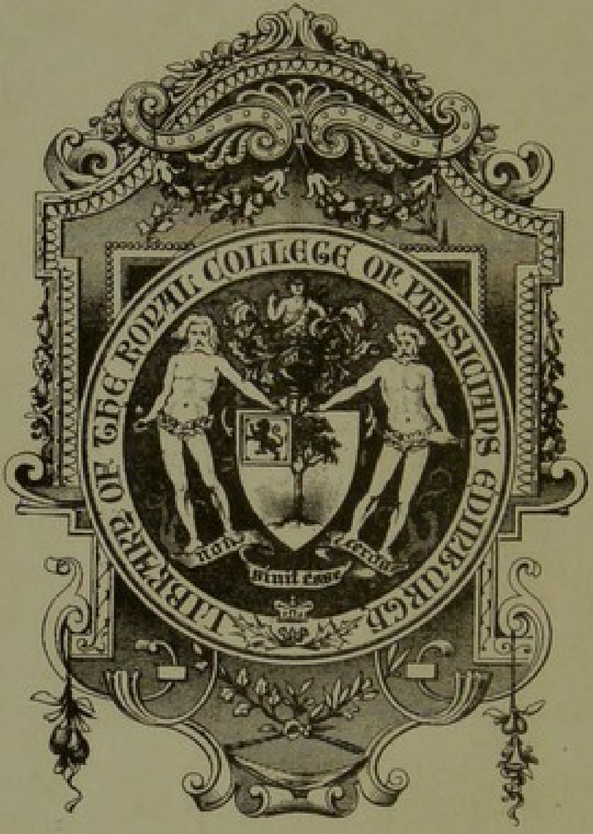
Exercises in quantitative chemical analysis : with a short treatise on gas analysis / by W. Dittmar.

Contributors

Dittmar William.
Royal College of Physicians of Edinburgh

Publication/Creation

Glasgow : W. Hodge, 1887.


LIBRARY OF THE ROYAL COLLEGE OF PHYSICIANS EDINBURGH

QUANTITATIVE CHEMICAL ANALYSIS.

With the Publishers' Compliments

EXERCISES
IN
QUANTITATIVE CHEMICAL ANALYSIS:
WITH A
SHORT TREATISE ON GAS ANALYSIS.

BY
W. DITTMAR, LL.D. (Edin.), F.R.S.; F.R.S.E.
PROFESSOR OF CHEMISTRY IN THE GLASGOW AND WEST OF SCOTLAND
TECHNICAL COLLEGE.

GLASGOW:
WILLIAM HODGE & CO., 123 HOPE STREET.
1887.

Glasgow:
Printed by Wm. Hodge & Co.,
123 Hope Street.

PREFACE.

A PRELIMINARY edition of this book, as many of my friends are aware, was issued a little over a year ago for the benefit of chiefly my own students. That edition, however, was little more than a reproduction of what had long had currency in my laboratory as a trypographed book. Hence this volume may be introduced as having already been used—and I hope not without success—in a largely-attended teaching laboratory for a series of years.

However it may stand with analysis generally, *quantitative* analysis can be taught only by examples; and in the earlier stages of the course the technicalities of the subject are the principal things to be taught. Hence our exercises on "analytical methods" (section 2) are arranged, not according to any scientific system, but so that, at any given point of his progress, the student has become familiar with as many different operations as could have been learned during the time.

To some of my readers the tone of the earlier exercises more especially may savour a little of mechanical drilling. Why tell the student so minutely what he has to do and hinder him from exercising his own ingenuity? Some ten years ago, if a book like the present had been placed before me, I should have asked this question myself. But I have since come to modify my views. The technicalities of quantitative analysis are the very things which the student is not likely to find out by himself. He had better be drilled into doing them correctly. What is the good, for instance, of letting him spoil a series of ammonia determinations by mismanaging his chloroplatinate precipitates? It surely is better to show him quite directly what he has to do; and if it is, why should not the book tell him, and thus save the time of the teacher? No fear of any talented student being spoiled by a course of judicious drilling. It is just he that must be made alive to the fact that no amount of scientific knowledge will enable a man to get through a quantitative analysis successfully unless he has the "canning" as well as the knowing, and unless he attends to all those little practical details which to him at first sight may appear to be irrelevant. Cheerful and conscientious devotion to all the protracted drudgery that may be involved in one's duty is certainly a lesson worth learning, and it is one of the educational functions of quantitative analysis to inculcate the lesson. And as to the talented student's weaker brother? Why, he *must* be drilled, or else he may learn nothing at all.

Of course, here, as everywhere, we must beware of extremes, and take care not to disgust the student with his work. It is as well, even at the earlier stages, to occasionally break the monotony of analytical work by the interpolation of an exercise in preparative chemistry. With students who have already been "broken in," a capital plan is to give them unnamed substances and let them *find* the exercise or set of exercises that they are meant to work, taking care not to give them any help except where it may become necessary to prevent sheer waste of time.

The section on Gas Analysis will, I hope, be welcome to many, because there is no treatise on the subject in any language, as far as I know, excepting, of course, Bunsen's *Gasometrische Methoden;* but it treats only of the great master's own methods.

In conclusion, I have much pleasure in acknowledging my indebtedness to my assistants, Messrs. John M'Arthur and Archibald Kling, for the valuable aid they have given me in preparing the book for and passing it through the press; to the same gentlemen and Messrs. Frank Lyall, James Robson, William Cullen, and Andrew Hodge, for the careful execution of test-analyses; and last, not least, to my publisher, for having spared no expense in bringing the book into a presentable form.

W. D.

CHEMICAL LABORATORY,
ANDERSON'S COLLEGE BUILDINGS,
GLASGOW, *September*, 1887.

CONTENTS.

PAGE

Table of Atomic Weights, - - - - - - - - - - xii

EXERCISES IN EXACT WEIGHING AND MEASURING.

1. Practice in the Routine Method of Relative Weighing, - - 1
2. The Method of Vibration, - - - - - - - - - 3
3. Absolute Weighing, - - - - - - - - - - 5
4. Reduction to the Vacuum, - - - - - - - - - 8
5. Weighing of Pre-determined Quantities of Liquids, - - 10
6. Making of Apparatus for the Exact Measurement of Liquids, - 10
7. Graduation of a Measuring Flask, - - - - - - - 11
8. Graduation of a Pipette for "Delivering" Pre-determined Volumes, 12
9. Determination of Specific Gravities of Liquids, - - - 12
10. Preparation and Adjusting of Standard Solutions, - - - 13

EXERCISES IN ANALYTICAL METHODS.

11. Determination of Filter Ashes, - - - - - - - - 16
12. Analysis of Chloride of Barium, - - - - - - - 17
    Rules regarding the Booking and Reporting of Analyses, - 19
13. Analysis of a Silver Coin, - - - - - - - - - 20
14. Sulphate of Iron and Potash, - - - - - - - - 22
15. Analysis of Sulphate of Magnesia and Potash, - - - - 24
    Tatlock's Method, - - - - - - - - - 25
    Finkener's Process, - - - - - - - - - 26
16. Analysis of Phosphate of Lime, - - - - - - - 30
17. Separation of Iron and Alumina, - - - - - - - - 33
18. Titrimetric Determination of Iron, - - - - - - 34
    The Bichrome Method, - - - - - - - - 37
    The Stannous Chloride Method, - - - - - - 39

PAGE

19. Analysis of Sulphate of Copper and Ammonia, - - - - 42
    Supplementary Methods, - - - - - - - - 46
20. Analysis of Carbonates, - - - - - - - - - 47
21. Separation of Iron, Manganese, and Calcium, - - - - 52
22. Spathic Iron Ore, - - - - - - - - - - 55
23. Preparation of a Standard Solution of Iodine, - - - - 56
24. Analysis of Bleaching Powder, - - - - - - - 60
25. Gas-Volumetric Analysis, - - - - - - - - 64
26. Native Oxide of Manganese, - - - - - - - 67
27. De Haen's Method for the Determination of Copper in Alloys, Ores, &c., - - - - - - - - - - - 75
28. Determination of Water by the "Direct" Method, - - - 76
29. Determination of Nitrogen by Varrentrapp and Will's Method, 79
    Notes regarding Special Classes of Substances, - - 82
30. Kjeldahl's Method of Nitrogen Determination, - - - 83
31. Schlœsing's Method of Nitric and Nitrous Acid Determination, 85
31*a*. Walter Crum's Method, - - - - - - - - 89
32. Quantitative Electrolysis, - - - - - - - - 91
32*a*. Electrolytic Separation of Copper and Nickel, - - - 100
33. Analysis of Brass, - - - - - - - - - - 101
34. Analysis of German Silver, - - - - - - - - 104
    Separation of Nickel and Cobalt, - - - - - 106
35. Analysis of Iron or Copper Pyrites, - - - - - - 111
    Assay for Sulphur, - - - - - - - - - 111
    Determination of the Metals, - - - - - - - 114
    Assaying for Copper, - - - - - - - - - 116
36. Analysis of Galena, - - - - - - - - - 119
37 Silicate Analysis, - - - - - - - - - - 122
38. Analysis of Chrome Iron Ore, - - - - - - - 128
    Assay for Chromic Oxide, - - - - - - - 128
    Complete Analysis, - - - - - - - - - 130
39. Separation of Lead and Antimony, - - - - - - 135
    By Means of Alkaline Sulphide, - - - - - - 135
    By Means of Chlorine, - - - - - - - - 136
40. Analysis of Gold and Silver Alloys by Cupellation, - - 140

PAGE

ELEMENTARY ANALYSIS OF COMBUSTIBLE CARBON COMPOUNDS.

41. Analysis of Ferrous Oxalate, - - - - - - - - 143
42. Analysis of Cane Sugar or Mannite, - - - - - - 146
43. Analysis of Benzoic Acid or Naphthalene, - - - - 147
44. The Old Method of Organic Analysis, - - - - - - 147
45. Analysis of Liquids, - - - - - - - - - - 149
46. Analysis of Nitrogenous Substances, - - - - - - 151
47. Determination of Nitrogen in Organic Substances by Dumas' Method, - - - - - - - - - - 152

GAS ANALYSIS.

Generalities and Theory, - - - - - - - - - 155
Proximate Analysis of Gas Mixtures, - - - - - - - 166
The Law of Gas Absorption and its Applications, - - - - 168
Ultimate Analysis of Gases generally, - - - - - - 173
Apparatus and Working Methods, - - - - - - - 179

Exercises—

1. *Making of a Bunsen Eudiometer*, - - - - - 208
2. *Calibration of the Eudiometer*, - - - - - 211
3. *Preparation of a Reduced Volume Scale for the Eudiometer*, - - - - - - - - - - - 212
4. *Making and Calibration of a Bunsen Absorption Tube*, 212
5. *Calibration of the Measurer in the Author's Apparatus*, 212
6. *Analysis of a Mixture of Air and Carbonic Acid*, - 212
7. *Analysis of a Mixture of Carbonic Oxide and Carbonic Acid*, - - - - - - - - - - 213
8. *Analysis of Marsh Gas*, - - - - - - - - 213
9. *Analysis of Ethylene*, - - - - - - - - 213
10. *Analysis of a Mixture of* H_2, CO, CH_4, *and* N_2, - - 215
11. *Extraction of the Absorbed Gases from a Water, and their Determination*, - - - - - - - 215

PROMISCUOUS EXERCISES IN APPLIED ANALYSIS.

1. Analysis of a Sea Water, - - - - - - - - - 219
Chlorine, - - - - - - - - - - - 219
Sulphuric Acid, Note (8), - - - - - - - - 313
Lime and Magnesia, - - - - - - - - - 224

PAGE
The Potash, - 225
Total (Bases as) Sulphates, - 226
The Carbonic Acid, - 227
Alkalinity, - 230
Total Salts (Tornoe's Method), - 231
The Bromine, - 232
Average Composition of Ocean-Water Salts, - 234
2. Stassfurth Potash Salts, - 235
Tatlock's Method, - 236
Our own Form of Finkener's Method, - 236
3. Cast-iron, - 238
The Total Carbon, - 238
The Sulphur, - 241
The Phosphorus, - 242
The Manganese, - 244
The Silicon, - 246
The Iron and Foreign Metals, - 246
Determination of the Silica, &c., present as Slag, - 247
Steel and Wrought-iron, - 247
4. Superphosphate of Lime, - 248
5. Guano, - 252
6. Milk, - 255
Albumenoids and Sugar, - 256
The Sugar, - 257
7. Soap, - 259
Fatty Acid, - 260
The Alkali Salts generally, - 261
The Glycerine, - 262
Resin, - 263
8. Butter, - 265
Foreign Fat, - 265
Rancidity, - 267
9. Assaying of Tanning Materials, - 267
Assaying of Sumach, - 267
10. Partial Analysis of Tea, - 271
11. Analysis of Wood Spirit, - 272
Determination of the Methyl-Alcohol, - 276

PAGE
Determination of the Acetone, - - - - - - 279
Dittmar and Fawsitt's Table of the Specific Gravities of Aqueous Methyl-Alcohols, - - - - - - 281
12. Determination of Ethyl-Alcohol, - - - - - - - - 284
Table giving the relation in Aqueous Ethyl-Alcohol between Specific Gravity and Percentage, - - - - - 286
Separation of Ethyl and Methyl-Alcohol, - - - - 292

NOTES.

(1) Theory of the Balance, - - - - - - - - - - 302
(2) Specific Gravities of Aqueous Hydrochloric Acids.—The Author's Differential Method of Specific Gravity Determination, - - - - - - - - - - 305
(3) Double Salts (Mg or Fe)$SO_4.K_2SO_4 + 6H_2O$, - - - - - 308
(4) To Ex. 24, - - - - - - - - - - - 309
(5) To Ex. 26, - - - - - - - - - - - 309
(6) Determination of Cobalt as Phosphate, - - - - - - 309
(7) On Platinum Solution and Platinum Residues, - - - 310
(8) Determination of the Sulphuric Acid in Sea Water, - - 313
(9) Greiner and Friedrich's new Stopcocks, - - - - - - 313

INDEX, - . - - - - - - - - - - - 315

ATOMIC WEIGHTS.

O = 16

After Lothar Meyer and Seubert's calculations. Exceptions: according to authorities quoted in the notes.

Name of Element.	Atomic Weight.		Name of Element.	Atomic Weight.	
	Symbol.	Value.		Symbol.	Value.
Aluminium,	Al	27·10	Molybdenum	Mo	96·2
Antimony,	Sb	119·9	Nickel,	Ni	58·7
Arsenic,	As	75·09	Niobium,	Nb	93·9
Barium,	Ba	137·20	Nitrogen,	N	14·046
Beryllium,	Be	9·1	Osmium,	Os	195·
Bismuth,[1]	Bi	208·0	Oxygen,	O	16·
Boron,	B	10·9	Palladium,	Pd	106·6
Bromine,	Br	79·952	Phosphorus,	P	31·04
Cadmium,	Cd	112·0	Platinum,[6]	Pt	195·5
Cæsium,	Cs	133·0	Potassium,	K	39·136
Calcium,	Ca	40·02	Rhodium,	Rh	104·3
Carbon,	C	12·00	Rubidium,	Rb	85·4
Cerium,	Ce	141·5	Ruthenium,	Ru	103·8
Chlorine,	Cl	35·454	Scandium,	Sc	44·1
Chromium,[3]	Cr	52·13	Selenium,	Se	79·07
Cobalt,	Co	58·7	Silicon,[7]	Si	28·399
Copper,	Cu	63·34	Silver,	Ag	107·93
Didymium,	Di	145·4	Sodium,	Na	23·053
Erbium,	E	166·4	Strontium,	Sr	87·52
Fluorine,	F	19·1	Sulphur,	S	32·06
Gold,[4]	Au	197·324	Tantalum,	Ta	182·7
Hydrogen,	H	1·0024	Tellurium,	Te	128·0
Gallium,	Ga	70·1	Thallium,	Tl	204·2
Indium,	In	113·7	Thorium,	Th	232·5
Iridium,	Ir	193·0	Tin,	Sn	117·6
Iodine,	I	126·85	Titanium,[8]	Ti	48·08
Iron,	Fe	56·02	Tungsten,	W	184·0
Lanthanum,	La	138·9	Uranium,	U	240·5
Lead,	Pb	206·9	Vanadium,	V	51·2
Lithium,	Li	7·02	Yttrium,	Y	89·8
Magnesium,[2]	Mg	24·37	Ytterbium,	Yb	173·
Manganese,[5]	Mn	55·0	Zinc,[9]	Zn	65·37
Mercury,	Hg	200·3	Zirconium,	Zr	90·6

---

[1] [2] Marignac ; Fres. Zeitschrift, 1884 ; 118.

[3] Siewert, as calculated by Clarke.

[4] Thorpe and Laurie ; Chem. Soc. Trans., 1887, p. 565.

[5] Dewar and Scott ; Marignac.

[6] Dittmar and M'Arthur ; Memoir communicated to the Roy. Soc. of Edin. in summer, 1887.

[7] Thorpe and Young ; Chem. Soc. Trans., 1887, p. 576.

[8] Thorpe ; Roy. Soc. Proc., 1883, p. 43.

[9] Mean of determinations by Marignac and by Baubigny (1884).

EXERCISES IN EXACT WEIGHING AND MEASURING.*

Ex. 1.—Practice in the Routine Method of Relative Weighing.

As a necessary preliminary to the actual practice of quantitative analysis, begin by learning to execute exact weighings by means of a precision balance. But a mere *knowledge* of the method is not sufficient: you must practise the art for hours and hours until you have it at your fingers' ends.

To enable you to do this, and to check the results, we keep a set of pieces of metal marked A, B, C, &c., of which the exact weights in grammes are noted down in a book. Procure this set, and then, in order to determine the several weights,

First, set your balance in order; *i.e.*, clean the case outside and inside, and remove every particle of dust from the instrument itself by means of a camel's-hair brush.

Second, "level" the instrument by working the screws at the bottom of the case until the spirit-levels inside stand at zero, which shows that the (plane) central support of the beam is exactly horizontal, and the zero of the scale lies vertically below the axis of rotation.

Third, see if your balance is in equilibrium. For this purpose shut the case, and, by letting down the arrestment, enable the beam to seek its position of rest. As a rule, it will *vibrate* about this position. Should it stand still, cause it to oscillate by sending a current of air down on one pan (using your hand as a fan), or else by placing the rider on the beam for an instant and then removing it. Follow the excursions of the needle, and note the

---

* *See* Note (1) at end of volume.

successive turning points. If in two consecutive excursions the needle goes as far to the one side of the zero as to the other, the position of rest is at zero; it agrees with that position in which the centre of gravity of the empty beam (by intention at least) is vertically below the axis of rotation; the balance is in equilibrium. Should it turn out that it is not, shift the little knob at the one end of the beam along the horizontal screw to which it is attached, forwards and backwards, until perfect equilibrium is established.

In order now to determine the relative weight of an object, place it on the left pan, and then try greater or lesser combinations of standards ("weights") on the right until the beam's position of rest lies within its angle of free play; that is, until the beam, when the arrestment is down, oscillates freely. It stands to reason that these trials must be executed in a systematic manner. Supposing we had found that P grammes is greater, while p grammes is less, than the weight sought for, the correct rule is to add to p that *one* weight which comes nearest to the value $\frac{1}{2}(P-p)$. Take care not to make any alteration in the charge on either pan without having first arrested the beam; and in letting down the arrestment, do it slowly so that the beam (as long as it is to any considerable extent out of equilibrium) in its descent keeps pace with the arrestment.

Supposing now equilibrium to be established to the extent above referred to, shut the case, allow the beam to oscillate, and note two consecutive excursions of the needle (neglecting the first, which is liable to be infected by irregularities), mark with the *plus* sign (+) what lies to the left, and with the *minus* sign (−) what lies to the right, of zero.

The algebraic sum[*] of the two readings, representing as it does the distance from the zero, in half-degrees, of that point which the needle would point to if the beam were in its position of rest, is proportional to the number of milligrammes ($\triangle$) which must be added to the lighter side to establish equilibrium. This distance we call the "deviation," and are in the habit of

---

[*] Supposing the needle to move (*a*) from -4 to $+6$; (*b*) from $+0{\cdot}5$ to $+4{\cdot}5$; (*c*) from -1 to $-1{\cdot}7$, the deviation would be respectively (*a*) $+(6-4)=+2$; (*b*) $+(0{\cdot}5+4{\cdot}5)=+5$; (*c*) $-(1+1{\cdot}7)=-2{\cdot}7$ half-degrees.

designating it by the symbol α. Determine approximately the relation between α and $\triangle$ by seeing to what extent the deviation is diminished by the addition of, say, 2 milligrammes to the lighter side. Supposing α had been $= +5°$ (half-degrees), and by taking away 2 mgms. been reduced to $+1°$, *i.e.*, by 4°, every 2° of deviation means approximately a plus or minus of 1 mgm. Take away $5 \div 2 = 2·5$ mgms., take another couple of readings, correct the remaining error, and so on until equilibrium is established to within as little as the balance is capable of indicating. Tabulate your results, and ask the Demonstrator to check them by comparison with the standard tables. If your results are unsatisfactory, do the whole work over again (without referring to your previous notes), and so on until you are able, without any effort, to effect a weighing with rapidity, and yet with unerring certainty.

Ex. 2.—The Method of Vibration.

A REFINEMENT on the ordinary routine method, which consists in this, that after having established equilibrium to within a few milligrammes, we determine the deviation with precision, and from it calculate the exact weight (of $\triangle$ mgs.) which is required to establish absolute equilibrium. To learn the method, determine the relation in your balance between charge P, overweight $\triangle$, and deviation α, as follows:—Bring the empty instrument into approximate equilibrium, and then, in order to determine the exact deviation, let down the arrestment, and take, say, four or six consecutive excursions of the needle (neglecting the first one) so that you have 3, 5, . . . , or a greater *odd* number of readings to calculate from: we leave it to you to find out why an *odd* number is in practice preferred to an even one. Supposing the needle to turn successively at

(2)	*(3)*	*(4)*	*(5)*	*(6)*
+4·2	−3·0	+4·0	−2·8	+3·8,

which results are conveniently taken down as follows:—

+4.2	4·0	3·8
−3·0	2·8,	

we have from (*2*) and (*3*) $a = +1{\cdot}2$ half-degrees.
„ (*3*) „ (*4*) $a = +1{\cdot}0$ „
„ (*4*) „ (*5*) $a = +1{\cdot}2$ „
„ (*5*) „ (*6*) $a = +1{\cdot}0$ „
Mean $= +1{\cdot}10 = a_0$.

Now, place successively 1, 2, 4 mgms. on one of the pans, again determine the deviation, and in each case calculate the overweight corresponding to 1 half-degree of deviation. Supposing we found, for the increase which a suffers by

	1	2	4	mgms.,	
$(a - a_0) =$	3·0	6·2	11·7	half-degrees,	
we have $\frac{\triangle}{a} =$	0·33	0·32	0·34	„	mean = ·33.

If, for simplicity's sake, we substitute a for $a - a_0$, $\frac{\triangle}{a}$, as the example illustrates, is constant; we will call it c, and consequently put down that for the empty instrument, $c = 1/3\ (0{\cdot}33 + 0{\cdot}32 + 0{\cdot}34) = 0{\cdot}33$ mgs. This being done, charge your balance, say, with 20 grms. on each side, establish equilibrium by adding small bits of thin wire, and determine the value which c now possesses. Do the same for charges of 40, 60, 80, 100 grms., and tabulate your results. The several values for c, in a good balance, will not differ much from one another, so that the c's corresponding to intermediate values can be obtained by interpolation. Draw a straight line, and lay down on it a scale of convenient units of length; at the points 0, 20, 40, 60, 80, 100, erect perpendiculars, and (choosing a convenient unit of length) make the lengths of them equal numerically to the c's corresponding to the charges of 0, 20, 40, &c., grms. Draw a continuous curve so that it passes, as nearly as possible, through the end-points of the perpendiculars, and take the length of the ordinates from the points 0, 10, 20, &c., of the base line. These lengths represent the △'s corresponding to 1°, at the charges 0, 10, 20, &c., grms. respectively. How such a table can be utilized for exact weighings need not be explained. In ordinary practice, however, it is best to strike a compromise between the strict method of vibration and the routine method explained in Ex. 1.

For the same charge, the value c depends on the distance of the centre of gravity of the empty instrument from the axis of rotation. Every complete balance has an arrangement (gravity bob) for varying that distance. The best method is so to adjust the bob that, for some medium charge, the weight-value of 1 half-degree is, say, exactly 1, $\frac{1}{2}$, or $\frac{1}{5}$ mgm., and to use this mean value of c for the approximate translation of deviations into differences of weight.

Ex. 3.—Absolute Weighing.

In Chemical Analysis, we have to do only with *weight-ratios*, not with absolute weights; hence we need not trouble ourselves about the *absolute* correctness of our set of gramme weights; and as we always, in weighing, place the substance on the left, and the weight standards on the right, pan, it does not matter if our balance is not exactly equal-armed. But we should not use a set of weights without having tested it for its relative correctness, and this involves absolute weighings, though the unit, even here, as a matter of principle, is arbitrary.

Exercise.—Procure a set of only approximately adjusted gramme weights such as are sold in Germany and France for commercial purposes, take out the pieces representing nominally 1, 1, 1, 2, 5, 10 grammes, and in order to determine their relative errors, adopt provisionally one of the grammes as your standard, and with it compare the rest, as follows:—

Place the standard 1 gramme on the right pan of a fine balance, and, by placing metallic objects (wire, &c.), on the left, establish approximate equilibrium. Allow the balance to vibrate, take down, say, four vibrations, and find the deviation a, as shown in the preceding exercise. Calculate the number of milligrammes $\triangle$ which correspond to the a, and book your results thus (we assume that $\triangle = 0{\cdot}5\ a$):—

In pan,	a	$\triangle$
(1)	say, $-2{\cdot}3$	$-1{\cdot}15$ mgs.

Now, take away that one gramme (1), and substitute another which we will call $(1)_1$, add the requisite number of milligrammes to establish approximate equilibrium, and again book your results. Supposing we find

(In pan)	a =	△ =
$(1)_1$ + 1 mg.	−4·0.	−2·0 mgs.,

obviously perfect equilibrium would have been established, or, in other words, the constant tare would have been exactly counterpoised

in the case of (1) by adding to it 1·15 mgs.,
„ „ $(1)_1$ „ „ 3·00 „

Hence,

$$(1)_1 + 3 \text{ mgs.} = (1) + 1{\cdot}15 \text{ mgs.},$$
$$\text{or } (1)_1 = (1) - (3 - 1{\cdot}15) = (1) - 1{\cdot}85 \text{ mgs.},$$

(1) being = unity, by assumption.

In a similar manner, determine the error in the third gramme piece $(1)_2$. Say you find it = (1) + 1·2 mgs. Now, clearly, any two of the three weights (1), $(1)_1$, $(1)_2$, when taken together, represent a known weight equal approximately to the 2-gramme piece (2), and the difference between, for instance, (1) + $(1)_1$ and (2) can be ascertained as you determined that between (1) on the one hand and $(1)_1$ or $(1)_2$ on the other. Suppose you had found

the constant tare equivalent to (1) + $(1)_1$ + 1·3 mgs.,
„ „ „ „ „ (2) − 3·7 mgs.,

then, as we know that $(1)_1$ = (1) − 1·85 mgs., we have (1) + $(1)_1$ + 1·3 mgs. = 2 × (1) − 1·85 + 1·3 mgs. = (2) − 3·7 mgs. Hence,

$$(2) = 2 \text{ units} - 1{\cdot}85 + 1{\cdot}3 + 3{\cdot}7 \text{ mgs., or}$$
$$(2) = 2 \text{ units} + 3{\cdot}15 \text{ mgs.}$$

In the same way, determine the values of the (5) and (10) in terms of the assumed unit (1) and of milligrammes, and all that we then need to be able to draw up a correction table for our set of weights is the exact relation between the milligrammes (*i.e.*, the rider) used and our unit (1). But this, if it had to be done by experiments independent of any guaranteed set of weights, would involve more work than the result, *in this case*, would be worth. Hence, you had better now assume the 10 grammes out of the fine set to be equal exactly to 10 grammes, and equal also to 10,000 times 1 mg. as counted by the rider, and, after having compared that "true" 10-gramme piece with the (10) in the bad set, calculate the values of your several pieces in terms of the new unit. Supposing we found

$(10) = (10 \times$ "1 gramme")[*] $+ 6{\cdot}7$ mgs, and before that
$(10) = 10 \times (1) - 9{\cdot}8$ mgs., then
$(10) \times (1) = 10$ grammes $+ 16{\cdot}5$ mgs., and
$(1) = 1$ gramme $+ 1{\cdot}65$ mgs.,

which value must be substituted for every one (1) in the provisional table of errors.

To make sure of your results, compare your several weights, (1), $(1)_1$, (2), &c., with the respective pieces in the set of precision weights, and compare the thus directly determined errors with the ones entered in your table. In order to learn something new, effect these comparisons as follows:—

After having brought the balance into equilibrium,[†] place the object on the left pan, and weigh it with precision grammes placed on the right pan, using the method of vibration for the final adjustment. Then reverse the position of object and weight proper, and again note down the result.

Supposing we found that the unknown weight x of the object was balanced

in the first case by 10·0126 grammes,
„ second „ by 10·0132 „

then, taking l' as being the length of the left arm, and l'' as being the length of the right arm of our balance,

$$x \times l' = 10{\cdot}0126 \text{ grammes} \times l'' \quad \text{Eq. (1)},$$
$$\text{and } x \times l'' = 10{\cdot}0132 \quad „ \quad \times l' \quad \text{Eq. (2)}:$$
$$\text{hence } x^2 l' l'' = 10{\cdot}0126 \times 10{\cdot}0132\, l' l'' \quad \text{Eq. (3)}:$$
$$\text{hence } x = \sqrt{10{\cdot}0126 \times 10{\cdot}0132},$$

or practically, as is easily proved, $x = \frac{1}{2}(10{\cdot}0126 + 10{\cdot}0132)$.

---

[*] *i.e.*, the value of the standard 10-gramme piece or ten "true grammes."

[†] Absolutely exact equilibrium is not needed. Assuming, for instance, the left pan were, in itself, by ϵ grammes too heavy (ϵ being something like, say, 0·01 grms. or less), then we have in lieu of eq. (3), $x \times (x + \epsilon) = (10{\cdot}0126) \times (10{\cdot}0132 + \epsilon)$, and we may well cancel $(x \times \epsilon)$ against $10{\cdot}0126 \times \epsilon$ without real error.

The method illustrated in this exercise is the same as the one which we use for determining the errors in a set of precision weights, except that what we ultimately adopt as our standard is an imaginary quantity, so chosen that the average error of the single piece of the set, when its value is expressed in terms of the standard, is reduced to a minimum. Observe that, even in the best sets of gramme weights, as made by the most eminent artists, the "unit," in passing from one set to another, is, strictly speaking, a variable quantity. What that quantity is, in the absolute sense, it is of no use to the chemist to know; but obviously, where two or more sets are used to supplement one another, it is necessary to determine the relations of the several units ("grammes") to one another.

Ex. 4.—Reduction to the Vacuum.

