg; and hitherto no vascular connexion has been traced between the chick and its shell.

SECTION IV.

ON THE LIQUIDS OF SEROUS AND MUCOUS SURFACES, &c., AND ON PURULENT MATTER.

The surface of the cellular membrane is moistened with a peculiar limpid transparent fluid called *lymph*, which is in very small quantity during health, but collects abundantly in some dropsical affections. Mr. Brande collected it from the thoracic duct of an animal which had been kept without food for twenty-four hours. Its chief constituent is water, besides which it contains muriate of soda and albumen, the latter being in such minute quantity that it is coagulated only by the action of galvanism. Lymph does not affect the colour of test paper; but when evaporated to dryness, the residue gives a green tint to the syrup of violets.

The fluid secreted by serous membranes in general, such as the pericardium, pleura, and peritoneum, is very similar to lymph. According to Dr. Bostock, 100 parts of the liquid of the pericardium consist of water 92 parts, albumen 5.5, mucus 2, and muriate of soda 0.5. The serous fluid exhaled within the ventricles of the brain in *Hydrocephalus internus* is composed, in 1000 parts, of water 988.3, albumen 1.66, muriate of potash and soda 7.09, lactate (acetate) of soda and

its animal matter 2.32, soda 0.28, and animal matter soluble only in water, with a trace of phosphates, 0.35. (Berzelius, in Med. Chir. Trans. vol. iii. p. 252.)

The liquor of the amnios, or the fluid contained in the membrane which surrounds the *fœtus in utero*, differs in different animals. That of the human female was found by Vauquelin and Buniva to contain a small quantity of albumen, soda, muriate of soda, phosphate and carbonate of lime, and a matter like curd which gives it a milky appearance. That of the cow, according to the same authority, contains the substance already described under the name of amniotic acid; but several other chemists, such as Prout, Dulong, Labillardière, and Lassaigne, have been unable to detect it. Lassaigne states, that this acid exists in the fluid of the allantois of the cow. Dr. Prout found some sugar of milk in the amnios of a woman. (An. of Phil. v. 417.)

Humours of the Eye.—The aqueous and vitreous humours of the eye contain rather more than 80 per cent of water. The other constituents are a small quantity of albumen, muriate and acetate of soda, pure soda, though scarcely sufficient to affect the colour of test paper, and animal matter soluble only in water, but which is not gelatine. (Berzelius.) The crystalline lens, besides the usual salts, contains 36 per cent of a peculiar animal matter, very analogous to albumen if not identical with it. In cold water it is soluble, but is coagulated by boiling. The coagulum, according to Berzelius, has all the properties of the colouring matter of the blood excepting its colour.

The tears are limpid and of a saline taste, dissolve freely in water, and, owing to the presence of free soda, communicate a green tint to the blue infusion of violets. Their chief salts are the muriate and phosphate of soda. According to Fourcroy and Vauquelin the animal matter of the tears is mucus; but it is more probably either albumen, or some analogous principle. Its precise nature has not however been satisfactorily determined.

Mucus.—The term *mucus* has been employed in very different significations. Dr. Bostock applies it to a peculiar animal matter which is soluble both in hot and cold water, is

not precipitated by corrosive sublimate or solution of tannin, is not capable of forming a jelly, and which yields a precipitate with sub-acetate of lead. The existence of this principle has not, however, been fully established; for the presence of muriatic and phosphoric acids, the latter of which is frequently contained in animal fluids, and the former scarcely ever absent, sufficiently accounts for the precipitates occasioned in them by the salts of lead or silver. But even supposing the opinion of Dr. Bostock to be correct, it would be advisable to give some new name to his principle, and apply the term *mucus* solely to the fluid secreted by mucous surfaces.

The properties of mucus vary somewhat according to the source from which it is derived; but its leading characters are in all cases the same, and are best exemplified in mucus from the nostrils. Nasal mucus, according to Berzelius, has the following properties. Immersed in water, it imbibes so much of that fluid as to become transparent, with the exception of a few particles which remain opaque. When dried on blotting paper, it loses its transparency, but again acquires it when moistened. It is not coagulated or rendered horny by being boiled in water; but as soon as the ebullition has ceased, it collects unchanged at the bottom of the vessel. It is dissolved by dilute sulphuric acid. Nitric acid at first coagulates it; but by continued digestion, the mucus gradually softens and is finally dissolved, forming a clear yellow liquid. Acetic acid hardens mucus, and does not dissolve it even at a boiling temperature. Pure potash at first renders it more viscid, but afterwards dissolves it. By tannin mucus is coagulated, both when softened by the absorption of water, and when dissolved either in an acid or an alkali.

Pus.—Purulent matter is the fluid secreted by an inflamed and ulcerated surface. Its properties vary according to the nature of the sore from which it is discharged. The purulent matter formed by an ill-conditioned ulcer is a thin, transparent, acrid, fetid ichor; whereas a healing sore in a sound constitution yields a yellowish-white coloured liquid, of the consistence of cream, which is described as bland, opaque, and inodorous. This is termed healthy pus, and is possessed of the following properties. Though it appears homogeneous to the naked

eye, when examined with the microscope it is found to consist of minute globules floating in a transparent liquid. Its specific gravity is about 1.03. It is insoluble in water; and is thickened, but not dissolved by alcohol. When recent it does not affect the colour of test paper; but by exposure to the air it becomes acid. The dilute acids have little effect upon it; but strong sulphuric, nitric, and muriatic acids dissolve it, and the pus is thrown down by dilution with water. Ammonia reduces it to a transparent jelly, and gradually dissolves a considerable portion of it. With the fixed alkalies it forms a whitish ropy fluid, which is decomposed by water.

The composition of pus has not been ascertained with precision; but its characteristic ingredient is more closely allied to albumen than the other animal principles.

Several attempts have been made to discover a chemical test for distinguishing pus from mucus. When these fluids are in their natural state, the appearance of each is so characteristic that the distinction cannot be attended with any difficulty; but on the contrary, when a mucous surface is inflamed, its secretion becomes opaque, and, as sometimes happens in some pulmonary diseases, acquires more or less of the aspect of pus. Mr. Charles Darwin, who examined this subject, pointed out three grounds of distinction between them. 1. When the solution of these liquids in sulphuric acid is diluted, the pus subsides to the bottom, and the mucus remains suspended in the water. 2. When pus and catarrhal mucus are diffused through water, the former sinks, and the latter floats. 3. Pus is precipitated from its solution in potash by water, while the solution of mucus is not decomposed by similar treatment. Dr. Thomson, in his system of chemistry, has given the following test on the authority of Grasmeyer. The substance to be examined, after being triturated with its own weight of water, is mixed with an equal quantity of a saturated solution of carbonate of potash. If it contain pus, a transparent jelly forms in a few hours; but this does not happen if mucus only is present. Dr. Young, in his work on Consumptive Diseases, has given a very elegant character for distinguishing pus, founded on its optical properties. But the practical utility of tests of any kind is rendered very questionable by the fact that inflamed mucous membranes may secrete genuine pus

without breach of surface, and that the natural passes into purulent secretion by insensible shades.

Sweat.—Watery vapour is continually passing off by the skin in the form of insensible perspiration; but when the external heat is considerable, or violent bodily exercise is taken, drops of fluid collect upon the surface, and constitute what is called sweat. This fluid consists chiefly of water; but it contains some muriate of soda and free acetic acid, in consequence of which it has a saline taste and an acid reaction.

SECTION V.

ON THE URINE AND URINARY CONCRETIONS.

The urine differs from most of the animal fluids which have been described by not serving any ulterior purpose in the animal economy. It is merely an excretion designed for ejecting from the system substances, which by their accumulation within the body would speedily prove fatal to health and life. The sole office of the kidneys, indeed, appears to consist in separating from the blood the superfluous matters that are not required or adapted for nutrition, or which have already formed part of the body, and been removed by absorption. The substances which in particular pass off by this organ are nitrogen, in the form of highly azotized products, and various saline and earthy compounds. This sufficiently accounts for the great diversity of different substances contained in the urine.

The quantity of the urine is affected by various causes, especially by the nature and quantity of the liquids received into the stomach; but on an average a healthy person voids between thirty and forty ounces daily. The quality of this fluid is likewise influenced by the same circumstances, being sometimes in a very dilute state, and at others highly concentrated. The urine voided in the morning by a person who has fed heartily, and taken no more fluids than is sufficient for satisfying thirst, may be regarded as affording the best specimen of natural healthy urine.

The urine in this state is a transparent limpid fluid of an amber colour, having a saline taste, and while warm emitting an odour which is slightly aromatic, and not at all disagreeable. Its specific gravity in its most concentrated form is about 1.030. It gives a red tint to litmus paper, a circumstance which indicates the presence either of a free acid or of a super-salt. Though at first quite transparent, an insoluble matter is deposited on standing; so that urine, voided at night, is found to have a light cloud floating in it by the following morning. This substance consists in part of mucus from the urinary passages, and partly of super-urate of ammonia, which is much more soluble in warm than in cold water.

The urine is very prone to spontaneous decomposition. When kept for two or three days it acquires a strong urinous smell; and as the putrefaction proceeds, the disagreeable odour increases, until at length it becomes exceedingly offensive. As soon as these changes commence, the urine ceases to have an acid reaction, and the earthy phosphates are deposited. In a short time, a free alkali makes its appearance, and a large quantity of carbonate of ammonia is gradually generated. Similar changes may be produced in recent urine by continued boiling. In both cases the phenomena are owing to the decomposition of urea, which is almost entirely resolved into carbonate of ammonia.

The composition of the urine has been studied by several chemists, but the most recent and elaborate analysis of this fluid is by Berzelius. According to the researches of this indefatigable chemist, 1000 parts of urine are composed of

Water,	933.00
Urea,	30.10
Uric acid,	1.00
Free lactic acid, lactate of ammonia, and animal matter not separable from them,	17.14
Mucus of the bladder,	0.32
Sulphate of potash,	3.71
Sulphate of soda,	3.16
Phosphate of soda,	2.94
Phosphate of ammonia,	1.65
Muriate of soda,	4.45
Muriate of ammonia,	1.50
Earthy matters, with a trace of fluate of lime,	1.00
Siliceous earth,	0.03

Besides the ingredients included in the preceding list, the urine contains several other substances in small quantity. From the property this fluid possesses of blackening silver vessels in which it is evaporated, owing to the formation of sulphuret of silver, Proust inferred the presence of unoxidized sulphur; and Dr. Prout, from the odour of phosphuretted hydrogen, which he thinks he has perceived in putrefying urine, suspects that phosphorus is likewise present. The urine also contains a peculiar yellow colouring matter which has not hitherto been obtained in a separate state. From the precipitate occasioned in urine by the infusion of gall-nuts, the presence of gelatine has been inferred; but this effect appears owing to the presence not of gelatine but of a small portion of albumen.

According to Scheele, the urine of infants sometimes contains benzoic acid, a compound which, when present, may be easily procured by evaporating the urine nearly to the consistence of syrup, and adding muriatic acid. The precipitate, consisting of uric and benzoic acids, is digested in alcohol, which dissolves the benzoic acid.

Notwithstanding the high authority of Berzelius, it is very doubtful if any free acid be present in healthy urine. Dr. Prout, with every appearance of justice, maintains that the acidity of recent urine is occasioned by super-salts, and not by uncombined acid. He is of opinion that the acid reaction is chiefly, if not wholly, to be ascribed to the super-phosphate of lime and super-urate of ammonia, salts which he finds may co-exist in a liquid without mutual decomposition. A very strong argument, which to me indeed appears conclusive, in favour of this view, is derived from the fact, that on adding muriatic acid to recent urine, minute crystals of uric acid are gradually deposited, as always happens when this acid subsides slowly from a state of solution; but, on the contrary, if no free acid is added, an amorphous sediment, which Dr. Prout regards as super-urate of ammonia, is obtained.

Such is a general view of the composition of human urine in its natural healthy state. But this fluid is subject to a great variety of morbid conditions, which arise either from the deficiency or excess of certain principles which it ought

to contain, or from the presence of others wholly foreign to its composition. As the study of these affections affords an interesting example of the application of chemistry to pathology and the practice of medicine, I shall briefly mention some of the most important morbid states of this fluid, referring for more ample details to the excellent treatise of Dr. Prout *.

Of the substances which, though naturally wanting, are sometimes contained in the urine, the most remarkable is sugar, which is secreted by the kidneys in diabetes. (Page 802.) Diabetic urine has a sweet taste, and yields a syrup by evaporation, is almost always of a pale straw colour, and in general has a greater specific gravity than ordinary urine. It contains a remarkably small proportion of azotized substances, so that it has no tendency to putrefy; but the presence of sugar renders it susceptible of undergoing the vinous fermentation.

The acidifying process which is constantly going forward in the kidneys, as evinced by the formation of sulphuric, phosphoric, and uric acids, sometimes proceeds to a morbid extent, in consequence of which two acids, the oxalic and nitric, are generated, neither of which exists in healthy urine. The former, by uniting with lime, gives rise to one of the worst kinds of urinary concretions; and the latter, in the opinion of Dr. Prout, leads to the production of purpurate of ammonia, by reacting on uric acid.

In severe cases of jaundice the bile passes from the blood into the kidneys, and communicates a yellow colour to the urine. The most delicate test of its presence is muriatic acid, which causes a green tint.

Though albumen is contained in very minute quantity in healthy urine, in some diseases it is present in large proportion. According to Dr. Blackall it is characteristic of certain kinds of dropsy, accompanied with an inflammatory diathesis, as in that which supervenes in scarlet fever; and Dr. Prout has described two cases of albuminous urine, in which, without any febrile symptoms, albumen existed in such quantity that spontaneous coagulation took place within the bladder. From the Medical Reports lately published by Dr. Bright, it ap-

* Inquiry into the Nature and Treatment of Gravel, Calculus, &c.

pears that dropsical effusions are sometimes owing to an inflammatory or diseased state of the kidneys; and in these cases the urine commonly contains so much albumen as to be rendered turbid by heat. So regular indeed is its occurrence, that Dr. Bright considers albuminous urine, in dropsical patients, to be a sign of renal disease.

In the blood of patients suffering under this malady, Dr. Bostock detected a crystalline substance resembling urea; and Dr. Christison, pursuing the inquiry, obtained urea with all its characteristic properties. (Edinb. Med. and Surg. Journ. Oct. 1829.)

In certain states of the system urea is generated in an unusually small proportion. This occurs especially in *diabetes mellitus*, and in acute and chronic inflammation of the liver, diseases in which urea is said sometimes to be wholly wanting; but the experience of Dr. Prout has led him to doubt if it is ever entirely absent. Dr. Henry has shown that urea, when mixed with a considerable proportion of sugar, cannot be discovered by the usual test of nitric acid; and, consequently, that though present in diabetic urine, it may easily be overlooked. The method by which he has succeeded in detecting it in such cases is by distillation, urea being the only known animal principle which is converted into carbonate of ammonia at a boiling temperature. (Med. Chir. Trans. ii. 127.) During the hysteric paroxysm, also, the animal matters of the urine are deficient, while its saline ingredients are secreted in unusual quantity. An excess of urea occasionally exists. The mode by which Dr. Prout estimates the proportion of this principle is by putting the urine in a watch-glass, and carefully adding to it nearly an equal quantity of nitric acid, in such a manner that the acid may collect at the bottom. If spontaneous crystallization ensue, an excess of urea is indicated; and the degree of excess may be inferred approximately by marking the time which elapses before the effect takes place. Undiluted healthy urine yields crystals only after an interval of half an hour; but the nitrate crystallizes within that interval when the urea is in excess.

An unusually abundant secretion of uric acid is a circumstance by no means uncommon. In some instances this acid makes its appearance in a free state; but happily it generally

occurs in combination with an alkali, especially with soda or ammonia. As the urates are much more soluble in warm than in cold water, the urine in which they abound is quite clear at the moment of being voided, but deposits a copious sediment in cooling. The undue secretion of these salts, if temporary, occasions scarcely any inconvenience, and arises from such slight causes, that it frequently takes place without being noticed. This affection is generally produced by errors in diet, whether as to quantity or quality, and by all causes which interrupt the digestive process in any of its stages, or render it imperfect. Dr. Prout specifies unfermented heavy bread, and hard boiled puddings or dumplings, as in particular disposing to the formation of the urates. These sediments have commonly a yellowish tint, which is communicated by the colouring matter of the urine; or when they are deposited in fevers, forming the lateritious sediment, they are red, in consequence of the colouring matter of the urine being then more abundant. In fevers of an irritable nature, as in hectic, the sediment has a pink colour, which is ascribed by Dr. Prout to the presence of purpurate of ammonia, and by Proust to rosacic acid. (Page 805-6.)