In chemistry, when we "weigh" a thing, what we want to measure is, not its weight in the strict sense of the word, but its "mass," *i.e.*, the quantity of matter which it contains. Our method of weighing really is a method of mass-measurement, founded upon the proposition that two things which (at a given place and time) are equal in weight are equal also in mass. If a thing weigh fifty times as much as our 1-gramme piece, its mass also is fifty times the mass of that 1-gramme piece; and this is what we mean by saying that it "weighs 50 grammes." But the proposition, in strictness, holds only when the weighings are made in vacuo, because when a body is plunged in air its weight is partly compensated for by the upward pressure of the air, which is equal to the weight of air displaced. Hence, when we have weighed an object, we should always by rights ascertain the difference between the volume V of the object and the volume v of the weights, and (if $V > v$) add to the weight registered the weight of $V - v$ unit-volumes of air. To give an idea of the magnitude of the correction as applied to ordinary cases, assume a quantity of water has been weighed by means of brass weights, and been found = 10 grms. Taking the volume of

1 grm. of water as our unit of volume, the weights of unit-volume of brass, water, air, are about 8, 1, 1/800 respectively. Hence, 10 grms. of water are 10 volumes by definition, and 10 grms. of brass are $10 \div 8 = 1{\cdot}25$ volumes; and $V - v = 10 - 1{\cdot}25 = 8{\cdot}75$; so many volumes of air weigh $8{\cdot}75 \div 800 = 0{\cdot}0109$ grms. Hence the *true* weight ("mass") of the water is 10·0109 grms., and not 10·0000. Most of the things which we weigh in the ordinary practice of analysis are nearer in specific gravity to water than they are to brass; hence the error which we commit when we neglect the correction is by no means insignificant. But its effect on the final result is in general far less than would appear from our example. A single weighing in chemistry is nothing more than one term of a ratio, and as both terms are affected by the error similarly (though not equally), the quotient is nearer the truth than the student may be inclined to think. Supposing, for instance, in addition to our mass of water we had weighed the same volume of sulphuric acid in order to determine the specific gravity, and found the apparent weight to be = 12 grms., then the corrected weight of the acid would be 12·0109, and the *true* specific gravity $= 12{\cdot}0109 \div 10{\cdot}0109 = 1{\cdot}1998$, which differs only by 0·0002 from the apparent specific gravity, $12 \div 10 = 1{\cdot}2000$. In practice, the correction can be neglected, unless we have to weigh a gas or other substance of very small density, and even then we may always neglect the weight of the air displaced by the weights, because obviously we have the right to assume as our unit of weight the weight which our 1-gramme piece has in air. It would even be a mistake not to do so, because our weights are adjusted by comparison against each other in air, and we would introduce an error by allowing, for instance, for the difference in density between the platinum of the decigrammes and the brass of the grammes and gramme-multiples. Our unit of weight, then, is variable with the density of the air we weigh in, but this is a matter of no moment practically. To calculate the weight of air displaced by the object, we divide its apparent weight by its specific gravity, and thus obtain a sufficient approximation to its volume. Taking the volume of 1 gramme of water (the cubic-centimetre) as unit volume, 1 cc. of air of t° and P mms. pressure weighs

$S = 0{\cdot}4648 \times P \div (273 + t)$ mgs. Hence, supposing a body in air of 15° and 750 mms. weighs apparently 44 grms., and its specific gravity is 4·0, its volume is $44 \div 4 = 11$ cc., and its real weight equals 44 grms. $+ (11 \times 0{\cdot}4648 \times 750) \div 288 = 44{\cdot}0133$ grms.

Ex. 5.—Weighing of Pre-determined Quantities of Liquids.

To practise this operation, and at the same time to procure a useful piece of apparatus, take a cylindrical test-glass of 4 to 6 ounces capacity; weigh into it successively 10, 20, . . 100 grms. of water; mark the several levels, first with pencil on a strip of paper fixed along the glass, and finally with a diamond. In reading the levels, to obtain constant results, we must adopt a definite *modus operandi*. The one adopted by us is this—Place the measure so that its axis is vertical, and the level of the liquid in the same horizontal plane with the observing eye, so that the meniscus appears as a band. Take the lower boundary of this band as defining the "level of the liquid."

Ex. 6.—Making of Apparatus for the Exact Measurement of Liquids.

THE most convenient unit for this purpose is the volume at the ordinary temperature of that quantity of water the apparent weight of which in air is equal to 1 gramme (of our set of weights). We will adopt this unit, and call it "fluidgramme," symbol "fgr." The value of our fluidgramme, it is true, is, strictly speaking, a variable quantity, as it depends on the temperature of the water, and the density of the air in which the weight is taken; but the effect of these variations rarely goes beyond the unavoidable uncertainty of the measurement. For the sake of precision, however, we will adopt standard conditions, and herewith define the fluidgramme as being "the volume at 15°C. of that quantity of water which, at 15°C. and

760 mms. barometric pressure, weighs apparently 1 gramme." The fluidgramme, as is seen from our definition, is almost identical with the cubic centimetre, or milli-litre of the French system. What, in commercial volumetric apparatus, figures as "cubic centimetre" or "litre," usually comes nearer to our fluidgramme and 1000 fluidgrammes respectively than to the standard units nominally adopted.

Ex. 7.—Graduation of a Measuring Flask.

To graduate a measuring flask, take a long-necked flask of, say, ½–1 litre's capacity, and after having cleaned and dried it, weigh into it the nearest convenient multiple of 10 grammes of water of 15°C., mark the level of the water with the diamond, and reckon the flask as holding "so many fluidgrammes." Instead of bringing the water to 15°C., we may, of course, use the stock of water we have at our disposal as it is, determine its actual temperature, and, by the following table, calculate the weight of water corresponding to the required volume.

1000 grammes of water (weighed in air of $t°$ and 760 mms., brass standards, uncorrected for displaced air) occupy at this temperature of $t°$ the volume of $(1000 + x)$ fluidgrammes = $(1000 + y)$ cubic centimetres.

t	x	y	t	x	y
+0°	−0·64	+1·25	+15°	+0·00	+1·89
4	0·78	1·12	16	0·15	2·04
8	0·68	1·21	17	0·30	2·20
9	0·63	1·27	18	0·47	2·37
10	0·56	1·34	19	0·66	2·55
11	0·47	1·43	20	0·85	2·74
12	0·38	1·52	21	1·06	2·95
13	0·27	1·63	22	1·28	3·17
14	0·14	1·76	23	1·51	3·39
15	0·00	1·89	24	1·75	3·63

Note.—In using this table you may always say, without appreciable error, $(1000 \pm x) : 1000 = 1000 : (1000 \mp x)$.

Ex 8.—Graduation of a Pipette for "Delivering" Pre-determined Volumes.

EXAMPLE chosen:—A pipette graduated to deliver ½, 1, 1½, 2 . . . up to 5 fgrs. To make such an instrument, select a glass tube as nearly as possible cylindrical, and make it into a pipette. Paste along it a narrow strip of paper, then fill it by suction with water to near the top and let the water run out again, taking care not to remove more of the last drop than goes out by itself when the end of the pipette is held against the wet side of the vessel used to receive the liquid. (This method must subsequently be strictly adhered to in the use of the instrument.) In order now to find the approximate position of the marks, tare a crucible with a little more than 5 grms. of water in it on a balance, and suck out water into the moist pipette until the crucible has lost exactly 5 grms. of its weight. Mark the level of the water in the pipette with a pencil. In a similar manner find the position of the ½ fgr. mark. The intermediate marks may be determined by measurement, which will give incidentally the length of tube corresponding to every centigramme of water. Now determine the exact actual capacities corresponding to the several marks by means of an exact balance, and correct the errors by linear measurement. Supposing the pipette when filled up to the 5 mark delivers 4·94 grms. instead of 5 grms., and the distance from the 4 to the 5 mark is 30 mms., we see that the mark must be shifted upwards through $0·06 \times 30 = 1·8$ mms. to assume its right position. Finally, mark the several points with the diamond.

Ex. 9.—Determination of Specific Gravities of Liquids.

EXAMPLE chosen:—Pure muriatic acid (which in this exercise means aqueous acid; by "hydrochloric acid" we mean the real substance HCl). Take a quantity of pure, fuming, muriatic acid, determine its approximate density by a Twaddell's hydrometer, and then dilute it with water so as to bring it down to 20° Twad. at 15°C. Supposing the acid showed 35° Twad. (which corresponds, by definition, to the specific gravity $(5 \times 35 + 1000) : 1000 = 1·175$), the excess of weight per 1 fgr. over that of the same volume of water is 35/20 of what it is meant to be. Hence, every 20 volumes of the acid must be diluted to 35 ÷ 20 × 20 = 35 volumes, which, if the two liquids when mixed did not *contract*, would give *exactly* what is wanted. [The acid being intended to be used in Ex. 10, work on such a scale as to produce about 300 cc.] After having made sure that the dilute acid really is of the intended density according to the hydrometer, determine the specific gravity more exactly by the successive application of the following two methods:—

1. Take a narrow-necked flask of about 50 or 100 fgrs. capacity, make a diamond mark on the neck, and determine its capacity when filled up to this mark with water of 15°C. Repeat the experiment with acid, taking particular care in this case to make sure of the temperature, as hydrochloric acid expands far more largely by heat than water does. Supposing the flask to hold 50 grms. of water and 55·21 of acid, the specific gravity of the latter, by definition, is 55·21 ÷ 50 = 1·1042.

2. Make a "plunger" (Fig. 1) which displaces about 20 grms. of water, charge it with mercury so that it weighs in all about 40 grms., attach to its upper end a very thin platinum wire, and then determine the loss in apparent weight which the plunger suffers when immersed in (*a*) water and (*b*) the acid at 15°C. These losses, according to a well-known hydrostatic proposition, equal the weights of liquid displaced, from which the specific gravity can easily be calculated.

FIG. 1.

Half actual size.

Ex. 10.—Preparation and Adjusting of Standard Solutions.

EXAMPLE chosen:—Preparation of a standard solution of hydrochloric acid containing exactly 1 gramme-equivalent, *i.e.*, HCl grms. = 36·45 grms. of real hydrochloric acid per litre. For a first approximation, deduce from the specific gravity of your muriatic acid (Ex. 9) its percentage of HCl by means of the table given in Note (2) at the end of this volume, and from that calculate how much has to be diluted to, say, 1000 fgrs. to produce the solution required. Supposing for the specific gravity found the table gives the percentage as 20·25; hence, 36·45 ÷ 20·25 × 100 = 180 grms. may be taken as representing approximately 36·45 grms. of chloride of hydrogen. Weigh out the calculated quantity of your acid, pour it into a litre flask, dilute to about 4/5 of a litre, mix the liquids by giving them a rotatory motion; then fill up exactly to the mark, shake up thoroughly (liquids don't mix by themselves), and preserve the mixture in a glass stoppered bottle, until, by Exs. 12 and 13, you have learned to determine chlorine quantitatively. You may then apply these methods to, say, 5 cc. of the approximately standardized dilute acid to ascertain its exact strength, and then correct it either by addition of water or of the mother-acid, as the case may be. As 5 cc. cannot be measured off with a sufficient degree of exactitude, it is better to determine the weight in grammes of, say, 100 cc. of your acid, to *weigh* the small quantity required for the chlorine determination, and to *calculate* the *exact* volume. To show how the correcting of the crude "standard" acid is effected, let us assume—

1. The actual quantity of HCl found in 1000 fluidgrammes, instead of being 36·45, were 36·7 grms. In this case all that is required is to dilute every 3645 volumes of acid with water to 3670 volumes; or, what is more exact *in practice*, to add to every 3650 volumes (which need not be measured with any high degree of exactitude) exactly 3670 − 3645 = 25 volumes of water.

2. Supposing now the acid only contained 36·1 instead of 36·45 grms. per 1000 fluidgrammes, to be able to easily rectify matters in this case, it is best to keep some of the original acid (of 20·25 per cent.) in reserve. Obviously what was weighed out of this stock for 1000 fluidgrammes of solution was only 36·1/36·45 of what ought to have been taken; hence, since 180 grms. had been used, 180 × 36·45 ÷ 36·1 = 181·75 grms. is what ought to have been taken. If we simply added the 1·75 grms. of stock acid, we should have to remove 1·75 ÷ 1·10 = 1·6 fluidgrammes of water by evaporation to bring down the volume to its proper limit. But clearly there is no need for this troublesome operation. We can calculate the stock acid

required to convert 1000 volumes of the stock acid as it is into, say, 1003 volumes of what it ought to be, thus: needed for 1003 fgrs., 1·003 × 181·75 = 182·29 grms.; 182·29 − 180 = 2·29 grms. = 2·08 fgrs. of stock to be added to 1000 fgrs. of the solution to form 1002·08 fgrs. of a mixture, which obviously requires to have added to it 3·00 − 2·08 = 0·92 fgrs. of water to be made all right. In this case, as in the former, only the small quantities of stock acid and of water added to the large volume of solution need be *accurately* weighed or measured. Finally, in order to make sure that everything was done correctly, again analyse the adjusted acid. The result should not differ more from the intended value of 36·45 grms. than by 0·05 grm. (or 0·1 grm. at the outside); the mean between the intended value, 36·45, and the one resulting from the final analysis is the most probable value of the *actual* "*titre*."

The student will notice that we *neglect* the unknown contractions involved in the mixings; in a case like the present we may do so without going wrong practically.

If the highest precision is demanded, the surest method is to ascertain the specific gravity of the acid to be produced, and to reduce all the quantities involved to *weight*. The contractions, then, are out of court.

In obedience to a general habit, we shall from now use the terms "cubic centimetre" and "litre" as designating the unit of volume used in graduating the respective measuring instrument and its thousand-fold respectively.

EXERCISES IN ANALYTICAL METHODS.

Ex. 11.—Determination of Filter Ashes.

In quantitative analysis, it is best to make a rule of using only Swedish paper, as this gives less ash per square unit than any other filter paper in commerce (except the ash-free filters lately introduced by Schleicher and Schüll). But, in any case, before using a filter paper, the exact amount of ash which it contains must be determined as follows:—

Cut out a stock of filters of the several sizes required in analysis. We are in the habit of naming the sizes by the length of their radii in centimetres, and speak of a No. 2, 3, 4, 4½, 5 filter when we mean a filter of 2, 3, 4, 4½, or 5 centimetres radius respectively. Take, say, three No. 8 filters, fold and roll them up tightly into a small parcel, and, after having wound the end of a platinum wire round it, kindle it, and let it burn itself out completely, *over a porcelain plate placed beneath it* to catch any particles. Put the ash into a small, clean, platinum crucible, burn off the charcoal completely, allow to cool, weigh the whole, remove the ash (by means of a feather if necessary), and weigh the empty crucible. The difference gives the weight of the ash. Supposing it amounts to n mgs., we have, for the ash yielded by a filter of r centimetres radius, the formula—

$$\text{Ash in mgrs.} = \frac{n}{3 \times 8^2} \times r^2 = kr^2. \quad \text{Calculate } k.$$

Multiply k successively by the squares of the radii of the several sizes, and enter the results in a table. As treatment with acids removes a large proportion of the ash of a paper, repeat the determination with three No. 8 filters which have been previously washed with hot 10 per cent. hydrochloric acid, and then with water, and add a second column to your table as giving the ashes of the filters when "exhausted by acids."

Ex. 12.—Analysis of Chloride of Barium.

SUBSTANCE.—Pure chloride of barium occurs in commerce. To make sure of the crystal water, recrystallize it from hot water, allow the crystals to drain, and dry them on filter paper in the air. Take about 3 grms. of the air-dry crystals, grind them up in a mortar, and keep the now absolutely homogeneous substance in a small corked preparation-tube.

Determination of the Water.—Weigh out, say, 1 grm. of salt in a tared porcelain crucible, and expel the water by very gradually raising the temperature to a dull-red heat, which maintain for about ten minutes. Allow to *cool,* and weigh. Now, again heat the crucible for about five minutes, allow to cool, and weigh again, and so on until the weight is constant to within ·5 mgr. at most. From the final loss of weight calculate the percentage of water.

To Determine the Chlorine.—Dissolve a known weight of substance (about 1 grm.) in a beaker in about 50 cc. of water, acidulate with nitric acid, and then add nitrate of silver, at last drop by drop, and stirring up diligently after each addition until the chlorine is completely precipitated. Avoid application of heat, and don't use an immoderate excess of reagent. Stir up the mixture until it has quite lost its milky appearance, allow it to settle in the dark (or in gaslight), and carefully decant the liquor through a 4½ filter. Stir up the precipitate with cold water, acidulated with nitric acid, again allow to settle, and decant through the filter. Repeat this operation once more, then wash the precipitate on to the filter, and wash it with water (cold) until the filtrate is free from acid and from barium. Dry the precipitate in the funnel, detach it as completely as possible from the paper, and incinerate the latter in a porcelain crucible. To remove the charcoal from the lid, place it, inside up, on a triangle over a Bunsen, and cover it with a bit of platinum foil; the charcoal will soon vanish. In a similar way the charcoal inside the crucible is removed by placing the crucible slantingly over the flame, and successively heating the several portions of the charcoal under a small reverberator of platinum foil placed over the edge and stretching down into, but not touching the inside of, the crucible. The small particles of chloride of silver which stuck to the filter are now converted into metal. To chlorinate them, dissolve them in one drop of nitric acid, add a drop of hydrochloric, and carefully evaporate to dryness. Now, add the bulk of the chloride of silver, and heat the crucible over a flame so as to just fuse the chloride at the lowest temperature. Allow to cool, weigh, deduct the weights of empty crucible and ash (as "exhausted by acid"), and, from the weight of the chloride, calculate the percentage of chlorine. $AgCl : Cl = 143{\cdot}38 : 35{\cdot}45 = 1 : 0{\cdot}24727$.

To Determine the Barium.—First boil down the wash-waters from the chloride of silver so far that, when united with the filtrate, the whole amounts to 100–150 cc. Place this liquid in a beaker, or better, in a Florence flask of 200–250 cc. capacity, heat to boiling, and *then* add excess of sulphuric acid so as to precipitate the barium. Keep up a boiling heat until the precipitate becomes compact and readily settles down. Allow the precipitate to settle down *completely*, decant the clear liquor through a 4½ filter, wash the precipitate twice by decantation with hot water acidulated with sulphuric acid; then collect it on the filter, continue washing with *pure* hot water until the last washings are free from sulphate and free acid. Dry the precipitate, detach it from the filter, incinerate the latter in a platinum wire spiral, add the ash to the precipitate, and ignite the whole for about a quarter of an hour in a tared platinum crucible, allow to cool in an exsiccator, and weigh. From the weight of the sulphate of baryta calculate the percentage of barium. $BaSO_4 \times 0{\cdot}5882 = Ba$.

During the evaporations, &c., involved in the above operations, practise the following two methods for the determination of the barium:—

1. Dissolve, say, 1 grm. of the salt in about 100 cc. of water, heat to boiling, precipitate the barium by sulphuric acid, and collect and weigh the precipitate as just explained.

2. Weigh out about 1 grm. into a platinum crucible, dissolve, over a water bath, in the least quantity of water, add a measured volume of a standardized sulphuric acid, presumably not *quite* sufficient to decompose the salt, evaporate to as near dryness as possible on a water bath; then place the crucible slantingly on a triangle, and complete the evaporation by heating the lid and the upper portions of the crucible by means of a Bunsen. Finally, heat the crucible to redness from below, allow to cool, and weigh. Moisten the residue with a *few drops* of sulphuric acid, evaporate, again ignite and weigh, and so go on until the weight of the residue is constant.

Each of the above analytical methods must be practised again and again if necessary, until you have them at your fingers' ends. Observe, the methods in this book are not selected on the principle of simplicity, but with the view of teaching you as much as possible by each exercise.

RULES REGARDING THE BOOKING AND REPORTING OF ANALYSES.

1. Keep one book for the data of the analyses; another for the calculations. Both to be paged, and every item in either book to be marked with the page corresponding to it in the other.

2. No need of a scroll book, as a rule. The weighings should go directly into the report book meant to be submitted to the teacher. Write distinctly.

3. All results to be given in, whether successes or no.

4. At end of report, summarize in the following style:—

1.—*Percentage of Water.*

Analysis,..........	1.	2.	3.	Mean.
Results,............	14·65	14·92	(16·33)	14·78

"( )" means excluded in calculating the mean. The numbers 1, 2, &c., refer to sections of the detailed report.

2.—*Percentage of Barium.*

Analysis,..........	1.	3.	5.	Mean.
Results,............	56·10	56·33	56·20	56·21

3.—*Percentage of Chlorine.*—Similarly.

Mean Results.

		Theory.	Found.
Barium,............Ba =	137·20	56·20	—
Chlorine,.........Cl_2 =	70·91	29·05	—
Water,.........$2H_2O$ =	36·01	14·75	—
	244·12	100·00	

Two decimals are plenty. Learn the methods of shortened decimal multiplication and division, and of logarithmic calculation. The four-place table in the author's "Tables to facilitate," &c., will be found convenient. It is so constructed that the uncertainty in even an interpolated logarithm is less than 1½ unit of the fourth place, and consequently corresponds to less than ± 0·00026, or 1/3850 of the number. The uncertainty in a number furnished for a given logarithm, even by *interpolation*, falls short of ± 0·000145, or 1/6900 of the value of the number. This is more than can be attained with an ordinary four-place table, and suffices in almost all cases.

Ex. 13.—Analysis of a Silver Coin.

DISSOLVE, say, 1 grm. of the alloy by heating it with 10 cc. of 1·2 nitric acid in a slanting Florence flask. If gold is present it remains as a black powder, which collect on a very small filter, ignite precipitate and filter in a small porcelain crucible, and weigh. To the filtrate (which should be in a beaker), add hydrochloric acid *drop by drop*, stirring up diligently after each addition, so that the chloride of silver coagulates, and you are able to see if the next drop produces an additional precipitate. In this way continue until the silver is completely precipitated by *the least practicable quantity of reagent.* Manipulate the precipitate as shown in Ex. 12, and from the weight of the chloride of silver calculate the silver. $AgCl \times 0·7527 = Ag$.

While the AgCl is drying, practise the following "titrimetric" method of silver determination:—

Volhard's Method.—By dissolving 1/10 $NCS.NH_4 = 7·6$ grms. of sulphocyanate of ammonium in water, and diluting to 1 litre, prepare a solution which contains approximately 1/10 $NCS.NH_4$ mgs., and consequently precipitates about 1/10 × Ag. mgs. = 10·793 mgs. silver per cc. To standardize this solution exactly, weigh out from 4 to 5 decigrms. of *pure silver*, dissolve it in 10 cc. of pure nitric acid, of 1·2 specific gravity, in a slanting flask, dilute with water to about 100 cc., add about 5 cc. of saturated solution of iron-alum, and then run in sulphocyanate from a burette until the *red* colour of ferric sulphocyanate, which makes its appearance locally from the first, *through the addition of the last drop of reagent*, has become permanent on stirring. Supposing 450 mgs. of silver have been taken, and 42·1 cc. of standard solution been required to effect a complete precipitation, 1 cc. of the latter may be put down as corresponding to 450 ÷ 42·1 = 10·689 mgs. of silver. This determination must be done twice at least (the two results should agree to within ± 1/1000, or, at most, 1/500 of their value), and the mean of the results be adopted. To determine the silver in the coin, just treat ½ grm. of it as you did the pure silver in determining the "titre" of the reagent. The rest requires no explanation. The copper may be determined by difference.*

You may now resume Ex. 10, and determine the exact weight of hydrochloric acid contained in every cc. of your standard muriatic acid by means of the following two methods:—*1st*, the one explained in Ex. 12; and *2nd*, as follows:—Weigh out (*i.e.*, indirectly measure off) a convenient quantity of your muriatic acid, and, from the result of the gravimetric analysis, calculate the weight of silver which that quantity of acid should be capable of precipitating. Supposing it is 1·106 grms., weigh out a little more than that, say 1·12 grms. of pure silver, dissolve it in nitric acid, dilute to 100 cc. or so, add the weighed-out sample of your muriatic acid, stir up violently, and allow to settle in the cold, and *in the dark*. Then pour off the clear liquor as completely as possible, add iron alum, and, by titrating with sulphocyanate, determine the weight of silver which is present in the solution. From the result you will see

---

* By intention, British coins contain 92·5 per cent., German and French coins 90·0 per cent., of real silver. The rest, apart from an occasional trace of gold, is copper.

whether or not it is worth while to recover and estimate the small remnant of dissolved silver contained in the moist precipitate. Deduct the silver found by titration from the silver originally taken, and, from the difference, calculate the hydrochloric acid, remembering that every Ag = 107·93 parts of silver corresponds to HCl = 36·45 parts of real hydrochloric acid.

Note.—In either case, you had better state your result in multiples of HCl mgs. per cc. Supposing, for instance, you obtained 145·3 mgs. of chloride of silver per cc., report the hydrochloric acid as being 145·3/143·38 × (HCl = 36·45) mgs., reducing the fraction 145·3/143·38 to a decimal. And, similarly, if with the second method you found 1 cc. of your acid precipitated exactly 109·1 of silver, report thus—109·1/107·93 × (HCl = 36·45) mgs. of chloride of hydrogen.

Ex. 14.—Sulphate of Iron and Potash.

$FeSO_4 K_2SO_4 + 6 H_2O$.

SUBSTANCE.—Dissolve 64 grms. of pure ferrous sulphate crystals and 29 grms. of pure powdered sulphate of potash* in 110 cc. of hot water and 1 cc. of 20 per cent. sulphuric acid; filter hot into a basin, and allow to crystallize. Throw away the mother liquor. Dry the crystals on filter paper by exposure to ordinary air. Do not re-crystallize your salt, or else it changes composition.

Determination of the Sulphuric Acid.—Dissolve 1-1·5 grms. of salt in about 100 cc. of water, with addition of 2-3 cc. of 20 per cent. HCl, heat to boiling, then add a slight excess of chloride of barium. Keep the mixture at a boiling heat until the precipitate of sulphate of baryta has settled. Manipulate the precipitate as shown in Ex. 12, except that you acidulate the wash-water with hydrochloric, instead of sulphuric, acid. From its weight calculate the percentage of sulphuric acid. $BaOSO_3 \times 0·3432 = SO_3$. Keep filtrate and wash-waters for the determination of the iron and potash.

---

* *See* Note (3) at end of volume.

To Determine the Iron.—Boil down the filtrate* (with addition of a few granules of chlorate of *baryta* to peroxidize the iron) to about 200 cc. Then add excess of ammonia, and boil off that excess again (in order to minimize the precipitation of barium). Collect the precipitate on a No. 5 filter, and wash it with hot water until the last drop of wash-water leaves no residue on evaporation on platinum foil. As this precipitate is always contaminated with barium, scrape it from the filter (before drying) as completely as possible by means of a platinum spatula, dissolve what sticks to the filter in hydrochloric acid, and use the liquor for dissolving the bulk of the precipitate. Precipitate the barium with a few drops of sulphuric acid in the heat, allow to settle, filter and wash the precipitate, and in the filtrate reprecipitate the iron with ammonia. Dry, detach the oxide as completely as possible from the paper, and place it in a tared platinum crucible. Incinerate the paper in a platinum spiral, add the ash to the precipitate, ignite, and weigh. From its weight calculate the percentage of ferrous oxide. $Fe_2O_3 \times 0{\cdot}9 = 2\ FeO$.

The Potash is determined in the filtrate obtained in the first precipitation of the oxide of iron. Concentrate the wash-waters by evaporation in a slanting flask, add the filtrate, and next precipitate the barium by addition of ammonia and carbonate of ammonia. Keep the mixture on a water bath until the carbonate of baryta has settled, then filter it off and wash it with hot water, always adding a few drops of carbonate of ammonia to increase the insolubility of the precipitate. Boil down the filtrate in a flask, and ultimately evaporate to complete dryness in a Berlin basin. Scrape out the *dry* residue, transfer it to a platinum crucible, put on the lid, and, by applying a flame, gradually and slowly burn off the ammonia salt, taking care never to let the temperature rise beyond *dull* redness. To recover the small quantity of salt sticking to the basin, dissolve it in a few cc.'s of sal-ammoniac solution, evaporate to dryness *in the basin*, scrape out that residue, and treat it like the first. The non-volatile residue should, by theory, consist of pure chloride of potassium,

---

* "Filtrate" always includes the washings as far as they contain anything of the substance to be determined in the filtrate.

but is generally not quite pure. Weigh the crude chloride, then see if it is quite soluble in water, and if the solution remains clear on adding a drop of carbonate of ammonia. If the mixture is *turbid*, filter off the small precipitate formed, evaporate the filtrate to *dryness* in the crucible, ignite gently to drive off the chloride of ammonium, and weigh the residue as (now sufficiently pure) chloride of potassium. Reduce to percentage of K_2O by eq. $2KCl \times 0·6319 = K_2O$.

The Water is determined by difference.

Theoretical Composition.

Ferrous oxide,	72·02	16·58
Sulphuric acid,	160·12	36·86
Potash,	94·27	21·70
Water	108·03	24·87
	434·44	100·01

Ex. 15.—Analysis of Sulphate of Magnesia and Potash.

SUBSTANCE.—Dissolve 53 grms. of crystallized sulphate of magnesia and 29 grms. of sulphate of potash in 150 cc. of boiling water, filter, and allow to crystallize. Do not re-crystallize your double salt.* Place the crystals on filter paper, and expose them to the air to dry.

The Water is determined as shown for chloride of barium in Ex. 12. Take care that the temperature, while fully up to, never rises beyond, dull redness, or else some of the SO_3 goes with the H_2O.

The Magnesia.—Dissolve 0·7 – 1 grm. of the salt in 40 cc. of water, add a few cubic-centimetres of sal-ammoniac, then 10 cc. of ammonia, which should produce a clear liquid. If a precipitate is produced, take it away by cautious addition of more sal-ammoniac. Then add a slight excess of phosphate of ammonia, and allow to stand for twelve hours in a *covered* beaker. In stirring the mixture, avoid touching the beaker with the glass rod, or else the parts of the precipitate which form at the scratches produced

---

* *See* Note (3) at end of volume.

will be very hard to remove. After having made sure that the precipitation is completely effected, collect the precipitate on a No. 5 filter, wash it with a mixture of 1 volume of 10 per cent. ammonia and 2 volumes of water until the last runnings are free from sulphate, dry it, separate it from the filter, incinerate the filter in a platinum spiral, and ignite precipitate and ash in a porcelain crucible until the weight remains constant, even at a bright red heat. The ignited precipitate is $P_2O_7Mg_2$; from its weight calculate the magnesia. $P_2O_7Mg_2 \times 0{\cdot}3623 = 2MgO$.

The Sulphuric Acid is determined by precipitation with chloride of barium, as shown in Ex. 14. From the weight of the sulphate of baryta calculate the percentage of sulphuric acid as SO_3. For the

Determination of the Potash, we recommend the following two methods. Both should be practised by the student:—

1.—Tatlock's Method.

Dissolve, say, 0·5 grm. of the double salt in 20 cc. of water and a few drops of hydrochloric acid, add a quantity of chloroplatinic acid solution, containing 1·3–1·4 grm. of metallic platinum, *i.e.,* about 2·5 times the quantity which is required, by calculation, to convert both the magnesium and the potassium into chloroplatinates, and evaporate over a water-bath until the residue, after cooling, forms a semi-solid magma.

[If the substance to be analysed contains chlorides, add a little water to the residue, and re-evaporate to expel the HCl eliminated from the $PtCl_6H_2$ as far as conveniently practicable. In our case there is no hydrochloric acid produced, as $PtCl_6H_2 + K_2SO_4 = PtCl_6K_2 + H_2SO_4$.]

After cooling, add 2·5 to 3 cc. of water,[*] allow to stand, with occasional stirring, for an hour; then throw the whole on a filter, No. 3, and use first the filtrate, and then about 10 drops of chloroplatinic acid solution, containing 5 grms. of metal per 100 cc. for rinsing the basin. Other 10 to 15 drops of reagent serve to bring the bulk, if not the whole, of what has remained of precipitate in the basin on the filter. After the platinic

---

[*] The intention is to extract the soluble parts with a $PtCl_6H_2$ solution, containing at least 5 grms. of metal per 100 cc.

liquor has drained off as completely as possible, use small successive instalments of strong alcohol, to bring all the precipitate on the filter and wash it free of chloride. About 20 cc. of alcohol suffice for this purpose (Mr. Tatlock recommends alcohol of "95 per cent."; but ordinary alcohol of 85 per cent. by weight no doubt is sufficiently strong). Dry the precipitate in the filter in a drying chamber below 100°C., and transfer the bulk to a watch-glass. To recover what sticks to the filter, replace the filter in the funnel, dissolve off the adhering salt in hot water, and evaporate the solution in a tared platinum crucible. Now add the bulk from the watch-glass, dry at 100°C. until constant, and weigh. $PtCl_6K_2 \times 0{\cdot}1940 = K_2O$.