So long as uric acid remains in combination with a base, it never yields a crystalline deposite; but when this acid is in excess and in a free state, its very sparing solubility causes it to separate in minute crystals, even within the bladder, giving rise to two of the most distressing complaints to which human nature is subject,—to gravel when the crystals are detached from one another, and when agglutinated by animal matter into concrete masses, to the disease called the *stone*. These diseases may arise either from uric acid being directly secreted by the kidneys, or, as Dr. Prout suspects, from the formation of some other acid, by which the urate of ammonia is decomposed. The tendency of urine to contain free acid occurs most frequently in dyspeptic persons of a gouty habit, and is familiarly known by the name of the uric or lithic acid diathesis. In these individuals the disposition to undue acidity of the urine is superadded to that state of the system which leads to an unusual supply of the urates.

A deficiency of acid in urine is not less injurious than its excess. As phosphate of lime in its neutral state is in-

soluble in water, this salt cannot be dissolved in urine except by being in the form of a superphosphate. Hence it happens that healthy urine yields a precipitate, when it is neutralized by an alkali; and if, by the indiscriminate employment of alkaline medicines, or from any other cause, the urine, while yet within the bladder, is rendered neutral, the earthy phosphates are necessarily deposited, and an opportunity afforded for the formation of a stone.

URINARY CONCRETIONS.

The first step towards a knowledge of urinary calculi was made in the year 1776 by Scheele, who showed that many of the concretions formed in the bladder consist of uric or lithic acid. The subject was afterwards successfully investigated by Drs. Wollaston and Pearson in this country, and by Fourcroy and Vauquelin in France; but the merit of having first ascertained the composition and chemical characters of most of the species of urinary calculi at present known, belongs to Dr. Wollaston. (Phil. Trans. for 1797.) The chemists who have since materially contributed to advance our knowledge of this department of science, are Dr. Henry, Mr. Brande, Dr. Prout, and the late Dr. Marcet, to whose "Essay on the Chemical History and Medical Treatment of Calculous Disorders," I may refer the reader who is desirous of studying this important subject.

The most common kinds of urinary concretions may be conveniently divided into six species: 1. The uric acid calculus; 2. The bone earth calculus, principally consisting of phosphate of lime; 3. The ammoniaco-magnesian phosphate; 4. The fusible calculus, being a mixture of the two preceding species; 5. The mulberry calculus, composed of oxalate of lime; and, lastly, The cystic oxide calculus. (Marcet.)

1. The uric acid forms a hard inodorous concretion, commonly of an oval form, of a brownish or fawn-colour, and smooth surface. These calculi consist of layers arranged concentrically around a central nucleus, the laminæ being distinguished from each other by a slight difference in colour, and sometimes by the interposition of some other substance.

This species is readily distinguished by the following cha-

racters. It is very sparingly soluble in water and muriatic acid. Digested in pure potash it quickly disappears, and on adding an acid to the solution, the uric acid is precipitated. It is dissolved with effervescence by nitric acid, and the solution yields purpurate of ammonia when evaporated. Before the blowpipe it becomes black, emits a peculiar animal odour, and is gradually consumed, leaving a trace of white ash, which has an alkaline reaction.

As a variety of this species may be mentioned urate of ammonia, a rare kind of calculus first noticed by Fourcroy. Mr. Brande and Dr. Marcet expressed a doubt of its ever forming an independent concretion; but its existence, as such, has been established by Dr. Prout. The calculus of urate of ammonia has the same general chemical characters as that composed of uric acid, from which it is distinguished by its solubility in boiling water, when reduced to powder, and by its solution in potash being attended with the disengagement of ammonia. It deflagrates remarkably before the blow-pipe. (Med. Chir. Trans. x. 389.)

2. The bone earth calculus, first correctly analyzed by Dr. Wollaston, consists of phosphate of lime. The surface of these calculi is of a pale brown colour, and quite smooth as if they had been polished. When sawed through the middle, they are found to be laminated in a very regular manner, and the layers in general adhere so slightly that they may be separated with ease into concentric crusts. Dr. Yellowly, in several bone-earth concretions, has detected small quantities of carbonate of lime, which appears to have been overlooked by others.

This calculus, when reduced to powder, dissolves with facility in dilute nitric or muriatic acid, but is insoluble in potash. Before the blowpipe it first assumes a black colour, from the decomposition of a little animal matter, and then becomes quite white, undergoing no further change unless the heat be very intense, when it is fused.

3. Phosphate of ammonia and magnesia was first described as a constituent of urinary calculi by Dr. Wollaston. It rarely exists quite alone, because the same state of the urine which leads to the formation of this species, favours the deposition of phosphate of lime; but it is frequently the prevailing in-

gredient. It often appears in the form of minute sparkling crystals, diffused over the surface or between the interstices of other calculous laminæ.

Calculi, in which this salt prevails, are generally white, and less compact than the foregoing species. When reduced to powder they are dissolved by cold acetic acid, and still more easily by the stronger acids, the salt being thrown down unchanged by ammonia. Digested in pure potash it emits an ammoniacal odour, but it is not dissolved. Before the blowpipe, a smell of ammonia is given out, it diminishes in size, and melts into a white pearl with rather more facility than phosphate of lime.

4. The fusible calculus, the nature of which was first determined by Dr. Wollaston, is a mixture of the two preceding species. It is commonly of a white colour, and its fracture is usually ragged and uneven. It is more friable than any of the other kinds of calculus, separates easily into layers, and leaves a white dust on the fingers. These concretions are very common, and sometimes attain a large size.

The fusible calculus is characterized by the facility with which it melts into a pearly globule, which is sometimes quite transparent. When reduced to powder, and put into cold acetic acid, the phosphate of ammonia and magnesia is dissolved, and the phosphate of lime, almost the whole of which is left, dissolves readily in muriatic acid.

5. The mulberry calculus, so named from its resemblance to the fruit of the mulberry, was first proved to consist of oxalate of lime by Dr. Wollaston. This concretion is sufficiently characterized by its dark-coloured tuberculated surface; but it may also be distinguished chemically by the following properties. Heated before the blowpipe, the oxalic acid is decomposed, and pure lime remains, which gives a strong brown stain to moistened turmeric paper. It is insoluble in the alkalies; but by digestion in carbonate of potash it is decomposed, and the insoluble carbonate of lime is left. When reduced to powder and digested in muriatic or nitric acids, a perfect solution is effected. It is not dissolved by acetic acid, a circumstance which distinguishes it from the ammoniaco-magnesian phosphate; and it is distinguished from phosphate of lime by being insoluble in phosphoric acid.

6. The cystic oxide was described by its discoverer Dr. Wollaston in the Philosophical Transactions for 1810. This concretion is not laminated, but appears as one uniform mass, confusedly crystallized through its whole substance, having somewhat the appearance of the ammoniaco-magnesian phosphate, though more compact. Before the blowpipe it emits a peculiarly fetid smell, quite distinct from that of uric acid, and is consumed. It is characterized by the great variety of re-agents in which it is soluble. It is dissolved abundantly by the muriatic, nitric, sulphuric, and oxalic acids; by potash, soda, ammonia, and lime-water; and even by the neutral carbonates of soda and potash. It is insoluble in water, alcohol, bi-carbonate of ammonia, and in the tartaric, citric, and acetic acids.

From the similarity which this substance bears to certain oxides in uniting both with acids and alkalies, Dr. Wollaston termed it an oxide, and gave it the name of *cystic*, on the supposition of its being peculiar to the bladder. Dr. Marcet, however, has found it in the kidney.

Cystic oxide is a rare species of calculus. In this country seven specimens only have been found;—two by Dr. Wollaston, two by Dr. Henry, and three by Dr. Marcet, Professor Stromeyer has met with two instances of it in one family, and in one of the cases the cystic oxide was also detected in the urine. M. Lassaigne has likewise found it in a stone taken from the bladder of a dog. From the analysis of this chemist, 100 parts of cystic oxide are composed of carbon 36.2, hydrogen 12.8, oxygen 17, and nitrogen 34.

It is remarkable that cystic oxide is never accompanied with the matter of any other concretion; whereas the other species are frequently met with in the same stone. They are sometimes so intimately mixed that they can be separated from one another only by chemical analysis, forming what is called a *compound* calculus; but more frequently the concretion consists of two or more different species arranged in distinct alternate layers. This is termed the *alternating* calculus.

Besides the calculi just mentioned, a few other species have been noticed. Two were described by Dr. Marcet under the names of *xanthic oxide* and *fibrinous calculus*, both of which are exceedingly rare. Xanthic oxide is of a reddish or yellow

colour, is soluble both in acids and alkalies, and its solution in nitric acid, when evaporated, assumes a bright lemon-yellow tint, a property to which it owes its name, and by which it is characterized. (ξανθος yellow.) The fibrinous calculus derives its name from fibrin, to which its properties are closely analogous. The third species consists chiefly of carbonate of lime, and is likewise of rare occurrence. It is probable that in some very uncommon cases, silica forms the principal ingredient of a stone; at least siliceous matter was found by Mr. Venables to be voided in one if not in two cases of gravel. (Journal of Science, N. S. vi. 234.)

From the solubility of urinary concretions in chemical menstrua, hopes were once entertained that reagents might be introduced into the urine through the medium of the blood, or be at once injected into the bladder, so as to dissolve urinary calculi, and thus supersede the necessity of a painful and dangerous operation. It has been found, however, that, for this purpose, it would be necessary to employ acid or alkaline solutions of greater strength than may safely be introduced into the bladder; and consequently all attempts of the kind have been abandoned. The last suggestion of this nature was made by Messrs. Prevost and Dumas, who proposed to disunite the elements of calculi by means of galvanism. This agent, however, though it may produce this effect out of the body, will scarcely, I conceive, be found admissible in practice.

SECTION VI.

ON THE SOLID PARTS OF ANIMALS.

BONE, HORN, MEMBRANES, TENDONS, LIGAMENTS, MUSCLES, &c.

Bones consist of earthy salts and animal matter intimately blended, the former of which are designed for giving solidity and hardness, and the latter for agglutinating the earthy particles. The animal substances are chiefly cartilage, gelatine, and a peculiar fatty matter called marrow. On reducing bones to powder, and digesting them in water, the fat rises and swims upon its surface, while the gelatine is dissolved.

By digesting bones in dilute muriatic acid, both the gelatine and earthy salts are dissolved, and the pure cartilage is left, which is flexible, but retains the original figure of the bone. The cartilage of bones is formed before the earthy matter, and constitutes the nidus in which the latter is deposited. In its chemical properties it is very analogous to coagulated albumen.

When bones are heated in close vessels, a large quantity of carbonate of ammonia, some fetid empyreumatic oil, and the usual inflammable gases, pass over into the recipient; while a mixture of charcoal and earthy matter, called animal charcoal, remains in the retort. If, on the contrary, they are heated to redness in an open fire, the charcoal is consumed, and a pure white friable earth is the sole residue.

According to the analysis of Berzelius, 100 parts of dry human bones consist of animal matters 33.3, phosphate of lime 51.04, carbonate of lime 11.30, fluate of lime 2, phosphate of magnesia 1.16, and soda, muriate of soda, and water 1.2. Mr. Hatchett found, also, a small quantity of sulphate of lime; and Fourcroy and Vauquelin discovered traces of alumina, silica, and the oxides of iron and manganese.

Teeth are composed of the same materials as bone; but the enamel dissolves completely in dilute nitric acid, and therefore is free from cartilage. From the analysis of Mr. Pepys, the enamel contains 78 per cent of phosphate and 6 of carbonate of lime, the residue being probably gelatine. The composition of ivory is similar to that of the bony matter of teeth in general.

The shells of eggs and the covering of crustaceous animals, such as lobsters, crabs, and the starfish, consist of carbonate and a little phosphate of lime, and animal matter. The shells of oysters, muscles, and other molluscous animals consist almost entirely of carbonate of lime and animal matter, and the composition of pearl and mother of pearl is similar.

Horn differs from bone in containing only a trace of earth. It consists chiefly of gelatine and a cartilaginous substance like coagulated albumen. The composition of the nails and hoofs of animals is similar to that of horn; and the cuticle belongs to the same class of substances.

Tendons appear to be composed almost entirely of gela-

tine; for they are soluble in boiling water, and the solution yields an abundant jelly on cooling. The composition of the true skin is nearly the same as that of tendons. Membranes and ligaments are composed chiefly of gelatine, but they also contain some substance which is insoluble in water, and is similar to coagulated albumen.

According to the analysis of Vauquelin, the principal ingredient of hair is a peculiar animal substance, insoluble in water at 212° F, but which may be dissolved in that liquid by means of Papin's Digester, and is soluble in a solution of potash. Besides this substance hair contains oil, sulphur, silica, iron, manganese, and carbonate and phosphate of lime. The colour of the hair depends on that of its oil; and the effect of metallic solutions, such as nitrate of silver, in staining the hair, is owing to the presence of sulphur.

The composition of wool and feathers appears analogous to that of hair. The quill part of the feather was found by Mr. Hatchett to consist of coagulated albumen.

Silk is covered with a peculiar varnish which is soluble in boiling water and in alkaline solutions, and amounts to about 23 per cent of the raw material. By digestion in alcohol it is also deprived of a portion of wax. The remaining fibrous structure has been examined in a very imperfect manner. By the action of nitric acid it is converted into a yellow crystalline substance of a bitter taste.

The flesh of animals, or *muscle*, consists essentially of fibrin; but independently of this principle, it contains several other ingredients, such as albumen, gelatine, a peculiar extractive matter called *osmazome*, fat, and salts, substances which are chiefly derived from the blood, vessels, and cellular membrane, dispersed through the muscles. On macerating flesh, cut into small fragments, in successive portions of cold water, the albumen, osmazome, and salts are dissolved; and on boiling the solution, the albumen is coagulated. From the remaining liquid, the osmazome may be procured in a separate state by evaporating to the consistence of an extract, and treating it with cold alcohol. By the action of boiling water, the gelatine of the muscle is dissolved, the fat melts and rises to the surface of the water, and pure fibrin remains.

The characteristic odour and taste of soup is owing to

the osmazome. This substance is of a yellowish-brown colour, and is distinguished from the other animal principles by solubility in water and alcohol, whether cold or at a boiling temperature, and by not forming a jelly when its solution is concentrated by evaporation. Like gelatine and albumen it yields a precipitate with infusion of gall-nuts.

The substance of the brain, nerves, and spinal marrow differs from that of all other animal textures. The most elaborate analysis of cerebral matter is by Vauquelin, who found that 100 parts of it consist of water 80, albumen 7, white fatty matter 4.53, red fatty matter 0.70, osmazome 1.12, phosphorus 1.5, and acids, salts, and sulphur 5.15. (Annals of Phil. i.) The presence of albumen accounts for the partial solubility of the brain in cold water, and for the solution being coagulated by heat, acids, alcohol, and by the metallic salts which coagulate other albuminous fluids. By acting upon cerebral matter with boiling alcohol, the fatty principles and osmazome are dissolved, and the solution in cooling deposits the white fatty matter in the form of crystalline plates. On expelling the alcohol by evaporation, and treating the residue with cold alcohol, the osmazome is taken up, and a fixed oil remains of a reddish brown colour, and an odour like that of the brain itself, though much stronger. These two species of fat differ little from each other; and both yield phosphoric acid when deflagrated with nitre.

SECTION VII.

ON PUTREFACTION.

When dead animal matter is exposed to air, moisture, and a moderate temperature, it speedily runs into putrefaction, during which every trace of its original texture disappears, and products of a very offensive nature are generated. The most favourable temperature is from 60° to 80° or 90° Fahr. Below 50° the process takes place tardily, and at 32° it is wholly arrested;—a fact, which is clearly evinced by the circumstance that the bodies of animals, which have been buried in snow or ice, are found unchanged after a long series of years. The necessity of a certain degree of moisture is shown by the

facility with which the most perishable substances may be preserved when quite dry. The preservation of smoked meat is chiefly owing to this cause; and, for a like reason, animals buried in the dry sand of Arabia and Egypt have remained for years without change.

It is probable that when moisture and warmth concur, putrefaction in animal matter which has not been heated to 212° will take place independently of atmospheric influence. But when animal matter has been boiled, and is then, without subsequent exposure, completely protected from air, it may be preserved for years, even though moist and in a temperature favourable to putrefaction. The practice of preserving every kind of food, both animal and vegetable, now a subject of extensive commercial enterprise, affords ample demonstration of this statement. The mode generally adopted is the following. Into a tin vessel is placed any kind of food, such as joints of meat, fish, game, and vegetables, dressed for the table; and into the interstices is poured a rich gravy, care being taken to have the vessel completely full. A tin cover, with a small aperture, is then carefully fixed by solder; and while the whole vessel is perfectly full, and at the temperature of 212°, the remaining aperture is closed. As the ingredients within cool and contract, a vacuum is formed if the operation has been skilfully conducted, and the sides of the vessel are in consequence slightly pressed in by the weight of the atmosphere. In this state the vessel may be sent to tropical climates without fear of putrefaction; and the most delicate food of one country be thus eaten in its original perfection, in a distant region, many months or even years after its preparation.

For reasons formerly mentioned, animal matters commonly undergo putrefaction more readily than those which are derived from the vegetable kingdom; (page 670) but they are not all equally disposed to putrefy. The acid and fatty principles are less liable to this change than urea, fibrin, and other analogous substances. The chief products to which their dissolution gives rise are water, ammonia, carbonic acid, and sulphuretted, phosphuretted, and carburetted hydrogen gases.

PART IV.

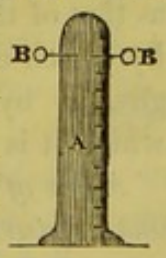
ANALYTICAL CHEMISTRY.

To enter into a detailed account of experimental and analytical chemistry is altogether inconsistent with the design and limits of the present work. My sole object in this department is to give a few concise directions for conducting some of the more common analytical processes; and in order to render them more generally useful, I shall give examples of the analysis of mixed gases, of minerals, and of mineral waters.

SECTION I.

ANALYSIS OF MIXED GASES.

Analysis of air or of gaseous mixtures containing oxygen. —Of the various processes by which oxygen gas may be withdrawn from gaseous mixtures, and its quantity determined, none are so convenient and precise as the method by means of hydrogen gas. In performing this analysis, a portion of atmospheric air is carefully measured in a graduated tube, and mixed with a quantity of hydrogen gas which is rather more than sufficient for uniting with all the oxygen present. The mixture is then introduced into a strong glass tube called Volta's Eudiometer, shown in the annexed wood cut, and is inflamed by the electric spark, the aperture of the tube being closed by the thumb at the moment of detonation. The total diminution in volume, divided by three, indicates



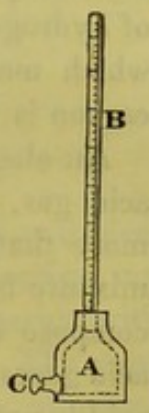
the quantity of oxygen originally contained in the mixture. This operation may be performed in a trough either of water or mercury. (Figs. 1 and 2.)

Instead of electricity, spongy platinum may be employed for causing the union of oxygen and hydrogen gases; and while its indications are very precise, it has the advantage of producing the effect gradually and without detonation. The most convenient mode of employing it with this intention is the following. A mixture of spongy platinum and pipe-clay, in the proportion of about three parts of the former to one of the latter, is made into a paste with water, and then rolled between the fingers into a globular form. In order to preserve the spongy texture of the platinum, a little muriate of ammonia is mixed with the paste; and when the ball has become dry, it is cautiously ignited at the flame of a spirit-lamp. The sal-ammoniac, escaping from all parts of the mass, gives it a degree of porosity which is peculiarly favourable to its action. The ball, thus prepared, should be protected from dust, and be heated to redness just before being used. To insure accuracy, the hydrogen employed should be kept over mercury for a few hours in contact with a platinum ball and a piece of caustic potash. The first deprives it of traces of oxygen which it commonly contains, and the second of moisture and sulphuretted hydrogen. The analysis must be performed in a mercurial trough. The time required for completely removing the oxygen depends on the diameter of the tube. If the mixture is contained in a very narrow tube, the diminution does not arrive at its full extent in less than twenty minutes or half an hour; while in a vessel of an inch in diameter, the effect is complete in the course of five minutes.

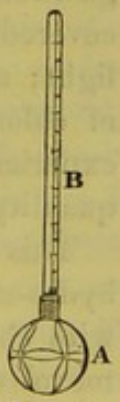
Mode of determining the quantity of nitrogen in gaseous mixtures.—As atmospheric air, which has been deprived of moisture and carbonic acid, consists of oxygen and nitrogen only, the proportion of the latter is of course known as soon as that of the former is determined. The only method, indeed, by which chemists are enabled to estimate the quantity of this gas, is by withdrawing the other gaseous substances with which it is mixed.

Mode of determining the quantity of carbonic acid in gaseous mixtures.—When carbonic acid is the only acid gas which

is present, as happens in atmospheric air, in the ultimate analysis of organic compounds, and in most other analogous researches, the process for determining its quantity is exceedingly simple; for it consists merely in absorbing that gas by lime water or a solution of caustic potash. This is easily done in the course of a few minutes in an ordinary graduated tube; or it may be effected almost instantaneously by agitating the gaseous mixture with the alkaline solution in Hope's eudiometer. This apparatus, as represented in the figure, is formed of two parts:—of the bottle A, capable of containing about twenty drachms of fluid, and furnished with a well-ground stopper C; and of the tube B, of the capacity of one cubic inch, divided into 100 equal parts, and accurately fitted by grinding to the neck of the bottle. The tube, full of gas, is fixed into the bottle previously filled with lime water, and its contents are briskly agitated. The stopper C is then withdrawn under water, when a portion of liquid rushes into the tube, supplying the place of the gas which has disappeared; and the process is afterwards repeated, as long as any absorption ensues.



The eudiometer of Dr. Hope was originally designed for analyzing air or other similar mixtures, the bottle being filled with a solution of hydro-sulphuret of potash or lime, or some liquid capable of absorbing oxygen. To the employment of this apparatus it has been objected, that the absorption is rendered slow by the partial vacuum which is continually taking place within it, an inconvenience particularly felt towards the close of the process, in consequence of the eudiometric liquor being diluted by the admission of water. To remedy this defect, Dr. Henry has substituted a bottle of elastic gum for that of glass, as in the annexed wood-cut, by which contrivance no vacuum can occur. From the improved method of analyzing air, however, this instrument is now rarely employed in eudiometry; but it may be used with advantage for absorbing carbonic acid or similar gases, and is particularly useful for the purpose of demonstration.



Mode of analyzing mixtures of hydrogen and other inflammable gases.—When hydrogen is mixed with nitrogen,

air, or other similar gaseous mixtures, its quantity is easily ascertained by causing it to combine with oxygen either by means of platinum or the electric spark. If, instead of hydrogen, any other combustible substance, such as carbonic oxide, light carburetted hydrogen, or olefiant gas, is mixed with nitrogen, the analysis is easily effected by adding a sufficient quantity of oxygen, and detonating the mixture by electricity. The diminution in volume indicates the quantity of hydrogen contained in the gas, and from the carbonic acid, which may then be removed by an alkali, the quantity of carbon is inferred.

An elegant mode of converting carbonic oxide into carbonic acid gas, suggested by Dr. Henry, is to mix it with rather more than its own volume of nitrous oxide gas, and fire the mixture by the electric spark. The two gases mutually decompose each other, and give rise to nitrogen and carbonic acid gases. For each measure of carbonic oxide one of carbonic acid is produced, one measure of nitrous oxide is decomposed, and one of nitrogen evolved. By employing a slight excess of pure carbonic oxide, the composition of nitrous oxide may be ascertained. The mixed gases occupy the same space after deflagration as before it; and the carbonic acid gas occupies the same space as the nitrous oxide which had been present. (Annals of Philosophy, xxiv. 301.)

When olefiant gas is mixed with other inflammable gases, its quantity is easily determined by an elegant and simple process proposed by Dr. Henry. (Page 354.) It consists in mixing 100 measures, or any convenient quantity of the gaseous mixture, with an equal volume of chlorine in a vessel covered with a piece of cloth or paper, so as to protect it from light; and after an interval of about ten minutes, the excess of chlorine is removed by lime water or potash. The loss experienced by the gas to be analyzed, indicates the exact quantity of olefiant gas which it had contained.

This method is not correct when the vapours of the dense hydro-carburets are present. Thus when oil gas is mixed with chlorine, the diminution in volume arises from the removal of the combustible vapours as well as of olefiant gas; for the former are equally disposed as the latter to unite with chlorine.

In mixtures of hydrogen, carburetted hydrogen, and carbonic oxide, the analytic process is exceedingly difficult and complicated, and requires all the resources of the most refined chemical knowledge, and all the address of an experienced analyst. The most recent information on this subject will be found in Dr. Henry's Essay in the Philosophical Transactions for 1824.

SECTION II.

ANALYSIS OF MINERALS.

As the very extensive nature of this department of analytical chemistry renders a selection necessary, I shall confine my remarks solely to the analysis of those earthy minerals with which the beginner usually commences his labours. The most common constituents of these compounds are silica, alumina, iron, manganese, lime, magnesia, potash, soda, and carbonic and sulphuric acids; and I shall, therefore, endeavour to give short directions for determining the quantity of each of these substances.

In attempting to separate two or more fixed principles from each other, the first object of the analytical chemist is to bring them into a state of solution. If they are soluble in water, this 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 the 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 potash, 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.

Analysis of Marble or Carbonate of Lime.—This analysis

is easily made by exposing a known quantity of marble for about half an hour to a full white heat, by which means the carbonic acid gas is entirely expelled, so that by the loss in weight the quantity of each ingredient, supposing the marble to have been pure, is at once determined. In order to ascertain that the whole loss is owing to the escape of carbonic acid, the quality of this gas may be determined by a comparative analysis. Into a small flask containing muriatic acid diluted with two or three parts of water, a known quantity of marble is gradually added, the flask being inclined to one side in order to prevent the fluid from being flung out of the vessel during the effervescence. The diminution in weight experienced by the flask and its contents, indicates the quantity of carbonic acid which has been expelled.

Should the carbonate suffer a greater loss in the fire than when decomposed by an acid, it will most probably be found to contain water. This may be ascertained by heating a piece of it to redness in a glass tube, the sides of which will be bedewed with moisture, if water is present. Its quantity may be determined by causing the watery vapour to pass through a weighed tube filled with fragments of the chloride of calcium, by which the moisture is absorbed.

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 muriatic 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, converted into quicklime by a white heat, and weighed; or the oxalate may be 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 in the form of the ammoniaco-phosphate is precipitated. 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 a few 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° F., acidulating at the same time by muriatic 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 sa line 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 muriate 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 either heated to low redness to expel the water, and weighed, or at once reduced to quicklime by a white heat. Of the dry carbonate, fifty parts correspond to twenty-eight of lime. The alkaline solution is acidulated with muriatic acid, and the sulphuric acid thrown down by muriate of baryta. From the sulphate of this earth, collected and dried at a red heat, the quantity of acid may easily be estimated.

The method of analyzing the sulphate of strontia and baryta is somewhat different. As these salts are difficult of decom-

position 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 muriatic 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 muriatic 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 iron and alumina, a solution of pure potash is added in moderate excess; so as not only to throw down those oxides, but to dissolve 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 on a sand-bath. Of this hydrated peroxide, forty-nine parts contain forty of anhydrous peroxide of iron. But the most accurate mode of determining its quantity is by expelling the water by a red-heat. 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 sal-ammoniac, when the muriatic acid unites with the potash, 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 muriatic 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 muriatic 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 liquid 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 iron be washed with cold water. Of this succinate, well dried at a temperature of 212° F., 90 parts correspond to 40 of the peroxide. 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 in-

tended 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 be proportionally small, it is precipitated as a sulphuret by hydrosulphuret of ammonia or potash. This sulphuret is then dissolved in muriatic acid, and the manganese thrown down as usual by means of an alkali. But if the manganese be 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 muriatic 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 peroxide, while any traces of lime or manganese, 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 potash or soda, the mass is taken up in dilute muriatic 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 bi-carbonate, 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 pre-

cipitated, substances which may be separated from each other by means of pure potash. (Page 872.) The manganese, lime, and magnesia, may then be determined by the processes above described.

Analysis of minerals containing a fixed alkali.—When the object is to determine the quantity of fixed alkali, such as potash or soda, it is of course necessary to abstain from the employment of these reagents in the analysis itself; and the beginner will do well to devote his attention to the alkaline ingredients only. On this supposition, he will proceed in the following manner. The mineral is reduced to a very fine powder, mixed intimately with six times its weight of artificial carbonate of baryta, and exposed for an hour to a white heat. The ignited mass is dissolved in dilute muriatic acid, and the solution evaporated to perfect dryness. The soluble parts are taken up in hot water; an excess of carbonate of ammonia is added; and the insoluble matters, consisting of silica, carbonate of baryta, and all the constituents of the mineral, excepting the fixed alkali, are collected on a filter. The clear solution is evaporated to dryness in a porcelain capsule, and the dry mass is heated to redness in a crucible of platinum, in order to expel the salts of ammonia. The residue is chloride of potassium or sodium.

In this analysis, it generally happens that traces of manganese, and sometimes of iron, escape precipitation in the first part of the process; and, in that case, they should be thrown down by hydrosulphuret of ammonia. If neither lime nor magnesia is present, the alumina, iron, and manganese may be separated by pure ammonia, and the baryta subsequently removed by the carbonate of that alkali. By this method the carbonate of baryta is recovered in a pure state, and may be reserved for another analysis. The baryta may also be thrown down as a sulphate by sulphuric acid, in which case, the soda or potash is procured in combination with that acid; but this mode is objectionable, because the sulphate of baryta is very apt to retain small quantities of sulphate of potash.

The analysis is attended with considerable inconvenience when magnesia happens to be present; because this earth is not completely precipitated either by ammonia or its carbonate, and therefore some of it remains with the fixed alkali. The

best mode with which I am acquainted, is to precipitate the magnesia, by phosphate of ammonia; subsequently recovering from the filtered solution the excess of phosphoric acid by acetate of lead, and that of lead by sulphuretted hydrogen. The acetate of the alkali is then brought to dryness, ignited, and by the addition of sulphate of ammonia converted into a sulphate.

In the preceding account, several operations have been alluded to, which, from their importance, deserve more particular mention. The process of filtering, for example, is one on which the success of analyses materially depends. Filtration is effected by means of a glass funnel B, into which a filter C, of nearly the same size and form, made of white bibulous paper, is inserted. For researches of delicacy, the filter, before being used, is macerated for a day or two in water acidulated with nitric acid, in order to dissolve lime and other substances contained in common paper, and it is afterwards washed with hot water till every trace of acid is removed. It is next dried at 212°, or any fixed temperature insufficient to decompose it, and then carefully weighed, the weight being marked upon it with a pencil. As dry paper absorbs hygrometric moisture rapidly from the atmosphere, the filter, while being weighed, should be inclosed in a light box made for the purpose. When a precipitate is collected on a filter, it is washed with pure water until every trace of the original liquid is removed. It is subsequently dried and weighed as before, and the weight of the paper subtracted from the combined weight of the filter and precipitate. The trouble of weighing the filter may sometimes be dispensed with. Some substances, such as silica, alumina, and lime, which are not decomposed when heated with combustible matter, may be put into a crucible while yet contained in the filter, the paper being set on fire before it is placed in the furnace. In these instances, the ash from the paper, the average weight of which is determined by previous experiments, must be subtracted from the weight of the heated mass.

The tests commonly employed in ascertaining the acidity or alkalinity of liquids are litmus and turmeric paper. The former is made by digesting litmus, reduced to a fine powder,

in a small quantity of water, and painting with it white paper which is free from alum. Turmeric paper is made in a similar manner; but the most convenient test of alkalinity is litmus paper reddened by a dilute acid.

SECTION III.

ANALYSIS OF MINERAL WATERS.

Rain water collected in clear 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 an insoluble compound with the acid 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 ex-

pelled, 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 muriates of lime and soda 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 (D. fig. 2.) 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. (Fig. 6.)

The different kinds of mineral water may be conveniently arranged for the purpose of description in the six divisions of acidulous, alkaline, chalybeate, sulphurous, 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 iron, in consequence of the facility with which these salts are dissolved by water charged with carbonic acid.