Another mode of manipulating the filter is to incinerate it in a small crucible (which converts the chloroplatinate into $Pt + 2KCl$), to wash the ash by decantation with hot water, and to weigh the (ignited) platinum. $Pt \times 2{\cdot}4936 = PtCl_6K_2$. $Pt \times 0{\cdot}4839 = K_2O$. The chloroplatinate, if dried at 100°C., retains an appreciable proportion of water; it, besides, is liable to include traces of sulphates. On the other hand, however, a small quantity of the chloroplatinate remains dissolved in the mother liquor, and another is dissolved by the wash liquors; and as a matter of experience the errors very nearly compensate one another.

Mr. Tatlock's method, indeed, gives very satisfactory results with any kind of salt that fairly falls within the denomination of (impure or pure) potash salt. It is not intended for the determination of small percentages of potassium in, for instance, what substantially consists of sodium salts. The principal advantages of the following method are that it is very widely applicable, and gives exact results, even if the potash to be determined is diffused through a large mass of foreign salts; besides, it is less wasteful of platinum than any of the older forms of the platinum process.

2.—FINKENER'S PROCESS.

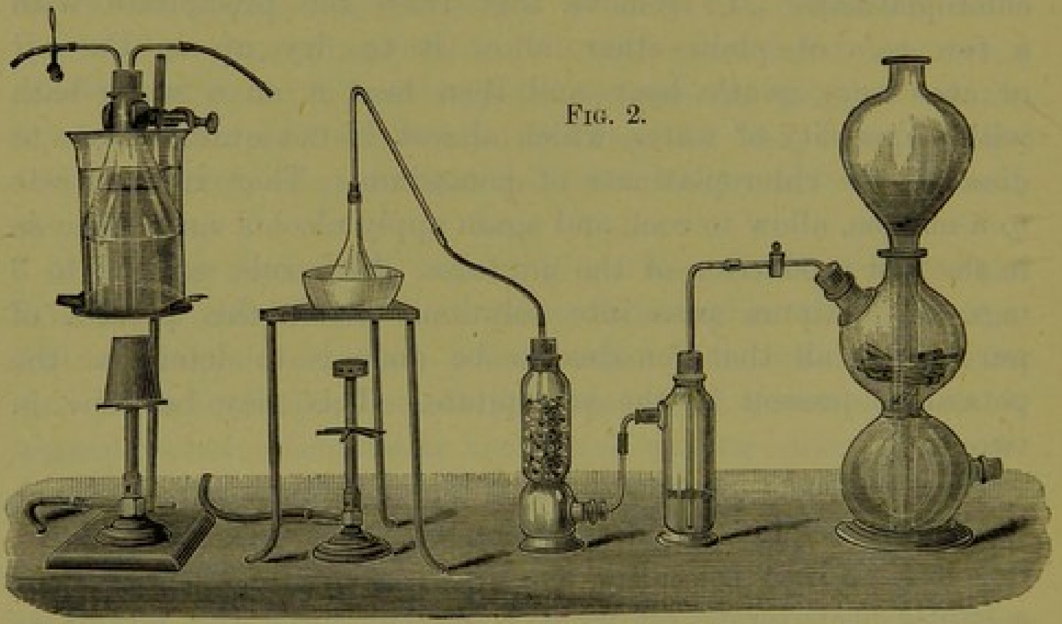
(*As modified by the* AUTHOR *and* MR. JOHN M'ARTHUR).

Dissolve, say, 1 grm. of salt in water, and add about 1·25 times the quantity of chloroplatinic acid required, by calculation, for the conversion of the *potassium* into chloroplatinate, *i.e.*, about 0·6 grm. of metallic platinum for 1 grm. of our double salt. Heat the mixture, and, if necessary, add more water, so that the chloroplatinate formed almost or quite dissolves in the hot liquid. Then evaporate on a water-bath to a very small volume, so that what is left forms, after cooling, a solid magma soaked in, say, 1 cc. of mother liquor; as soon as salt begins to separate out, you must stir up to prevent the formation of large crystals. After cooling, add, first, about 10 cc. of absolute alcohol, and then, after some time, 5 cc. of ether, mix well, and allow the basin to stand under a bell jar for one or two hours, or until the precipitate (a mixture of chloroplatinate of potassium and sulphate of magnesia in the present case; if Na_2O or CaO were present they would go down in similar forms) has settled completely. Decant off the liquid through a filter and wash with ether-alcohol, 1 volume of ether to 2 of alcohol. The precipitate as thus obtained usually contains a small quantity of foreign chloroplatinate. To remove this, rinse the precipitate with a few cc.'s of plain ether, allow it to dry up in the air or at a very gentle heat, and then heat it on a water-bath with a quantity of water, which almost, if not quite, suffices to dissolve the chloroplatinate of potassium. Then re-evaporate to a magma, allow to cool, and again apply alcohol and ether as in the first production of the mixture. As a rule, some 2 to 3 mgs. of platinum pass into solution. After this process of purification all that remains to be done is to determine the potassium present in the precipitate. This may be done in two ways.

First method.—Decant the clear liquor through a filter, No. 4, wash the precipitate by decantation with ether-alcohol as above, dry it (*i.e.*, both the filter and the contents of the basin) at a gentle heat, scrape off what is on the filter and add it to what is in the basin. Incinerate the filter and add also the filter-ash. Then place a glass funnel over the salt in the basin (*see* Fig. 2), and, while sending a pretty brisk current of hydrogen gas through the stem over the substance, raise the temperature of the latter to about 300°C. by means of an Argand or rose burner, and keep up this heat until the chlorine of the $PtCl_4$ part of the salt is completely expelled as HCl. The residue now consists of metallic platinum *plus* sulphates ($MgSO_4$ in our case). Extract them, the bulk by means of water, the last remnant (and other impurities that may be present) by means of warm hydrochloric acid; collect the platinum on a No. 3 filter, wash, ignite, and weigh it. From the weight calculate the potash. (*Vide supra.*) The filtrate from the metallic platinum must be tested by sulphuretted hydrogen, and any PtS_2 that may come down collected, washed, and ignited, to be recovered as metal.

A more exact form of the method is to dissolve all the precipitate in hot water (about 100 cc. for 0·5 to 1 grm. of platinum in the precipitate), and precipitate the platinum as such by hydrogen gas. *Requirements.*—(1.) A "Kipp" affording a continuous supply of washed hydrogen. (2.) An Erlenmeyer flask, holding about twice the volume of the liquid, provided by means of a well-fitting india-rubber "cork" with an inlet tube terminating 1 to 2 centms. above the liquid, and an outlet tube commencing just below the cork and terminating in a short bit of india-rubber tubing. (2*a*.) A pinch-cock to close the latter. (3.) A large beaker rigged up as a hot-water bath. (4.) A carbonic acid apparatus. The flask is filled with hydrogen. When

Fig. 2.



Wet Way. Reduction of K_2PtCl_6 in the Dry Way.
One-tenth actual size.

all the air is out, the outlet is closed with the pinch-cock; but the communication with the Kipp maintained. The flask is immersed almost totally in the water bath, which is kept at 80° to 90°C. until all the platinum is eliminated, which is seen by the disappearance of all colour from the solution. Before opening the flask the hydrogen must be displaced by *air-free* carbonic acid to avoid explosions. The rest explains itself.

Second method.—After having washed the mixture of $PtCl_6K_2$ and $MgSO_4$ with ether-alcohol, digest it in a cold, saturated solution of sal-ammoniac, which readily dissolves the $MgSO_4$ (and Na_2SO_4, if present), but does not change the chloroplatinate if not allowed to act for an unnecessarily long time. Collect the residual $PtCl_6K_2$ on a small filter, wash it as quickly as possible with sal-ammoniac solution until the last runnings are free from SO_3, run alcohol through the precipitate once to remove part of the sal-ammoniac, then dry it (not completely, but only so that the filter can be safely lifted out of the funnel), and, lastly, ignite precipitate and filter at a *dull* red heat in a porcelain crucible. Heat the residue in an atmosphere of hydrogen, and extract the chloride of potassium by means of water. The potassium now can be determined in three ways—1, by igniting and weighing the platinum (this is the safest plan); 2, by evaporating the KCl solution to dryness, igniting gently to expel any (NH_4) Cl that may have remained, and weighing the KCl; 3, (if the (NH_4) Cl is sure to be away), by determining the chlorine in the KCl solution.

The *Second* (sal-ammoniac) method comes in useful chiefly for the analysis of substances poor in potash. In their case the Finkener process serves only for, so to say, concentrating the potassium so as to bring it within the range of the ordinary forms of the platinum process. The recrystallization process is dispensed with. The crude mixture of sulphates and potassium chloroplatinate, after having been washed and dried, is reduced dry in hydrogen as explained, the chloride of potassium extracted by water, and then determined as chloroplatinate, preferably as follows:—The calculated amount of chloroplatinic acid, *plus* about a quantity representing 50–100 mgs. of metallic platinum, is added to the dissolved chloride of potassium, the whole evaporated to a magma on a water-bath, as usual, and after cooling, washed judiciously, first with 0·5 cc. of water, then again with 0·5 cc. of water, or 0·5 cc. of 5 per cent. reagent should the excess of platinum not produce about this strength in 0·5 cc. of added water, then with small instalments of alcohol of about 74 per cent. by weight, and lastly, with nearly or perfectly absolute alcohol. The chloroplatinate is dried at 100°, and weighed as such.*

Theoretical Composition.

Magnesia,.............	MgO	=	40·37	.... 10·02
Potash,................	K_2O	=	94·27	.... 23·40
Sulphuric acid,.......	$2SO_3$	=	160·12	.... 39·75
Water,................	$6H_2O$	=	108·03	.... 26·82
			402·79	99·99

Ex. 16.—Analysis of Phosphate of Lime.

EXAMPLE chosen:—Hydrated di-calcic phosphate, $P_20_5(2CaO.H_2O) + x\mathrm{Aq}$.

Determination of the Water.—Ignite 0·7 to 1·5 grms. in a platinum crucible repeatedly until the weight is constant, and from the loss calculate the percentage of water. The residue, being *pyrophosphate,* is *not* available for the following determinations.

Determination of the Lime.—Dissolve 1 to 1·5 grms. of substance in the least quantity of hydrochloric acid, dilute with water to about 50 cc., and to the *cold* liquid add ammonia until alkaline; then add acetic acid, drop by drop, until the precipitate is redissolved. If an insoluble precipitate remains, filter it off, ignite, and weigh it as P_20_5 (Fe_20_3 or Al_20_3). To precipitate the lime in the filtrate, add a measured volume of an approximately standardized solution of oxalate of ammonia, which is sure to be more than equivalent to the lime present. Allow the mixture to stand in the cold for about half-an-hour, then put it on a water

---

* *See* Note (4) at end of volume.

bath until the oxalate of lime has completely settled. Filter off the oxalate on a No. 5 filter, wash it with hot water, dry, and heat it with the filter in a close platinum crucible until the paper is completely charred. In order now to burn the charcoal, shift the lid a little to one side so that the crucible is only three-fourths covered, and give it the full heat of a good Bunsen until the residue is white. Weigh the crucible, then heat for five minutes over the blow-pipe and weigh again, and so continue until the weight is constant, which shows that the residue has been converted into pure (CO_2-free) lime. The filtrate serves for the

Determination of the Phosphoric Acid.—Evaporate filtrate and washings to about 100 cc., add 25 cc. of ammonia, then magnesia mixture in sufficient quantity, and allow to stand for twelve hours in a covered beaker. Collect and weigh the precipitate as shown in Ex. 15 for magnesia. $(P_2 0_5\ 2MgO) \times 0{\cdot}6377 = P_2 0_5$. While the above operations are progressing, start an independent determination of the phosphoric acid by means of

The Molybdenum Process, which is of great importance on account of its almost absolutely general applicability. Dissolve 0·1 to 0·15 grm. of substance in nitric acid, add enough of a nitric solution of molybdate of ammonia to precipitate the whole of the $P_2 0_5$ (which means at least 40 parts of $Mo0_3$ for every 1 part of $P_2 0_5$ present),* and keep the mixture over a water bath, at about 40°C., for five or six hours, when the $P_2 0_5$ may be assumed to be completely precipitated. But to make sure of this, decant off some of the clear liquor into a large test-tube, add about one-third of its volume of reagent, heat gently for a while, and observe the effect. Supposing the precipitation to be complete, decant the liquor through a No. 4 filter as completely as possible, and wash the yellow precipitate four times by decantation with small quantities (of about 10 cc.) of reagent, or of a liquid prepared by dissolving 15 grms. of nitrate of ammonia in water acidulated by 1 cc. of nitric acid, and diluting to about 100 cc. In order now to determine the $P_2 0_5$ in the precipitate, dissolve what is on the filter in the least quantity

---

* In calculating the reagent, assume your preparation to contain 75 per cent. of $P_2 0_5$.

of ammonia, and use the resulting liquid for dissolving the bulk of the precipitate which was left in the precipitating vessel. To the solution (which should be perfectly clear) add hydrochloric acid, drop by drop, until the yellow precipitate locally formed is somewhat slow in disappearing; then add magnesia mixture to precipitate the P_20_5 as phosphate of magnesia and ammonia, which is filtered off and washed with dilute ammonia. It is always contaminated with *molybdenum*. To remove this, dissolve the precipitate in the least quantity of hydrochloric acid, pass H_2S into the heated solution, allow to stand until the precipitate has settled, then filter and reprecipitate by ammonia after addition of a little magnesia mixture. The precipitate now is pure, and can be manipulated as usual.

According to Finkener,* the phospho-molybdate of ammonia can be weighed directly. For this purpose, precipitate in the usual way, keeping the bulk of the precipitate in the beaker, and wash with an acidified 20 per cent. solution of nitrate of ammonia. Transfer the precipitate to a tared porcelain crucible (preferably a shallow, flat-bottomed one), evaporate to dryness, and heat on a piece of wire-gauze, over a very small flame, till vapours cease to be evolved. Most of the precipitate can be washed over mechanically; what of it sticks to the filter or beaker is dissolved in ammonia; the ammonia solution is added to the precipitate. But according to Finkener, an acid reaction must be established by HNO_3 before evaporating. Weigh and calculate the P_20_5. The precipitate contains 3·794 per cent. of P_20_5. Although it may be slightly discoloured, this will not appreciably affect the final result.

From the percentages found, calculate the formula of the salt—that is, assuming the salt to be $1P_20_5 + xCaO + yH_2O$, find x and y; x should be very nearly equal to 2; y, in a preparation which has not been specially dried under definite conditions, is subject to variation.

Supposing you find $x = 2{\cdot}02$, $y = 4{\cdot}2$, calculate the percentages corresponding to $P_20_5\,(2CaO.H_20) + 3{\cdot}2\ H_2O$, and contrast them with the direct result of your analysis.

---

* Ber. Deutsch. Chem. Ges., 1878, p. 1639.

Ex. 17.—Separation of Iron and Alumina.

WEIGH out about 1 grm. of potash alum, and ·5 grm. of standardized sulphate of iron (*see* Ex. 18), dissolve in water, add hydrochloric acid, and a few drops of nitric, and boil, to peroxidize the iron. Then dilute to about 20 cc., add enough of pure potash to produce a strong permanent precipitate, then place the mixture in a nickel or platinum basin.* Now add excess of strong caustic potash, and keep at a boiling heat, stirring up continually with a platinum rod to prevent actual boiling, until the Al_2O_3 can be assumed to have passed into solution, and dilute, first as far as possible in the metal basin, then by instalments more largely in a Berlin basin provided with a good spout, and filter off the ferric hydrate. Wash the precipitate thoroughly with hot water: the result is that substantially the iron and alumina are separated from each other. But, in general at least, what should be ferric oxide retains a more or less considerable portion of the alumina. This alumina must be extracted by re-dissolving the precipitate in hydrochloric acid, and repeating the treatment with alkali. The crude ferric oxide obtained cannot be ignited and weighed as it is, because it contains combined fixed alkali. It must be dissolved in hydrochloric acid, reprecipitated by ammonia, and ignited as before explained.

From the Alkaline Liquors precipitate the alumina by adding an excess of sal-ammoniac, and heating the mixture until the ammonia liberated is substantially expelled. The test for seeing whether the sal-ammoniac is in excess is, after expulsion of the ammonia, to add some more of the salt, and see if this causes an additional evolution of ammonia. If not, the decomposition of the aluminate is accomplished, and all that remains to be done is to collect the alumina on a filter, to wash it thoroughly with hot water, dry, ignite, and weigh it. The best way of manipulating the alumina is to allow it to dry up in the filter at a gentle heat, until the paper ceases to be actually wet, and the precipitate has shrunk considerably without having become hard and dry; and in this condition to put it, wrapped up in the filter,

---

* If a platinum basin is used, the acid liquor may go in directly.

into a platinum crucible, and ignite it, finally in the presence of air, until all the charcoal is burned away.

For a check, determine the iron and alumina conjointly by precipitating with ammonia and sal-ammoniac. Compare your results with the numbers demanded by the synthesis.

On this occasion, you should learn to work the Bunsen pump. Ask the Demonstrator to show you how to use it.

Ex. 18.—Titrimetric Determination of Iron.

THE method is founded upon the fact that strongly acid dilute solutions of ferrous salt are readily oxidized into ferric salt by addition of permanganate of potash. This reagent forming intensely pink or violet solutions, while dilute iron and manganous solutions are practically colourless, the end-point of the oxidation process is easily seen by the appearance of a permanent red colour in the mixture.

REQUIREMENTS.

(1.) *Standardized Ferrous Sulphate.*—Dissolve 100 grms. of the ordinary *pure* salt in 250 cc. of water and 10 cc. of 60 per cent. sulphuric acid, heat the solution for a while with a quantity of small iron nails, and then filter it through a double filter straight into half a litre of strong alcohol, with constant agitation of the latter. The greater part of the salt comes down as a fine crystal meal. Collect this on a funnel over a small perforated cone of vegetable parchment, and, with the help of the filter pump, suck off the mother-liquor, and wash off the adhering remnant of the latter by means of alcohol. After having dried the salt on filter paper (which should be renewed after the tangible liquor is gone), crush the lumps by gentle pressure, and expose the salt on a bed of fresh paper to the air in a dry place (*not* in artificially dried air) until it has lost every trace of stickiness and rolls over a sheet of paper like gunpowder. Lastly, sift off and reject the coarser parts, and preserve the powdery salt in a dry, well-stoppered bottle. To determine the iron, heat, say, 2 grms. in a platinum crucible, finally to bright redness in the presence of air, until the residue no longer changes weight, *i.e.*, has become pure Fe_2O_3. Before accepting the result, make sure of the absence of FeO and of SO_3 by dissolving a little of the oxide in hydrochloric acid, and applying the well-known tests. The (unavoidable) ferricum amounts to very little; yet it had better be determined, in some 5 grms., by titration with stannous chloride (*vide infra*), and allowed for.

(2.) *A Solution of Permanganate of Potash*, so adjusted that 1 cc. = 5·6 mgs. metallic iron.* Since Mn_2O_7 contains 5 × "O" available for oxidation of iron, and every 1"O" oxidizes $2FeSO_4 + 1H_2SO_4$ into $Fe_2(SO_4)_3 + H_2O$;

$$\begin{aligned} K_2OMn_2O_7 \text{ grms.} &= 10 \text{ Fe grms.} \\ 316 \text{ grms.} &= 560 \text{ grms.; or} \\ 3{\cdot}16 \text{ grms.} &= 5{\cdot}60 \text{ grms.} \end{aligned}$$

As the salt is never absolutely pure, the solution cannot be standardized synthetically. Weigh out, say, 2 × 3·2 = 6·4 grms. of permanganate, dissolve in a mortar by successive instalments of water, and dilute to 2 litres.

To determine the exact strength of the solution, weigh out 0·8 to 1·0 grm. of the ferrous sulphate, dissolve in 200 to 300 cc. of water previously mixed with about 20 cc. of 20 per cent. H_2SO_4, and drop in permanganate solution from a Gay-Lussac burette until the last drop added produces a permanent red colour. Calculate the iron corresponding to 1 cc. of permanganate in multiples of 5·6 mgs.

Supposing you find 1 cc. = 1·012 × 5·6 mgs. of iron, then obviously every 1 lit. of the reagent requires the addition of ·012 lit., or 12 cc. of water. Add the calculated quantity of water, and repeat the standardization. All these standard titrations ought to be done in duplicate at least, and not to be accepted unless the results agree to 0·1 or 0·2 cc. per about 30 cc. of reagent used.

The application of the process to solutions containing iron as *ferrous sulphate* requires no explanation. The following points, however, must be attended to:—

---

* We often use the symbol = for "equivalent to" (in the sense of the reaction considered).

1. The iron solution must be so dilute that 1 lit. contains at most 1 grm. of metal.

2. The solution must be cold.

3. There must be a large excess of H_2SO_4, far more than the chemical equation demands.

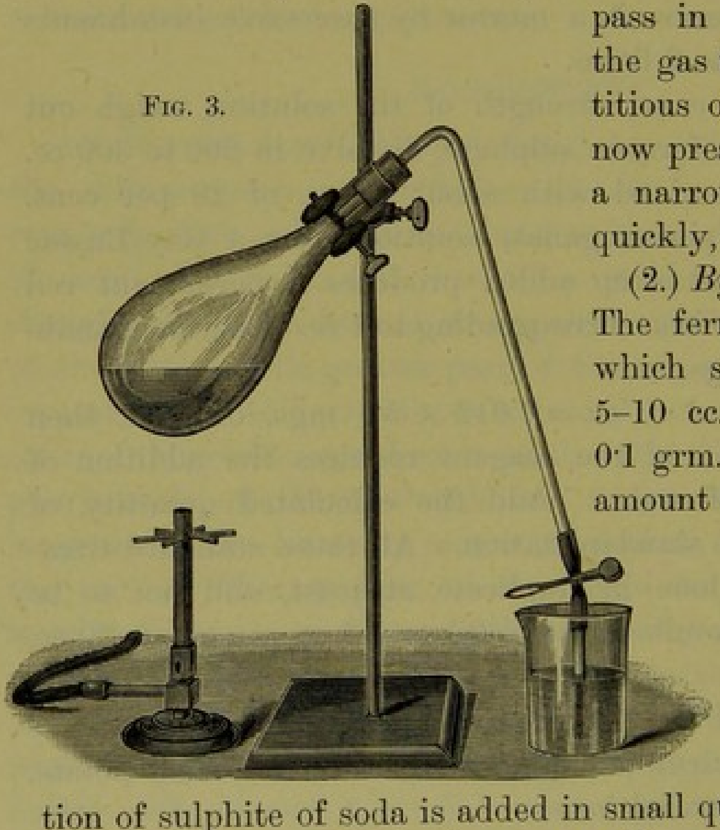
4. The solution must be free from chlorides, or else the HCl takes up part of the reagent, forming Cl_2 and water:—$Mn_2O_7 + 14HCl = 7H_2O + 2MnCl_2 + 5Cl_2$. This, however, can be remedied by addition of a sufficiency of *sulphate of manganese* (Zimmermann). Prepare a solution of 20 grms. ordinary crystallized $MnSO_4\ 4H_2O$ to 100 cc. In titrating, about 20 cc. of this solution should be added per 60 cc. of 20 per cent. HCl used in dissolving the substance to be analysed.

When the iron is given as *ferric* salt, its reduction to *ferrous* salt may be effected by the following methods:—

(1.) *By Sulphuretted Hydrogen.*—Pass H_2S into the solution until it is completely reduced, boil off the H_2S, filter quickly, pass in a few extra bells of the gas to correct any adventitious oxidation, boil off the now present excess of H_2S in a narrow-necked flask, cool quickly, and titrate.

(2.) *By Sulphite of Soda.*—The ferric chloride solution, which should contain about 5–10 cc. of HCl, and about 0·1 grm. of metallic iron, and amount to 100 cc., is placed in a 300 cc. flask with a long neck, diluted to 200 cc., and heated nearly to boiling. The heat is then removed, and a saturated solution of sulphite of soda is added in small quantities till 15–20 cc. in all have been added. As soon as the solution of the sulphite has been all added, an india-rubber stopper provided with a

Fig. 3.



syphon-shaped outlet-tube, as shown by Fig. 3, is inserted, and the liquid boiled briskly. The boiling is continued until the steam, when passed through a dilute solution of permanganate containing a little H_2SO_4, no longer destroys the colour of the reagent. As soon as this test shows that all the SO_2 has been boiled away, the tube is dipped into a beaker containing pure water, the boiling continued for a short time, and the clip then closed, the lamp being, of course, removed at the same time. After a minute or two, the clip is opened and the flask allowed to fill itself up to about the beginning of the neck. The contents are then cooled and the titration is proceeded with, after addition of the requisite quantity of sulphate of manganese. [P. T. Austen and G. P. Hurff; *Chemical News*, vol. xlvi. (1882), p. 288.]

To practise the method of permanganate titration, apply it

(1) To a known weight of pianoforte wire dissolved in dilute sulphuric acid. Good wire contains from 99·6 to 100 per cent. of metal. Calculate for 99·8, and the titration should correspond with that to ± 0·2 or 0·3 per cent.

(2) To the case of iron and alumina in Ex. 17. Produce a mixed precipitate of Fe_2O_3 and Al_2O_3, containing an exactly known weight of iron; dissolve in hydrochloric acid, reduce by means of sulphurous acid, add sulphate of manganese, and titrate.

APPENDIX.

The following two additional methods are given here for future reference. The student is not meant to take them up now; he makes better use of his time by practising gravimetric work.

The Bichrome Method

was invented at about the same time by Penny and by Schabus; and it is worth noting that in the latter's hands it virtually led to the discovery of an error in the then atomic weight of chromium. In principle it is similar to the permanganate method, only bichromate of potash is used as an oxidant, and the end point is sought for by taking out a drop of the titration mixture from time to time, and examining it with ferricyanide of potassium.

The Ferricyanide is used as a ½ per cent. solution, which is best made extemp. from a compact crystal previously washed with water to remove any superficial ferrocyanide. The solution does not keep long, especially not in the light. Before use it must be tested with pure ferric chloride, with which it should strike a brown colour, free of all shade of green. For immediate use drops of the solution are distributed on a flat porcelain plate or in the several cavities of a porcelain slab as used for water-colour painting.

The Bichrome solution can be standardized synthetically. As

$$Cr_2O_6 + 6FeO = 3Fe_2O_3 + Cr_2O_3$$

1/60 of 294·54 grms. = 4·909 grms. of the *pure* reagent dissolved to 1 lit. give a solution of which every cc. peroxidizes 1/10 Fe = 5·6 mgs. of ferrosum. The principal impurity in the salt to guard against is sulphate. To test for it dissolve 1 grm. in 10 per cent. hydrochloric acid, and heat with a few drops of alcohol to reduce the CrO_3 to Cr_2Cl_6. Dilute the dark green solution, add chloride of barium, and allow to stand for twelve hours. Then decant off all except a few drops into another vessel, and dilute the small residue with water. The least quantity of sulphate of baryta becomes visible. To dehydrate the salt it is powdered, and, after having been kept near its fusing point for about ten minutes, fused at the lowest sufficient temperature. On freezing it breaks up into numberless little fragments, and thus spontaneously assumes a convenient form for being weighed out. The titre, as calculated from the synthesis, ought to be perfectly correct; but unfortunately there is no method for proving the absence of surplus chromic acid in the salt, and besides, as a matter of principle, it is better to determine the *iron-titre* experimentally by means of standardized ferrous sulphate. For this purpose about 1 grm. of the iron salt is weighed out exactly, dissolved in 70–100 cc. of water, previously mixed with enough of sulphuric acid to prevent the formation of basic salt in the oxidation. There is no need of any such large excess of acid as is required in the permanganate process. About 95 per cent. of the calculated volume of the bichrome solution are now added out of a burette, and a drop of the mixture is taken out and tested with the ferricyanide solution to make sure that it still contains unoxidized ferrosum, and strikes a blue colour with the reagent. More bichrome is now added in less and less instalments, until a drop, when taken out, no longer gives a *greenish* colour with ferricyanide. Supposing the oxidant at the end to have been added in instalments of 0·2 cc., and the ferrosum reaction to have ceased after addition of 32·2 cc., 32·1 ± 0·1 is put down as the volume equivalent to the weight of ferrosum employed. Should the end point have been overstepped, this is easily set right by adding a known, small, additional weight of iron salt; the final titre is calculated from the mean of 3–4 well-agreeing titrations.

In the determination of an *unknown* weight of dissolved ferrosum, the finding of the end point is, of course, not so easy as in the case of the standardization; but one soon learns to interpret the shades of blue or green observed in the drop tests, and to finish an analysis without wasting any appreciable quantity of the ferrosum over them.

Iron given as *ferricum* must, of course, be reduced to ferrosum by means of sulphuretted hydrogen or sulphite of soda, as above explained. Penny recommends stannous chloride as a reducing agent (*vide infra*), but we do not like to use it, because every drop of stannous chloride that is added over and above the exact quantity needed of course vitiates the result. To obtain exact results we must work on only *moderately* dilute solutions, because the delicacy of even the ferricyanide test is limited, and, strictly speaking, the negative end-reaction comes out, not when the ferrosum is *all* oxidized, but when it is reduced to a small weight r per unit volume of mixture. If the iron solution is very dilute and not susceptible of concentration, this r must be ascertained synthetically and allowed for.

Unlike the permanganate process, the bichrome one is *not* affected injuriously by the presence of chlorides. This is a great advantage, because hydrochloric acid is, so to say, the natural solvent for iron ores, while sulphuric acid, as a rule, attacks them only very sluggishly.

THE STANNOUS CHLORIDE METHOD

is founded upon the fact that strongly acid solutions of ferric chloride are most intensely yellow *in the heat*, and *in the heat* readily reduced (and decolorized) by stannous chloride.

$$Fe_2Cl_6 + SnCl_2 = SnCl_4 + 2FeCl_2.$$

Fresenius has established the conditions under which the reaction takes its normal course, and thus translated it into an exact method for the determination of *ferricum*.

Requirements:—(1.) *A Standard Solution of Ferric Chloride.*—Pure ferric oxide is made by heating pure ferrous oxalate in a basin, and then in a platinum crucible in the presence of air until the weight is constant. (Make sure, by direct testing, that ferrous oxide is absent.) $1/20\ Fe_2O_3 = 8{\cdot}00$ grms. of such oxide are dissolved by prolonged digestion in strong, *pure* hydrochloric acid, and the solution is diluted to 1 litre.

(2.) *A Standard Solution of Stannous Chloride.*—A weighed quantity of pure granulated tin is boiled with pure hydrochloric acid until a sufficiency of the metal is dissolved. The solution is decanted off, and the residual metal washed, dried, and weighed roughly, to see what weight of it has dissolved. For every 3 grms. of dissolved tin the solution is diluted (with boiled out water) to 1 litre to obtain a liquid which decolorizes about half its volume of standard iron solution.

(3.) As a useful, though not indispensable, auxiliary, a solution of *iodine* in iodide of potassium, containing 3 to 5 grms. of free iodine per litre. It is standardized empirically against the tin solution. The ordinary standard solution (*see* Ex. 23) will do.

Standardization of the Tin Solution.

The tin solution readily takes up oxygen from the air, and its titre therefore is eminently variable. It is best kept in a tall bottle, provided with a narrow (clipped) syphon for letting out liquid, and an air inlet tube drawn out to a fine point. The titre then remains constant for at least the space of 2-3 hours. Even for a few analyses a large supply (say one Winchester quartful of solution) had better be made. In the course of time the solution becomes absolutely useless through formation of metastannic acid. Mulder recommends to connect the air space in the bottle permanently with a Kipp (or similar contrivance) yielding carbonic acid on demand; but this complication is worth employing only when the reagent is being used habitually day after day.