The best mode of determining the quantity of carbonic acid is by heating a portion of the water in a flask, as in the annexed figure, and receiving the carbonic acid by means of a bent tube, in a graduated jar filled with mercury.

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. Michaels, South America, 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, sulphuretted hydrogen, and muriate of soda.

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 muriatic or sulphuric acid; but most frequently it is in the form of proto-carbonate, held in solution by free carbonic acid. On exposure to the air, the protoxide is oxidized, and the hydrated peroxide subsides, causing the ochreous deposite, 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 an alkali 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. Sulphurous waters, of which the springs of Aix la Chapelle, Harrowgate, and Moffat afford examples, contain sulphuretted hydrogen, and are easily recognised 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 inferred by transmitting it through a solution of acetate of lead, and weighing the sulphuret which is generated.

5. Those mineral springs are called saline which do not belong to either of the preceding divisions. The salts which are most frequently contained in these waters are sulphates, muriates, and carbonates of lime, magnesia, and soda. Potash 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. Muriatic acid is detected by nitrate of silver, and sulphuric acid by muriate of baryta; and if an alkaline carbonate be present, the precipitate occasioned by either of these tests will contain a carbonate 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. Potash is known by the action of muriate of platinum. (Page 428.) 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 recognised by the rich yellow colour which it communicates to flame. (Page 431.) 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 319.)

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 muriatic acid is precipitated by nitrate of silver. The mixed sulphate and carbonate is exposed to a low red heat, and weighed; and the latter is then dissolved by dilute muriatic acid, and its quantity determined by weighing the sulphate. The chloride of silver, of which 146 parts correspond to 37 of muriatic 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 precipi-

tating 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 of course gives the quantity of that alkali; or it may be procured in a separate state by the process described in the foregoing section.

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 muriatic acids, lime, and soda, it is obvious that three cases are possible. The liquid may contain sulphate of lime and muriate of soda, or muriate of lime 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 soda. 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. 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. (Page 154.)

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. According to the analysis of Dr. Murray, 10,000 parts of water from the Frith of Forth contain 220.01 parts

* Philosophical Transactions of Edinburgh, vol. vii.

of common salt, 33.16 of sulphate of soda, 42.08 of muriate of magnesia, and 7.84 of muriate of lime. Dr. Wollaston has detected potash in sea water, and it likewise contains small quantities of hydriodic and hydrobromic acids.

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 Dr. 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, Dr. 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 Dr. 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, I found to contain 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.)

TABLE

Showing the Composition of several of the principal Mineral Waters. (From Dr. Henry's Elements.)

[N. B. The temperature, when not expressed, is to be understood to be 49° or 50° Fahrenheit.]

I. Carbonated Waters.

Seltzer. Bergman.

In each wine pint.

Carbonic acid	17 cub. in.

Specific gravity 1.0027.

Carbonate of soda	4 grs.
——— of magnesia	5
——— of lime	3
Chloride of sodium	17
	29

Carlsbad (Temperature 165° Fahr.) Berzelius.

In a wine pint.

Carbonic acid	5 cub. in.

In 1000 parts by weight.

Sulphate of soda	2.58714 grs.
Carbonate of soda	1.25200
Chloride of sodium	1.04893
Carbonate of lime	0.31219
Fluate of do.	0.00331
Phosphate of do.	0.00019
Carbonate of strontia	0.00097
——— of magnesia	0.18221
Phosphate of alumina	0.00034
Carbonate of iron	0.00424
——— of manganese,	a trace
Silica	0.07504
	5.46656

Spa. Bergman.

Specific gravity 1.0010.

In each wine pint.

Carbonic acid	13 cub. in.
Carbonate of soda	1.5 gr.
——— of magnesia	4.5
——— of lime	1.5
Chloride of sodium	0.2
Oxide of iron	0.6
	8.3

Pyrmont. Bergman.

Specific gravity 1.0024.

In each wine pint.

Carbonic acid	26 cub. in.
Carbonate of magnesia	10. grs.
——— of lime	4.5
Sulphate of magnesia	5.5
——— of lime	8.5
Chloride of sodium	1.5
Oxide of iron	0.6
	30.6

Pouges. Hassenfratz.

In each wine pint.

Carbonic acid	30 cub. in.
Carbonate of soda	10. grs.
——— of magnesia	1.2
——— of lime	12.
Chloride of sodium	2.2
Oxide of iron	2.5
Silica	0.5
	28.4

Composition of Mineral Waters,—Continued,

II. Sulphureted Waters.

Aix la Chapelle. Bergman.

Temperature 143°.

In each wine pint.

Sulphureted hydrogen	5.5 cub. in.
Carbonate of soda.....	12. grs.
——— of lime.....	4.75
Muriate of soda	5.
	21.75

Cheltenham, Sulphur Spring.

Brande and Parkes.

Specific gravity 1.0085.

In each wine pint.

Carbonic acid	1.5 cub. in.
Sulphureted hydrogen.....	2.5
Sulphate of soda	23.5 grs.
——— of magnesia	5.
——— of lime	1.2
Muriate of soda	35.
Oxide of iron	0.3
	65.

Leamington, Sulphur Water.

Scudamore.

Specific gravity 1.0042.

Sulphureted hydrogen, quantity not ascertained.

In each pint.

Muriate of soda	15. grs.
——— of lime	7.96
——— of magnesia	3.30
Sulphate of soda.....	11.60
Oxide of iron	a trace.
	37.86

Moffat. Garnet.

Nitrogen	0.5 cub. in.
Carbonic acid	0.6
Sulphureted hydrogen ...	1.2
Muriate of soda	4.5 grs.

Harrogate Water.

New Well, at the Crown Inn.

(West, Quart. Journ. xv. 82.)

Specific gravity 1.01286 at 69°.

One wine gallon contains

Sulphureted hydrogen	6.4 cub. in.
Carbonic acid	5.25
Azote	6.5
Carbureted hydrogen	4.65
	22.8

Also,

Muriate of soda.....	735. grs.
——— of lime.....	71.5
——— of magnesia.....	43.
Bi-carbonate of soda.....	14.75
	864.25

Old Well.

Sp. gr. 1.01324 at 60°.

Sulphureted hydrogen ..	14.0 cub. in.
Carbonic acid	4.25
Azotic gas	8.
Carbureted hydrogen ..	4.15
	30.4

Also,

Muriate of soda	752.0 grs.
——— of lime	65.75
——— of magnesia.....	29.2
Bi-carbonate of soda.. ..	12.8
	859.75

III. Saline Waters.

Seidlitz. Bergman.

Specific gravity 1.0060.

In a pint.

Carbonate of Magnesia.....	2.5
——— of lime	0.8
Sulphate of magnesia	180.
——— of lime	5.
Muriate of magnesia	4.5
	192.8

Cheltenham, pure saline. Parkes and Brande.

In each pint.

Sulphate of soda	15.
——— of magnesia	11.
——— of lime	4.5
Muriate of soda.....	50.
	80.5

Composition of Mineral Waters,—Continued.

LEAMINGTON, saline. Scudamore.

Specific gravity 1.0119.

In a pint.

Muriate of soda	53.75
——— of lime	28.64
——— of magnesia	20.16
Sulphate of soda	7.83
Oxide of iron	a trace.
	110.38

LEAMINGTON, Lord Aylesford's spring. Scudamore.

Specific gravity 1.0093.

In a pint.

Muriate of soda	12.25
——— of lime	28.24
——— of magnesia	5.22
Sulphate of soda	32.96
Oxide of iron	a trace.
	78.67

BRISTOL. Carrick.

Temp. 74°. Specific gravity 1.00077.

In each pint.

Carbonic acid	3.5 cub. in.
Carbonate of lime	1.5 grs.
Sulphate of soda	1.5
——— of lime	1.5
Muriate of soda	0.5
——— of magnesia	1.
	6 0

BATH. Phillips.

Temp. 109° to 117°. Sp. gr. 1.002.

In each pint.

Carbonic acid	1.2 cub. in.
Carbonate of lime	0.8
Sulphate of soda	1.4
——— of lime	9.3
Muriate of soda	3.4
Silica	0.2
Oxide of iron	a trace.
	16.3

BATH. Solid contents. Scudamore.

Muriate of lime	1.2 grs.
——— of magnesia	1.6
Sulphate of lime	9.5
——— of soda	.9
Silica	.2
Oxide of iron	.01985
Loss, partly carb. of soda	.58015
	14.

BUXTON. Scudamore.

Sp. gr. at 60°. 1.0006. Temp. 82°.

In a wine gallon.

Carbonic acid	1.5 cub. in.
Nitrogen	4.64
Muriate of magnesia	.58 grs.
——— of soda	2.40
Sulphate of lime	.6
Carbonate of lime	10.40
Extractive and vegetable matter	0 50
Loss	0.52
	15.

Or, according to Dr. Murray's views,

Sulphate of soda	0.63
Muriate of lime	0.57
——— of soda	1.80
——— of magnesia	0.58
Carbonate of lime	10.40
Extract and loss	1.02
	15.00

MATLOCK BATH. Scudamore.

Temp. 68°. Sp. gr. 1.0003.

Free carbonic acid.
Muriates and sulphates of magnesia, lime, and soda?
in very minute quantities not yet ascertained.

Composition of Mineral Waters,—Continued.

IV. Chalybeate Waters.

Tunbridge. Scudamore.

Specific gravity 1.0007.

In each gallon.

Muriate of Soda	2.46
——— of lime	0.39
——— of magnesia	0.29
Sulphate of lime	1.41
Carbonate of lime	0.27
Oxide of iron	2.22
Traces of manganese, vegetable fibre, silica, &c.	0.44
Loss	0.13
	7.61

Cheltenham. Brande and Parkes.

Specific gravity 1.0092.

In a pint.

Carbonic acid	2.5 cub. in
Carbonate of soda	0.5
Sulphate of soda	22.7
——— of magnesia	6.
——— of lime	2.5
Muriate of Soda	41.3
Oxide of iron	0.8
	73.8

Brighton. Marcet.

Specific gravity 1.00108.

Carbonic acid gas	2½ cub. in.
Sulphate of iron	1.80 grs.
——— of lime	4.09
Muriate of soda	1.53
——— of magnesia	0.75
Silica	0.14
Loss	0.19
	8.50

Harrogate, Oddie's chalybeate.

Scudamore.

Specific gravity 1.0053.

In each gallon.

Muriate of soda	300.4
——— of lime	22.
——— of magnesia	9.9
Sulphate of lime	1.86
Carbonate of do.	6.7
——— of magnesia	0.8
Oxide of iron	2.40
Residue, chiefly silica	.40
	344.46

APPENDIX.

TABLE of Chemical Equivalents, Atomic Weights, or Proportional Numbers, Hydrogen being taken as Unity.

In preparing the following tabular view of the atomic weights, I have chiefly consulted the table published by Dr. Thomson in his First Principles of Chemistry, and by Mr. Phillips in the new series, 10th volume, of the Annals of Philosophy. From the full account already given of the Laws of Combination and of the Atomic Theory, it will be superfluous to describe the uses of the table. The only explanation required on this subject relates to the ingenious contrivance of Dr. Wollaston, called the *Scale of Chemical Equivalents.* This useful instrument 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 88 parts, or one equivalent of sulphate of potash contain 40 parts of sulphuric acid and 48 of potash; 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 potash on the fixed part of the scale, the numbers opposite to the terms sulphuric acid and potash will give the precise quantity of each

contained in 100 parts of the compound. In the original scale of Dr. 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 Mr. Boswell Reid of Edinburgh.

Acid, acetic,	50 or 51	Acid, perchloric, (chl. 36 + 0.56)	92
c. 1 w*.	59 or 60	phosphorous, (p. 15.71 + 12)	27.71
arsenic, (a. 38 + ox. 20 Berz.)	58	phosphoric, (p. 15.71 + 20)	35.71
arsenious, (a. 38 + ox. 12 Berz.)	50	saccholactic,	104
benzoic,	120	selenious, (sel. 40 + 0.16)	56
boracic, (b. 8 + 0.16)	24	selenic, (s. 40 + 0.24)	64
c. 2 w.	42	succinic,	50
bromic, (b. 78.26 + ox. 40 Berz.)	118.26	sulphuric, dry (s. 16 + 0.24)	40
carbonic, (c. 6 + 0.16)	22	liquid, sp. gr. 1.4838, 1 w.	49
chloric, (chl. 36 + 0.40)	76	sulphurous, (s. 16 + 0.16)	32
chloriodic, (chl. 72 + iod. 124)	196	tartaric,	66
chloro-carbonic, (chl. 36 + carb. oxide, 14)	50	c. 1 w.	75
chlorocyanic (chl. 36 + cyan. 26)	62	titanic,	48
chromic, (chr. 32 + ox. 20)	52	tungstic, (t. 96 + 0.24)	120
citric,	58	uric,	72
c. 2 w.	76	Alcohol, (ole. gas 14 + aq. vap. 9)	23
columbic,	152	alum, anhydrous,	262
fluoboric,	68?	+ c. 25 w.	487
hydro-fluoric,	19.86	Alumina,	18
formic,	37	sulphate,	58
fluosilicic,	26.86?	Aluminium,	10
gallic?	62	Ammonia, (nit. 14 + hyd. 3)	17
hydriodic, (iod. 124 + hyd. 1)	125	Antimony,	44
hydrobromic, (b. 78.26 + h. 1.)	79.26	chloride, (ant. 44 + chl. 34)	80
hydrocyanic, (cyan. 26 + hyd. 1)	27	iodide, (ant. 44 + iod. 124)	168
hyposulphurous, (s. 32 + 0.8)	40	oxide, (ant. 44 + 0.8)	52
hyposulphuric, (s. 32 + 0 40)	72	deutoxide,	56
iodic, (iod. 124 + 0.40)	164	peroxide,	60
malic, (Liebig)	57	sulphuret,	60
manganeseous?	52	Arsenic,	38
manganesic,	60	sulphuret, (realgar)	54
molybdous,	64	†sesquisulphuret, (orpiment)	62
molybdic,	72	persulphuret,	78
muriatic, (chl. 36 + hyd. 1)	37	Barium,	70
nitric, dry (nit. 14 + 0.40)	54	chloride, (b. 70 + chl. 36)	106
liquid (sp. gr. 1.5) 2 w.	72	iodide, (b. 70 + iod. 124)	194
nitrous, (nit. 14 + 0.32)	46	oxide, (baryta)	78
oxalic,	36	peroxide?	86
c. 3 w.	63	phosphuret,	85.71
		sulphuret,	86
		Bismuth,	72
		chloride, (b. 72 + chl. 36)	108

* C means crystallized, w, water; and the numeral before w, expresses the number of equivalents of water which the crystals contain.

† 1 Proportion of arsenic, and $1\frac{1}{2}$ sulphur.

Bismuth, oxide, . . 80
iodide, (b. 72 + iod. 124) 196
phosphuret, (b. 72 + p. 12) 87.71
sulphuret, (b. 22 + s. 16) 88
Boron, . . . 8
Bromine, . . (Berz.) 78.26
Cadmium, . . . 56
chloride, (cad. 56 + chl. 36) 92
oxide, . . 64
iodide, . . . 144
phosphuret, . 71.71
sulphuret, . . 72
Calcium, . . . 20
chloride, (cal. 20 + chl. 36) 56
iodide, . . . 144
oxide, (lime) . . 28
phosphuret, . . 35.71
sulphuret, . . 36
Carbon, . . . 6
bisulphuret, (c. 6 + s. 32) 38
chloride, . . 42
perchloride, . . 120
oxide, . . . 14
phosphuret, . 21.71
Cerium, . . . 50
oxide, . . . 58
peroxide, . . 62
Chlorine, . . . 36
hydrocarburet, (chl. 36 + olef. gas 14) . . 50
oxide, (chl. 36 + 0.8) . 44
peroxide, . . 68
Chromium, . . . 32
oxide, . . . 40
Cobalt, . . . 26
chloride, (cob. 26 + chl. 36) 62
iodide, . . . 150
oxide, . . . 34
peroxide, . . 38
phosphuret, . . 41.71
sulphuret, . . 42
Columbium, . . 144
Copper, . . . 64
chloride, (cop. 1 + chl. 1.) 100
bi-chloride, (c. 1 + chl. 2) 136
iodide, (c. 1 + iod. 1) . 188
oxide, (c. 1 + 0.1) . 72
peroxide, (c. 1 + 0.2) . 80
phosphuret, . . 79.71
sulphuret, . . 80
bi-sulphuret, . . 96
Copper, (Thomson) . . 32
Cyanogen, (carb. 2 + nit. 1) . 26
Cyanuret of sulphur, (cy. + 1 s. 2.) . . . 58
Ether, (olef. gas 2 + wat. vap. 1.) . . . 37
Fluorine, . . 18.86
Glucinium, . . . 18
Glucina, . . . 26
Gold, . . . 200
chloride, (g. 1 + chl. 1.) 236
Gold, bichloride, (g. 1. + chl. 2.) 272
iodide, (g. 1. + iod. 1) 324
oxide, (g. 1. + 0.1) . 208
peroxide, (g. 1 + 0.3) 224
sulphuret, (g. 1 + s. 3) 248
Hydrogen, . . . 1
arseniuretted, (a. 1. + h. 1.) 39
carburetted. (c. 1 + h. 2) 8
olefiant gas, (c. 2 + h. 2) 14
seleniuretted, (s. 1 + h. 1) 41
sulphuretted, (s. 1 + h. 1) 17
bisulphuretted, (s. 2 + h. 1) 33
Iodine, . . . 124
Iridium, . . (Berz.) 99
Iron, . . . 28
chloride, (I. 1 + chl. 1) 64
perchloride, (I. 1 + chl. 1½) 82
iodide, (I. 1 + iod. 1) . 152
oxide, (I. 1 + 0.1) . 36
peroxide, (I. 1 + 0.1½) 40
sulphuret, (I. 1 + s. 1) 44
bisulphuret, (I. 1 + s. 2) 60
Lead, . . . 104
chloride, (l. 1 + chl. 1) 140
oxide, (l. 1 + 0.1) . 112
deutoxide, (l. 1 + 0.1½) 116
peroxide, (l. 1 + 0.2) 120
phosphuret, (l. 1 + p. 1) 119.71
sulphuret, (l. 1 + s. 1) 120
Lithium, . . 10
chloride, (l. 1 + ch. 1.) 46
iodide, . . . 134
oxide, (lithia) . . 18
sulphuret, . . 26
Magnesium, . . . 12
chloride, (m. 1 + chl. 1) 48
oxide, . . . 20
sulphuret, . . 28
Manganese, . . . 28
chloride, (m. 1 + chl. 1) 64
perchloride, (m. 1 + chl. 4) 172
oxide, (m. 1 + 0.1) . 36
deutoxide, (m. 1 + 0.1½) 40
peroxide, (m. 1 + 0.2) 44
sulphuret, . . 44
Mercury, . . . 200
chloride, (calomel) m. 1 + chl. 1) . . 236
bichloride, (corrosive subl.) 272
iodide, (m. 1 + iod.) 324
biniodide, (m. 1 + iod. 2) 448
oxide, (m. 1 + 0.1) 208
peroxide, (m. 1 + 0.2) 216
sulphuret, . . 216
bisulphuret, . . 232
Molybdenum, . . 48
oxide, (m. 1 + 0.1) . 56
deutoxide, (m. 1 + 0.2) . 64
Molybdic acid, (m. 1 + 0.3) . 72
Nickel, . . . 26
chloride, (m. 1 + chl. 1) 62
iodide, . . . 150

Nickel, oxide, (n. 1 + 0.1) . 34
peroxide, (n. 1 + 0.1½) . 38
phosphuret, . . 41.71
sulphuret, . . 42
Nitrogen, . . . 14
bicarburet, (cyanogen) . 26
chloride, (n. 1 + chl. 4) . 158
iodide, (n. 1 + iod. 3) . 386
oxide, (n. 1 + 0.1) . . 22
deutoxide, . . 30
Oxygen, ... 8
Palladium, . (Berz.) about 53
oxide, . . 61
Phosphorus, . (Berz.) 15.71
chloride, (p. 1 + chl. 1) . 51.71
bichloride, . . 87.71
carburet, . . . 21.71
sulphuret, . . 31.71
Platinum, . (Berz.) about 99
chloride, (p. 1 + chl. 1) . 135
bichloride, . . 171
oxide, . . . 107
deutoxide, . . 115
sulphuret, . . . 115
bisulphuret, . . 131
Potassium, . . . 40
chloride, (p. 1 + chl. 1) . 76
iodide, . . . 164
oxide, (potash) . . 48
peroxide, (p. 1 + 0.3) . 64
phosphuret, . . 55.71
sulphuret, . . 56
Rhodium . (Berz.) about 52
oxide, . . 60
peroxide . . 64
Selenium, . . . 40
Silica, . . . 16
Silicium, . . . 8
Silver, ... 110
chloride, (s. 1 + chl. 1) . 146
iodide, . . . 234
oxide, (s. 1 + 0.1) . 118
phosphuret, . . 125.71
sulphuret, . . 126
Sodium, . . . 24
chloride, (s. 1 + chl. 1) . 60
iodide, . . . 148
oxide, (soda) . . 32
peroxide, (s. 1. + 0.1½) . 36
phosphuret, . . 39.71
sulphuret, . . . 40
Strontium, . . . 44
chloride, . . . 80
iodide, . . . 140
oxide, (strontia) . . 52
phosphuret, . . 59.71
sulphuret, . . 60
Sulphur, . . . 16
chloride, (s. 1 + chl. 1) . 52
iodide, (s. 1. + iod. 1) . 140
phosphuret, . 31.71
Sulphuretted hydrogen, . . 17
Bisulphuretted hydrogen, . 33
Tellurium, (Berzelius) . . 32
chloride, . . 68
oxide, . . . 40
Tin, ... 58
chloride, (t. 1 + chl. 1) . 94
bichloride, . . . 130
oxide, . . 66
deutoxide, . . 74
phosphuret, . . 73.71
sulphuret, . . 74
bisulphuret, . . 90
Titanium, . . . 32
oxide, . . . 40
Titanic acid, . . . 48
Tungsten, . . . 96
oxide, (brown,) (t. 1 + 0.2) 112
Tungstic acid, (t. 1 + 0.3) 120
Uranium, . . . 208
oxide, . . . 216
peroxide, . . 224
Water, . . . 9
Yttrium, . . . 34
Oxide, (Yttria) . . . 42
Zinc, ... 34
chloride, . . . 70
oxide, . . . 42
phosphuret, . . 49.71
sulphuret, . . 50
Zirconium, . . . 40
Zirconia, . . . 48

SALTS.

Acetate of alumina, (Ac. 1 + Al. 1.) 68
c 1 w. . . . 77
ammonia, (Ac. 1 + Am. 1.) 67
c. 7 w. . . . 130
Baryta, (Ac. 1 + B. 1.) . 128
c 3 w. . . . 155
cadmium, (c 2 w.) . 132
copper per-oxide, (Ac. 1 + C. 1.) 130
c. 6 w. com. verdigris, . 184
binacetate, . . 180
c. 3 w. distilled verdigris, . 207
subacetate, (Ac. 1 + C. 2.) 210
lead, . . . 162
c. 3 w. . . . 189
lime, . . . 78
magnesia, . . 70
mercury, (protoxide) c. 4 w. 294
potash, . . . 98
silver, . . . 168
strontia, c. 1 w. . . 111
zinc, ... 92
c. 7 w. . . . 155
Arseniate of lead, (A. 1 + 1.1) 170
lime, . . . 86
magnesia, . . 78
potash, . . 106
Binarseniate of potash, c. w. . 90
Arseniate of soda, . . 110

Binarseniate of soda, c. w. . 176
Arseniate of strontia, . 114
silver, . . 180
Arsenite of lime, (A. 1 + L. 1) 78
potash, . . 98
Arsenite of soda, . . 82
silver, . . 168
Carbonate of ammonia, (C. 1 + A. 1) . . . 39
Sesquicarbonate of ammonia, (C. 1½ + A. 1 + w. 1.) . 59
Bicarbonate of do 1 w. . . 70
Carbonate of baryta, . . 100
copper, . . 102
iron, (protoxide) . . 58
lead, . . . 134
lime, . . . 50
magnesia, . . . 42
manganese, . . 58
potash, . . 70
Bicarbonate of potash, . . 92
c. 1. w. . . 101
Carbonate of soda, . . 54
c. 10 w. . . 144
Bicarbonate of soda, c. 1 w. . 85
Carbonate of strontia, . . 74
zinc, . . . 64
Chlorate of baryta, (Ch. 1 + B. 1) 154
lead, . . 188
mercury, . . 284
potash, . . 124
Chromate of baryta, . . 130
lead, . . 164
mercury, . . 260
potash, (Chr. 1 + P. 1) . 100
Bichromate of potash, . . 152
Muriate of ammonia, (M. 1 + A. 1) 54
baryta, c. 1 w. . . 124
lime, c. 6 w. . . 119
magnesia, . . 57
strontia, c. 8 w. . . 161
Nitrate of ammonia, (N. 1 + A. 1) 71
baryta, . . . 132
bismuth, c. 3. . . 161
lead, . . . 166
lime, . . 82
magnesia, . . 74
mercury protoxide, c. 2 w. . 280
potash, . . . 102
silver, . . . 172
soda, . . . 86
strontia, . . 106
Oxalate of ammonia, (Ox. 1 + A. 1) 52
c. 2 w. . . 71
baryta, . . . 114
Binoxalate of baryta, . 150
Oxalate of cobalt, . . 70
lime, . . . 64
nickel, . . 70
potash, . . . 84
c. 1 w. . . 93
Binoxalate of potash, . . 120
c. 2 w. . . 138
Quadroxalate of potash, . 192
c. 7 w. . . . 255
Oxalate of strontia, . . 88
Binoxalate of strontia, . . 124
Phosphate of ammonia, c. 2 w. 70.71
baryta, . . 113.71
lead, . . . 147.71
lime, . . . 63.71
magnesia, . . 55.71
soda, . . . 67.71
c. 12½ w. . . 180.21
Sulphate of alumina, . . 58
ammonia, c. 1 w. . 66
baryta, . . . 118
Sulphate of copper, (S. 1 + perox. 1) 120
Bisulphate of ditto, . . 160
c. 10 w. (blue vitriol) . 250
Sulphate of iron, (protoxide) . 76
c. 7 w. (green vitriol) . 139
lead, . . . 152
lime, . . . 68
c. 2 w. . . 86
lithia, c. 1 w. . . 67
magnesia, c. 7 w. . 123
mercury, (S. 1 + perox. 1) 258
Bisulphate of mercury, (peroxide) 296
potash, . . 88
Bisulphate of potash, c. 2 w. . 146
Sulphate of soda, . . 72
c. 10 w. . . 162
strontia, . . . 92
zinc, . . . 82
c. 7 w. . . 145
Sulphate of alumina and potash, 262
c. 25 w. (alum) . . 487
Nitrate of lead, (T. 1 + L. 1) . 178
lime, . . . 94
potash, . . 88
Bitartrate of potash, . . 180
c. 2 w. (cream of tartar) . 198
Tartrate of antimony and potash, c. 3 w. (tartar emetic) . 363

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	66° F.	0.616		100° F.	1.86	1.860
33	0.207		67	0.655		101	1.92	
34	0.214		68	0.676		102	1.98	
35	0.221		69	0.698		103	2.04	
36	0.229		70	0.721	0.726	104	2.11	
37	0.237		71	0.745		105	2.18	2.100
38	0.245		72	0.770		106	2.25	
39	0.254		73	0.796		107	2.32	
40	0.263	0.250	74	0.823		108	2.39	
41	0.273		75	0.854	0.860	109	2.46	
42	0.283		76	0.880		110	2.53	2.456
43	0.294		77	0.910		111	2.60	
44	0.305		78	0.940		112	2.68	
45	0.316		79	0.971		113	2.76	
46	0.328		80	1.00	1.010	114	2.84	
47	0.339		81	1.04		115	2.92	2.820
48	0.351		82	1.07		116	3.00	
49	0.363		83	1.10		117	3.08	
50	0.375	0.360	84	1.14		118	3.16	
51	0.388		85	1.17	1.170	119	3.25	
52	0.401		86	1.21		120	3.33	2.300
53	0.415		87	1.24		121	3.42	
54	0.429		88	1.28		122	3.50	
55	0.443	0.416	89	1.32		123	3.59	
56	0.458		90	1.36	1.360	124	3.69	
57	0.474		91	1.40		125	3.79	3.830
58	0.490		92	1.44		126	3.89	
59	0.507		93	1.48		127	4.00	
60	0.524	0.516	94	1.53		128	4.11	
61	0.542		95	1.58	1.640	129	4.22	
62	0.560		96	1.63		130	4.34	4.366
63	0.578		97	1.68		131	4.47	
64	0.597		98	1.74		132	4.60	
65	0.616	0.630	99	1.80		133	4.73	

Table II. continued.

Temp.	Force of Vapour.		Temp.	Force of Vapour.		Temp.	Force of Vapour.	
	Dalton.	Ure.		Dalton.	Ure.		Dalton.	Ure.
134° F.	4.86		175° F.	13.62	13.550	216° F.	32.46	33.400
135	5.00	5.070	176	13.92		217	33.09	
136	5.14		177	14.22		218	33.72	
137	5.29		178	14.52		219	34.35	
138	5.44		179	14.83		220	34.99	35.540
139	5.59		180	15.15	15.160	221	35.63	36.700
140	5.74	5.770	181	15.50		222	36.25	
141	5.90		182	15.86		223	36.88	
142	6.05		183	16.23		224	37.53	
143	6.21		184	16.61		225	38.20	39.110
144	6.37		185	17.00	16.900	226	38.89	40.100
145	6.53	6.600	186	17.40		227	39.59	
146	6.70		187	17.80		228	40.30	
147	6.87		188	18.20		229	41.02	
148	7.05		189	18.60		230	41.75	43.100
149	7.23		190	19.00	19.000	231	42.49	
150	7.42	7.530	191	19.42		232	43.24	
151	7.61		192	19.86		233	44.00	
152	7.81		193	20.32		234	44.78	46.800
153	8.01		194	20 77		235	45.58	47.220
154	8 20		195	21.22	21.100	236	46.39	
155	8.40	8.500	196	21.68		237	47.20	
156	8.60		197	22.13		238	48.02	50.300
157	8.81		198	22.69		239	48.84	
158	9.02		199	23.16		240	49.67	51.700
159	9.24		200	23 64	23.600	241	50.50	
160	9.46	9.600	201	24.12		242	51.34	53.600
161	9.68		202	24.61		243	52.18	
162	9.91		203	25.10		244	53.03	
163	10.15		204	25.61		245	53.88	56.340
164	10.41		205	26.13	25.900	246	54.68	
165	10.68	10.800	206	26.66		247	55.54	
166	10.96		207	27.20		248	56.42	60.400
167	11.25		208	27.74		249	57.31	
168	11.54		209	28.29		250	58.21	61.900
169	11.83		210	28 84	28.880	251	59.12	63.500
170	12.13	12.050	211	29.41		252	60.05	
171	12.43		212	30.00	30.000	253	61.00	
172	12.73		213	30.60		254	61.92	66.700
173	13.02		214	31.21		255	62.85	67.25
174	13.32		215	31.83		256	63.76	

Table II. continued.