To determine the titre, a known volume (say 20 cc.) of the iron solution is run into an Erlenmeyer standing on a flat sand-bath charged with perfectly *white* sand. By means of a bent glass tube connected with a Kipp discharging carbonic acid by means of a *stiff* joint, an atmosphere of carbonic acid is established in the flask, and (let us at once add) maintained to the end. The liquid is mixed with some pure hydrochloric acid, heated to incipient ebullition, and the tin solution is run in from a Mohr's burette, until the last drop, by converting an almost colourless into a perfectly colourless liquid, produces a peculiar transitory blue. The volume of the tin solution used is noted down, and the volume of the iron solution equivalent to one volume of tin calculated (from, of course, a number of agreeing titrations). The outlet tube of the tin burette should be made of a long *narrow* tube, and be bent thus,  so that, while the outlet tube hangs in the titration flask, the burette is not being heated by the vapours. But it is not always (and not with all persons equally) easy to catch the end point. Hence, in general, it is an improvement to intentionally add a slight excess of tin, to allow to cool (in carbonic acid), to add starch solution, and then iodine solution, until the appearance of a permanent blue colour. To ascertain the saturation-ratio between the tin and the iodine solutions, under the circumstances of the analysis, undo the blue colour by adding, say, 2–3 cc. of tin, and then run in iodine again until the blue colour reappears. As the strength of the tin is variable, while that of the iodine solution is practically constant, the *titre* of the latter had better be referred to the iron solution. Supposing, for instance, we find

1 cc. of tin solution = 0·480 cc. of iron solution,
1 cc. „ „ = 2·1 cc. of iodine solution,

we note down that every 1 cc. of iodine is equivalent to 0·48 ÷ 2·1 = 0·229 cc. of iron.

To determine an *unknown* weight x mgs. of ferricum, add pure, strong hydrochloric acid to convert it virtually into Fe_2Cl_6, and establish a strongly acid reaction, and then proceed as in the standardization of the tin. Supposing t cc. of tin and i cc. of iodine to have been used, 1 cc. of tin $= k$ cc. of iron, and 1 cc. of iodine $= n$ cc. of iron solution, then we have the chemical equation,—t cc. of tin $= x$ mgs. of ferricum $+ i$ cc. of iodine $= x$ mgs. of ferricum $+ ni$ cc. of ferricum solution $= kt$ cc. of ferricum solution. Hence, arithmetically, $x = (kt - ni) \times 8{\cdot}0$ mgs. of ferric oxide, or $(kt - ni) \times 5{\cdot}6$ mgs. of ferricum.

If the iron solution is given as ferrosum, it must be converted into ferricum, which is done best by means of a current of chlorine, followed, of course, by expulsion of the surplus chlorine by prolonged gentle heating.

It stands to reason that the method may be reversed for the determination of an unknown weight of stannosum by means of ferric chloride; but it is worth pointing out that it will *not* do in such a case to run the ferric solution into the stannosum solution until a yellow colour begins to appear, because experience has shown that in this latter procedure the free oxygen (O_2) dissolved in the reagent-solutions takes part in the oxidation of the tin, while it does not in the normal process as described.

Ex. 19.—Analysis of Sulphate of Copper and Ammonia.

$$CuSO_4(NH_4)_2SO_4 + 6H_2O.$$

DISSOLVE 250 grms. of pure blue vitriol and 132 grms. of pure sulphate of ammonia in 800 cc. of water at a boiling heat, filter while hot, and allow to crystallize. Dry the crystals in the air on filter paper. Take a sample of 3–4 grms., grind it up to make absolutely sure of its being homogeneous, and preserve it in a corked preparation-tube for the following exercise:—

Determination of the Copper.—Dissolve, say, 1 grm. of the salt in 100 cc. of water, add 2 cc. of 20 per cent. sulphuric acid, heat to boiling, and pass sulphuretted hydrogen through the hot liquid until all the copper is precipitated. Collect the sulphide on a No. 5 filter, wash it with hot water, and dry it. Detach the precipitate from the filter, and incinerate the latter in a platinum spiral; place precipitate and ash in a porcelain crucible provided with a perforated lid (*see* Fig. 4), and heat it over a Bunsen, while a pretty lively current of hydrogen gas is being passed through the crucible by means of a porcelain (or hard glass) tube inserted into the perforation. The precipitate is thereby converted into a mixture of metal and sulphide. To produce a definite sulphide, allow to cool in hydrogen, add a pinch of pure sulphur and again heat in hydrogen, first gently, then more strongly, and lastly, for about twenty minutes, with the full heat of a good Bunsen. Now allow to cool in hydrogen, and weigh. The precipitate now is sure to—at least substantially—consist of Cu_2S; but it is better to repeat the last operation (*i.e.*, addition of sulphur and ignition in hydrogen) until the weight is constant to within, at most, ± 1 mg. $Cu_2S \times 0{\cdot}9996 = 2CuO$.

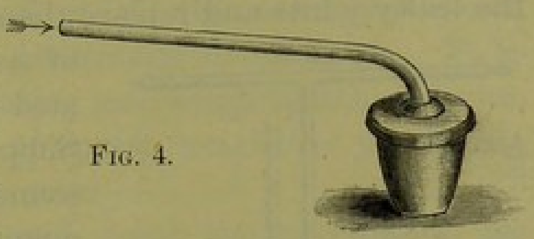


FIG. 4.

To Determine the Ammonia.—Construct the distillation apparatus represented in Fig. 5.* *a* is a Florence flask of 100 cc.'s capacity, communicating with a U-tube *b*, with inflated bulbs immersed in a cold-water bath. The U-tube, when filled up to the upper edge of the bulbs, should hold at least 120 cc. of water. *c* is a tower filled with glass beads or fragments of porcelain; it communicates with an aspirator for reducing the pressure within the apparatus. Before using the apparatus make sure of all the joints being air-tight, by attaching a small mercury manometer (Fig. 6) to the end of *c*, sucking out air so as to reduce the pressure by about $\frac{1}{2}$ or 1 inch of mercury, closing the suction-tube, and

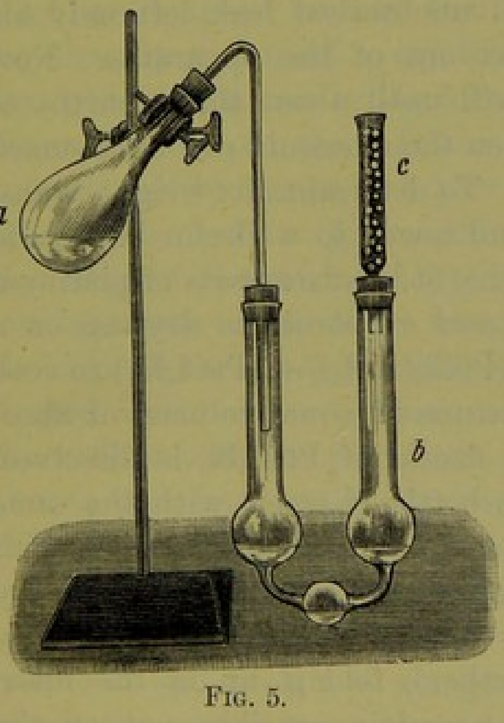


FIG. 5.

---

* Another apparatus for the same purpose is described in Ex. 30 on Kjeldahl's method.

allowing to stand for, say, ten minutes. If the mercury maintains its level, the apparatus is sufficiently tight. If not, discover the leaky joints and replace them by better ones; the application of sealing-wax, &c., cannot be tolerated in a quantitative apparatus. Supposing the apparatus to be in a sound condition, place a weighed quantity (about 1 grm.) of the salt in the flask, and, on the other hand, run a mixture of 1 cc. of 20 per cent. hydrochloric acid and 5 cc. of water into the U-tube through the tower. Now pour on the salt about 40 cc. of 10 per cent. caustic *soda* (not potash), attach the U-tube and the aspirator to the tower, and, by sucking a little air out of the apparatus, reduce the pressure by about 2 inches of water, so that, if there should be a small unobserved leak left, only air can get in, but nothing can get out of the apparatus. Now apply heat to the flask, and distil until about three-fourths of the contents are driven over, when the ammonia can be assumed to have passed over completely. To determine its weight, transfer the contents of the U-tube and tower to a Berlin basin, add an excess of chloroplatinic acid (*i.e.*, at least six parts of platinum for every one part of ammonia), and evaporate to dryness on a water-bath. Allow the residue ($PtCl_6(NH_4)_2 + xPtCl_6H_2$) to cool, treat it with ether-alcohol (a mixture of equal volumes of absolute alcohol and ether) until the excess of $PtCl_6H_2$ is dissolved, and then, by means of a wash-bottle charged with the same liquid, sweep the precipitate on a No. 4 filter, and wash it with ether-alcohol until the last runnings are colourless. Then dry the precipitate (at first *outside* the drying chamber, at a very gentle heat on account of the ether), fold it up in the filter, place it in this condition in a porcelain crucible, put on the lid, and next apply a very gentle heat until the charring of the paper is completed. Then gradually raise the temperature to ultimately a red heat. The precipitate is now reduced to spongy

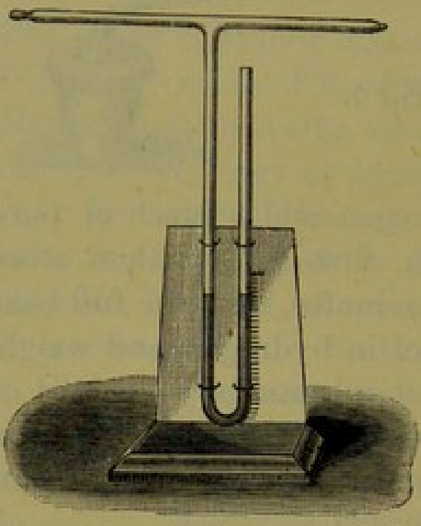


FIG. 6.

platinum, accompanied by charcoal, which coats the lid and the inside of the crucible. Burn away this charcoal as shown for chloride of silver in Ex. 12, and weigh the now pure metal. From its weight calculate the percentage of ammonia. $Pt \times \cdot 17508 = 2NH_3$. Instead of isolating and weighing the platinum of the chloroplatinate, we may, of course, weigh the precipitate itself, which may be done in two ways—

(1.) After having collected and dried the precipitate, we transfer the bulk of it to a tared crucible, and to recover the particles sticking to the paper replace the filter in the funnel, dissolve them by means of hot water, and evaporate the solution to dryness over the bulk of the salt by means of a water-bath. The residue is dried at 100° in an air chamber until constant.

(2.) We collect the precipitate on a filter previously dried (until constant in weight) at 100° (and weighed), and at the end weigh filter and precipitate conjointly. As filter paper is very hygroscopic, both the filter and the filter *plus* precipitate must be weighed within two well-fitting watch-glasses held together by means of a suitable clip. The most exact *modus operandi* in this case is the following:—Prepare two equal sized filters, put one on the left, the other on the right pan of the balance, and by means of a pair of scissors clip off bits from the apex of the heavier filter until it just balances the other. At this stage of the work the filters should not be *handled* directly, but by means of an ivory forceps. Put the entire filter inside the clipped one on the funnel, and collect the precipitate in this double filter. After washing and preliminary drying, dry the inner filter with the precipitate on one of the couple of watch-glasses, and meanwhile keep the tare filter in the same drying chamber in, say, a small porcelain dish. Immediately after the last weighing of the precipitate, take it and its filter out of the watch-glasses, substitute the tare filter as it comes out of the chamber, and weigh it along with the watch-glass couple to obtain the correct tare to be subtracted.

$$PtCl_6(NH_4)_2 \times 0{\cdot}07688 = 2NH_3.$$

The Sulphuric Acid is determined by precipitation with chloride of barium as usual.

The Water is determined by difference.

Theoretical Composition.

Oxide of copper, CuO,	=	79·34	19·85
Ammonia, $2NH_3$,	=	34·11	8·54
Sulphuric acid, $2SO_3$,	=	160·12	40·07
Water, $7H_2O$,	=	126·03	31·54
		399·60	100·00

SUPPLEMENTARY METHODS.

Requirements:—The standard muriatic acid of Ex. 10 and a *standard solution of caustic alkali*. Dissolve 30 grms. of pure caustic potash (purified by alcohol) in distilled water, and dilute to 1 lit. To determine the strength of the solution, charge two burettes, one with the acid, the other with the alkali. Run into a beaker about 20 cc. of the acid, colour it with a few drops of *neutral* litmus solution, and run in alkali until, by addition of the last drop, the mixture, after stirring, is blue throughout its entire mass. That the mixture on standing gradually turns violet is owing to the unavoidable presence of carbonic acid, which gradually acts on the litmus, and therefore must not be taken into consideration. Mark down the volumes of acid and alkali used as being equivalent to each other. Now undo the neutrality of the liquid by running in an additional small volume of acid; again neutralize with alkali, and note the volumes of the reagents used. So go on 5–6 times. From each couple of readings, calculate the ratio, $\frac{\text{acid volume}}{\text{alkali volume}} = k$, and take the mean of the well-agreeing numbers. In order *to determine the ammonia*, distil about 2 grms. of the salt with excess of caustic alkali, collect the ammonia in a properly adjusted volume of your standard acid, and, by titration, determine the acid left unsaturated, taking care to determine the point of saturation several times, as in the standardization of the alkali, to obtain as close an approximation to the truth as possible. Supposing the acid used was Acc and the alkali used was Pcc, then $(A - kP)$ cc. is the volume of acid equivalent to the ammonia;

and if 1 cc. of the standard acid was = to exactly 36·45 mgs. of real HCl, the ammonia amounts to (A – kP) × 17·05 mgs.*

Determination of the Sulphuric Acid.—Dissolve 2–3 grms. of salt in 200 cc. of water, pass H_2S into the hot solution until all the copper is down, filter off the precipitate, boil down the filtrate to 100–200 cc., and, after cooling, determine the free acid by titration. This (assuming the salt to be a compound of $CuSO_4$ and $(NH_4)_2SO_4$), gives the acid combined with the oxide of copper (by theory 20·03 per cent.). To determine the rest, add to the mixture a volume of additional standard alkali equal to a little more than was required for the first titration; boil down the mixture in a Berlin basin until the vapours no longer smell of ammonia, or colour turmeric paper. Then add standard acid out of the burette to produce a decidedly acid reaction, and lastly, titrate back with alkali until neutral. The additional alkali used, when corrected for the standard acid added, measures the sulphuric acid combined with the ammonia (again 20·03 per cent. by theory).

Ex. 20.—Analysis of Carbonates.

Example chosen:—Iceland spar; or pure precipitated carbonate of lime as used in Lawrence Smith's method of Silicate Analysis. (*See* Ex. 37).

The carbonic acid in this as in most other carbonates can be determined in two ways, namely, by decomposing a known weight by means of a suitable acid, and weighing the carbonic acid which goes off, either *indirectly* by identifying it with the loss of weight which apparatus, substance, and reagents conjointly suffer in consequence of the withdrawal of the carbonic acid, or else *directly* by collecting it in an apparatus charged with potash or other chemical absorbent for carbonic acid, and

---

* *Note to more advanced students.*—To obtain the highest attainable precision, the ratio *k* must be determined in a solution as dilute, and containing about as much $(NH_4)_2SO_4$ as the titration mixture in the analysis did. *Neutral* $(NH_4)_2SO_4$ is made by precipitating an ammoniacal solution of ordinary pure salt with strong alcohol, washing the precipitated crystal meal with alcohol, and drying in the air.

ascertaining the increase of weight suffered by the absorption apparatus. The second method is susceptible of a higher degree of exactitude than the first; hence, in the instruction concerning it, we introduce certain refinements omitted in the first, although equally needful theoretically on both sides.

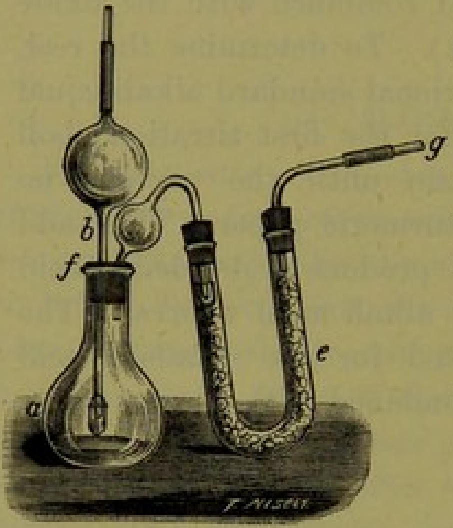


Fig. 7.

(1.) *The Indirect Method.*—Construct an apparatus according to Fig. 7. *a* is a flask of about 100 cc.'s capacity; *e*, a U-tube charged with granulated porous chloride of calcium as used in organic analysis; *b*, a pipette of 15–20 cc.'s capacity, which must be provided either with a stopcock at *b*, or else with a small india-rubber cap at the top, and in any case with a small "thimble" below, which is tied to a contracted portion of the stem by means of a thin platinum wire fused to the edge of the thimble; *f* is a very carefully fitted in and perforated cork or india-rubber stopper. To execute an analysis, place, say, 1 grm. of substance in the flask, and add about 5 cc. of water. Charge the pipette with about 15 cc. of 10 per cent. hydrochloric acid, and put the apparatus together as shown by the figure, taking care that none of the acid gets in contact with the substance before it is wanted. Now, in order to cause the apparatus to quickly assume a constant weight, plunge it into a mass of water of the temperature of the balance-room up to almost the rim (without wetting the cork), wipe off the water, suspend the apparatus at the balance, and determine its weight repeatedly at intervals of about five minutes until two consecutive weighings agree to within 1 mg. While the apparatus is being left to itself, both the top end of the pipette and the exit end of the U-tube are closed with india-rubber caps; the latter cap, however, must be removed before the weight is determined. Decompose the carbonate by *gradual* addition of acid from out of the pipette, then gently heat the contents, finally to *near* boiling, and, by gently shaking the flask round, expel the dissolved carbonic acid; lastly, remove the cap of the pipette and suck at the *g* end, by means of an india-rubber tube, until all the liberated carbonic acid can be assumed to be displaced by air. Now put on the caps, allow the apparatus to cool, and, in order to bring its outside as nearly as possible into the same condition as it was at first, keep it for a sufficient time immersed in a water-bath of the temperature of the balance-room. Then wipe off the water, remove the outlet cap, and determine what the weight now amounts to. The rest requires no explanation.

(2.) For executing *the direct method* rig up the apparatus (Fig. 8). The flask *a* should be of 100–150 cc.'s capacity. The stem of the funnel should extend to near the bottom of the flask; the outside portion of it is shaped so that, supposing the stem to have once been filled with liquid, this liquid will, under all circumstances, be partly retained by the tube so as to prevent egress of gas. The flask, through an ascending, rather wide tube, communicates with a small U-tube *b*, charged with pumice impregnated with dehydrated sulphate of copper* to absorb HCl vapours. A thimble placed in the U-tube *b* (Fig. 9) below the entrance end of the tube from the flask serves to collect that part of the water and hydrochloric acid which has condensed

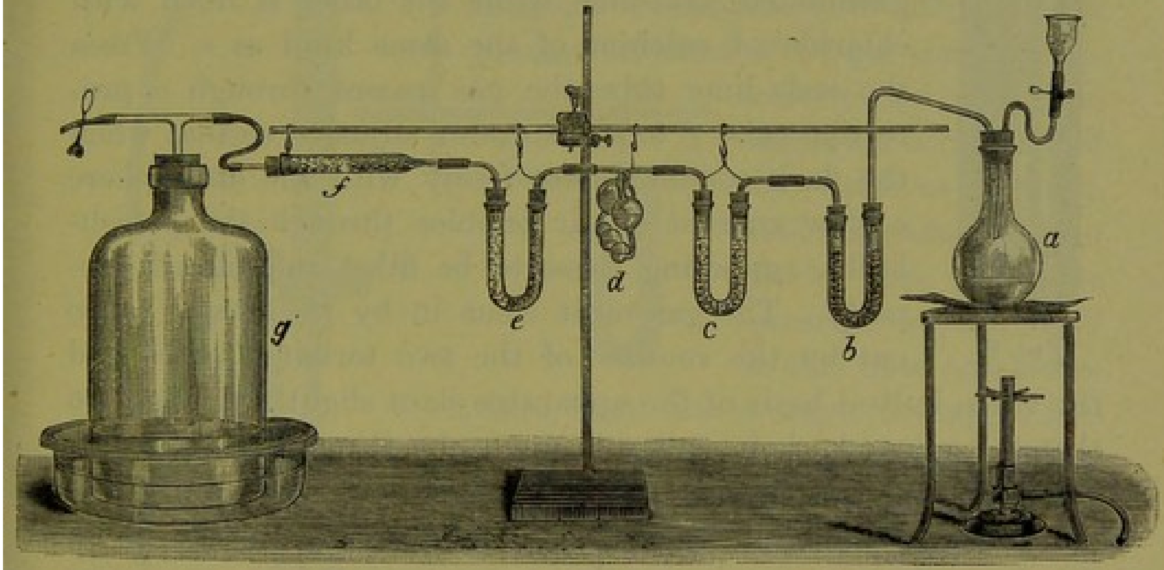


Fig. 8.

---

* Soak fragments of pumice in solution of sulphate of copper, and heat them in a platinum dish until white.

during the descent of the gas through that tube. From the sulphate of copper tube (supposing carbonic acid to be evolved in the flask) the gas passes next through a chloride of calcium U-tube *c* to be dried, and thence through the Liebig bulbs *d* charged with liquid caustic potash (1 part of sticks to $1\frac{1}{2}$ parts of water), where the carbonic acid is almost completely absorbed; but a small quantity escapes absorption, and besides, some of the water of the ley is always carried away as vapour by the unabsorbed part of the gas (the air). To condense both is the function of the little U-tube *e*, of which the limb nearer to the potash-bulb is charged with granulated soda-lime, while the other is filled with chloride of calcium of the same kind as *c*. From the soda-lime tube the gas passes through a protection tube *f* to an aspirator adjusted so that when the flask communicates freely with the atmosphere a slow current of air bubbles through the potash-bulbs, supposing these to be filled and placed properly. The gas must come in by the *larger* to go out by the *smaller* of the two terminal bulbs, and the three-bulbed basis of the apparatus slant slightly upwards so that the gas *ascends* in going through the three bulbs. To fill the bulbs, put a sufficiency of the ley into a crucible, dip in the entrance (*i.e.*, the major bulb) end, and, while taking care to let the base slant upwards in the sense explained, suck at the outlet end by means of a long enough india-rubber tube to enable you to see what you are doing, until a slow current of air, sucked through after the ley, sends a *little* of the latter up into the outlet bulb (*see* Fig. 10). The inlet end which dipped into the ley must be carefully cleaned, the outside in an obvious manner, the inside by means of filter paper rolled round a thin knitting wire. To make sure that no ley hangs about the outside of the apparatus, finish up by dipping it as far as safe

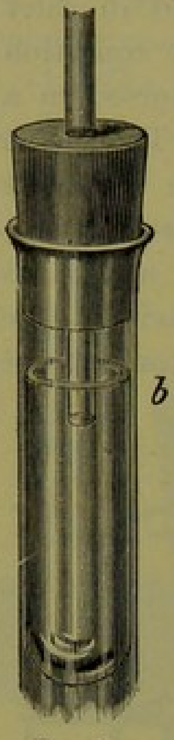


FIG. 9.

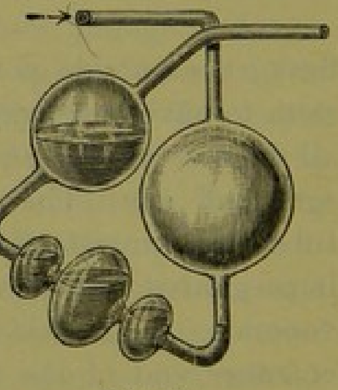


FIG. 10.

into a mass of water, and then wiping it dry by means of a soft towel or linen handkerchief. Supposing the water to be of the temperature of the balance-room, the immersion process is always useful as bringing the bulbs more quickly to a constant weight.

The aspirator arrangement is only meant to make assurance doubly sure; don't trust to its compensating for actual leaks, but test your apparatus before use by means of the mercury manometer represented by Fig. 6, p. 44. Supposing this point to be satisfactorily settled (the potash-bulb and soda-lime tube are supposed to have been carefully tared before), the analysis itself is easy. Decompose your carbonate by gradual addition of 10 per cent. hydrochloric acid, expel the dissolved carbonic acid by cautious heating, and then, after having made sure that the pressure in the flask is less than one atmosphere, suck air through the apparatus by means of the aspirator until all the carbonic acid can be assumed to have been swept into the potash-bulb.

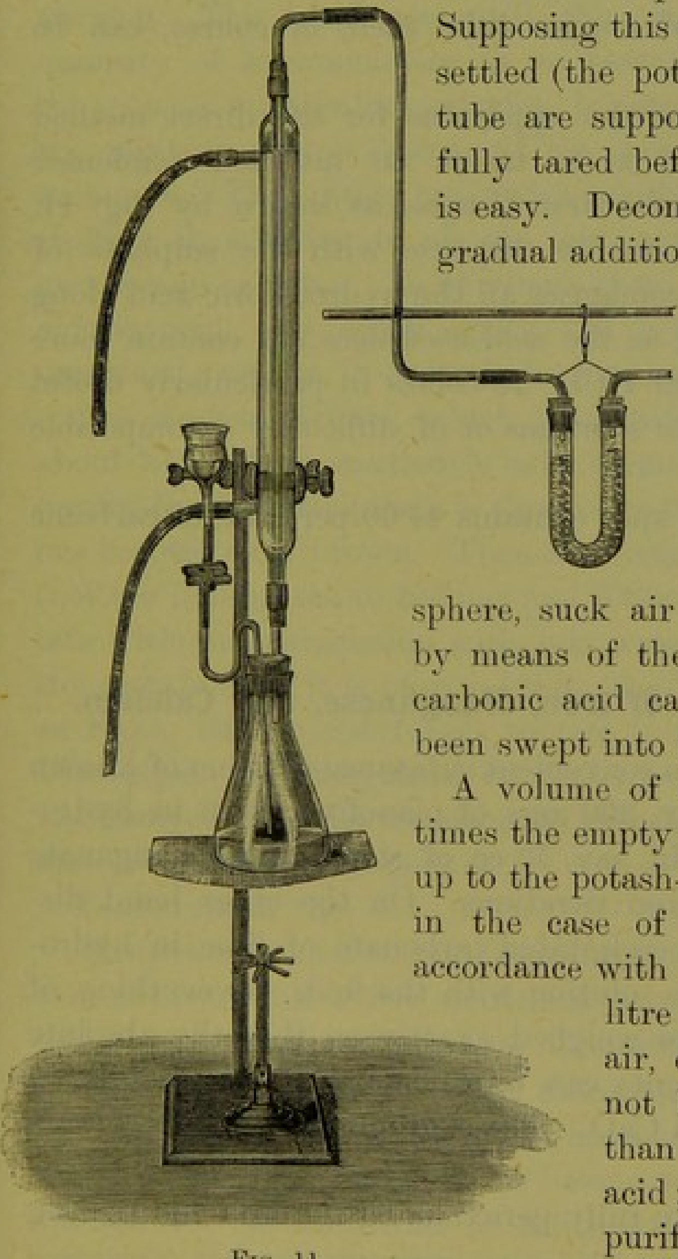


FIG. 11.

A volume of air equal to, say, three times the empty space in the apparatus up to the potash-bulb is sufficient, which, in the case of your apparatus, if in accordance with the figure, means half a litre of air. Half a litre of air, even in a laboratory, is not likely to contain more than half a mg. of carbonic acid; yet it is better to purify the air before allowing it to enter the apparatus by means of a soda-lime tube attached to the funnel by means of a well-fitting cork. The sulphate of copper tube *in the present case*, in the hands of a careful operator, is almost ornamental; but in an apparatus meant to be preserved, it is as well to have it so as to be at liberty, where necessary, to use stronger acid.

Whenever the bases in the carbonate form soluble sulphates, dilute sulphuric acid should be employed instead of hydrochloric acid, on account of its absolute non-volatility from aqueous solutions. The sulphate of copper tube then, of course, can be dispensed with.

An improvement upon the apparatus for the direct method (introduced by Classen) is to insert an inverted condenser between the flask and the first U-tube, as shown by Fig. 11. The condenser enables one to dispense with the sulphate of copper tube, because it condenses all the hydrochloric acid along with the water as long as the acid used does not contain more than 20 per cent. of real HCl. It comes in particularly useful in the analysis of dilute solutions or of difficultly decomposible carbonates.

Theoretically, Iceland spar contains 44·00 per cent. of carbonic acid (CO_2).

Ex. 21.—Separation of Iron, Manganese, and Calcium.

SUBSTANCE.—To obtain a convenient substance-solution of known composition, dissolve, say, 300 mgs. of pianoforte wire in hydrochloric acid, and drop in, say, 50 cc. of standard permanganate of potash as used for iron titrations. On the other hand, dissolve, say, 100 mgs. of precipitated carbonate of lime in hydrochloric acid, and mix the solution with the first. Everything, of course, to be measured or weighed exactly, so that the absolute weights of the components can be calculated* conveniently in terms of FeO, MnO, and CaO. The solution is meant to contain a remnant of ferrosum.

Separation.—Begin by fully peroxidizing the iron by heating

---

* Constants needed for the calculations:—$Mn_2\,O_7\,K_2\,O = 316·3$; $10\,Fe = 560·0$; $2\,Mn = 110$; $CaO\,CO_2 = 100$; $CaO = 56$.

with a few granules of chlorate of potash. Expel the chlorine oxides by gentle heating, and next boil for some time, so that any manganic chloride that may be present assumes, through the action of the hydrochloric acid the state of manganous salt. Then allow to cool, and dilute to about half a litre; add sal-ammoniac if necessary, and then ammonia until it predominates. From the moment when a permanent precipitate begins to form, the ammonia should be added by drops and with constant stirring. This and, more still, the presence of a considerable quantity of sal-ammoniac, is an essential condition of success. As soon as an alkaline reaction is established, at once heat up the mixture, and boil it until the vapours no longer smell of ammonia. Then filter hot, and wash with hot water. The precipitate, in addition to all the iron, contains part of the manganese and calcium. To eliminate them, re-dissolve it in hydrochloric acid, and again apply the process of separation just explained; or else, in order to learn something new, use

The Acetate Method, which is as follows:—After diluting to about half a litre, cautiously add ammonia in the cold until the locally-formed precipitate is slow in re-dissolving, and the liquid has become dark brown. Then add (neutral) acetate of ammonia (not too little), heat to boiling, and filter *hot.** Wash the precipitate without intermission with hot water containing a little of the acetate until it is pure. Ignite the precipitate, and weigh it as Fe_2O_3, but do not forget to test it for manganese with the blow-pipe. (If manganese be present, the precipitate must be re-dissolved, and the remnant of manganese recovered, weighed, and brought into account).

To determine the

Manganese and Calcium, concentrate the filtrate by evaporation to about half a litre, neutralize (exactly) with ammonia, and add a *slight* excess of sulphide of ammonium to precipitate the manganese as sulphide. The manipulation of this precipitate presents certain difficulties, which, however, according to Fresenius, are overcome by taking care to have a sufficiency—not too much, though—of sal-ammoniac in the mixture, to use colourless, or

---

* *Prolonged* boiling brings the precipitate into a condition in which it refuses to "filter" properly.

almost colourless, sulphide of ammonium (instead of the ordinary yellow reagent), and otherwise operating as follows:—The precipitation is effected at a gentle heat in a flask (conveniently an Erlenmeyer), which should not be much larger than necessary; boiled-out warm water is then added so as to almost fill the flask, which is corked and allowed to stand in a warm place for 24 hours or longer until the sulphide has settled completely. The clear supernatant liquor is now syphoned off into another flask and kept there, meanwhile, protected against access of air. The precipitate is mixed with warm air-free water containing a little sal-ammoniac and sulphide of ammonium, the flask corked up again and put aside to allow the contents to clear up. This second liquor is syphoned off and preserved like the first. With a large precipitate the process is repeated once more (with plain sulphide of ammonium this time); but in our case one washing by decantation will do. Supposing it to be effected, the wash-waters are filtered first (beginning with the more dilute one), and only then the precipitate is collected on the filter, and washed with warm water containing a little sulphide of ammonium.