Temp.	Force of Vapour.		Temp.	Force of Vapour.		Temp.	Force of Vapour.	
	Dalton.	Ure.		Dalton.	Ure.		Dalton.	Ure.
257° F.	64.82	69.800	280° F.	88.75	101.900	303° F.	115.32	147.700
258	65.78		281	89.87	104.400	304	116.50	
259	66.75		282	90.99		305	117.68	150.560
260	67.73	72.300	283	92.11	107.700	306	118.86	154.400
261	68.72		284	93.23		307	120.03	
262	69.72	75.900	285	94 35	112.200	308	121.20	157.700
263	70.73		286	95.48		309	122.37	
264	71.74	77.900	287	96.64	114.800	310	123.53	161.300
265	72.76	78.040	288	97.80		311	124.69	164.800
266	73.77		289	98.96	118.200	312	125.85	167.000
267	74.79	81.900	290	100.12	120.150	313	127.00	
268	75.80		291	101.28		314	128.15	
269	76.82	84.900	292	102.45	123.100	315	129.29	
270	77.85	86.300	293	103.63		316	130.43	
271	78.89	88.000	294	104.80	126.700	317	131.57	
272	79.94		295	105.97	130.400	318	132.72	
273	80.98	91.200	296	107.14		319	133.86	
274	82.01		297	108.31	133.900	320	135.00	
275	83.13	93.480	298	109.48	137.400	321	136.14	
276	84.35		299	110.64		322	137.28	
277	85.47	97.800	300	111.81	139.700	323	138.42	
278	86.50		301	112.98		324	139.56	
279	87.63	101.600	302	114.15	144.300	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	13.00	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	304°	30.00
165	86.40	135	12.15	254.3	143.70	307.6	32.60
170	92.80	140	13.90	258.6	151.60	310	33.50
175	99.10	145	15.95	260	155.20	315	35.20
180	108.30	150	18.00	262	161.40	320	37.06
185	116.10	155	20.30	264	166.10	322	37.80
190	124.80	160	22.60			326	40.20
195	133.70	165	25.40			330	42.10
200	142.80	170	28.30			336	45.00
205	151.30	173	30.00			340	47.30
210	166.00	178.3	33.50			343	49.40
		180	34.73			347	51.70
		182.3	36.40			350	53.80
		185.3	39.90			354	56.60
		190	43.20			357	58.70
						360	60.80
						362	62.40

TABLE IV.

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 V.

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	52.602	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	1.2528	34.271	1.0540	7.970
1.4228	60.572	1.2462	33.474	1.0485	7.273
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
1.3973	55.790	1.2084	28.692	1.0159	2.391
1.3948	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 VI.

Table of Lowitz showing the Quantity of absolute Alochol 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	0·889	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	0·809	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	0·878	34	66	0·948	0·951	0	100	1·000	
67	33	0·875	0·879	33	67	0·950	0·953				

TABLE VII.

Tables showing the Specific Gravity of Liquids, at the Temperature of 55° Fahr. corresponding to the Degrees of Baumé'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

DESCRIPTION OF THE PLATES.

Fig. 1. Mercurial trough made of cast iron. A is the body of the trough, B B the hollow or reservoir for containing the mercury, and C the shelf for supporting inverted glasses filled with mercury. *e* is a hole for receiving the beak of a retort ; *f* a hollow in the side of the trough, against which the neck of the retort rests; and D an inverted jar full of mercury for collecting gas.

Fig. 2. A represents the hydro-pneumatic trough nearly filled with water. B is the shelf of the trough for supporting the jar C, which is full of water, and inverted in that liquid. D is a plain retort, the beak or open extremity of which, E, dips under the surface of the water, and terminates under the shelf. As the gas issues from the retort, it passes through a funnel-shaped aperture purposely made in the shelf, and is collected in the inverted jar. F is an argand lamp, and G a stand with rings; the one for supporting, and the other for applying heat to the retort.

Fig. 3. Woulfe's apparatus, intended for transmitting gases through liquids. The gas generated in the bottle A is transmitted through the solutions contained in B and C, or through any number of bottles similarly disposed; and if any portion of the gas is not absorbed, it may be collected by means of the tube D.

Fig. 4. A bottle with two necks for collecting hydrogen, carbonic acid, or other gases which do not require heat for their evolution. By means of the tube B, dilute acid may be introduced into the bottle during an experiment, without the necessity of withdrawing the cork and re-admitting the air. The gas, as it is formed, passes along the bent tube C; and it may be collected by placing the free extremity of the tube under the water of the hydro-pneumatic trough. The same apparatus is very convenient for transmitting gases through liquids.

If heat is necessary to the production of the gas, the plain retort in figure 2 may be employed; or the tube C of figure 4 may be fixed by means of a cork into a common digesting flask. If a liquid is to be added during the course of the operation, the tubulated retort, figure 10, should be used, to the tubular B of which the bent tube B, figure 4, may be adapted.

Fig. 5. Welter's safety tube, for connecting the bottles of Woulfe's apparatus. By means of this contrivance gas is allowed to escape, should the pressure within the apparatus be too great; or air is admitted into the vessel, should any sudden condensation ensue. The bulb A should be half filled with some liquid, such as water or mercury.

Fig. 6. A still for the purpose of distillation. A is the boiler; B is the head or capital; C the refrigerator to be filled with cold water; D a convoluted metallic tube called the worm, the exterior of which is kept cool by the water in the refrigerator, in order to condense the vapour within; E the lower extremity of the worm at which the condensed vapour issues.

Fig. 7. Davy's safety lamp. A represents the body of the lamp, with a small bent wire for cleaning the wick. B is the cage of wire gauze with which the flame is surrounded.

Fig. 8. Earthen ware table furnace, sold by Watkins and Hill, Charing Cross. A is the fireplace; C the lower part of the furnace for containing the grate and ash-pit; B a cover which is the beginning of the flue; E the flue. *aa* are small pieces of pottery, which may be removed at pleasure either for the purpose of adding fuel, or that the neck of a retort may pass out. *bb* are similar pieces of earthenware to act as dampers for regulating the supply of air. *cc* a tube represented in a position for being heated to redness.

Fig. 9. A section of the same furnace as figure 8.

A similar furnace, made with sheet-iron, and lined with refractory clay, is well known by the name of Knight's furnace. These furnaces are converted into excellent wind furnaces by lengthening the flue with funnel pipe; and they are made into blast furnaces by supplying a draught of air by bellows. By removing the cover B, a vessel may be placed directly over the burning fuel, or be heated by means of a sand bath. The fuel should be either charcoal or coke.

Fig. 10. A tubulated retort and receiver. A the body of the retort; B the tubular with its stopper, and C the beak or neck. D is the receiver, and E its tubular and stopper. This apparatus is much employed for distilling liquids which from their nature or small quantity cannot be distilled in the ordinary still. The tubular admits of fresh fluid being added without discontinuing the process. The tubular in the receiver is convenient either for draining off the distilled liquid, or allowing the escape of gaseous matter. Plain retorts and receivers are similar to those represented in the figure, but have not any tubular.

Fig. 11. The Alembic with its receiver. A the body in which the fluid is placed, B its head, fitted accurately to A by grinding, and D the tube for conducting the distilled liquid into the receiver C. The glass Alembic was formerly much used for distillation, but is now almost entirely superseded by the retort.

Fig. 12. Hessian crucible made of coarse pottery ware, capable of supporting intense heat without fusing.

Fig. 13. Evaporating capsule, made either of Wedgewood ware or porcelain.

Plate 1.

Fig. 1.

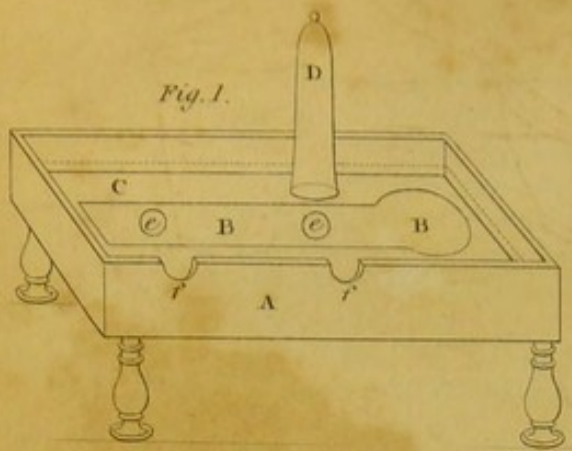


Fig. 3.

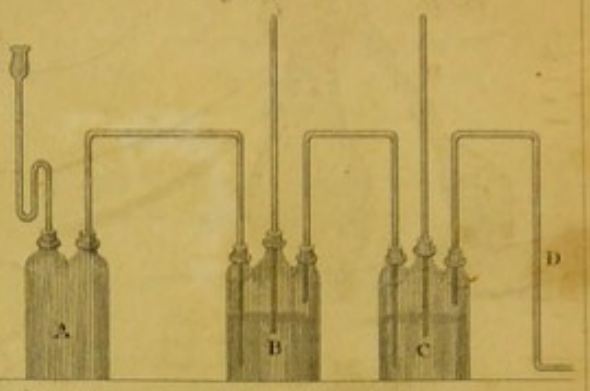


Fig. 6.

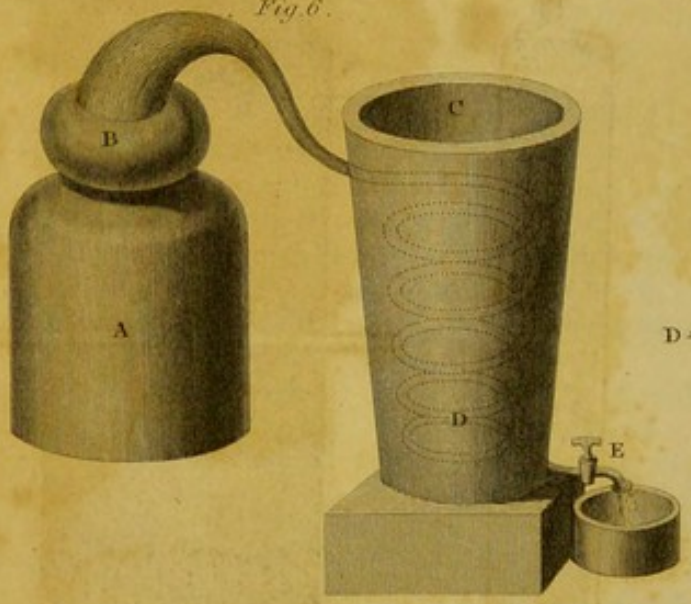


Fig. 4.

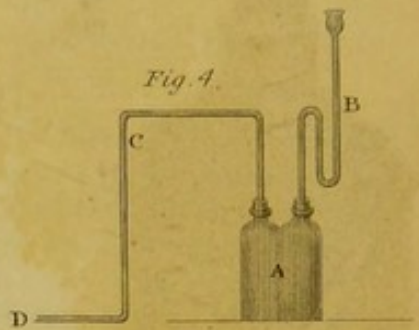


Fig. 5.

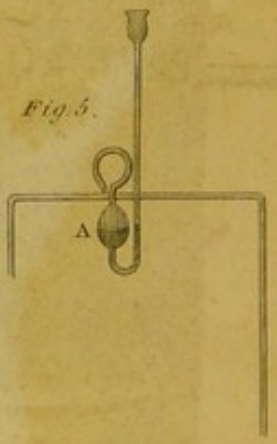


Fig. 2.

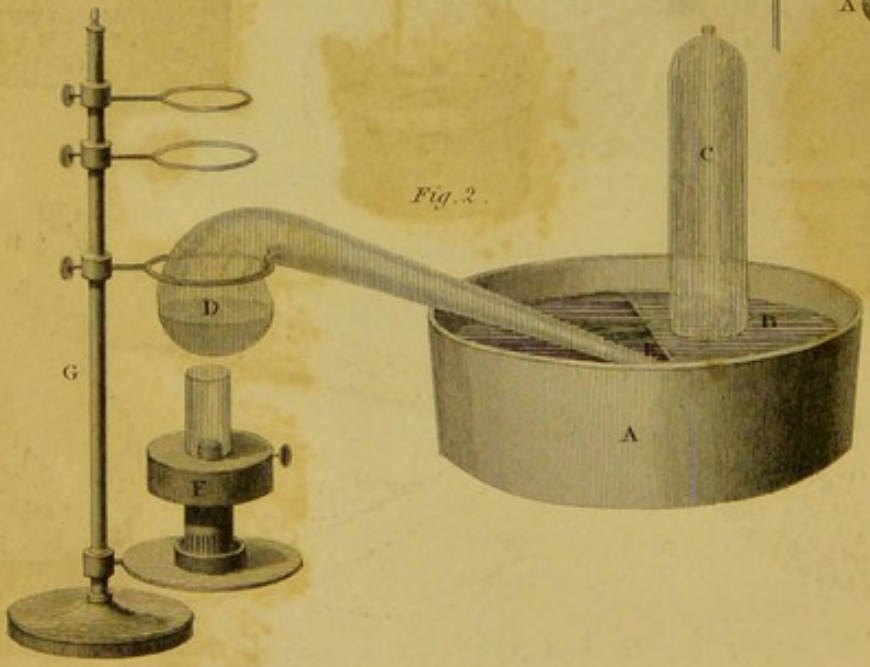


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Plate 2.

Fig. 11.

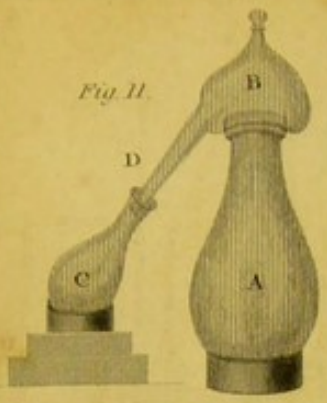

Fig. 12.

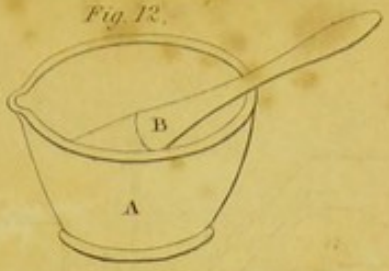

Fig. 13.

Fig. 8.

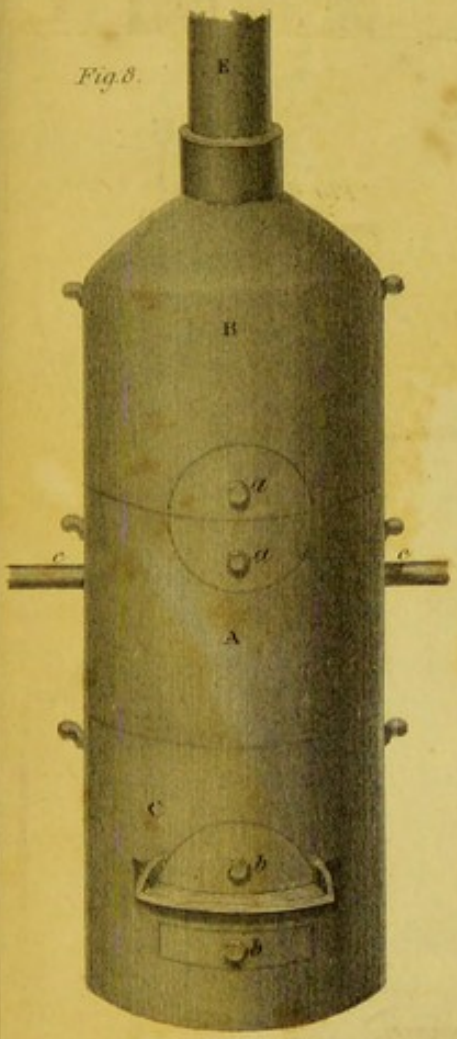

Fig. 7.

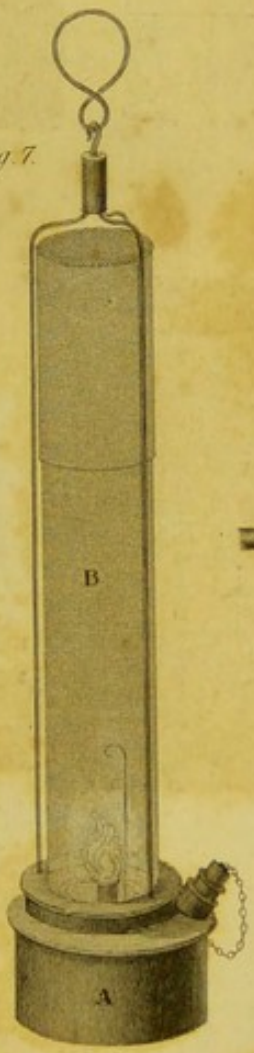

Fig. 9.

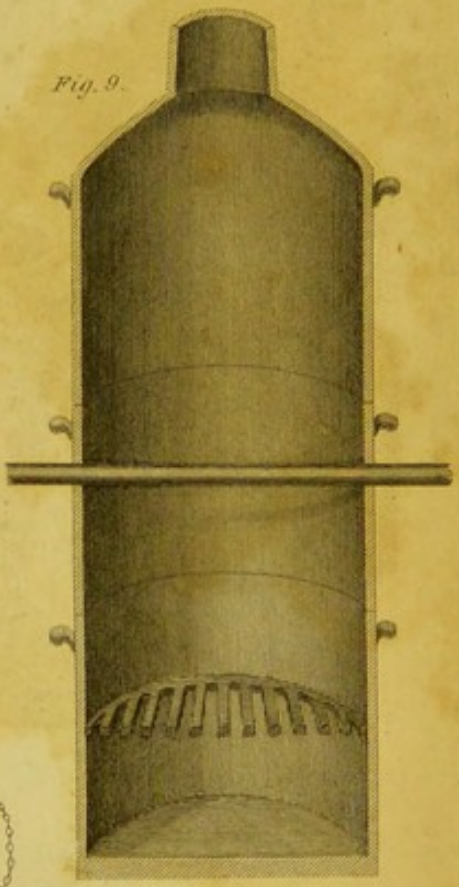

Fig. 10.

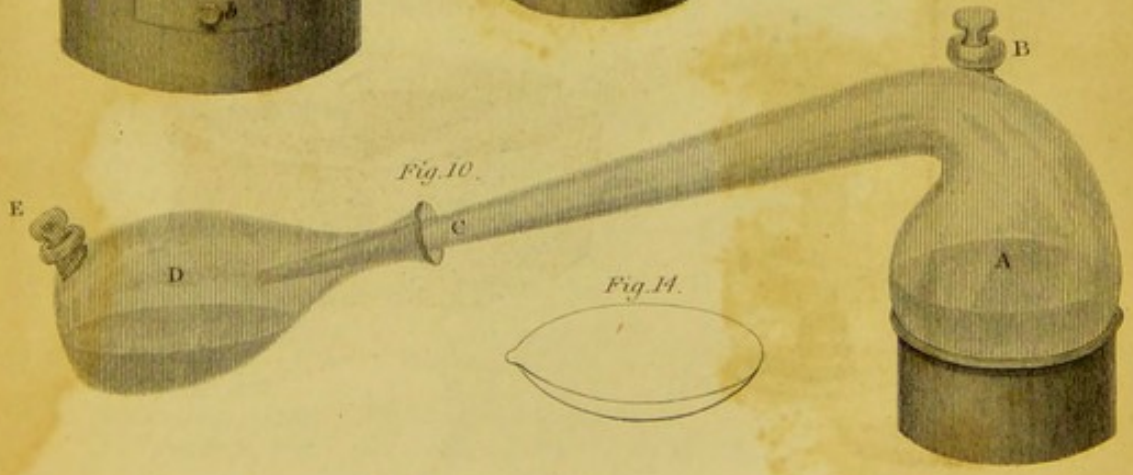

Fig. 14.

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GENERAL INDEX.

A

Acetates, 677
Acetous fermentation, 778
Acidifying principles, 588
Acids, definition of, 588
  nomenclature of, 141
Acids, acetic and acetous, 675
  vegetable, 674
  amylic, 750
  animal, 802
  amniotic, 807
  antimonic and antimonious, 529
  arsenic, 510
  arsenious, 505
  auric, 566
  benzoic, 693
  boletic, 698
  boracic, 282
  bromic, 331
  butyric, capric, caproic, 811
  camphoric, 697
  carbazotic, 701
  carbonic, 251
  caseic, 844
  ceric, 664
  chloric, 303
  chloriodic, 323
  chloro-cyanic, 386
  chloro-carbonic, 309
  chloro-chromic, 518
  chlorous, 300
  cholesteric, 813
  chromic, 516
  citric, 690
  columbic, 524
  cyanic, 382
  cyanous, 383, 385
  ellagic, 695
  erythric, 805
  ferro-cyanic, 390
  ferruretted chyazic, 392
  fluo-boric, 339
  fluo-chromic, 518
  fluoric, 337
  fluo-silicic, 467
  formic, 806
  fulminic, 385
  gallic, 604
  hippuric, 806
  hircic, 811
  hydriodic, 317
  hydro-bromic, 329
  hydro-chloric, 294
Acids, hydro-cyanic, 376
  hydro-fluoric, 335
  hydro-selenic, 368
  hydro-xanthic, 396
  hypo-nitrous, 236
  hypo-phosphorous, 280
  hypo-sulphuric, 270
  hypo-sulphurous, 269
  igasuric, 699
  indigotic, 702
  iodic, 320
  iodous, 322
  kinic, 699
  lactic, 807
  lampic, 736
  lithic, 802
  malic, 691
  manganesic and manganeseous, 477
  margaric, 719 & 810
  meconic, 700 and 707
  mellitic, 699
  molybdic and molybdous, 519
  moroxylic, 698
  mucic, 697
  muriatic, 294
  nitric, 240
  nitro-muriatic, 299
  nitrous, 237
  oleic, 719 and 810
  oxalic, 681
  oxymuriatic, 289
  pectic, 700
  perchloric, 304
  phocenic, 811
  phosphatic, 280
  phosphoric, 274
  phosphorous, 279
  prussic, 376
  purpuric, 804
  pyro-citric, 691
  pyroligneous, 675
  pyromalic, 692
  pyromucic, 698
  pyrophosphoric, 277
  pyro-tartaric, 686
  pyro-uric, 804
  rheumic, 698
  rosacic, 805
  saccholactic, 697
  sebacic, 811
  selenic, 286
  selenious, 286
  silicic, 465
Acids, silico-fluoric, 468
  sorbic, 698
  stearic, 810
  suberic, 699
  succinic, 696
  sulpho-naphthalic, 359
  sulphuric, 264
  sulphurous, 261
  sulphuretted chyazic, 393
  sulpho-cyanic, 393
  sulpho-vinic, 734
  tartaric, 685
  titanic, 539
  tungstic, 521
  uric, 802
  zumic, 699
Adipocire, 812
Aeriform bodies, 4
Affinity, chemical, 144
  table of, 145
  elective simple, 145
  elective double, 149
  disposing, 208
  quiescent and divellent, 149
  by what causes modified, 152
  measure of, 160
Agedoite, 768
Air, atmospheric, 217
Alabaster, 610
Albumen, 795
  vegetable, 764
  incipient, 841
Alcohol, 727
Alembic, fig. 11
Algaroth, powder of, 527
Alizarine, 692
Alkali, volatile, 342
Alkalimeter, 640
Alkalies, definition of, 588
  native vegetable, 703
  decomposition of, by galvanism, 124
Alloys, 583
Aloes, bitter of, 701
Althea, 716
Alum, 611
Alumina, 452
Aluminium and its oxide, 450
Amalgams, 582
Amalgam, ammoniacal, 216
Amber and its acid, 724

Ambergris and ambreine, 813
Ammonia, 342
solution of, 344
character of the salts of, 343
Ammoniuret of copper, 616
Amnios, liquor of, 847
Amidine, 747
Analysis defined, 6
Analysis, proximate and ultimate, of organic substances, 671
of minerals, 869
of gases, 865
of mineral waters, 877
Animal chemistry, 792
proximate principles, 792
substances, analysis of, 672
oils and fats, 808
heat, 830
fluids, 815
Antimony, regulus of, crude antimony, 526,
oxides of, 527
chlorides of, 529
sulphurets of, 530
golden sulphuret of, 531
glass, crocus and liver of, 531
alloys of, 583
tartarized, 688
Anthracite, 742
Apparatus for generating gases, fig. 4
Woulfe's, fig. 3
Aqua regia, 299
Arbor Dianæ, 563
Saturni, 550
Archil, 759
Argentine flowers of antimony, 527
Arrow root, 750
Arseniates, 633
Arsenical solution of, 634
Arsenic, 503
compounds of oxygen, 504
tests of, in mixed fluids, 506
alloys of, 583
chloride of, 511
sulphurets of, 513
Arsenites, 634
Asparagin, 768
Asphaltum, 740
Atmospheric air, 217
analysis of, 865
weight of, 218
Atom, what, 175
Atomic theory, Dalton's view of, 174
Berzelius's view of, 187
Atomic weights, table of, 886
what, 176
Atropa, 716
Attraction, chemical, 5 and 144
cohesive, 3
terrestrial or gravity, 3
Aurum, musivum, 497
Azotic gas, 215

B

Balloons, 203
Balsams, 724
Barilla, 641
Barium, 437
oxides of, 438
chloride and sulphuret of, 440
Barley, malting of, 784
Barometer, correction of, for the effects of heat, 29
Baryta, 438
Basis, in dyeing, what, 754
Bassorin, 768
Battley's sedative liquor, 706
Baumé's hydrometer, degrees of, reduced to the common standard, 898
Bell metal, 584
Benzoates, 694
Bile and biliary calculi, 836
Bismuth and its oxide, 536
magistery of, 537
chloride, bromide, and sulphuret of, 537
alloy of, 583
Bitter principle, 772
Bituminous substances, 739
Black dye, 761
Black drop, 708
Black lead, 487
Bleaching, 293
Bleaching powder, 446
Blende, 489
Blood, 815
Blow-pipe, with oxygen and hydrogen, 205
with oxygen gas, 206
Blue, Prussian, 660
dyes, 754
Boa constrictor, urine of, 803
Boiling point of liquids, 63
Bones, 860
Borates, 637
Borax, 637
Boracite, 638
Boron, 282
chloride of, 310
Brain, analysis of the, 863
Brass, 584
Brazil wood, 691
Bromates, 628
Bromine, 325
Bronze, 584
Brucia, 711
Butyrine, 811
Butter, 811
of antimony, 529

C

Cadmium, 492
oxide of, 493
Caffein, 769
Calamine, 489
Calcium and oxide of lime, 443
chloride of, 445
Calcination, 405
Calculi, urinary, 856
biliary, 839
salivary, 834
Calomel, 557
Caloric, 9
communication of, 11
radiation of, 15
effects of, 23
expansion produced by in solids, 25
liquids, 28
gases, 32
specific, 45
capacities of bodies for, 44
of fluidity, 55
sensible and insensible, 46
latent, 45
sources of, 80
quantity of, in bodies, 58
Calorimeter, 46
Calx, 405
Camphor, 721
Camphorates, 697
Cannon metal, 584
Canton's phosphorus, 448
Caoutchouc, 725
Capacity for caloric, 44
Carbon, 247
compounds of, with hydrogen, 346
nitrogen, 375
chloride of, 305
sulphuret of, 395
Carbonates, general properties of, 638

Carbonates, particular description of, 639-646
Carbonic acid, 251
oxide, 255
Carbo-sulphurets, 395
Carburetted hydrogen, 346
Carmine, 759
Cartilage, 860
Caseous matter, 842
Caseous oxide, 766 and 845
Cassius, purple powder of, 568
Cassava, 750
Catechu, 761
Cathartin, 769
Caustic, lunar, 623
Cerate, 726
Cerin, 726
Cerium and oxides, 534
Cerulin, 757
Ceruse, 645
Cetine, 812
Chalk, 644
Chameleon mineral, 476
Charcoal, 247
animal or ivory black, 247
Cheese, 842
Chemical affinity or attraction, 144
action, changes which accompany it, 149
Chemistry, definition of, 5
organic, 7
inorganic, 7
nomenclature of, 141
Chinoidea, 711
Classification of chemical substances, 6
Chlorates, general characters of, 625
of potash and baryta, 625
Chloric ether, 352
acid, 303
Chloride of boron, 310
bromine, 332
carbon, 305
cyanogen, 386
iodine, 323
nitrogen, 304
phosphorus, 308
sulphur, 308
lime, 446
Chloride of soda, 433
Chlorides, metallic, 407
Chlorine, 289
and hydrogen—muriatic acid, 294
and oxygen, 300
protoxide of, 300
peroxide of, 302
Chlorine, nature of, 311
Chloriodic acid, 323
Chloro-carbonic acid, 309
Chlorophyle, 773
Cholesterine, 813
Chromium, 514
compounds of, with oxygen, 515
Chromates, 635
of iron, 635
Chrome yellow, 636
Cinchona bark, active principle of, 708
Cinchonia, 708
Chyle, 840
Cinnabar, 559
Citrates, 691
Coke, 742
Coal, 740
gas, 361
Cobalt, 497
oxygen, 498
Cocculus indicus, principle of, 714
Cochineal, 759
Cohesive attraction, 3
Cohesion, 3
influence of, over chemical action, 152
Cold, artificial methods of producing, 58 and 69
Colocyntin, 772
Colouring matter, 753
Colours, adjective and substantive, 754
Columbium and its acid, 523 and 524
Combination defined, 5
laws of, 163
Combining proportions explained, 164
Combustion, 197
theories of, 197
spontaneous, 718
Composition of bodies how determined, 6
Conductors of caloric, 11
Congelation, 54
Cooling of bodies, 22
Copal, 723
Coppernickel, 560
Copper, 542
oxides of, 543
chlorides of, 546
sulphurets of, 546
ammoniuret of, 616
alloys of, 584
ammoniacal sulphate of, 615
sheathing, preservation of, 128
Cork, 769
Corrosive sublimate, 555
Corydalin, 714
Coumarin, 722
Cream of milk, 841
Cream of tartar, 687
Crocus of antimony, 531
Cryophorus, 70
Crystallization, 594
Crystallization of salts, 594
water of, 591
Curcuma paper, 760
Curd, 842
Cuticle, 861
Cyanogen, 375
Cyanurets, 415
of chlorine, 386
of bromine, 389
of iodine, 389
metallic, 415
Cyanuret, red, of iron and potassium, 659
Cynopia, 715
Cystic oxide, 859

D

Decomposition, simple, 145
double, 148
Decrepitation, 592
Deflagration, 405
Deliquescence, 590
Delphia, 715
Derosne, salt of, 708
Destructive distillation, 671
Detonating powders, 625
Dew, formation of, 21
Diamond, 250
Differential thermometer 36
Digesting flask, 878
Dippel's oil, 809
Disenfecting liquid, 433
Distillation, apparatus for, fig. 6
Dragon's blood, 723
Dutch gold, 584
Dyes, 753

E

Earths, 421 and 450
Ebullition, 63
Efflorescence, 592
Egg shells, 861
Eggs, 845
Elaine, 719
Elastic gum, 725
Elasticity, its effect on chemical affinity, 156
Elective affinity, 144
Electricity, 89
Electrical machine, 95
Electro-magnetism, 133
Electro-negative and electro-positive bodies, 131

Electro-chemical theory, 126
Electrometer, 102
Elements, what, and how many, 6
Emetia, 714
Emetic tartar, 688
Emulsion, 718
Epsom salts, 611
Equivalent, chemical, what, 168
scale table of, 886
Erythrogen, 839
Essential oils, 719
salt of lemons, 684
Ether, 731
acetic, muriatic, hydriodic, 738 and 739
hydro-bromic, 739
chloric, 352
nitrous, 737
pyro-acetic, 676
sulpho-cyanic, 739
sulphuric, 732
Ethiops mineral, 560
per se, 553
Euchlorine, 300
Eudiometer, 224
Hope's, 867
Volta's, 865
Evaporation, 68
cause of, 71
limit to, 73
Expansion, 24
of solids by heat, 25
liquids by do. 28
gases by do. 32
Extractive matter, 712
Eye, humours of, 847

F

Farina, 747
Fat of animals, 803
Feathers, 862
Fecula, 747
Fermentation, 773
Ferro-cyanates, 657
Fibre, woody, 751
Fibrin, 793
Filter, 876
Fire-damp of coal mines, 343
Flame, 349 and 350
Fixed oils, 717
Flask for digesting, 878
Flesh of animals, 862
Flint, 464
Flowers of sulphur, 260
Fluidity caused by caloric, 54
Fluoric acid, 337
Fluoboric acid, 339
borates, 638
Fluo-silicic acid gas, 467
silicates, 469
Fluorine, 334
Fluor spar, 654
Flux, white and black, 681
Food of plants, 789
Freezing mixtures, 59
in vacuo, Leslie's method, 70
Frigorific mixtures, table of, 59 and 60
Fulminating gold, 567
mercury, 385
platinum, 572
silver, 385
Fulminic acid, 385
Fuming liquor of Libavius, 496
Fungin, 769
Funnel, 876
Fusion, 55
watery, 592
Fusible metal, 584
Fustic, 760