According to Finkener, the precipitation of the manganese can be effected promptly and successfully by adding the sulphide of ammonium to the neutralized liquid at a boiling heat, boiling for about ten minutes, and filtering off through a double filter. The precipitate is washed with hot water containing sulphide of ammonium. According to the Author's experience (*see* his "Manual of Analysis," pp. 96 and 97), precipitated manganese sulphide is decomposed by boiling sal-ammoniac; hence, the volatilized sulphide of ammonium must be replaced from time to time by fresh reagent.

Of our various methods for bringing precipitated sulphide of manganese into a weighable form, no one is quite satisfactory. Perhaps the best gravimetric* method is Rose's, who, after incineration of the filter, mixes precipitate and filter ash with sulphur, and ignites in hydrogen, &c., as explained for copper, Ex. 19. The thus ignited precipitate is MnS. $MnS \times 0{\cdot}8155 = MnO$, and $MnS \times 0{\cdot}6318 = Mn$.

---

* More advanced students may consult the section on manganese under "Cast-iron."

In the filtrate from the sulphide of manganese, the calcium, after due concentration, is determined by precipitation with oxalate of ammonia in the presence of free ammonia in the heat. The mixture must be allowed to stand hot until the oxalate has settled completely; it is then filtered off, washed hot, ignited, and weighed as CaO. (*See* Ex. 16).

The student, after having learned this method of separation with solutions of known composition, may apply it in the complete analysis of a (manganiferous) spathic iron ore.

Ex. 22.—Spathic Iron Ore.

Impure MCO_3, where M = chiefly Fe, but in general includes Mn, Ca, Mg. The quantitative should be preceded by an exhaustive qualitative analysis.

Powder a supply of the ore, dry it at 100°C., and analyse it in this condition. For the determination of the metals, prepare a standardized

SUBSTANCE-SOLUTION as follows:—Dissolve 5 grms. of substance in hydrochloric acid, and next evaporate to dryness to render the silica insoluble; then separate out the silica (*plus* insoluble silicates) as shown in the Exercise on Silicate Analysis. The impure silica is filtered off, ignited, weighed, and calculated as "*gangue*." The filtrate is diluted to 500 cc. or other convenient volume, and aliquot parts are used for the determinations. We are in the habit of doing these fractionations both by volume and by weight, and of calculating from the recorded weights (*see* Exercise on Sea Water); but in this case volume-measurement will suffice.

The Metals are determined as explained in the preceding Exercise,—it being remembered, however, that the sesquioxide precipitate may contain alumina, which, if present, must be eliminated and determined as explained in Ex. 17, and that the oxide of iron may contain silica. This silica remains when the ignited precipitate is dissolved in strong hydrochloric acid, and thus becomes weighable.

As the presence of alumina involves a second precipitation of the oxide of iron, in its presence *one* precipitation of the mixed sesquioxides will do; but the filtrate from the (re-precipitated) alumina-free ferric oxide must, of course, be worked up along with the first filtrate from the sesquioxides (for manganese, lime, and *magnesia*). The *magnesia* is determined in the filtrate from the oxalate of lime by means of phosphate of ammonia, as explained in Ex. 15.

For *the Carbonic Acid, see* Ex. 20.

To check the results, determine the iron titrimetrically in an aliquot part of the substance solution, and ascertain by direct experiment what percentage of fixed residue the ore leaves when ignited—finally in the presence of air—until the weight is constant. This percentage must agree with that calculated from the separate determinations, assuming the metals to remain as Fe_2O_3, Mn_3O_4, CaO, MgO respectively.

Note.—The united ammoniacal filtrates (containing the manganese, &c.) *may* contain such masses of ammonia salt that it is necessary to remove these—by evaporation to dryness and calcination of the residue—before the determination of the protoxides is proceeded with. The calcined residue is dissolved in water, with addition of hydrochloric acid.

Ex. 23.—Preparation of a Standard Solution of Iodine.

A SOLUTION of iodine in iodide of potassium which contains an exactly known weight of free iodine per cc. is susceptible of manifold applications as a titrimetric agent. For its preparation the most exact method is a

Direct Quantitative Synthesis.—The necessary pure iodine is best prepared by Stas' method. A quantity (say 50 grms.) of commercial *re-sublimed iodine* is dissolved by grinding it up in a mortar with 75 grms. of water, and the least sufficient quantity—about 35 grms. will do—of iodide of potassium. As the solution is almost opaque, allow to stand for a time, decant off the liquor, and, if any undissolved iodine is left, bring it into solution by means of the least sufficient quantities of iodide of potassium and water. Filter the solution through a bunch of glass wool stuck into the throat of a funnel, and dilute it with ten times its volume (or if necessary, more) of water to precipitate as large a proportion as possible of the dissolved iodine. The precipitated iodine is quite free from bromine and chlorine; these remain in the mother-liquor. Wash it by decantation with pure cold water, collect it on glass wool, allow to drain, and next dry it further on a plate of unglazed porous stoneware. To dry the preparation further, keep it in a shallow basin over perfectly anhydrous nitrate of calcium under a bell-jar for a number of days. For its final purification distil it from out of a very short-necked retort heated by means of an air-bath which quite encloses it. The first instalment of vapours often contains a little water, and therefore is collected separately. As soon as the water is gone, the rest of the vapours are allowed to fall into a large wide-necked Erlenmeyer, where they condense, assuming, as a rule, the form of a semi-fused compact mass. This is taken out, ground up coarsely, and dried finally over *fresh* nitrate of calcium. By re-subliming (the compact mass) in instalments from out of a watch glass (which is being heated very slowly on a piece of sheet-iron or asbestos paste-board) into a beaker placed over the watch glass, the iodine is obtained in isolated crystals, which are more easily dehydrated finally than a powder prepared in a mortar.

Small quantities of precipitated iodine are best sublimed at once in this way, the first instalment of vapour being allowed to go off *with the moisture*.

After having produced a supply of pure anhydrous iodine, it is expedient to at once weigh out, say, 3–4 portions exactly in glass tubes and seal them up for future use. If there is a sufficient quantity, prepare from it a quantity of exactly standardized solution by weighing out some 5 grms. exactly, dissolving them in strong solution of 10 grms. of iodide of potassium, and diluting to 1000 cc.

Such synthetically-produced iodine solution, however, is expensive; hence it had better be used only for the exact standardization of a larger supply of roughly standardized solution made either from ordinary iodine weighed out approximately, or from the mother-liquor obtained in the Stas process of purification by adding some more iodide of potassium to it to preclude future precipitation of iodine, standardizing it roughly in the first instance, and diluting with the calculated volume of water. For an exact standardization, prepare first an *auxiliary solution of thiosulphate of soda* by dissolving 10 grms. of the *pure* salt $Na_2S_2O_3 5H_2O$ in water, and diluting to 1 litre. When this solution is mixed with iodine solution, the salt is oxidized into tetrathionate in exact accordance with the equation—

$$2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6.$$

On titrating a given volume of the iodine solution by added thiosulphate solution over a white underground, the end point of the reaction can be seen very sharply, without the use of starch solution, by the disappearance of the last trace of yellow colour. Of course, the addition of a little *clear* starch solution near the end of the reduction facilitates the recognition of the end point. Supposing unit volume of thiosulphate requires for its oxidation, according to one experiment, n volumes of the normal iodine solution, and, according to another, n′ cc. of the iodine solution to be standardized, both contain the same weight of free iodine. It stands to reason that a directly weighed-out small quantity of dry iodine dissolved in iodide of potassium solution and conveniently diluted may be substituted for the synthetically-standardized solution. The *titre* is noted by stating the free iodine per cc. as a multiple of I = 126·85 mgs. The iodine solution, when kept in a good glass-stoppered bottle in a cool place and away from direct sunlight, retains its *titre* for a long time. It must not be measured in a Mohr's burette, because the vulcanized india-rubber of the pinch-cock reacts with the free iodine. The thiosulphate solution is not quite so stable as the iodine solution; but if made from *pure* salt, it changes only very slowly. After long standing it deposits sulphur. As soon as this change shows itself, the solution must be thrown away and renewed.

Examples of Applications.—By means of standardized iodine solution we can determine—

(1.) *Arsenious Acid* given as dissolved alkaline arsenite. The solution must be free from caustic alkali, and should not contain an immoderate quantity of carbonate. Dilute moderately, add starch solution, and titrate with iodine, stirring up constantly, until the liquid becomes permanently blue. Then add sesquicarbonate of ammonia, which, in general, will cause the colour to disappear; if so, drop in more iodine solution until the mixture is blue and retains the colour on addition of a little more of the sesquicarbonate (Mohr). If enough of the latter is present to ensure to the mixture an alkaline re-action even at the end, the process goes on in accordance with the equation—

$$As_2O_3 + 2H_2O + 2I_2 = 4HI + As_2O_5.$$

(2.) *Antimonious Oxide* Sb_2O_3, given as dissolved tartar-emetic, or in similar conditions, behaves like arsenious acid.

(3.) *Dissolved Thiosulphate.*—Even in solutions acid by hydrochloric acid, the reaction goes on, as above explained, if the solution is sufficiently diluted, and the thiosulphuric acid formed by the hydrochloric acid has had no time to suffer its characteristic spontaneous decomposition into sulphur and sulphurous acid.

(4.) *Dissolved Sulphurous Acid*, H_2SO_3.—The solvent must be *air-free* water, and the solution so dilute that it contains no more than about three parts of SO_2 per 10,000 parts (Bunsen), or else the sulphuric acid formed—

$$H_2SO_3 + H_2O + I_2 = 2HI + H_2SO_4$$

acts backwards on the 2HI produced in the sense of the same equation read from the right to the left. Hence, any free sulphuric acid present from the first (in calculating the water to be added) must be taken into account as representing so much sulphurous acid. SO_2 per H_2SO_4.

By the combined application of *iodine and thiosulphate* we can determine (1), and obviously, free iodine; (2) free chlorine or bromine, because these, by mere addition of excess of iodide of potassium solution, furnish their equivalent of free iodine; (3) hypochlorous acid. Every HClO, from an excess of dissolved hydriodic acid (KI + enough of HCl), liberates I_2; hence, conversely, every $I_2 = 2 \times 126{\cdot}85$ mgs. of iodine liberated indicate HClO mgs. of hypochlorous acid, or $O = 16$ mgs. of active oxygen, or $Cl_2 = 70{\cdot}9$ mgs. of active chlorine.

(5.) The loosely combined part of the oxygen in any peroxide which, either when brought into contact with iodide of potassium solution liberates a quantity of iodine equivalent to the loose oxygen, or which, when distilled with hydrochloric acid, liberates a similar equivalent of chlorine. Examples :—MnO_2, CrO_3, &c.

Ex. 24.—Analysis of Bleaching Powder.

Exs. 24, 26, and 27 include cases of iodine titration. The student may single these out and practise them before taking up the Exercises in their entirety.

In the analysis of a bleaching powder the most important item is the proportion of real $Cl-Ca-OCl$ ($=caCl+caOCl$) which is contained in it. In practice, however, it is customary not to report the percentage of $CaOCl_2$, but that of the chlorine equivalent to the oxygen of the hypochlorite, which happens to be equal in weight to the chlorine in the $CaOCl_2$.

Of the numerous methods for the

Determination of the "Active" Chlorine,

we select the following three. Whether you choose one or another, begin by weighing out 10 grms. of the "bleach," grinding them up in a porcelain mortar with a good spout with water so as to form a *uniform* paste, and diluting to 1000 cc. Aliquot parts of the turbid solution (to be referred to as the "liquor"), rendered uniform immediately before by turning the close flask upside down two or three times, are measured off for the several determinations.

(1.) *Bunsen's Method.**—Measure off 10 cc. of liquor = 100 mgs. of substance, and add about 1 grm. of solid iodide of potassium, which dissolves readily with liberation of some iodine. To liberate *all* the iodine due ($O+2HI=H_2O+I_2$), acidify with hydrochloric acid, dilute to about 50 cc., and titrate with thiosulphate solution previously standardized by means of standard iodine solution. The method is easy and exact; but the imperfect

---

* As modified by Rud. Wagner. In the original method very dilute sulphurous acid served as the reducing agent.

stability of the thiosulphate is an inconvenience. Hence, whenever bleaching powder tests have to be carried out frequently,

(2.) *Penot's method* deserves the preference. This method measures more directly the *oxygen* of the hypochlorite by ascertaining the weight of arsenious acid, As_2O_3, which it is capable of converting into arsenic acid, As_2O_5. $1/40 \times As_2O_3 = 4{\cdot}95$ grms. of pure powdered white arsenic are placed in a litre flask along with about 11 grms. of *pure* carbonate of soda, Na_2CO_3, or 30 grms. of the dekahydrated crystals, and some water, and the whole is heated over a water-bath until the arsenic is dissolved. A short-necked funnel suspended in the neck of the flask prevents loss by spirting. The (cooled down) solution is diluted to 1000 cc. Every 1 cc. requires $1/10\ Cl = 3{\cdot}545$ mgs. of chlorine for its exact oxidation,* a convenient *titre* for general purposes.†

Where the solution is used only for "bleach" testing, it is, of course, better to adjust it so that 1 cc. = exactly (say) 2 mgs. of chlorine. $4\ Cl \times 1{\cdot}3974 = As_2O_3$. Another requisite is *iodide of potassium and starch paper*, prepared by soaking strips of Swedish filter paper in a very dilute, clear starch solution containing some iodide of potassium, and allowing them to dry in a pure atmosphere. To make an analysis, measure of, say, 20 cc. of liquor = 200 mgs. of substance, and titrate with the arsenite until you have reached the exact point when a drop of the mixture no longer produces a blue stain (indicative of unchanged RClO) on a bit of the test paper placed on a porcelain slab. Should you have overstepped the end point, this can be set right by either adding another cc. of liquor, and resuming the addition of arsenite, or by adding sesquicarbonate of ammonia and some

---

* The student, for his information, should titrate the arsenite, after addition of sesquicarbonate of ammonia, by means of his iodine solution, and compare the analytical with the synthetical result for the arsenious acid. The two results should agree fairly, but they will not agree absolutely, because the respective chemical equations, though right enough as such, as *theories of the processes of titration* are only approximately correct. This remark applies to the majority of titrimetric processes; hence an obvious general rule for the standardization of a solution as a special reagent. For an example: iodine solution intended for determinations of arsenious acid had better be standardized with arsenious acid, although the iodine method is in itself more exact.

† Standard arsenite has a standing as a general reducing agent in titrimetric analysis.

starch solution, and titrating back with iodine solution.* But with some practice it is easy enough to catch the end point to within ±0·1 cc., and even less.

(3.) *Duflos' method*, although antiquated now, affords an instructive exercise to the student. It is founded upon the fact that hypochlorites in aqueous solutions are readily reduced by sulphurous acid with formation of sulphuric acid. $CaCl_2O + SO_2 = CaCl_2 + SO_3$. The sulphuric acid is determined gravimetrically by means of chloride of barium. Both it and the sulphurous acid are embodied in *one* reagent, prepared by dissolving 40 grms. of chloride of barium in 700 cc. of boiled-out water, adding 300 cc. of freshly made saturated sulphurous acid water, and allowing the mixture to stand in a well-closed bottle until the unavoidably formed sulphate of baryta has settled completely. By means of the syphon arrangement described for stannous chloride in Ex. 18, p. 40, it is easy to draw off portions of the clear liquid for immediate use.

According to Sims, 1 cc. of sulphurous acid water saturated completely at 20°C. contains 0·104 grms. of SO_2; hence 10 cc. of our reagent should contain about 400 mgs. of chloride of barium $= 1{\cdot}65 \times BaCl_2$ mgs., and 312 mgs. of sulphurous acid $= 5 \times SO_2$ mgs., or amply enough of barium for, say, 71 mgs. of chlorine equal to about 200 mgs. of bleaching powder, and far more than enough of sulphurous acid; but an ample excess *should* be employed in the analysis.

To make a determination, run a sufficiency of clear reagent into an Erlenmeyer previously filled to overflowing with carbonic acid gas, add the predetermined volume of bleach liquor, and allow the action to go on for a while in the cold, maintaining an atmosphere of air-free carbonic acid; then dilute moderately with boiled-out water, and add some hydrochloric acid to prevent permanent precipitation of sulphate of lime, and at last boil off the surplus sulphurous acid. Collect the sulphate of baryta, and weigh it.† $BaSO_4 \times 0{\cdot}3040 = Cl_2$ and $BaSO_4 \times 0{\cdot}06859 = O$.

---

* Which had better be standardized empirically by means of the arsenite solution.

† Should the bleach contain sulphate, the $BaSO_4$ corresponding to it must, of course, be determined, and deducted as a correction.

The other Components.

The Chlorate.—Most bleaching powders contains a little chlorate. For its exact determination, however, we have no really satisfactory method. Duflos', it is true, gives the total oxygen present as RClO or $RClO_3$, and, were we quite sure that Penot's gives only the hypochlorite oxygen, the chlorate could be obtained by the combined application of the two. But, apart from the uncertainty of this assumption, it is questionable whether the two methods conjointly afford a sufficient degree of precision for the determination by difference of the small quantity of chlorate under analysis. The student should try and see what he can do.

The Total Chlorine.—By boiling the liquor with excess of sulphurous acid solution under an inverted condenser, it is easy to reduce all the oxidized chlorine to chloride. The surplus sulphur dioxide is removed by heating the *sufficiently-diluted* mixture on a water-bath, and the chlorine determined as usual. By deducting the chlorines of the hypochlorite and chlorate, we obtain the chlorine which was present from the first as chloride.

The Carbonic Acid is liberated by means of a mixed solution of hydrochloric acid and enough of stannous chloride to fix the active chlorine as $SnCl_4$, and determined by the *direct* method. (*See* Ex. 20).

The Sulphuric Acid, Silica, "Sand."—A known weight of substance is decomposed by hydrochloric acid in the heat, the solution evaporated to dryness, and the silica (and "sand") eliminated as in a silicate analysis, care being taken not to expel any of the sulphuric acid. The impure silica is weighed as such; a separation of it into silica proper and sand is not worth the trouble. In the solution the sulphuric acid is determined as usual.

An aliquot part of the hydrochloric solution might serve for the determination of the

Lime and Magnesia (and the traces of iron and alumina which are usually present); but on account of the great preponderance of the former, an exact separation can be effected only by means of sulphuric acid, which may as well be applied to an aliquot part of the *liquor*. A measured volume of it is reduced by means of sulphurous acid, which just produces the sulphuric acid needed for the $CaCl_2O$; to satisfy the surplus lime a little more sulphuric acid is added, the whole reduced by evaporation to a small volume, and the sulphate of lime brought down, after cooling, by adding from a half to one volume of alcohol, and allowing to stand over night. The sulphate of lime is filtered off, washed first with aqueous, then with strong alcohol and ignited, to be weighed as sulphate of lime. $CaSO_4 \times 0{\cdot}4116 = CaO$. From the alcoholic filtrates the alcohol is expelled by evaporation in the presence of enough of water to prevent etherification. The iron is then peroxidized with a little chlorine water, precipitated (with the alumina) by ammonia, the excess of the latter boiled off, and the precipitate filtered off to be weighed after ignition. From the filtrate any remnant of lime is eliminated by oxalate of ammonia, and the magnesia then determined as usual.

The Water may be determined by means of the direct method, as given in Ex. 28, for ferrous sulphate. The column of hot chromate of lead retains the chlorine carried away by the steam; but it is easier, of course, to determine it by difference.

In reporting, give first the several components as determined; then express each as a multiple of the respective formula value, *e.g.*, the lime as $x \times 56$, the total chlorine as $y \times 35{\cdot}45$, the active oxygen as $z \times 16$ parts; then combine the chlorous and basilous radicals into multiples of $CaOCl_2$, $CaCl_2$, $CaSO_4$, &c., to obtain the percentages of chloro-hypochlorite, chloride, sulphate, &c.

A novel method, invented by Lunge, for the determination of the active oxygen in bleaching powder is appended as affording an example of what is called "gas-volumetric analysis."

Ex. 25.—Gas-Volumetric Analysis.

LUNGE'S method is founded upon the fact ascertained by him that the hypochlorite, when brought into contact with peroxide of hydrogen in aqueous solution, is reduced by and with the reagent thus: $RClO + H_2O_2 = RCl + H_2O + O_2$. The process is carried out in a flask whose atmosphere communicates directly with that of a gas-measuring tube, and the oxygen measured as an *increase* of volume in the atmosphere common to both ("gas-volumetrically"). Lunge recommends to mix 10 grms. of bleach with enough of water to produce 250 cc. of (turbid) liquor, and to use 5 cc. of the latter, representing 200 mgs. of substance. Supposing these to contain $71 = Cl_2$ mgs., the active oxygen amounts to $\frac{1}{2}$ O_2 mg. = 11 cc. about. The same quantity of oxygen must be contributed by the reagent, which in its customary form contains ten times its volume of loose oxygen. Hence, 2 cc. of reagent (instead of 1·1) are ample.

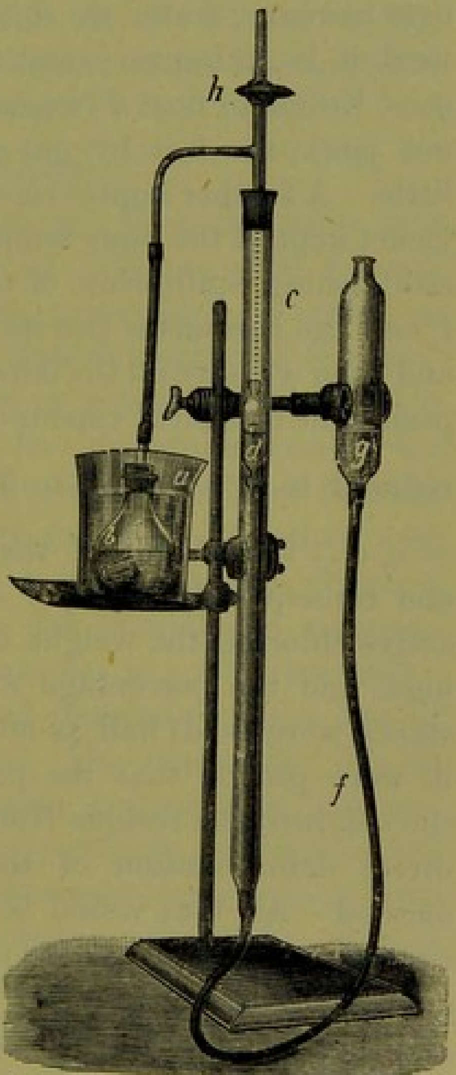


Fig. 12.

The apparatus (Fig. 12) consists of a flat-bottomed flask of, say, 50 cc.'s capacity, wide enough in the neck to enable one conveniently to slide in a flat-bottomed thimble and let it stand upright in the bulb of the flask. By means of a well-fitting india-rubber cork the flask can be made to communicate with an inverted Mohr's burette, the lower end of which communicates through an attached narrow india-rubber tube with a reservoir. The bleach liquor is run into the flask; the reagent placed in the thimble within the former. The burette is charged with water (or mercury) from out of the reservoir, and things are so arranged that, the burette (*i.e.*, cock *h*) being open, the two liquid levels coincide nearly with the top mark of the graduation. The flask is now joined on air-tight after having been immersed in a large beaker containing water of the temperature of the laboratory, the reservoir placed so that the pressure inside is exactly at that of the atmosphere, and the level in the gas-measurer noted down.

Now the cock *h* is closed, the flask tilted over, so that liquor and reagent mix and the reaction allowed to take its course, care being taken to always keep the pressure at that of the atmosphere—approximately at least. After 1–2 minutes the reaction is completed. The pressure is now adjusted to exactly that of the atmosphere, and the increase of gas volume ascertained to obtain the volume of the oxygen. Lunge recommends to collect the gas over mercury; water, we think, will do equally well. If water be used, it is an improvement to provide the Mohr burette with a *good* Erdmann float *d* (we mean one which fits close, and yet does not jam); the loss by gas-absorption, then, is reduced to very little. A further improvement is to enclose the burette in a water jacket kept at the same temperature as that in the beaker. After establishing equilibrium of temperature, we read the temperature *t*, and the barometer (let its height, reduced to 0°C., be $=$ B mm.), and then we have all the data for calculating out the result. Supposing the tension of vapour of water at t° to be $= p$; the gas volume reduced to $T = P$; say to $T = 1^\circ$ and $P = 1$ mm., is $\frac{v \times (B - p)}{273 + t} = v_0$ cc.; the weight of the oxygen $= v_0 \times 0{\cdot}03212 \times 16$ mgs.; and consequently as O_2 of oxygen evolved corresponds to Cl_2 of active chlorine, the weight of the latter is $v_0 \times 0{\cdot}03212 \times 35{\cdot}45$ mgs., and the percentage x of the latter (as 200 mgs. of substance were used) half as much, *i.e.*, $x = 0{\cdot}5693 \times v_0$. Supposing it were proved that the peroxide of hydrogen does not touch the *chlorate*, the residue from the Lunge test might serve for the direct determination of the oxygen in the latter by Duflos' method. All that would be necessary would be to destroy the surplus peroxide by means of platinum black, or (after diluting and acidifying) by means of the exact quantity of permanganate, and then to apply the Duflos reagent in an atmosphere of carbonic acid, as above explained.

Perhaps a better, and certainly a simpler, method would be, after (or perhaps without) destruction of the surplus peroxide, to next eliminate the chloride chlorine by means of nitrate of silver *in the cold*, and in the filtrate determine the *chlorate* chlorine by reducing the ClO_3 with sulphurous acid. The Cl of the ClO_3 assumes the form of chloride of silver, which is easily freed from the admixed sulphite by dilute nitric acid, and thus made fit for the balance.

Ex. 26.—Native Oxide of Manganese.

THE variety of minerals which our heading includes, from the standpoint of the analyst, can all be viewed as compounds $MnO_2 + x\,MnO + y RO$, where R may include Fe, Co, Ni, Ba, Ca, Mg, H_2, but be absent; the value of x varies from 2 (in Hausmannite, Mn_3O_4) to *nil* (in pure pyrolusite, MnO_2).

METHODS OF ASSAYING.

"Manganese," as it is called in commerce, is used chiefly as a material for generating chlorine, and its value as such depends substantially, if not entirely, on its percentage of actual or potential MnO_2. But the most exact determination of this percentage, in reference to a given cargo or consignment of ore, is of little value unless accompanied by *two* determinations of the moisture, namely, one with a large average sample of the ore, pounded up quickly though not very finely, and another with the finely-powdered analyst's sample as it goes to the chemical balance. These two determinations for commercial purposes must be carried out by drying both samples in a conventionally-fixed (though arbitrary) manner, and determining the loss of weight as representing the *moisture*. The reason for this is, that even the air-dry ore always contains a greater or less proportion of hygroscopic water, which is subject to considerable spontaneous variation. According to Fresenius (an acknowledged authority on the matter), all the moisture goes away only at 120°C.; yet the customary drying temperature is 100°C.

If the ore is meant to be used as a material for making ferro-manganese or manganese preparations, such as sulphate, &c., the percentage of manganese metal is the most important item in the assay; but the nature and quantity of the impurities in this case form a more important element in the valuation than they do in the case which we considered first. Methods for the mere assaying for *manganese* (Mn) are given in the Exercise on Cast-iron; we here confine ourselves to the determination of the binoxide or active oxygen.

Of the many methods proposed,

Fresenius and Will's unquestionably is the one best adapted to the requirements of the technical assayer. It is founded upon the fact that binoxide of manganese, when brought into contact with aqueous sulphuric and oxalic acids, is readily reduced to manganous sulphate with evolution of $2 \times CO_2$ of carbonic acid for every one MnO_2 of pure binoxide. $MnO_2 + H_2SO_4 + H_2C_2O_4 = MnSO_4 + 2H_2O + 2CO_2$.

The carbonic acid is easily determined by one of the two methods given in Ex. 20. $2CO_2 \times 0{\cdot}9886 = MnO_2$; $2CO_2 \times 0{\cdot}1818 = O$.

The sulphuric acid must not be too dilute if the reaction is to progress at a convenient rate; on the other hand, it must not be allowed in its concentration to come too near the condition of undiluted vitriol, or else some of the oxalic acid may be converted into $H_2O + CO + CO_2$. This condition, however, almost takes care of itself. It is more important to point out that, according to Luck, ferric oxalate, which is always liable to be present, at temperatures about 70°C. breaks up with formation of carbonic acid and ferrous salt. If such decomposition is allowed to happen in an ore containing iron in only the ferric form, so much Fe_2O_3 is mis-determined as MnO_2.

The ore to be analysed must be very finely powdered, or else the decomposition of the last particles proceeds very sluggishly. But finely-powdered manganese ore is very hygroscopic. Perhaps the best method is to preserve a sufficient supply of the fine powder in its air-dry condition in preparation tubes, and to weigh out—best at the same time—one portion for the determination of the moisture, and another for the assay proper. The oxalic acid is best used in the form of neutral potash salt, $K_2C_2O_4 H_2O = 184$; hence 1 grm. of real binoxide requires 2·12 grms. of this salt. Fresenius and Will prescribe 2·5 grms. for 1 grm. of high-class ore. For the execution of the assay, the inventors recommend the apparatus represented in Fig. 13. Flask *A* should hold about 120 cc.; flask *B*, about 100 cc. when filled up to the neck. *B* is charged with oil of vitriol up to about the middle of its belly. The weighed ore sample (3–5 grms.) goes into *A*, along with the requisite quantity of oxalate, and about 40 cc. of water.

The apparatus is then put together and tared. To start the reaction, some of the vitriol in *B* is made to flow over into *A* by sucking at *d* with a piece of india-rubber tubing, while *b* is closed with an india-rubber cap, and then allowing the atmosphere to press the acid over. This operation is repeated until all the binoxide is dissolved, which, as a rule, requires 5–10 minutes. In order now to expel the dissolved carbonic acid, a somewhat large quantity of vitriol is allowed to run into *A* so as to heat the mixture to near 70°C. The carbonic acid stagnating in the apparatus is then sucked out by means of an india-rubber tube attached to *d*—the cap at *b* being, of course, removed—the apparatus allowed to *cool completely*, and then weighed again.

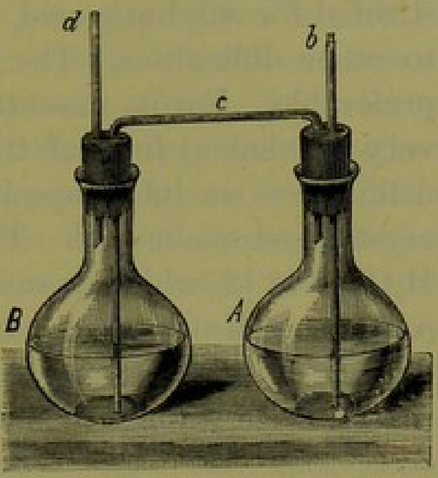


FIG. 13.*

Supposing C grms. of carbonic acid to have been evolved from P grms. of ore, the percentage of MnO_2 is

$$x = \frac{C \times 0{\cdot}9886 \times 100}{P}$$

Where such tests are made habitually, it is obviously expedient to weigh out exactly 3, 4, or 5 times 0·9886 grms. of ore, to facilitate the computation. In a completely equipped chemical laboratory the best *modus operandi* is to decompose, say, 1 grm. of ore (even less will do), and weigh the carbonic acid directly. If the ore contains carbonates, these must be decomposed, and their carbonic acid expelled before the oxalic acid is added. In this case, the inverted-condenser form of the apparatus comes in particularly useful.

The Permanganate Methods.—The MnO_2 is allowed to act on a weighed sufficiency of (*a*) standardized ferrous sulphate, or (*b*) oxalic acid in dilute sulphuric acid, and the surplus reducing agent left at the end determined by titration with permanganate. If form (*a*) is preferred, the reaction must be carried out in an atmosphere of carbonic acid to prevent oxidation of ferrosum by

---

* Taken from Fresenius' "Quantitative Analyse."

the atmosphere; it offers the additional inconvenience that the ore sometimes is rather slow in dissolving. Hydrochloric, substituted for sulphuric acid, works more promptly; but this leads to other difficulties. The oxalic acid *modus* is, on the whole, preferable. For its execution, neutral oxalate of ammonia is a very convenient form of the reagent, on account of the greater definiteness in its composition as compared with, for instance, crystallized oxalic acid. The air-dry crystals are $C_2O_4(NH_4)_2 + H_2O = 142{\cdot}12$, which quantity, of course, requires $O = 16$ parts of oxygen, or $MnO_2 = 87{\cdot}0$ parts of binoxide of manganese for its oxidation. The permanganate had better be standardized expressly with a weighed quantity of the oxalate. For this purpose, some 300 mgs. of the salt are dissolved in 10 per cent. sulphuric acid, conveniently, but not necessarily, along with some manganous sulphate, and permanganate dropped in until the liquid becomes permanently pink. If no manganous sulphate was added, the oxidation at first goes on very sluggishly, even on gentle heating, but it becomes more and more rapid as the amount of manganous salt increases. From the volume of permanganate added, the weight of surplus oxalate is calculated, to be deducted from the weight of salt taken. From the remainder the MnO_2 is calculated. In making an analysis, it is expedient to work on a *relatively* large scale, so that aliquot parts of the mixture (of $MnSO_4$ and surplus $C_2O_4H_2$) produced can be used for repeated determination of the excess of oxalate. If the mixture, as usual, is turbid,* it should be filtered before applying the permanganate, or else the change of colour is not seen with sufficient distinctness. The process of fractional filtration may be employed, *i.e.*, we may dilute the whole to, say, 500 cc., filter off, say, 100 cc. through a dry filter, and, neglecting the volume of the precipitate, look upon these 100 cc. as representing one-fifth of the whole solution.

Bunsen's Method.—A small known weight of the substance † is distilled from out of a small flask with hydrochloric acid of 20 per cent.; the chlorine evolved is passed into excess of solution of iodide of potassium, and the liberated iodine determined

---

* It is as well to make sure that the turbidity includes no oxalate of lime.

† Calculate for 50–100 cc. of thiosulphate.

by titration with thiosulphate, *i.e.*, comparison with the standard iodine solution. The distillation flask should not be larger than necessary; it is best made before the blow-pipe out of a piece of stout glass tubing of 4–6 mms. inner width. Another piece of the same tubing serves for a delivery tube. Both the entrance end of the latter and the edge of the flask are ground flat, and the two are so united by means of a piece of good, stout india-rubber tubing (previously de-sulphurized by treatment with hot, dilute caustic soda, and carefully washed) that the two ground edges touch each other inside. For the reception of the iodide of potassium solution, Bunsen uses a small untubulated retort. The solution is made so dilute that it just fills the belly of the retort, which when used is fixed to a clamp-stand in an inverted position, the neck slanting at about 45°. In this arrangement the greater part of the gas-evolution tube must be as narrow as at all convenient and permissible, and its end drawn out to a narrow point, so that, if the liquid threatens to go back, it does so slowly, and can be driven forward again by increasing the flame below the flask. The several safety contrivances which have been proposed to render the going back of the iodide impossible are all of no use. Another arrangement which generally works better in beginners' hands, is to put the iodide solution into a bulbed U-tube, provided with an attached bead-tube for catching any stray iodine, and kept cold by immersion in a water-bath. The connection of the flask with the U-tube is effected by means of a perforated paraffined cork. The end of the gas-evolution tube goes through this cork down to near the highest level which the liquid can possibly reach.

Whichever *modus operandi* we may adopt, we must remember that aqueous hydriodic acid absorbs oxygen from the air, especially at higher temperatures, with elimination of iodine. Hence, in the case of the retort-modus especially, the iodide solution should be prepared with boiled-out water; and in the case of the U-tube method, the U-tube should be filled with carbonic acid before starting the distillation. The substance is best weighed out direct in the tared dry flask, which is next filled with carbonic acid. Air-free, but cold, hydrochloric acid is then added, and the delivery tube joined on without delay. The iodine liquor must be cooled down (if necessary) by application of cold water,* and, after sufficient dilution with (cold) boiled-out water, be titrated with thiosulphate without delay. Every I = 126·85 mgs. of iodine liberated correspond to $\frac{1}{2}$O = 8 mgs. of oxygen, or $\frac{1}{2}MnO_2$ = 43·50 mgs. of binoxide.

Note.—If the ore contains a ferrous compound (such as magnetic oxide of iron, Fe_3O_4), the iron-permanganate and the Bunsen methods determine only that part of the active oxygen which is present over and above that needed for the peroxidation of the ferrosum. This, however, in the eyes of the assayer, is rather an advantage than a defect, because the ferrous oxide acts in the chlorine maker's still exactly as it does in the assay. In the case of the Fresenius and Will method the effect of the iron in the ore is not quite so definite. In general, only part of the ferrosum will be peroxidized at the expense of the MnO_2; on the other hand, the ferric oxide produced or originally present may oxidize oxalic acid into carbonic acid, and thus acts in the opposite way. According to Luck, almost the whole of the ferrous oxide of the ore becomes ferric oxide if some 6 cc. of 10 per cent. acetate of soda solution are added to the (3 grms. of) ore in the decomposition flask; and the method then becomes *technically* correct.

In the oxalic acid and permanganate method, in which the decomposition usually proceeds slowly, and the ferric oxide has no chance as an oxidizing agent, the result should be exact in a technical sense. In a

Complete Analysis, the determination of the moisture must be supplemented by that of the *chemically combined water*, which is effected by means of the "direct" method given in Ex. 28. The residue left in the boat should be weighed, because its weight affords a check on the rest of the determinations conjointly. In it the metals are present as Mn_3O_4, Fe_2O_3, CaO, MgO respectively; the nickel probably remains as NiO. About the cobalt we cannot venture upon any statement; but both it and the nickel together always form only a small fraction of the whole.

---

* The sensibility of the iodide of starch test decreases perceptibly as the temperature rises, from even ordinary low to ordinary high values.—(Fresenius.)

A further check might be obtained by reducing the first residue in hydrogen, so as to obtain a mixture containing the respective elements as MnO, Fe, Co, Ni, CaO, MgO, SiO_2. For the

Determination of the Metals, the ore is dissolved in hot hydrochloric acid, the solution evaporated to dryness, and the silica eliminated and weighed, as in a silicate analysis. This "silica," of course, includes any undecomposible silicates that may be present; but, as a rule, the analysis of the mixture offers no interest, and it is sufficient to report it *in toto* as "gangue." Only in the hands of a very negligent worker could the "gangue" include undecomposed free or combined MnO_2; but the residual silicate may be manganiferous, and its determination be required. The filtrate from the silica is diluted to a known volume, and aliquot parts of it serve for the several determinations. We will assume, in the first instance, that the qualitative analysis has proved the presence of only iron, manganese, calcium, and magnesium. In this case the first step is to separate

The Iron, which, of course, is present as ferricum, from the divalent metals. If there is relatively much iron present (we mean much for a manganese ore), a good method for its elimination is to neutralize the solution by cautious addition of carbonate of soda solution, *i.e.*, to add such solution until a permanent precipitate threatens to form, and then to add a sufficiency (but not more than necessary) of carbonate of baryta milk *in the cold.* Only the iron is precipitated; the manganese, &c., remain dissolved. After the precipitate has settled, it is filtered off and treated as a mixture of ferric hydrate and carbonate of baryta. From the filtrate the dissolved baryta is eliminated by the least sufficiency of dilute sulphuric acid as sulphate, and the manganese precipitated after neutralization with ammonia by means of sulphide of ammonium, as fully explained in Ex. 21.

In the filtrate from the sulphide of manganese, the calcium and magnesium, after due concentration, are determined by the usual methods.

If only little iron is present the use of carbonate of baryta can be dispensed with. It suffices to add carbonate of soda drop by drop until a small portion of the manganese has gone down visibly, and then to allow the mixture to settle. The precipitate

($Fe_2O_3 + x MnCO_3$) is dissolved in hydrochloric acid, the solution boiled to reduce the manganese to manganous chloride, and the two metals are then separated, as explained in Ex. 21. The ammoniacal manganiferous filtrates are, of course, added to the main portion and worked up along with it.

We will now pass to the components not taken into account in our explanation.

Alumina, if present, goes with the iron, and from it is separated by caustic potash, as shown in Ex. 17. Observe that neither the acetate of ammonia nor the carbonate of baryta process separates out alumina as completely as they do iron. A little reflection will show how small quantities of alumina which escaped precipitation can be recovered.

Barium, if present, must be determined in a special portion of the substance solution by means of sulphuric acid. In the case of a manganese ore, and in the hands of a thinking analyst, there is no fear of its getting mixed up with the calcium.

Cobalt and Nickel.—Small quantities of these two metals are often present, but their exact determination is by no means easy.

Assuming the oxide of iron to have been eliminated by fractional precipitation, the cobalt and nickel pass into the manganese liquors,* from which they can be recovered by fractional precipitation with sulphide of ammonium. This reagent is added, drop by drop, until, instead of a black, a flesh-coloured precipitate is produced. The mixture is then boiled, which will cause some of the precipitated sulphide of manganese to re-dissolve, but will not affect the sulphides of nickel and cobalt. Collect the (black) precipitate on a filter, wash it with hot water, and extract the manganese by treatment with hot, dilute, acetic acid. A small quantity of the nickel and cobalt will probably pass into solution. If so, they must be recovered by a repetition of the process described. The cobalt-nickel sulphide is dissolved in

---

* The iron (Fe_2O_3) precipitate may include some cobalt or nickel. The best method for their extraction is Schwarzenbach's. Dissolve in hydrochloric acid and dilute to at least half a litre for every 1 grm. of iron present. Neutralize in the *cold* with carbonate of ammonia, *i.e.*, add of this reagent drop by drop until the liquor is dark-brown and opalescent, though still free of tangible precipitate. Then boil and filter hot. The cobalt and nickel are in the filtrate, from which they can be precipitated with sulphide of ammonium.

aqua regia, the metal is precipitated by dilute caustic potash (hot), the hydrate washed, ignited, and reduced in hydrogen. The spongy metal is washed to remove adhering alkali, re-ignited in hydrogen, and weighed. For the *separation* of cobalt and nickel, *see* Appendix to Ex. 34.

Ex. 27.—De Haen's Method for the Determination of Copper in Alloys, Ores, &c.

(As modified by E. O. Brown.)

The method is founded upon the fact that solutions of cupric salts when mixed with iodide of potassium are decomposed with precipitation of the copper as subiodide, Cu_2I_2, and liberation of iodine. $CuX_2 + 2KI = 2KX + CuI + I$. The iodine is determined by titration with thiosulphate. The thiosulphate had better be standardized empirically by means of a known weight of pure metallic copper. 0·3 to 0·5 grm. of pure electrotype copper is dissolved in nitric acid,* the solution boiled to expel nitrous fumes, and diluted with water. Carbonate of soda solution is now added until a permanent precipitate has formed, and the precipitate re-dissolved in acetic acid. To the solution excess of iodide of potassium is added, and the liberated iodine titrated with thiosulphate, some starch solution being added *towards* the end to enable one to find the end point notwithstanding the presence of the cuprous iodide precipitate.

To assay, for instance, a cupreous pyrites, 3–10 grms. are dissolved in nitric acid or aqua regia, and the solution is evaporated to dryness with excess of sulphuric acid to convert the metals into sulphates.† The residue is treated with water, the solution filtered, and from the filtrate the copper re-precipitated as sulphide by thiosulphate of soda. The washed precipitate is dried, ignited,

---

[*] In the method described for the assays the metal is always brought into the form of *sulphate* before the addition of the iodide; hence it would no doubt be better to do the same in the standardization of the reagent, *i.e.*, convert the dissolved metal into sulphate by evaporation with sulphuric acid before proceeding further.—W. D.

[†] For another method of disintegration, *see* Ex. 35 on Iron Pyrites.

dissolved in nitric acid; the solution again evaporated with sulphuric acid to eliminate traces of lead, the residue re-dissolved, and the solution filtered. The filtrate is treated as the copper solution is in the standardization.

The above is taken from a memoir by James W. Westmoreland in the "Soc. of Chem. Ind. Journal" for 1886, p. 48. Westmoreland has subjected the process to a long series of severe critical tests, and found it to give very exact results, even in the presence of any foreign metals likely to occur in a copper ore.

In the *absence of certain metals* the precipitation of the copper as sulphide can no doubt be dispensed with, and the sulphate solution as obtained directly from the substance be neutralized, &c., and titrated. Unfortunately, it does not appear from Westmoreland's memoir what metals one may allow to be present without falling into error; all he says in this respect is, that lead *must*, and that iron had better be, removed.

Ex. 28.—Determination of Water by the "Direct" Method.

In many hydrated substances, although they may lose their water readily enough on ignition, this component cannot be deduced from the loss of weight observed, because what really remains, through some cause or other, differs in its weight from the anhydride of the original substance. In such cases, what is usually done is to expel the water from a known weight of substance by heating it in a current of dry air, and after removal of what there may be of foreign vapours, to collect the water in a tared chloride of calcium tube, and weigh it directly. To begin with an easy case (which is within the reach of the ordinary indirect method so that you can check your result by means of the latter), procure a supply of—

(1.) *Pure Selenite* ($CaSO_4 . 2H_2O$). Grind up a few grammes into a fine homogeneous powder, which preserve in a stoppered tube while constructing the necessary apparatus (Fig. 14). It consists of a hard Bohemian-glass tube *a b*, supported by the gutter of a combustion furnace about 35 ctms. long. The end *a*, which projects about 7 ctms. beyond the end of the gutter, communicates with a perspirator affording a current of *dry* air, and provided with a stopcock to regulate the current. A little thimble into which the end of the perspirator's exit-tube projects (*see* Fig. 15) serves to prevent back currents. The end *b* of the combustion tube is drawn out, and serves to attach a U-tube, filled with chloride of calcium, by means of an india-rubber tube, as shown in the figure. The two glass tube ends must *touch* each other within the india-rubber. During the analysis this joint is enclosed in an air chamber *c*, kept at 105°–110° by means of a special lamp to prevent condensation of the water. Such a chamber is easily made out of asbestos pasteboard, thin brass wire serves to sew up the seams; but one made of thin sheet-iron is better. Before starting the actual analysis, insert a plain glass tube in the india-rubber end at *b*, and, while keeping up a temperature of 105°–110° there by means of the chamber, dry the combustion tube by heating it in the furnace and driving a rapid current of dry air through it until the moisture may be

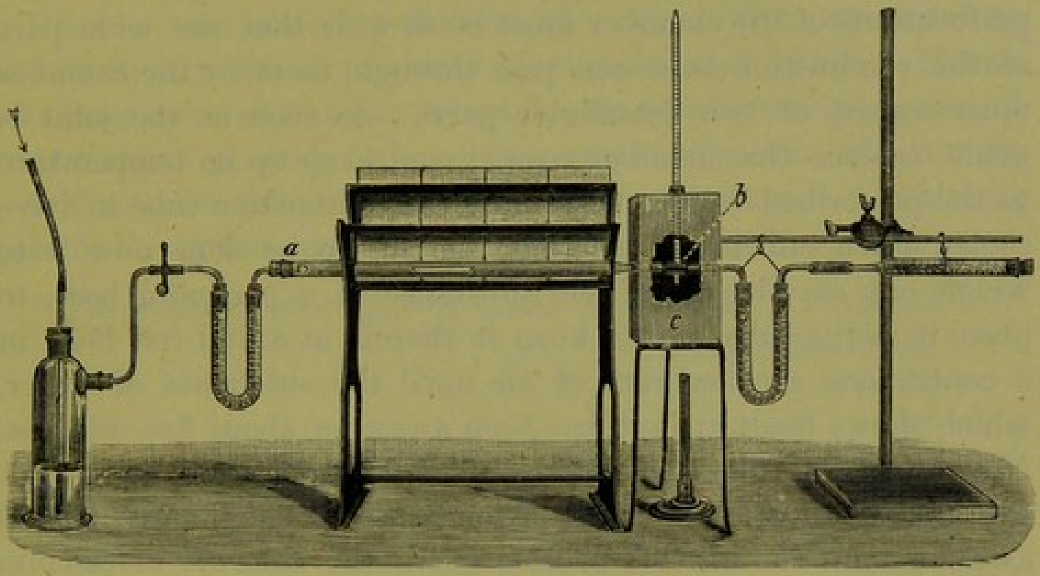


Fig. 14.

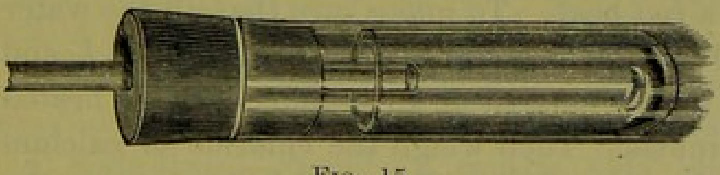


Fig. 15.

presumed to be gone; then slacken the current of air, and while allowing the combustion tube (but not the air chamber) to cool, weigh the chloride of calcium tube, and attach it at *b*, in lieu of the plain tube. To enable one to make this exchange, either the perforations of the chamber must be so wide that the wide part of the combustion tube can pass through them, or the chamber must consist of two detachable parts. As soon as the joint is made, replace the chamber over it, and keep up its temperature to the prescribed value. Assuming the combustion tube to have cooled down sufficiently, all that remains to be done now is to weigh out, say, 1 grm. of the substance in a platinum boat, to place it in the tube, and to keep it therein at a dull-red heat, in a continuous slow current of air until the sublimate of water, which shows itself at first, has been away for about five minutes. Now allow the tube (but not the air chamber) to cool, and weigh the chloride of calcium tube. To make sure that the water is all away, resume the heating process (with the chloride of calcium tube replaced), and, after about ten minutes' heating, again stop the heat and weigh the U-tube. As a rule, the weight will be the same as before; if not, the process must be repeated until the weight remains constant; which shows that all the water has been expelled and collected in the U-tube. Finally weigh the boat; the loss which it has suffered should be equal to the gain of the U-tube to within 1 or 2 mgs. After having by this exercise learnt to work the method, apply it to

(2.) *Sulphate of Iron and Potash*, with this modification, however, that about 15 ctms. of the front (*b*) part of the tube are filled with closely-packed granulated chromate of lead (as used for organic analysis), which, before the boat goes in, must be thoroughly dried at a red heat. To make sure that all the water is really gone, attach the tared chloride of calcium tube at *b*, and keep it there, while a slow current of air is going over the heated chromate, for ten minutes. Then weigh the chloride of calcium tube, and see if it has gained anything. If it has, repeat the process until the weight of the U-tube is constant to ± 0·5 mg. During the analysis the chromate must be kept hot to absorb the sulphur dioxide which goes off along with the water.

Notes.—During the heating processes take care to protect the chloride of calcium tube against the radiant heat of the chamber by means of a screen of asbestos pasteboard.

The column of chromate of lead is kept in its place by means of two plugs of asbestos.

Observe that ordinary chloride of calcium gives up water to absolutely dry air, as produced by the action of vitriol. Hence, whatever method you may adopt for the *preliminary* drying of your current of air, before entering the combustion tube it must pass through a tube charged with the same chloride of calcium as is in the U-tube intended for the reception of the water.

Theoretical percentage of water in selenite = 20·93.
" " " the iron salt = 24·87.

Ex. 29.—Determination of Nitrogen by Varrentrapp and Will's Method.

PRINCIPLE.—All nitrogen compounds which contain their nitrogen in direct combination with hydrogen, or metals, or carbon, when ignited with caustic soda, give off their nitrogen as ammonia. The H_2O in the $Na_2O\ H_2O$, by its hydrogen, supplements the NH_2 or (NH), or $N \equiv$ of the substance, into NH_3, while the O oxidizes the rest; the CO_2 produced combining with the Na_2O of the reagent. In practice the caustic soda is used in the form of soda-lime, because the unmixed reagent attacks the glass too violently.

REQUIREMENTS.

1. A combustion tube of the form shown in Fig. 16; convenient width = 14 mms. inside; length = 520 mms.
2. A nitrogen bulb; see *h* in the figure.
3. A copper or brass mixing wire; *i.e.*, a stout wire about 600 mms. long, terminating in a kind of short corkscrew.
4. *Soda-lime.*—Procure a caustic soda which is as free as possible from *nitrates;* dissolve 500 grms. of it with 5 grms. thiosulphate of soda* in 1000 cc. of water in a cast-iron pot, add 750 grms. of quicklime in small fragments, cover the

---

* To destroy traces of nitrates.

pot with a tinned-iron plate, and allow the lime to slake. Then put the pot over a fire, and evaporate to dryness with constant agitation with an iron spatula. Transfer the dry mass to a Hessian or iron crucible, and expose it to a dull-red heat for one to two hours. After cooling, take out the mass, pound it up in an iron mortar, and pass the whole through a wire-gauze sieve of 7 meshes per linear inch. From the product separate out the powdery part by means of a sieve with 22 meshes to the inch. Preserve the granulated part and the powder separately in dry, well-corked phials. The phials intended for immediate use should be of about 100 cc.'s capacity, and not have lips at the neck, so that the contents can be more conveniently poured into a combustion tube.

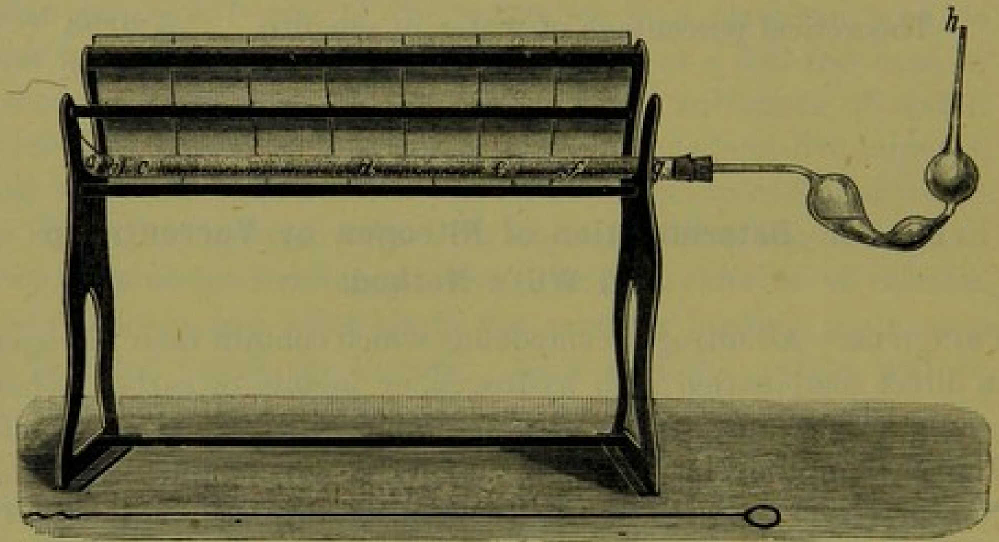


FIG. 16.

a is a plug of asbestos; *b*, a mixture of zinc dust and fine soda-lime; *c*, a small quantity of fine soda-lime; *d*, mixture of substance and fine soda-lime; *e*, plug of asbestos; *f*, granulated soda-lime; *g*, plug of asbestos.

5. A supply of zinc dust.
6. Asbestos, to be ignited strongly before use.

ANALYSIS.

Good substances to practise upon are *hippuric acid, oxamide*, or *urea*. Powder up a gramme or two, dry it at 100°C., and preserve in a preparation tube. For immediate use in the analysis prepare a substance tube, the outer width of which is no more than half at most of the inner width of the combustion tube.

Modus Operandi.—Stop up the lower end *a* of the tail of the combustion tube with a loose stopper of asbestos, and introduce a layer of a mixture of one part of zinc dust and one part of fine soda-lime *b* (about 4 ctms.). Shove down a plug of asbestos *c*, and add about 8 ctms. of fine soda-lime. Now put in about the half of the substance to be analysed from out of the previously weighed substance tube, pour on a quantity of soda-lime powder, and mix the two intimately by means of the wire, taking care to keep the first 4 ctms. or so of soda-lime free from substance. Add now another supply of powdery soda-lime, introduce the rest of the substance, add more soda-lime, and mix first this upper portion by itself and then the two portions into one homogeneous mass. Withdraw the wire, and, holding the tube vertically, gently tap it, so that the mixture falls down into its natural position, but take care to keep it pretty loose; then add a small quantity of plain soda-lime and a plug of asbestos *e*. Fill up the rest of the tube with granulated soda-lime, and again insert an asbestos plug at *g* to keep this part of the reagent in its place. Close the tube with a plain cork, and tap it thoroughly on a table so as to form a *canal* all over the powdery part of the contents. The quantity of substance to be used for an analysis depends on its richness in nitrogen. With rich substances aim at producing 50 to 150 mgs. of ammonia; but even of the poorest substance more than 1 grm. should *not* be used.

Charge the bulbs with about 15 cc. of 5 per cent. hydrochloric acid, by filling them from *h* like a pipette, and, by means of a first-class cork provided with a carefully made perforation, attach them to the end of the combustion tube. The next thing is to make sure that the apparatus is perfectly tight. For this purpose slip a narrow india-rubber tube over *h*, suck out some of the air, and then (using your fingers as a pinchcock to govern the backward flow of air) let in air so as to drive the liquor all into the pear-shaped bulb. If the liquor retains its level for about ten minutes the apparatus may be pronounced safe. Now place the tube in a combustion furnace, and next heat the granulated soda-lime to dull redness, beginning at the exit end. Then heat the mixture, progressing very gradually and slowly in the same way, until the decomposition is complete, which is seen by the mass (which becomes black at first) regaining a light-grey colour, and by the gas evolution coming practically to an end. Now heat the zinc dust to evolve hydrogen, and thereby drive the gas contents of the tube into the bulbs. At last detach the bulbs, empty their contents into a Berlin basin, rinse them twice with water and add the rinsings, and next evaporate on a water bath to about one-half or one-third of the original volume to expel volatile organic products. Now add excess of chloroplatinic acid, and proceed as shown in Ex. 19. $Pt \times 0{\cdot}14421 = N_2$.

Instead of weighing it as platinum, the ammonia may be titrated. In this case, however, we must work on a comparatively large scale to obtain a sufficiently exact result. This method does not work in cases when the hydrochloric acid at the end is strongly coloured.

Sometimes during the combustion the tube gets filled with relatively pure ammonia, while no fresh gas is being evolved; the hydrochloric acid then rushes back most violently, and you may lose your analysis. To be prepared for this, keep the india-rubber tube attached to *h*, and as soon as the liquid threatens to go back, clip it with your fingers, so as to slacken the speed of the backward flow of air. The possibility of this emergency is avoided, and the process rendered more easy of execution generally, by connecting the tail end of the combustion tube with a Kipp's apparatus for hydrogen gas, and letting a slow current of hydrogen go through from beginning to end. The hydrogen had better be *moist*.

NOTES REGARDING SPECIAL CLASSES OF SUBSTANCES.

1. *Cyanides and other substances*, which, by themselves, would give nearly pure ammonia, or ammonia and steam. Along with these add a small quantity of powdered sugar, to produce carburetted hydrogens.

2. *Substances consisting largely of cellulose or other carbohydrates.* These, especially when they contain much water, cause the soda-lime to *swell up* so as sometimes to obstruct the tube. This can be avoided by substituting for the powdery soda-lime a mixture of caustic soda and magnesia, easily made

from calcined magnesia and caustic soda by a process similar to that used for soda-lime.

Ex. 30.—Kjeldahl's Method of Nitrogen Determination.

This method, though as unlike it as it could possibly be in its technical aspects, naturally joins on to Varrentrapp and Will's, because it is founded upon a similar general principle, and, as far as our present experience goes, has the same range of applicability.

Requirements.—1. *Strongest oil of vitriol, i.e.*, as good an approximation to real H_2SO_4 as can conveniently be procured. Ordinary vitriol, distilled down in a current of air till it is reduced to Marignac's acid, $12SO_3.13H_2O$, will do.

2. *Sulphuric anhydride;* or phosphoric anhydride, which, conjointly with sulphuric acid, represents a certain quantity of SO_3. We are in the habit of using a very strong crystallized acid, $H_2SO_4 + xSO_3$, which is to be had in commerce.* These reagents must be free from every trace of nitrous and nitric acid.

In describing the method, we will assume that the substance to be analysed is an extract or syrup (for which class of substances it was originally invented). A quantity of substance, which should not contain more than 1 grm. of dry organic matter, and which *need* not represent more than, say, 50 mgs. of ammonia, is introduced into a pear-shaped, long-necked flask of about 150 cc.'s capacity, and next dried there as far as possible by heating the flask in a steam or air bath, and blowing air through it. The residue then is dissolved in 10 cc. of strongest oil of vitriol ("1"), the flask placed slantingly over a flame on a wire-gauze support, and heated, ultimately to near the boiling point of sulphuric acid, until the organic matter is decomposed as far as possible with evolution of sulphurous acid, carbonic acid, &c. The flask is now allowed to cool, the product mixed with 5 cc. (or more) of crystallized acid ($H_2SO_4 + xSO_3$), or an equivalent quantity of sulphuric or phosphoric anhydride,† and the heating

---

* From Chapman, Messel & Co., 36 Mark Lane, London, E.C.

† Kreusler recommends to use from the first a solution prepared by *gradual* addition of 200 grms. of P_2O_5 to 1 lit. of distilled H_2SO_4. 20 cc. suffice for 1–1·5 grms. of dry organic matter.

resumed and continued until the resulting liquor is no longer *darkly* coloured. On long-continued heating it becomes almost colourless; but the reaction need not, in general, be pushed so far. According to Kulisch (Fres. Zeitschr., year 1886, p. 150), the action of the vitriol is very greatly accelerated by the addition of a little mercury.

According to Kjeldahl, about two hours' heating, reckoning from the first addition of acid, suffices as a rule to effect a sufficient decomposition; but Kreusler, working chiefly on albumenoids, finds that 4–6 hours' heating is required, for at least this class of substances. When the sulphuric acid has done its work, powdered permanganate of potash is added, very cautiously, to the hot liquid, until after the disappearance of all brownish colour, the liquid assumes a greenish (or, if phosphoric anhydride was used, a bluish green) colour, from excess of reagent. Kjeldahl recommends to dust in the permanganate by means of a small sieve made out of a wide glass tube, slightly contracted at one end, and near it provided with a septum of wire-gauze. Only during the actual addition of an instalment of permanganate the lamp is removed. When the end-point has been reached, the flask is kept over a very much reduced flame for another 5–10 minutes, and then allowed to cool. The product

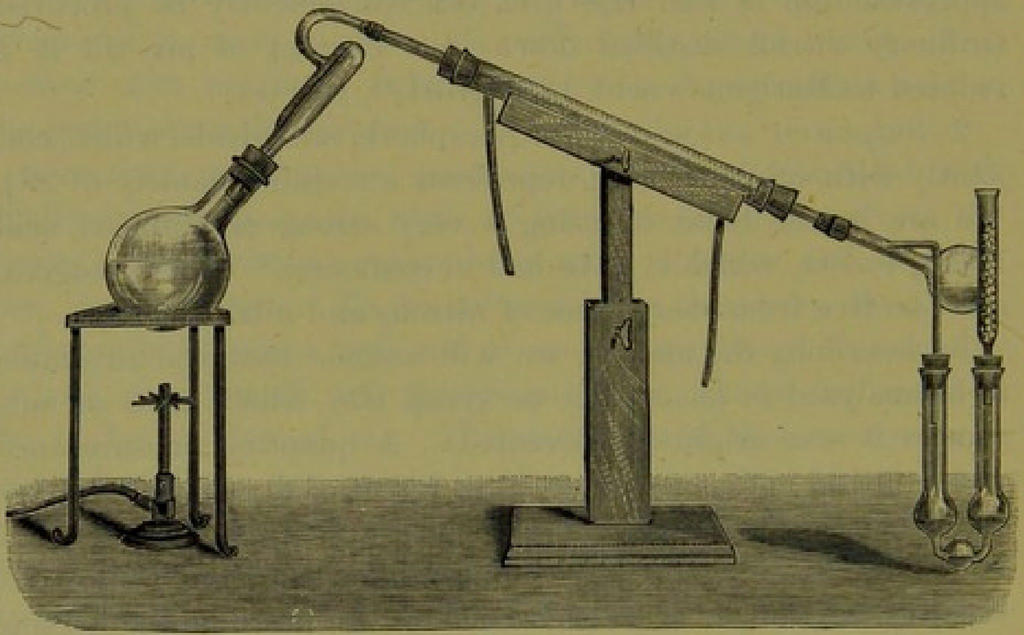


FIG. 17.

now contains all the nitrogen of the substance as sulphate of ammonia, and all that remains to be done is to dilute the product with water, to eliminate the ammonia by distillation with caustic soda, and determine it by platinum or otherwise. The caustic soda is employed conveniently in the form of a roughly standardized ley (2 parts of fused alkali, and 5 parts of water, Kreusler), so that the volume required can be determined beforehand. A convenient distillation apparatus (*see* Fig. 17) is a globular flask of 500–700 cc., connected with a Liebig's condenser by means of an adapter, which serves to collect any projected drops of liquid, and return them to the flask. According to Kreusler, the acid intended to receive the ammonia may be contained in an open beaker. If the outlet end of the condenser tube dips into the acid, there is no fear of any ammonia being lost. A few pieces of zinc placed in the flask prevent bumping; but before resorting to this expedient, we must make sure that the soda contains no nitrates or nitrites, which would give ammonia with the nascent hydrogen. The best *final* test for the absence of nitrogen oxides from the reagents is to make a blank experiment with, say, 0·3–0·5 grm. of cane sugar. The ammonia should not amount to more than a fraction of a mg., and if so, the quantity found may be subtracted from the ammonia obtained in the actual analysis as a correction. If it amounts to over 1 mg., the reagents must be rejected, and better preparations be procured.