G

Galena, 547
Gallates, 696
Gall-nuts, 761
Gall-stones, 839
Galvanic battery or trough, 113 and 114
arrangements, 107 and 112
Galvanism, 106
effects of, 121
chemical agency of, 123
electrical agency of, 121
connexion of, with magnetism, 133
theories of its production, 115
Gases, 719
condensation of, 79
law of expansion of, 33
conducting power of, 14 and 15
formula for correcting the effects of heat on, 33
specific caloric of, 47
their bulk influenced by moisture, and the formula for correcting its effect, 75
Gases, mode of drying, 78
Gas, from coal and oil, 361
apparatus for generating, fig. 4
Gastric juice, 834
Gelatine, 798
Germination, 783
Gilding, 583
Glass, 465
expansion of, by heat, 27
of antimony, 531
Glauber's salt, 608
Gliadine, 767
Glucina, 456
Glue, 798
Gluten, 765
Glycerine, 719, 809
Gold, 564
oxides of, 566
chlorides of, 567
fulminating compound of, 567
sulphuret of, 568
alloys of, 581
mosaic gold, 497
Golden sulphuret of antimony, 530
Gong, Indian, 584
Goulard's extract, 679
Gouty concretions, 802
Graphite, 487
Gravel, urinary, 855
Gravitation, 2
Gravity, effect of, on chemical action, 161
specific modes of determining, 139
Growth of plants, 786
Gum, 756
elastic, 725
Gum-resins, 724
Gunpowder, 621
Gypsum, 610

H

Hematin, 759
Hair, 862
Harrowgate water, 886
Hartshorn, spirit of, 342
Heat, animal, 830
intense, how generated, 205
Hiccory, wild American, 760
Hircine, 811
Homberg's pyrophorus, 612
Honey, 745
stone, 699
Hoofs, 861
Hordein, 749
Horn, 861
Horn-lead, 551
Horn-silver, 563
Humours of the eye, 847
Hydracids, salts of, 646
Hydrates, nature of, 209
Hydriodates, 651
Hydro, in what manner employed, 210

Hydro-carburet of chlorine, 352
iodine, 354
bromine, 354
Hydro-cyanates, 657
Hydrogen, 202
peroxide of, 211
arseniuretted, 512
carburetted, 346
and carbon, new compounds of, 355
phosphuretted, 369
potassuretted, 429
seleniuretted, 368
sulphuretted, 364
telluretted, 542
with metals, 420
Hydrometer, Baumé's, degrees of, reduced to the common standard, 898
Hydro-sulphuric acid, 366
Hydro-sulphurets or hydro-sulphates, 655
Hygrometer, 76
Hyper-oxymuriates, 625
Hypo-phosphorous acid, 280
Hypo-nitrous, 236
Hypo-sulphurous acid, 269
sulphuric acid, 270

I

Ice. See Water.
Imponderables, 6
influence of, over chemical action, 162
Incandescence, 85
Indigo, 755
acid of, 701
resin of, 701
Indigogene, 758
Ink, 696
sympathetic, 499
Insolubility, influence of; on affinity, 152
Inulin, 770
Iodates, 626
Iodic acid, 320
Iodide of nitrogen, 324
Iodides, metallic, 409
Iodine, 320
and hydrogen—hydriodic acid, 317
and phosphorus, 325
Iodine and sulphur, 325
Ipecacuanha, emetic principle of, 714
Iridium, 576
Iron, 479
oxides of, 483
chlorides of, 486
Iron, sulphuret, phosphuret, and carburets of, 487
Isinglass, 798
Ivory black, 247
Jelly, animal, 798
vegetable, 751

K

Kermes mineral, 531
Kelp, 641
King's yellow, 514

L

Labarraque's soda liquid, 433
Lakes, 753
Lamp without flame, 736
safety, 348 and fig. 7
Lampblack, 723
Lard, 809
Latent heat, 45
Lateritious sediment, 806
Laws of combination, 163
Law of multiples, 167
Lead, 547
oxides of, 549
chloride of, 551
iodide and sulphuret of, 551—552
phosphuret and carburet of, 552
alloys of, 583
Lemons, acid of, 690
essential salt of, 684
Leyden jar, 100
Libavius, fuming liquor of, 496
Ligaments, 862
Light, 81
chemical effects of, 84
Light, heating power of, 83
magnetizing power of, 85
modes of determining its intensity, 87
Lignin, 751
Lime, 443
water and hydrate of, 444
milk of, cream of, 444
chloride of, 446
phosphuret of, 448
stone, 644
Liniment, volatile, 718
Liquefaction, 54
Liquids, expansion of, by heat, 28
conducting powers of, 14
Liquorice-root, sugar of, 746
Litharge, 549
Lithia, 436
Lithates, 803
Lithium, 436
Litmus, 759
paper, 876
Liver of antimony, 531
sulphur (hepar sulphuris), 413
Logwood, 759
Luna cornea, 563
Lunar caustic, 562
Lupulin, 770
Lymph, 846

M

Madder, 760
Magistery of bismuth, 537
Magnesia, 448
Magnesium, 448
Magnetism, electro, 132
Malachite, 645
Malates, 692
Maltha, 740
Malting, 784
Manganese, 469
oxides of, 470
chloride and sulphuret of, 477 and 479
fluoride of, 478
Manganesiates, 477
Manna and mannite, 746
Marble, 644
Massicot, 549
Matter, properties of, 1
Meconic acid, 700 & 707
Medullin, 770
Membranes, 862
Mercurial trough, fig. 1
Mercury, 552
oxides of, 553
chlorides, 555
cyanuret and sulphurets of, 559
iodide of, 558
fulminating, 385
muriate, (corrosive sublimate) 555
submuriate of (calomel, 557
Metallic combinations, 580
general properties of, 399
Metals, 399
table of discovery of, 399
specific gravity, 400
fusibility of, 402
reduction of, 405
combustibility of, 404

Metals, compounds of, with chlorine, 407
iodine, 409
bromine, 410
sulphur, 411
selenium, 415
cyanogen, 415
phosphorus, 419
hydrogen, 420
classification of, 420
Meteoric stones, 480
Milk, 841
sugar of, 801
Mindererus's spirit, 678
Mineral chameleon, 476
Mineral tar, 740
pitch, 740
Mineral yellow, 551
Mineral waters, analysis of, 877
Minium, 551
Molasses, 745
Molybdates, 520
Molybdenum, 519
compounds of, with oxygen, 519
sulphuret of, 520
Mordaunt, 754
Morphia, 704
Mother of pearl, 861
Mucilage, 750
Mucus, 847
Mutiples, law of combination in, 167
Muriates, 647
Muriatic ether, 738
Muscle, 862
converted into fat, 812
Mushrooms, peculiar substance of, 769
Myrica cerifera, wax from, 726
Myricin, 726

N

Nails of animals, 861
Naphtha, 739
from coal tar, 358
Naphthaline, 358
Narcotine, 708
Neutral salt, characters of, 589
Neutralization, 150
Nickel, 500
oxides of, 502
Nitrates, general characters of, 618
particular descriptions of, 618 to 624
Nitre, 620
Nitric acid, 240
oxide, 232
Nitrites, general characters of, 624
Nitrogen gas, 215
protoxide of, 229
deutoxide of, 232
Nitrous acid, 237
gas, 232
oxide, 229
Nomenclature, 141

O

Oil, Dippel's animal, 809
of vitriol, 264
of wine, 734
gas, 361
Oils, animal, 808
fixed, 717
volatile, or essential, 719
Ointment, 726
Olefiant gas, 350
Olive oil, 717, 719
Olivile, 771
Opium, active principle of, 704
Organic chemistry, 668
substances, character of, 668
Orpiment, 513
Osmazome, 862
Osmium and its oxide, 576
Oxalates, 683
Oxalic acid, crystallized, composition of, 681
Oxidation, 195
Oxide, cystic, 859
xanthic, 859
Oxides, what, 195
nomenclature of, 141
Oxygen, 193
Oxy-hydrogen blow-pipe, 205
Oxiodine,
Oxymuriatic acid, 289
Oxymuriate of potash, 625

P

Palladium and its oxide, 573
Pancreatic juice, 834
Paper, preparation of, for tests, 876
Papin's digester, 65
Particles integrant and component, 5
Patent yellow, 551
Pearls, 861
Pearlash, 639
Pericardium, liquor of the, 846
Perspiration, fluid of, 850
Petroleum, 740
Pewter, 584
Phenecin, 757
Phlogiston, 198
Phosgene gas, 309
Phosphates, general characters of, 628
particular description of, 629 to 632
Phosphatic acid, 280
Phosphorescence, 86
Phosphoric acid, 274
ether, 734
Phosphorous acid, 279
Phosphorus, 272
with oxygen, 274
oxides of, 281
with chlorine, 308
with iodine, 325
Canton's, 448
Phosphuret, metallic, 419
Phosphuret of lime, 448
Phosphuretted hydrogen gas, 369
Photometer, 87
Picromel, 836
Picrotoxia, 714
Pinchbeck, 585
Piperin, 770
Pitchblende, 532
Pitch, mineral, 740
Pit coal, 740
Plants, growth of, 786
food of, 789
Plaster of Paris, 610
Plasters, 723
Platinum, 569
chlorides and oxides of, 570
sulphuret of, 571
alloys of, 585
fulminating, 572
Plumbagin, 772
Plumbago, 487
Pluranium, 580
Pollenin, 770
Polycroite, 761
Potash, 425
tests of, 428
Potash, 425
Potassium, 423
oxides of, 425
Potassium, chloride and iodide of, 429
with hydrogen, sulphur, and phosphorus, 430
Potato, starch of, 747
Precipitate, red, 554
Precipitation explained, 151
Pressure, influence of, on the bulk of gases, 140
Proportions in which bodies combine, 163

Proportional numbers defined, 169
table of, 886
Prussian blue, 660
Prussiates, 657
Prussiate triple, 658,
Purple powder of Cassius, 568
Purpurate of ammonia, 805
Pus, 848
Putrefaction, 780 and 863
Putrefactive fermentation, 780 and 863
Pyrites, iron, 486
copper, 546
Pyro-acetic ether, 676
and pyroxilic spirit, 752
Pyrometer, 40
Pyrophorus of Homberg, 612

Q

Quantity, its influence on affinity, 158
Quercitron bark, 760
Quick lime, 443
Quicksilver, 552
Quills, 862
Quina, 708

R

Radiant heat, 15
Rays, luminous, 81
calorific, 82
chemical, 84
Realgar, 513
Red lead, 550
dyes, 759
Reduction of metals, 405
Regulus of antimony, 526
Rennet, 842
Repulsion opposed to cohesion, 25
Resins, 722
Resin of copper, 546
Respiration, 823
Retinasphaltum, 740
Retort, D. fig. 2
Rhéin, 771
Rhodium, 574
oxides of, 575
Rhubarbarin, 771
Rhutenium, 580
Rochelle salt, 688
Rouge, 760
Rusting of iron, 482

S

Saccharine fermentation, 774
Safety lamp, 349
Safflower and saffron, 760
Sago and salep, 750
Sal-ammoniac, 647
Salifiable base, 589
Saliva, 833
Salt, common, 432
of sorrel, 684
petre, 624
spirits, of 297
Salts, general remarks on, 587
nomenclature of, 142 and 143
classification of, 590
affinity of for water, 591
crystallization of, 591
double and triple, 594
Sanguinaria, 716
Sarcocoll, 771
Saturated solution, what, 159
Saxony blue, 757
Scale of equivalents, 886
Scheele's green, 508
Sea water, 881
Secreted animal fluids, 833
Sealing wax, 723
Sediment of the urine, 855
Seignette, salt of, 688
Selenic acid, 286
Selenite, 610
Selenious acid, 286
Selenium, 284
oxide of, 285
Seleniuretted hydrogen, 368
Seleniurets, metallic, 415
Serosity, and serum, 816
Serous membranes, fluid of, 846
Shells, 861
Silica, 464
Silicates, 465
Silicated alkali, 465
Silicium, 462
Silk, 862
Silver and its oxide, 560
chloride of, 563
iodide, cyanuret, and sulphuret of, 564
fulminating compounds of, 385 and 563
alloys of, 586
Skin, 862
Smalt, 497
Soap, 719 and 809
Soda, 431
tests of, 431
Sodium, 430
oxides of, 431
chloride, 433
Solania, 715
Solar rays, 81
Solder, 583
Solids, expansion of, by heat, 25
liquefaction of, 54
conducting power of, 11
specific caloric of, 51
Solution, 158
Sorrel, salt of, 684
Spar, Iceland, 644
fluor, 654
heavy, 609
Specific gravity, 139
caloric, 45
Speculum metal, 584
Spectrum, prismatic, 82
Spelter, 489
Spermaceti, 808
Spirit proof, 729
of wine, 727
pyroxylic and pyro-acetic, 752
Starch, 747
Starkey's soap, 720
Steam, temperature of, 65
elasticity of, 66
latent, heat of, 67
Steam engine, principle of, 66
Stearine, 719 and 809
Steel, 488
new alloys of, 585
Still, common, fig. 6
Strontia, 441
Strontium, 441
oxides and chloride of, 442
Strychnia, 711
Suberin, 769
Succinates, 697
Suet, 809
Sugar, 743
of lead, 678
of grapes, 745
of liquorice root, 746
of milk, and diabetes, 801
Sugar-candy, 744
Sulphates, general characters of, 607
particular description of, 608 to 617
Sulphites, sulphuretted, 269
general characters of, 617
Sulpho-cyanates, 662
Sulphur, 259
compounds of, with oxygen, 261
chlorine, 308
carbon, 395
selenium, 398
Sulphurets, metallic, 411
Sulphurous acid, 261

Sulphuretted hydrogen, 364
Sulphuric acid, 264
table of, 896
ether, 732
Sulphur, balsam of, 720
Supporter of combustion, 193
Surturbrand, 741
Sweat, 850
Synthesis defined, 6

T

Tallow, 809
Tannin, 761
artificial formation of, 764
Tanno-gelatine, 763
Tantalum, 523
Tapioca, 750
Tar mineral, 740
Tartar, cream of, 687
soluble, 687
emetic, 688
Tartrates, 686
Tears, 847
Teeth, 861
Telluretted hydrogen gas, 542
Tellurium and its oxide, 541
Temperature, what, 43
Tenacity of different metals, 401
Tendons, 861
Thermometer, 35
differential, 36
formula for converting the expression of one into another, 28
graduation of, 37
Thermometer, register, 41
Thorina, 459
Tin and oxides of, 494
chlorides and sulphurets of, 496
alloys of, 583
Tincal, 637
Titanium and its compounds with oxygen, 538
Tombac, 585
Trona, 642
Treacle, 745
Trough, galvanic, 113
hydro-pneumatic, fig. 2
mercurial, fig. 1
Tungsten and its compounds with oxygen, 520 and 521
Turpeth mineral, 616
Turmeric, a dye, 760
paper, 760
Turnsol, 759
Turpentine, oil of, 720
Type, metal for, 584

U

Ulmin, 769
Ultra-marine, 433
Uranium and oxides, 532 and 533
Urates, 803
Urea, 799
Urine, 850
Urinary concretions, 856

V

Vacuum, boiling in, 65
evaporation, 68
Vaporization, 61
cause of, 62
Vapour, dilatation of, 62
density of, 62
elastic force of, 65
latent heat of, 67
limit of, 73
table of elastic force, 895
Vegetable acids, 674
alkalies, 703
extract, 772
jelly, 751
chemistry, 671
substances, 671
Vegetation, 786
Veratria, 713
Verdigris, 679
Verditer, 645
Vermilion, 559
Vinegar, 675
Vinous fermentation, 775
Vitriol blue, 615
green and white, 613 and 614
oil of, 264
Volta's eudiometer, 865
pile, 112
theory of, 115
Volumes, theory of, 182

W

Water, composition of, 207
properties of, 209
expansion of, in freezing, 30
latent heat of, 55
Water, boiling and freezing point of, 37
solubility of gases in, 210
of crystallization, 591
rain, snow, spring, well, river, 877
of the sea and the Dead Sea, 882
Waters, mineral, 883
acidulous, alkaline, chalybeate, sulphurous and siliceous, 877
Waters, saline, 879
Wax, 735
Welding, 480
Welter's tube of safety, fig. 5
Wheat flour, 747
Whey, 842
White lead, 645
White copper, 585
Wine, quantity of alcohol in, 731
oil of, 734
Wires, tenacity of, 402
Woad, 754
Woody fibre, 751
Wool, 862
Woulfe's apparatus, fig. 3

X

Xanthic oxide, 859
Xanthogen, 396

Y

Yeast, 767
Yellow, mineral, or patent, 551
Yellow, king's, 514
chrome, 636
dryes, 760
Yttria and its base, 458

Z

Zaffre, 790
Zero absolute, 60
Zymome, 767
Zinc, 489
oxide and chloride of, 490 and 491
sulphuret of, 491
Zirconia and its base, 460

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