Ex. 31.—Schlœsing's Method of Nitric and Nitrous Acid Determination.

Principle.—If a nitrate or nitrite be heated with an excess of a solution of ferrous chloride in *strong* hydrochloric acid, the nitrogen acid is completely converted into nitric oxide, whose reduced volume measures the nitrogen present as nitric or nitrous acid.

REAGENTS:—1. *A strong solution of ferrous chloride;* best prepared extemp. by dissolving fine iron wire (by theory 3·1, in practice, say, 10 parts of iron for 1 of N_2O_5) in 20 per cent. hydrochloric acid. 2. Hydrochloric acid of 30 per cent. or more.

Assuming the nitrate to be given as a solution, a quantity (containing from 50–100 mgs. of N_2O_5, if conveniently possible) is introduced into a pear-shaped flask of about 150 cc.'s capacity, which is provided with a narrow, drawn-out neck, so that a stout quill-sized india-rubber tube can be drawn over it. This serves to join on a narrow gas evolution tube, so that the evolved gas can be collected over water. The india-rubber tube should not be too thin in the body; and yet sufficiently so to enable one to see by its shape whether the pressure within the flask is above or below that of the atmosphere. A Mohr's clip, attached to the india-rubber joint (but meanwhile kept open by a wedge of wood stuck in between its two sides), enables one at a moment's notice to compress or open the india-rubber joint. The *modus operandi* is as follows:—The nitrate solution is heated and kept boiling until all the air can be assumed to be expelled, and the volume of the liquid is reduced to, at most, 5 cc. The clip is now closed, and the lamp withdrawn, the gas evolution tube having previously been dipped into the ferrous chloride solution, contained in a beaker. By cautiously opening the clip, we now suck in the iron solution, and after it a sufficient volume of the strong hydrochloric acid, taking care to allow no air to enter the flask or even the gas evolution tube. The latter is now adjusted to its right position under a graduated glass tube filled with water and placed for gas collection in a trough. The contents of the flask are then cautiously heated until the india-rubber joint—*i.e.*, the part nearest to the flask, which, on starting, was in a collapsed condition—has assumed its normal shape, and begins to expand. The clip is now opened and slipped off, so that it hangs at the tube by its ring, and the boiling continued until it is seen by the changes of colour in the boiling liquid that the reaction is over. The boiling is continued for some five minutes, to make sure of all the nitric oxide having gone over, and the india-rubber tube closed again, the lamp having been withdrawn immediately before. The tube with the nitric oxide in it is allowed to cool, transferred to a deep cylinder full of water in such a way that the hydrochloric acid in the tube falls down into the cylinder, and its place is taken by pure water. Adjust the position of the tube so that about 1–2 ctms. of water are suspended in it, wait till temperature-equilibrium is established, read off the volume, temperature and barometric pressure, and measure the height of the suspended column of water to obtain the data for calculating the reduced volume of the nitric oxide, and from it the weight of N_2O_5 (or N_2O_3) present in the substance analysed. The tension P mms. of the gas, supposing it to be dry and at its observed volume (V cc.) and temperature (t), is: Barometer reduced to 0° *minus* [suspended column of water, $\div$ 13·6 + tension of water at $t°$].

The weight of the nitric oxide is

$$\left\{ \frac{V\,P}{273 + t} \times 0{\cdot}0321 \right\} \times \frac{NO}{2} \text{ mgs.,}$$

and the corresponding weight of, say, nitrate of potash,

$$\left\{ \frac{V\,P}{273 + t} \times 0{\cdot}0321 \right\} \frac{KNO_3}{2} \text{ mgs.}$$

Nitric oxide being appreciably soluble in water, and besides characteristically prone to unite with oxygen, in the presence of water into N_2O_3 and N_2O_5, the method as described is obviously infected with a number of errors, some tending to increase, others to lessen, the volume of gas obtained. The best mode of correcting for this is, after a preliminary analysis, to carry out two experiments side by side of one another, one with the substance to be analysed, and the other with a known weight of pure nitrate of potash, so adjusted, that by calculation it yields the same weight of nitric oxide. If the two gases are measured under precisely the same conditions, their volumes are proportional, *very* nearly, to the respective quantities of nitrogen present. Supposing, for instance, the analysis yields 29 cc., the standard experiment 30 cc. of nitric oxide, the nitric acid in the substance is 29/30 of that in the standard nitrate. The following

Modus operandi of Kreusler's eliminates all the errors alluded to very completely. A glance at his apparatus (Fig. 18) almost enables one to divine his mode of procedure. Flask T is a reservoir for previously boiled out hot water, which is constantly kept simmering by means of a small flame beneath it. The syphon $n\ z$ is filled with water by blowing in at s, allowed to run for a little while, and then stopped in its action by closing clip x. The nitrate solution goes into R, and the first step is to boil it down (clips x and w closed; clips g and m open), and utilize the steam for expelling the air from S. After a time m is closed, and the steam blown off through w. When all the air may be presumed to be out, x is opened (to be kept open to the end) and w closed. A jet of lukewarm (relatively cold) water directed against S causes this tube to fill from T, and enables one to see any remaining air-bells, which are let out through m. Supposing by this time the liquid in R to have got sufficiently reduced, g is closed, the lamp withdrawn, and the flask charged through the funnel i, first with the ferrous chloride, then with fuming hydrochloric acid, and lastly with some 20 per cent. acid, to prevent the formation of gas-bells in the funnel tube. A Schiff's nitrogen-measurer,* charged with air-free 7 per cent. caustic soda, is now joined on at m, but without meanwhile undoing the clip there, and the nitric oxide evolved and driven over into S, to be collected there over hot water. At last the clip m is opened, the reservoir of the Schiff having been lowered

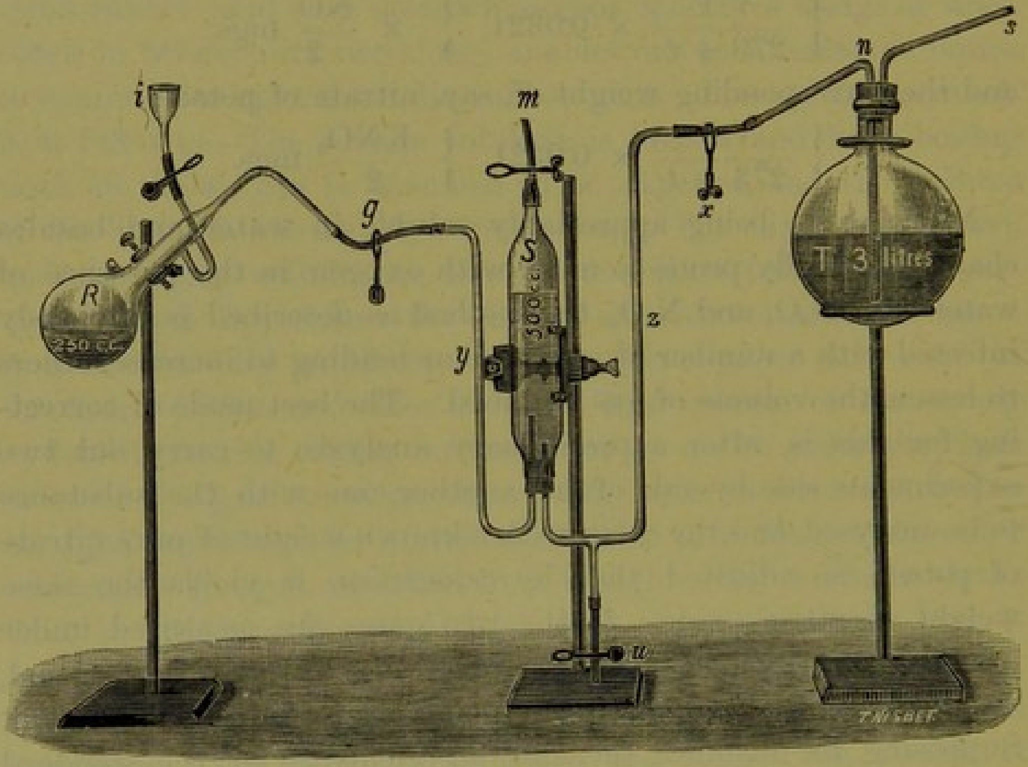


Fig. 18.

---

* As represented in the Exercise (47) on Dumas' Method of Nitrogen Determination.

before, so as to suck over the gas into the latter, where it is allowed to cool under, and at last measured at, the pressure of the atmosphere. Bunsen's *Gasometrische Methoden* (second edition) contains a table giving the tensions of vapour of water given out by such a caustic soda. If this table is not at hand, subtract from the tension of pure water the following correction:—

At 10° to 15°C.	1·1 mms.	(Kreusler.)
At 15° to 25°C.	1·4 „	

and the result is right to within ± 0·2 mms. of mercury.

Ex. 31a.—Walter Crum's Method.

By way of appendix to Schlœsing's, we will describe Walter Crum's method for the determination of nitric or nitrous acid, which is founded upon the fact that a nitrate or nitrite, when shaken with sufficiently strong oil of vitriol and mercury, is decomposed completely, even in the cold, so that all the nitrogen is eliminated as nitric oxide. Lunge's nitrometer, represented in Fig. 19, is a convenient apparatus for the execution of the method. It consists of a graduated glass tube *a*, the lower contracted end of which, by means of a stout narrow india-rubber tube, communicates with a plain tube *b* serving as a mercury reservoir, and which terminates above into a funnel *f*, the stem of which bears a peculiar kind of stopcock, the construction of which is seen from the supplementary figures I., II., III.

To prepare the apparatus for use, it is charged with mercury through tube *b* (the cock being in position I.), so that the measurer *a* is full up to the top end of the straight boring of the cock. Care must be taken to see that there are no air-bells anywhere in *a*, or in the india-rubber tube, or in the lower portion of *b*. There must be *one* continuous mass of mercury from the stopcock on to the meniscus in tube *b*, which, of course, at this stage stands at a level with the meniscus in *a*. The cock is now turned so that both its ways are stopped, and the reservoir tube *b* lowered, so that the pressure at the top of the measurer is decidedly less than that of the atmosphere.

Supposing now we wish to analyse a sample of *nitrous vitriol* as produced in a Gay-Lussac tower, we measure off 0·5 to 5 cc. of the given vitriol into the funnel, and by cautiously turning the cock into (or rather towards) position I., cause the liquid to be sucked into *a* without allowing any air to follow. To recover what sticks to the funnel, this latter is rinsed, once with 3 cc. and then with other 2–3 cc. of pure vitriol, and the rinsings are sucked into *a* as explained, to be shut up, air-free, by turning the cock into position II.

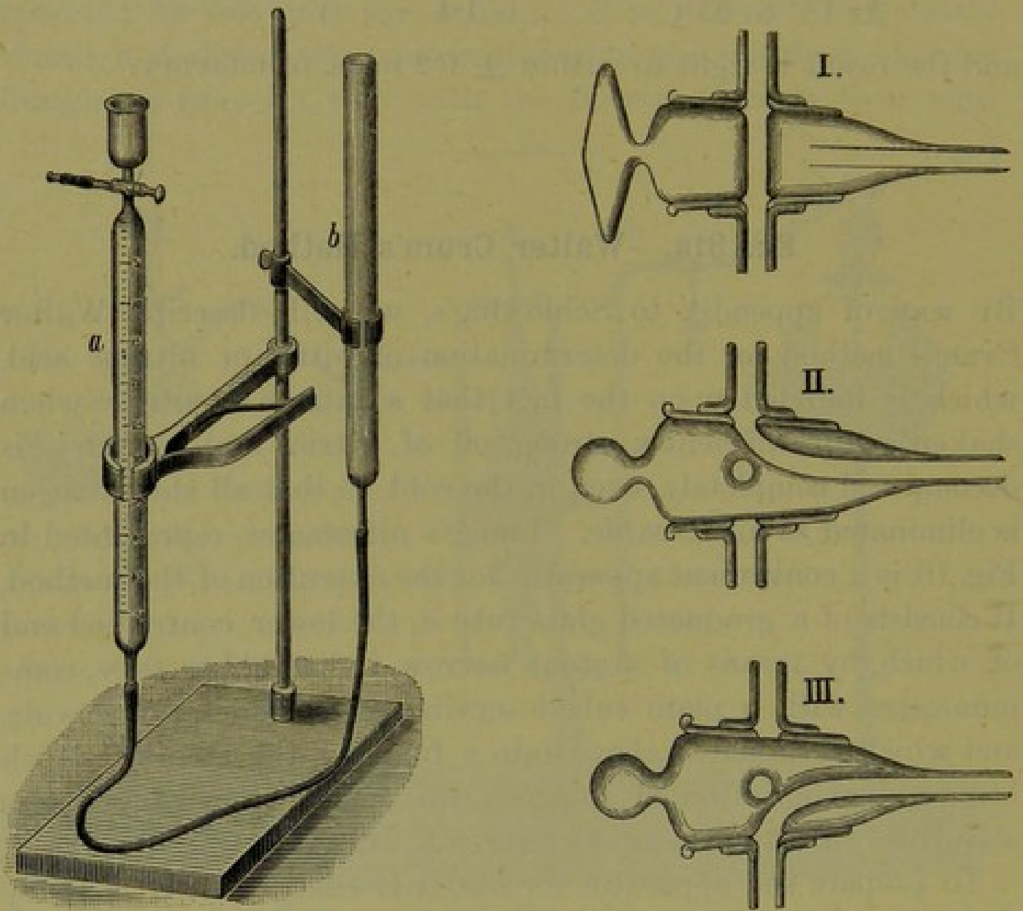


Fig. 19.*

In order now to induce the reaction, tube *a* is taken out of its clamp, and its contents are agitated by inclining the tube so as to make it almost horizontal, and then suddenly bringing it back into a vertical position. This is done again and again for some two minutes, until it ceases to cause renewed gas evolution.

---

* Taken from Winkler and Lunge's Technical Gas Analysis. Van Voorst, London.

This point having been reached, tube b is adjusted so that the pressure of the nitric oxide in a is equal to that of the atmosphere. To fulfil this condition the mercury meniscus b must be above that in a by the number x of millimetres, which exactly balances the h mm. of acid liquor in a. If this liquor has the specific gravity s, that of mercury being 13·6, we obviously have—

$$x \times 13{\cdot}6 = h \times s\,;\ \text{or}\ x = \frac{hs}{13{\cdot}6}$$

A solid nitrate or nitrite given for analysis is dissolved in the least sufficiency of water, the solution sucked into the measurer, and what sticks to the funnel washed in by means of pure concentrated oil of vitriol. At least three volumes of the latter must be used for every two of aqueous liquor introduced.

Even in this case the nitric oxide, in the calculation, may be assumed to be *dry*.

The final reading of the volume of gas produced must of course be postponed until the froth within a has subsided, and until the gas can be assumed to have the temperature of the surrounding atmosphere. The pressure is then finally readjusted, &c., &c.

As shown by Walter Crum, his method applies to nitrates of cellulose (gun-cotton, &c.) as well as to inorganic nitrates. A known weight of the gun-cotton is dissolved in the funnel in oil of vitriol, the solution sucked in, and the analysis completed as usual.

Ex. 32.—Quantitative Electrolysis.

WHEN a galvanic current is passed through the solution of a heavy-metallic salt, the general result is that the salt is decomposed into *metal* which goes to the negative electrode as such, and into *acid-rest* which goes to the positive electrode (chlorine or bromine as such; the sulphate-rest SO_4 as $SO_3 + \frac{1}{2}O_2$, &c.). Such a process is available for the quantitative determination of the respective metal, if it is possible to establish conditions under which the *whole* of the metal separates out (within a reasonable time) as a *coherent* deposit on the negative electrode, so that its weight can be determined exactly by weighing the electrode before and, along with the deposited metal, after the electrolysis. Of course the electrodes must consist of a solid, not in itself liable to change of weight during the process, which in practice means that they must consist of platinum.

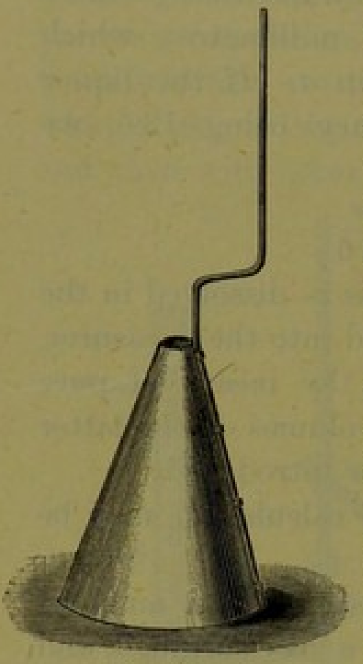


Fig. 20.

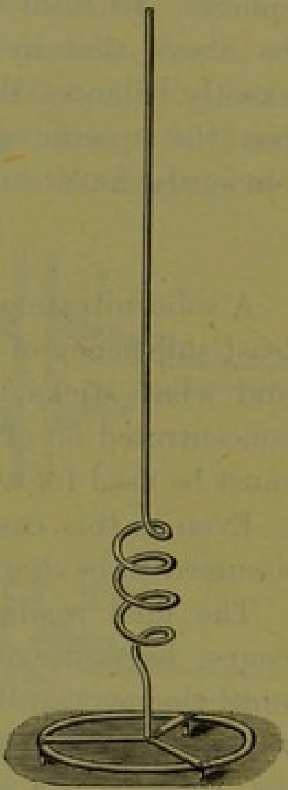


Fig. 21.

The decomposition cell and its electrodes may assume a variety of forms. In the so-called *Mansfeld apparatus*, which was introduced by Luckow, the negative electrode consists of a platinum cone, represented in Fig. 20, while the positive is made of stout platinum wire, and shaped as shown by Fig. 21. Both our figures give about one-fourth of the actual size. To effect an electrolysis, the solution is placed in a beaker somewhat higher but not much wider than necessary to accommodate the cone; the positive electrode stands within the cone, as indicated in Fig. 22, which at the same time represents a water-bath, enabling one, if necessary, to raise the temperature of the contents. This apparatus is used very largely at the famous Mansfeld copper works in Germany in the assaying of ores for copper, and it works very well for this purpose.

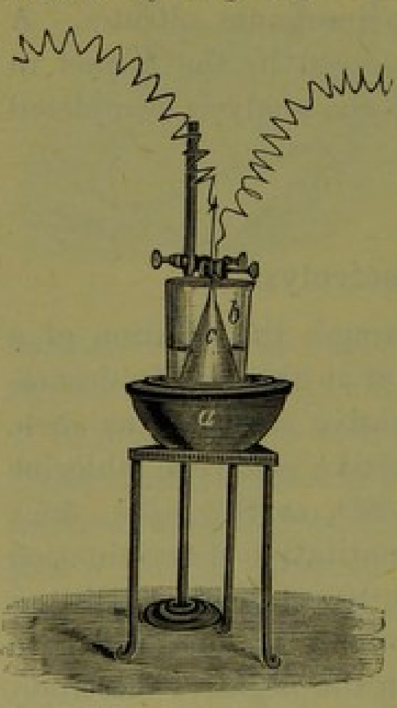


Fig. 22.

For *general* purposes, another apparatus of Luckow's invention is preferable. In it the negative electrode consists of a platinum basin, shaped as shown by Fig. 23, which accommodates the solution to be operated upon. Classen recommends the following dimensions—Diameter = 90 mm.; depth = 42 mm.; capacity = 225 cc. Such a basin needs not weigh more than some 35–38 grms. The positive electrode (Fig. 24) consists of a stout circular disc of sheet-platinum, with a long stout platinum wire riveted vertically to its centre.

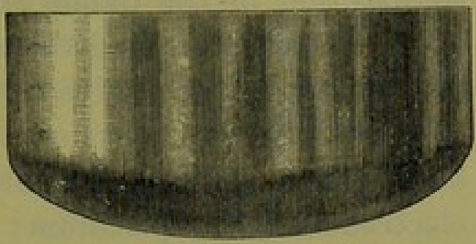


FIG. 23.

When used, the basin stands on a metallic ring, forming part of a metallic stand (Fig. 25), while the stem of the disc is held by a metallic screw-clip, cemented on to the end of an arm of the same stand, of which arm the middle portion is made of glass or vulcanite. A second screw-clamp, forming part of the same mass of metal as the first, serves to attach the positive* wire of the battery; the negative wire is attached to a screw-clip fixed to a lower point of the pillar of the stand.

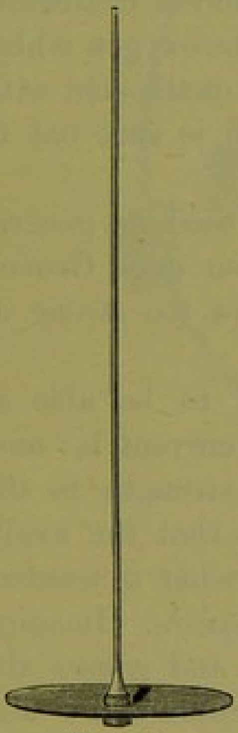


FIG. 24.

As all electrolyses which come into consideration for us involve gas evolutions from the positive electrode, the decomposition cell must be covered by a concave glass plate to catch projected droplets of liquid, or rather by two semi-circular concave plates provided at their open sides with the necessary notches to let the wires of the electrodes pass through, and constituting conjointly

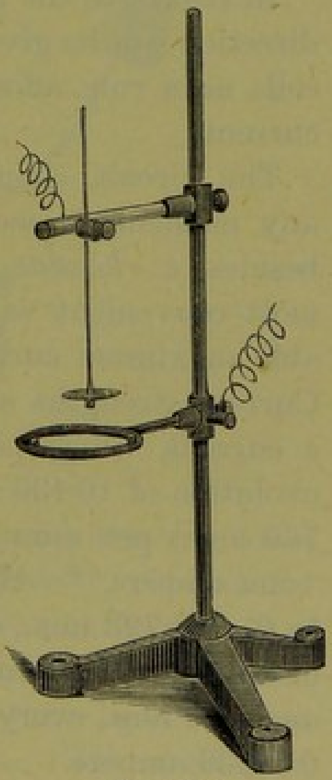


FIG. 25.†

---

* In the case of a Grove battery, the positive wire goes to the platinum, and the negative to the zinc pole of the battery.

† Taken from Classen's book.

a watch-glass-shaped cover. In any given case, the success of the analysis depends chiefly on the proper adjustment of (1) the composition of the liquid to be electrolyzed, and (2) the density of the current, meaning the number of *ampères* (*vide infra*) per square unit in the section of the body of current passing through the electrolyte. Chlorides, at least plain chlorides, are unfit for our purpose, because the chlorine which goes to the positive electrode attacks platinum; nitrates *may* work; sulphates, if their solution is of the proper degree of acidity or alkalinity, work well in many cases. According to Classen, the soluble double oxalates, which are produced from almost all heavy metals by addition to their neutralized sulphate or chloride solutions of excess of alkaline oxalate, lend themselves characteristically well for electrolysis generally, because the oxygen which goes to the positive electrode is taken up by the oxalic acid with formation of carbonic acid, a bye-product which is sure not to cause inconvenient secondary reactions.

In regard to the power of the battery to be used no general direction can be given, except by saying that four good Grove's cells, as a rule, afford an amply sufficient (if not too strong a) current.

The circuit should include a galvanometer, to be able at any moment to see what the strength of the current is; and, besides, a *rheostat*, to be able to reduce this strength to the most convenient value. This, of course, implies that the available maximum current-strength is in excess of what is wanted. Current-strengths are customarily stated in *ampères*. Imagine a current, which passes through a voltameter, and causes the evolution of 10·436 cc. of *Knallgas* ($H_2 + \frac{1}{2}O_2$) (reduced to 0° and 760 mm.) per minute of time; such a current is said to be of "one ampère."* Hence, supposing the Knallgas to be reduced to 0° and 793 mm., one "ampère" corresponds to exactly 10 cc. of Knallgas per minute. If the gas be measured *moist* at 15°C. and 760 mm., every cc. of gas evolved per minute corresponds to 0·08933 ampère.

The Author is in the habit of using a special kind of galvano-

---

* The statement, of course, refers to the current-strength as it is in the given connection; if the voltameter be taken out, the current-strength rises immensely.

meter, represented in Fig. 26, which Sir William Thomson, some time ago, had the kindness of designing for him. It is a small tangent galvanometer, constructed on the Helmholz principle, in so far as the centre of the needle is not *in*, but removed horizontally from, the centre of the ring which conveys the current by a distance equal to half the radius of the ring. This latter consists of a solid copper strip, and has a diameter of about 22

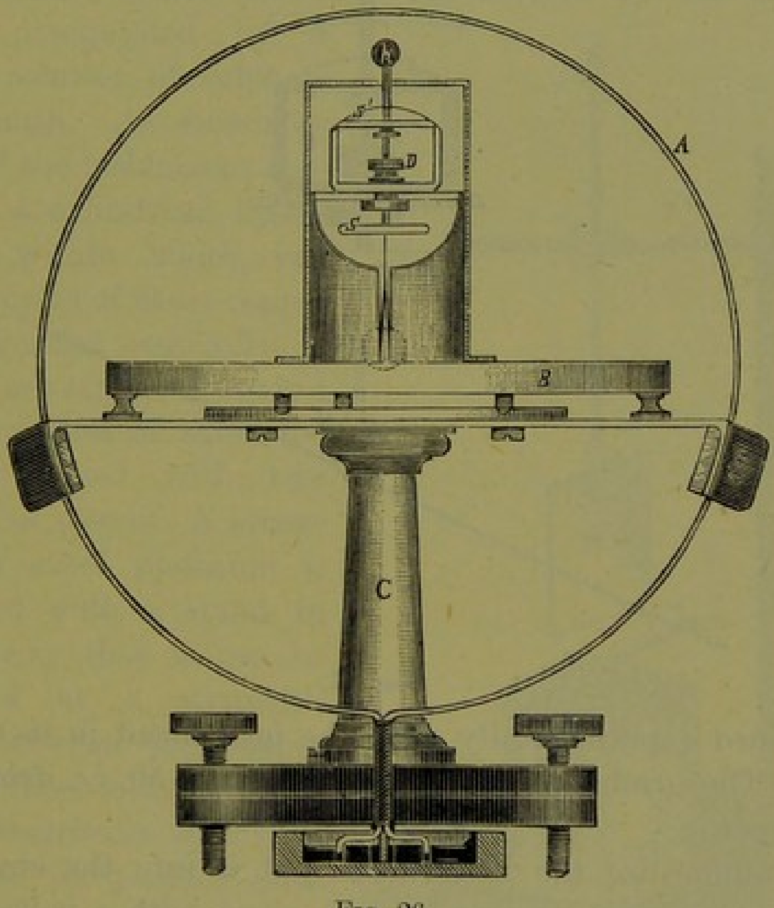


FIG. 26.

centimetres. The two ends of the strip dip, each into a mass of mercury, to enable one to make the necessary connections without disturbing the adjustment of the galvanometer.

The needle consists of a small circular magnetized disc of steel. Crossways to it there is fixed on a long, very light, hollow aluminium wire, which serves as an index. The needle, as shown by Fig. 27, is suspended from an elliptical spring, which keeps the thread from snapping. A little wooden peg *k*, terminating in a ball above, which passes through a perforation in the glass lid of the suspension arrangement, enables one to arrest the needle by pushing it down to the floor of the limb-box, which latter is covered with a glass plate. Each of the two ends of the index points to a graduation which gives tenth-ampères directly, in this sense, that the reading 10 x corresponds to $(1 + a)$ x ampères, where $(1 + a)$ is a factor, which must be determined experimentally with the instrument in its *intended place*. The graduations go from -50 to $+50$, *i.e.*, from -5 to $+5$ ampères.

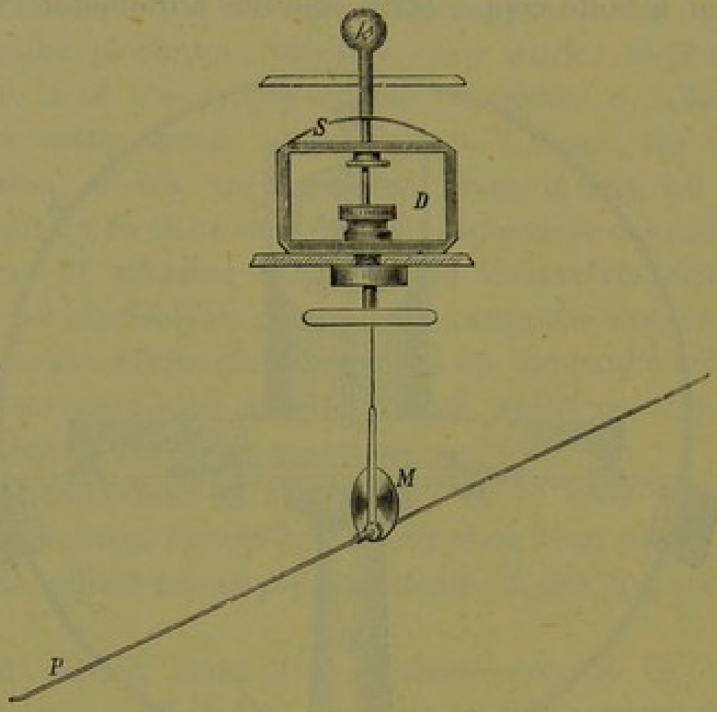


FIG. 27.

To standardize the instrument, put it into the circuit of a sufficiently strong constant battery, along with a voltameter,* a rheostat, and a commutator (an arrangement for reversing the current), and, at each of a properly selected series of current-strengths, determine the corresponding values for the volume of gas evolved per minute (at $t°$ and B mm.) and the mean of the two readings of the needle, always once with the current going one way, and then with the current reversed, to eliminate the zero and orientation errors. If the first of such a couple of readings is $+3{\cdot}84$, the second $-4{\cdot}00$, then $\frac{1}{2}(3{\cdot}84 + 4{\cdot}00) = 3{\cdot}92$

---

* Bunsen's *Knallgas* apparatus (*see* section on "Gas Analysis") will do.

is put down as *the* reading. Instead of calculating the above factor $(1 + \alpha)$, which cannot be expected to be quite a constant in practice, it is better to embody the relation between readings and ampères in a curve drawn within a system of rectangular co-ordinates, so as to do as full justice as possible to all the good observations.

Instead of a voltameter properly so called, a *copper-voltameter* may be used, which measures the current by the weight of copper precipitated by it from a solution of sulphate per minute. As shown by Fig. 28,* the instrument consists of a cylindrical lipless beaker, within which two square pieces of sheet copper are suspended vertically in the blue-vitriol solution (three volumes of saturated solution mixed with two volumes of water). A square plate of sheet platinum is connected with a stand in such a way that it can be immersed at a moment's notice between the copper plates. These latter are connected electrically with each other and the positive pole. The platinum plate is the terminal of the negative pole of the battery. The platinum plate is weighed before and, along with the deposit of copper formed on it, after the experiment (*vide supra*). Kittler recommends one square-decimeter of platinum surface for currents up to three ampères. Every one ampère corresponds to 19·686 mgs. of copper precipitated per minute, or every 1 mg. of copper corresponds to 0·0508 ampère.

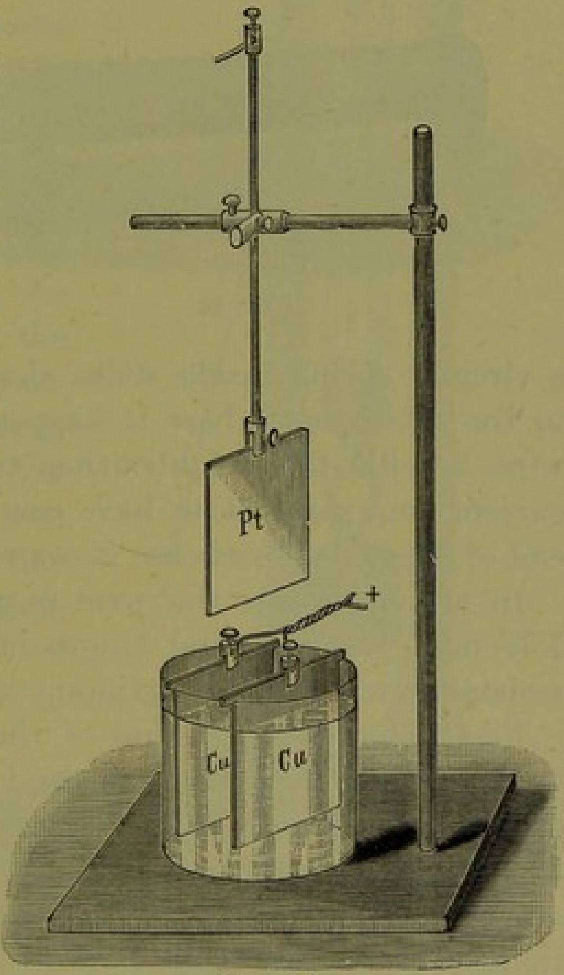


Fig. 28.

---

* Taken from Kittler's Elektrotechnik, vol. i., p. 170. (Stuttgart, Enke.)

My galvanometer was made by Mr. James White's successors, Sauchiehall Street, Glasgow. I can confidently recommend it for the purposes of quantitative electrolysis. The needle shows a degree of steadiness (I mean relative independence of the vibrations of the floor) which at first quite surprised me.

Fig. 29 represents a rheostat, which Mr. White's successors supplied along with the galvanometer. It consists of a wooden cylinder, with two parallel screw-lines cut into its surface. The two grooves accommodate two independent wires, A and B. Both these wires terminate in screw-clamps, situated at the same end of the cylinder. A belt of brass, provided with a circular spring inside, slides along the cylinder from one end to the other, and, where it happens to stand, unites a turn of wire A with the neighbouring turn of wire B, so that the current, supposing it to have come *via* A, returns *via* B to the end of the cylinder whence it came.

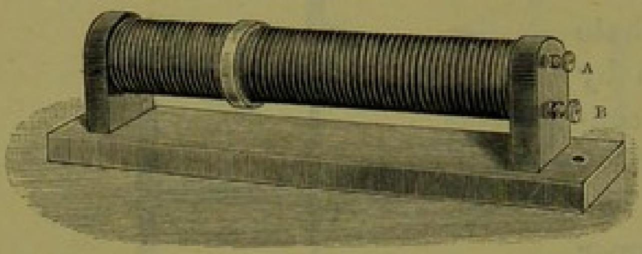


Fig. 29.

In my apparatus the wire is of platinoid,* its thickness is 1·37 mm., and the total length of A + B is 17·8 metres. The resistance, when at its maximum, amounts to 4·9 *ohms*.

Fig. 30 represents a kind of rheostat which Professor Blyth has devised for electrolytic and similar work. It consists of a wooden framework about five feet high, which serves as a support for six grooved pulleys, arranged in two blocks according to the ordinary block and tackle system. The three pulleys in the lower block are of wood, while in the upper, two are of wood and the third (the outside one) is of brass. One end of a fine iron wire is attached to the upper part of the framework, and the wire, after passing round the pulleys, is coiled upon a wooden or metal drum, by means of which the lower block with its attached weight can be raised. The

---

* Platinoid is practically German silver, with an addition of 1 or 2 per cent. of tungsten (Bottomley; Roy. Soc. Proc., 1884-5, vol. xxxviii., p. 341).

axis of the drum is screwed and moves in a nut, so that while revolving it has, at the same time, a longitudinal motion in the direction of the axis. The object of this is to prevent overlapping of the coils while the wire is being wound on. When the apparatus is used as a rheochord, the current is led through the iron wire by means of two terminals, one attached to the fixed end of the wire, and the other to the upper block which contains the brass pulley. At this point electrical contact is made simply by the pressure of the wire on the pulley. As the weight is raised, more and more wire is taken out of the circuit. In the apparatus represented, the iron wire used is 0·3536 mm. = 0·014 inch thick, and the greatest distance between the centres of the two blocks is 1·2 metre = 4 feet. With it a difference of resistance of from seven *ohms* to half an *ohm* can readily be obtained.

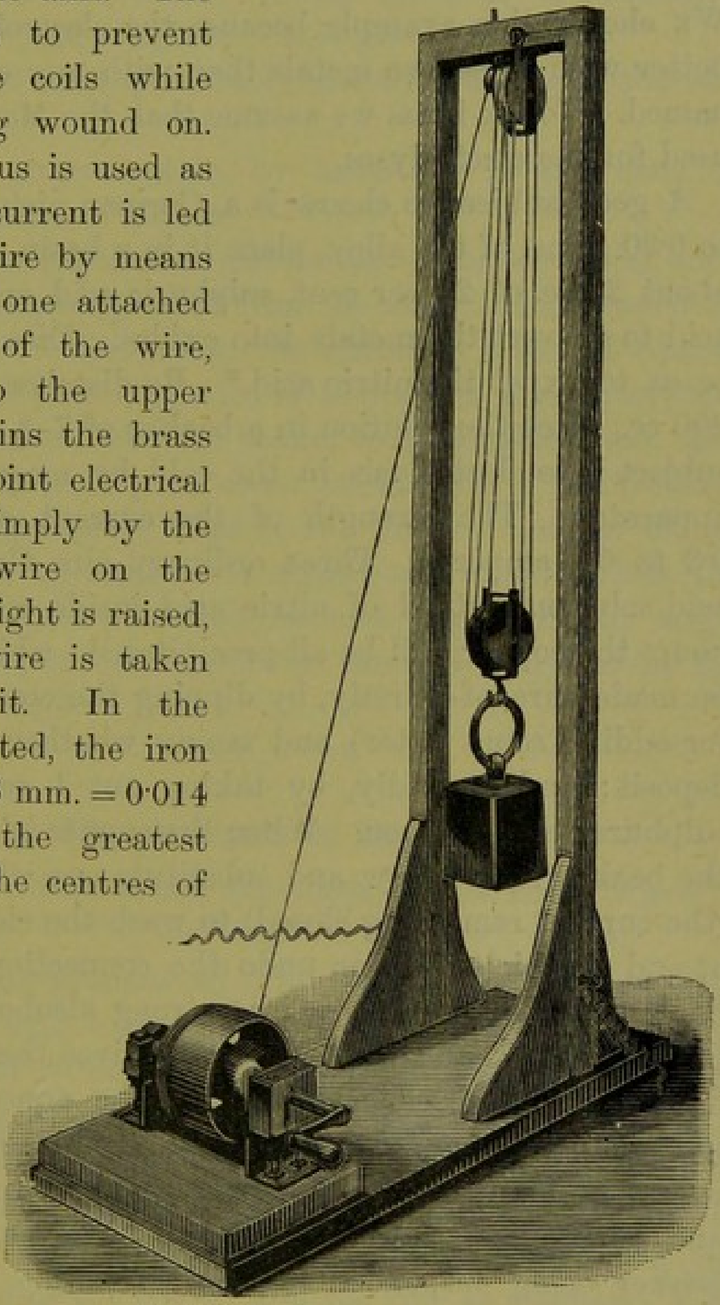


Fig. 30.

A special book on quantitative electrolysis (founded largely on researches of his own) was published lately by Classen.* Referring to it for fuller information, we satisfy ourselves with giving the following Exercise.

---

* Quantitative Analyse durch Electrolyse, von Alex. Classen. Berlin, 1886.

Ex. 32a.—Electrolytic Separation of Copper and Nickel.

We choose this example because the electrolytic method works better with these two metals than with any others that could be named. To fix ideas we assume that the Mansfeld apparatus is used for the electrolyses.

A good subject to choose is a German nickel coin. Take 0·25 to 0·30 grms. of the alloy, place it in a basin under a funnel, add about 20 cc. of 20 per cent. sulphuric acid, and enough of nitric acid to convert the metals into oxides. Dissolve, and evaporate so as to expel the nitric acid.* Re-dissolve in water, dilute to 200 cc., place the solution in a beaker of 7–8 ctms. diameter, and subject it to electrolysis in the cold by means of the Mansfeld apparatus. The strength of the current should be equal to 0·3 to 0·6 ampères. Three ordinary size Groves with chromic acid solution instead of nitric acid inside will do. After some hours the copper will be all precipitated; which, however, should be made sure of—firstly, by dipping the cone a little further in (or adding some water), and seeing whether there is any fresh deposit; and, secondly, by taking out 1 cc. and testing with sulphuretted hydrogen. When the copper is all down, withdraw the beaker from below and substitute one with 200 cc. of water (the current remaining closed) to wash the electrodes. (See note at end of article.) Then undo the connections, give the cone a final wash by plunging it into strong alcohol, dry it in an air-bath at 100°C., and weigh it. This gives the copper. To determine the nickel, concentrate first the aqueous washings, then the mother-liquor, the whole to about 100 cc., add a slight excess of ammonia and 4 grms. of solid oxalate of ammonia, and electrolize again, this time, however, in the heat, the beaker being suspended in a steam-bath.

The current (of 1·1 to 1·3 ampères) is passed through the solution until 1 cc. of the liquor, when tested with sulphide of ammonium, after expelling the excess of ammonia by heating,

---

* The presence of a remnant of nitric acid rather promotes the precipitation of the copper, but we are not quite sure that it does not interfere with the subsequent precipitation of the nickel. (*See* under "Assaying for Copper," Ex. 35).

shows that all the nickel is down. This (according to Classen, whom we follow here as far as the nickel is concerned) will be the case after about two hours. Wash the cone, as explained for the copper, dry, and weigh it. This gives the nickel.

For the first trial take, preferably, known weights of the two separate metals.

German nickel coins contain, by intention, 25 per cent. of nickel and 75 per cent. of copper.

Note.—Classen insists that, whenever an oxidizable metal, such as copper, has been precipitated from an acid liquid, it must be washed completely while within the current. This, of course, is easily done. All that is needed is to apply a narrow syphon and transfer the liquor from the beaker to a suitable vessel, and at the same time to pour pure water on the top of the (nickel) solution so as to gradually displace it. In this manner oxidation of the copper precipitate is completely avoided, but the quantity of wash-liquor produced becomes inconveniently large. With a compact deposit of copper our method, as given in the exercise, is safe enough.

Ex. 33.—Analysis of Brass.

Alloy of copper and zinc, usually contaminated with traces of iron and lead.

DISSOLVE about one gramme of alloy in dilute sulphuric, with the help of nitric, acid, and chase away the excess of the latter. Treat the residue of sulphates with water, filter off the sulphate of lead, wash it first with dilute sulphuric acid, then with alcohol, and weigh it, best on a tared filter dried at 120°C. as $PbSO_4$. The alcohol is applied only after the copper and zinc are removed, so that the alcoholic wash-liquors can be thrown away. In the filtrate which contains the copper and the zinc as sulphates, both these metals can be determined *electrolytically*, the copper as shown in Exs. 32 and 35; the *zinc* according to Classen, as follows:—(Assuming about 100 mgs. of zinc to be present, *i.e.*, that only about 0·5 grm. of alloy was taken originally), concentrate the liquor by evaporation to about 100 cc., neutralize very nearly, but not quite, with ammonia; dissolve in the liquid

2–3 grms. of oxalate of ammonia, dilute to 150–200 cc., and electrolize at 70–80°C. in the basin apparatus, Figs. 23–25, using a current of 0·8 to 1 ampère. The metallic deposit is washed first with hot water (without interrupting the current), then with alcohol, and after having been dried on the electrode at 80°–100°, weighed. The zinc precipitate after drying "sticks so fast" to the electrode that it is difficult to dissolve it off with dilute acid. As a rule the acid leaves a dark coating, which can be removed only by igniting the electrode (basin), and then again applying acid. Hence it is expedient to provide the basin with a coating of silver, copper, or tin before taring it and using it for the precipitation of the zinc (Classen).* If iron be present it passes into the zinc precipitate. Its determination is easily effected by dissolving the whole in dilute sulphuric acid and titrating the iron with permanganate.

The *ordinary* method is to separate the copper and zinc by means of sulphuretted hydrogen in the presence of a sufficiency of free mineral acid. For this purpose the (acidified) sulphate solution is heated to near boiling, and sulphuretted hydrogen passed through it until all the copper is precipitated as sulphide, which latter is filtered off and washed with hot water until the last washings are proved to be free of zinc and free acid. The copper precipitate is free of zinc (ZnS) only if the solution contained a very considerable surplus of sulphuric acid, but it is not quite easy to hit the exact degree of acidity. Hence the best course is to make sure that there is a sufficiency of acid, even at the risk of leaving a little of the copper in solution, and, should any copper remain unprecipitated, to bring it down from the filtrate, after dilution, by applying the sulphuretted hydrogen in the *cold*. The precipitate of sulphide of copper obtained in this second precipitation must be washed, first with very dilute sulphuretted hydrogen water acidified to about the same extent as the mother-liquor is with sulphuric acid, and then with unacidified

---

* In other words, part of the zinc deposit is an alloy of zinc and platinum, which gives off its zinc to acid only after the base metal has been oxidized by ignition in air. I fear a platinum basin will not stand this ordeal many times without getting rotten.

(H_2S) water. The two copper precipitates are ignited together, and after treatment with sulphur and hydrogen at a red heat, weighed together as Cu_2S, as shown in Ex. 19. To make quite sure that the sulphide is free of zinc, dissolve the ignited precipitate in fuming nitric acid of 1·5 specific gravity (at a *gentle* heat to keep the sulphur from running together into a globule), add a little sulphuric acid, chase away the nitric by evaporation, dilute and precipitate the copper with sulphuretted hydrogen, to test the filtrate for zinc by means of sulphide of ammonium. If sulphide of zinc is produced it must, of course, be collected and weighed (*vide infra*) to be allowed for. If the quantity of zinc thus recovered is small, it may be presumed to have been present in the ignited precipitate in the form of ZnS (beside Cu_2S).

From the united filtrates from the copper, the zinc, after expulsion of the sulphuretted hydrogen by boiling, may be precipitated by boiling with an excess of carbonate of soda in a platinum (or nickel) basin.* The precipitate of basic carbonate is filtered off, washed *completely* with hot water until all the alkali is proved to be away, then dried, ignited (in porcelain), and weighed as ZnO. The filter, of course, must be incinerated by itself, under circumstances which reduce the unavoidable loss of zinc (by volatilization as metal) to a minimum. A good method is to soak the filter in nitrate of ammonia, dry it, and then burn it in instalments in an open porcelain crucible. But a better method is to re-place the empty filter in its funnel, dissolve away the adhering oxide of zinc in boiling acetic acid, mixed with a little nitric, to evaporate the solution to dryness, finally in a porcelain crucible, and ignite the residue. The bulk of the basic carbonate is now added, and the whole ignited until the weight is constant. $ZnO \times 0{\cdot}8034 = Zn$. The oxide of zinc includes the iron (if any is present) as Fe_2O_3. To determine the iron, dissolve the ignited precipitate in hot ammoniacal sal-ammoniac as far as conveniently possible, and filter off the precipitate ($Fe_2O_3 + x ZnO$). Then dissolve this in the least quantity of hydrochloric acid, add ammonia to neutralize the acid, then

---

* Remember that nickel does not stand *acid* solutions (*see* Ex. 17, on Separation of Iron and Alumina); nor does it stand treatment with ammonia.

acetate of ammonia, boil, filter off the basic acetate of ferricum, ignite and weigh it as Fe_2O_3. (*See* Ex. 21, p. 53.) Another method is to take an aliquot part of the filtrate from the sulphide of copper, boil off the sulphuretted hydrogen, and determine the iron by titration with specially diluted permanganate, taking care to determine, and allow for, the small volume of reagent required to produce the end-reaction. (*See* Ex. 18.) In either case the weight of the zinc precipitate must be corrected for the weight of ferric oxide contained in it.

Another mode of separating out the *copper* is to precipitate it from the (lead free) sulphate solution, as sulphocyanate of cuprosum. The solution for this purpose should not be too dilute. It is neutralized very nearly with carbonate of soda, mixed with a sufficiency of sulphocyanate of *potassium* and sulphurous acid in excess, and allowed to stand cold over night. The precipitate is filtered off, washed, and either dried at 100°C. to be weighed as Cu.NCS, or, what is better, ignited with sulphur in hydrogen, and weighed as cuprous sulphide. $Cu(NCS) \times 0{\cdot}5216 = Cu$. From the filtrate the zinc is precipitated as carbonate, as explained above.

Another method for the determination of the *zinc* is given in the following exercise.

Ex. 34.—Analysis of German Silver.

Alloy of (chiefly) copper, nickel, and zinc. Ordinarily present impurities: lead, iron, and cobalt.

Convert about 1 grm. of the alloy into sulphates, eliminate the lead (as $PbSO_4$) and the copper (as CuS by sulphuretted hydrogren),* as shown in the Exercise (33) on Brass.

To Analyse the Filtrate, neutralize it with ammonia exactly, then, for every 1 mg.-atom of zinc., *i.e.*, 65·4 mgs., add about 4 mg.-equivalents, *i.e.*, $4 \times C_2H_3ClO_2$ mgs. of chlor-acetic acid, previously neutralized with ammonia, and 10 mg.-equivalents, *i.e.*, $10 \times C_2H_3ClO_2$ mgs. of free chlor-acetic acid, keep at 50°–60°C. over a water-bath, and precipitate the zinc by a

---

* Or electrolytically. *See* Exs. 32–35.

current of sulphuretted hydrogen. Sulphide of zinc thus produced filters and washes quite easily. It is quite different in this respect from the ordinary sulphide of ammonium precipitate. It may, indeed, be filtered off without allowing it to settle completely. It is washed with dilute sulphuretted hydrogen water, acidulated with a little chlor-acetic acid, and lastly with plain dilute sulphuretted hydrogen water. It is then dried, separated carefully from the filter, and, after addition of the filter ash and some sulphur, ignited in hydrogen over a good Bunsen, as shown for copper in Ex. 19, to be weighed ultimately as ZnS. $ZnS \times 0{\cdot}6709 = Zn$. Solid chlor-acetic acid can be had from Trommsdorff, Erfurt, or Kahlbaum, Berlin, as "purum," at 20 marks the kilogramme. $4 \times C_2H_3ClO_2 = 378{\cdot}0$ decigrammes dissolved to a decilitre in water gives a convenient solution. The filtrate from the sulphide of zinc contains all the nickel, cobalt, and iron. To simplify explanations we will assume, in the first instance, that iron is absent. To eliminate the nickel and cobalt conjointly add ammonia in excess, then excess of *colourless* sulphide of ammonium, and boil until the precipitate has become compact. Filter it off, wash it with hot water, dry it, and dissolve it with the filter ash in nitric acid of 1·5, evaporate with sulphuric acid to produce sulphates (as explained in Exercise on Brass, for copper). From the sulphate solution the nickel and cobalt may be precipitated electrolytically, as explained for nickel in Ex. 32.

For most practical purposes the cobalt (which never amounts to much) needs not be separated from the nickel, because it is quite equivalent to the latter metallurgically. But the problem is important scientifically, and we therefore append to this exercise a few methods for its solution. We will, however, first dispose of the

Iron, of which traces are, as a rule, present in the alloy. For its determination the filtrate, from the sulphide of zinc, is freed of its sulphuretted hydrogen by boiling, the iron peroxidized by addition of a small granule of chlorate of potash and boiling again, and the iron then precipitated by addition of excess of ammonia. The precipitate is a very impure hydroxide, which must be purified by re-dissolving it in hydrochloric acid and re-precipitating it by the Schwarzenberg process. (*See* foot-note on p. 74, Ex. 21.) This process may have to be repeated before the iron is fit to be ignited and weighed as Fe_2O_3. From the united filtrates the nickel and cobalt are precipitated as sulphides, as explained above.

Note on the Chlor-acetic Acid Process.—This method for the separation of zinc from nickel, cobalt, iron, &c., was worked out in Oswald's laboratory, Riga, by P. von Berg. It has been tested in our laboratory by Mr. Frank Lyall, who obtained the following very satisfactory results:—

Zinc Oxide taken.* (Mgs.)	Admixtures.	ZnS obtained. (Mgs.)	ZnO corresponding. (Mgs.)
315·0	None.	377·5	315·3
315·0	0·515 grm. of $NiSO_4$, $7H_2O$.	376·0	314·0
315·0	0·523 grm. of $CoSO_4$, $7H_2O$.	376·0	314·0
315·0	1·5 grm. of $Fe(NH_4)_2$, S_2O_8, $6H_2O$.	374·5	312·8

SEPARATION OF NICKEL AND COBALT.

All our methods for the solution of this problem start with the presumption that the solution to be operated upon contains no other heavy metals than these two, or, in other words, that any iron, manganese, &c., that may have been present originally, have already been eliminated by suitable methods, which, in the case of manganese, as we may say in passing, is not an easy condition to fulfil.

(1) *Liebig's Process* is of purely historical interest now, but the student ought to know it. It is based upon the fact that a solution of $Co(NC)_2 + 4K(NC)$, which contains free hydrocyanic acid, if boiled, passes into one of cobalticyanide $Co(NC)_3\,3K(NC)$, with evolution of hydrogen from the extra $(NC)H$, while the corresponding nickel salt remains unchanged. The metals had

---

* As a standard solution of $ZnSO_4$, analysed by evaporating a known volume to dryness, and igniting the residue, so as to convert it into ZnO.

better be used as nitrates; in this case the precipitation of the nickel (present as $Ni(NC)_2 + x\,KNC$) can be effected by boiling the solution with oxide of mercury. The nickel goes down as NiO, and is recovered by igniting the precipitate (in a good draught place). From the filtrate the cobalt, present as $(NC)_6Co'''K_3$ is precipitated, after cautious neutralization with nitric acid, by mercurous nitrate. The precipitate $(NC)_6Co'''Hg_3$ is washed with water, dried, and next heated strongly in air (in a draught place); the residue, lastly, in hydrogen, which yields weighable metallic cobalt.

(2) *Rose's Process* (also superseded now).—The metals are made into chlorides, and the solution is diluted to about a litre per gramme of total metal present. The solution is saturated with chlorine in the cold, mixed with carbonate of baryta, and allowed to stand cold. The *cobalt* goes down as Co_2O_3, the nickel remains dissolved—substantially, not exactly. By re-dissolving the cobalt precipitate in hydrochloric acid, and repeating the treatment with chlorine and carbonate of baryta, the nickel in it can to a great extent be eliminated, and a better separation be effected.

(3) *The Nitrite Process*, as worked out by Stromeyer.—(Succeeds best with nitrates or sulphates, but may be applied to chlorides). The reagent is a solution of nitrite of potassium, which, according to our experience, had better be freed from its silica, which is almost invariably present, by cautiously acidifying with acetic acid, and removing the precipitated silica. The mixed solution is neutralized by adding caustic potash until a small permanent precipitate is produced, which is then removed by addition of acetic acid. A very considerable excess of nitrite is then added, and enough of acetic acid to produce a strongly acid reaction. Stromeyer says that the mixture must be very concentrated, and be allowed to stand for some forty-eight hours to deposit all its cobalt. According to our own experience, a prompt precipitation of the cobalt can be effected from even *moderately dilute* solutions, by pouring the mixture (of metallic solution, nitrite, and acetic acid) into a fresh quantity of previously acidified reagent. After a few hours' standing, the cobalt is all precipitated as "Fischer's salt" $\left(\left.\begin{matrix}Co_2O_3\\ K_2O\end{matrix}\right\} 5N_2O_3 + x\,H_2O\right)$, which must be washed, first with a solu-

tion of acetate of potash, and lastly with alcohol, for the removal of the acetate of potash.* The alcoholic washings must not be allowed to mix with the nickel filtrate. From the filtrate the nickel may be recovered by precipitation with caustic potash; but we have found it better to first destroy the nitrogen-acids by evaporation with hydrochloric acid, and then to precipitate the nickel by means of colourless sulphide of ammonium in the heat. The precipitate (NiS) is easily filtered off and washed. It is dissolved as sulphate, and the metal determined electrolytically (*see* Ex. 32a). The Fischer's salt is dissolved in hot hydrochloric acid, the chlorine, &c., expelled, the metal precipitated as sulphide (as explained), the sulphide re-dissolved as sulphate, and the latter electrolyzed, we should say, were we quite sure that the method gives exact results. In a series of test-experiments on the electrolytic determination of cobalt by the old method (electrolysis of the sulphate in alkaline solution of sulphate of ammonia), we found it extremely difficult to obtain exact results with unmixed cobalt. The method worked admirably with nickel, even if moderately cobaltiferous; with pure cobalt solution we always obtained dull-looking deposits, which weighed more than the cobalt contained in them. Besides, a small portion of the cobalt often escaped precipitation. Classen's oxalate process may give better results;† but we do not know whether it does. Meanwhile, we prefer to determine nickel and cobalt conjointly by electrolysis, and, in the separation of the two metals by means of nitrite, to determine only the nickel directly, and the cobalt by difference. If a direct determination is required, precipitate the cobalt as hydrate by caustic potash in the heat (which must not be too strong, or else cobalt remains dissolved), wash the precipitate thoroughly, reduce it in hydrogen in a Rose's crucible, wash away the alkali by water, and heat again in hydrogen. The ultimate product is metallic cobalt, which, however, had better be tested by dissolving

---

* It is perhaps not superfluous to point out that in this case soda may *not* be substituted for potash.

† From a series of test-analyses made in our laboratory by Mr. A. B. Robertson, after the above had gone to the press, it indeed appears that exact results can be obtained with Classen's process, though not as easily as with nickel.

it in nitric acid, to see if there is not a residue of *silicon* or *carbon*, or both. If so, the residue must be collected on a weighed filter, dried at 110°, and weighed, to be allowed for.

Perhaps a better method would be to make the cobalt into a strong, acid-free solution of chloride, precipitate by pure oxalic acid, and ignite the washed and dried oxalate. The residue is semi-oxidized metal, which is easily rendered purely metallic by ignition in hydrogen. A small quantity of cobalt may escape precipitation, but this is easily recovered as sulphide, and brought into a weighable form. Possibly the phosphate process, to be given below (under 5), would work well as a means for bringing the cobalt into a weighable form.

(4) *The Nitroso-β-Naphthol Method.*

(M. ILINSKI and G. v. KNORRE.*)

Reagent.—A solution of nitroso-β-naphthol† in acetic acid containing 50 per cent. of $C_2H_4O_2$.

The metals are brought into solution as sulphates or chlorides. The solution is mixed with a little hydrochloric acid, heated gently, and mixed with a sufficiency of a hot solution of the reagent. After cooling make sure that a further addition of reagent gives no additional precipitate; allow to stand for some hours, then wash, once with cold and then repeatedly with hot hydrochloric acid of about 12 per cent. until the nickel is removed, and lastly with hot water. The precipitate is very voluminous, but is easily washed. It is a cobaltic salt of the formula $C_{10}H_6O(NO)_3Co'''$. When heated by itself it explodes; but, if mixed with a few knife-points of (pure) oxalic acid, and then heated gradually in a covered porcelain crucible, its decomposition proceeds quietly and without loss. This operation should be carried out in a Rose's crucible, so that one can finally heat in an atmosphere of hydrogen, and thus reduce the ash to metallic cobalt, which goes to the balance. (*See* Ex. 19, Determination of Copper.) From the filtrate from

---

* Fres. Zeitschrift for 1885, vol. xxiv., p. 595. Original in Ber. d. d. Chem. Gesellschaft, vol. xviii., p. 699.

† To be had from C. A. F. Kahlbaum, Berlin, Schlesische Strasse, 16–19, at ten marks the hectogramme.

the cobalt, the nickel, it appears, can be precipitated quantitatively by means of caustic potash. But the inventors prefer to determine nickel and cobalt first conjointly in some way and then to determine the cobalt by nitroso-β-naphthol, to find the nickel by difference. In a few test-analyses made in this laboratory the method gave very fair results for the cobalt (the nickel was left undetermined).

(5) *The Phosphate Process.*

(DIRVELL'S as modified by Dr. JOHN CLARK.*)

The solution containing the metals as chlorides, nitrates, or sulphates, which should be moderately concentrated, is mixed with phosphate of ammonia (about five parts of the salt, $PO_4(NH_4)_2H$ for one part of $Ni + Co$), and with hydrochloric acid (about five parts of acid of 20 per cent. for every one of phosphate), and the mixture boiled for several minutes. It is then removed from the flame, and, while it is still hot, ammonia is added in small instalments till the precipitate first produced is re-dissolved. The solution is then stirred vigorously; the cobalt separates out as a beautiful, purple, crystalline precipitate of the composition $PO_4Co(NH_4) + H_2O$. A few drops of ammonia are then added, and the beaker is kept on a water-bath for a few minutes to give the precipitate time to settle. The precipitate is collected on a filter, washed with cold water, dried, and ignited, to be reduced to and weighed as pyrophosphate, $P_2O_5 2CoO$, containing 40·4 per cent. of cobalt. The filtrate contains the nickel, associated, however, with a little remnant of cobalt. It is heated to and kept at 100°C. until a little of the nickel has come down. The precipitate (ammonio-phosphates of nickel and cobalt), is filtered off, dissolved in hydrochloric acid, and its cobalt estimated as above explained. The filtrate, of course, is united with the principal filtrate. From the filtrate the nickel is best precipitated by sulphuretted hydrogen, *i.e.*, extemporised colourless $(NH_4)_2S$, as NiS. (*See* above.) The test-analyses published by Dr. Clark gave very satisfactory results. From these analyses it appears that Dr. Clark prefers to use the metals as chlorides, although the sulphate and nitrate forms, as far as tried, worked well.

---

* "Chem. News," for 1883, part 2, vol. xlviii., p. 262.

Dirvell-Clark's certainly is the most *elegant* of all known processes for the separation of nickel and cobalt. How it compares with the nitroso-β-naphthol and nitrite methods in point of *exactitude* we are unable to say. In a few trials with Dirvell's *original* process we always found that a little of the cobalt escaped precipitation, while a little of the nickel passed into the cobalt precipitate.

Ex. 35.—Analysis of Iron or Copper Pyrites.

SUBSTANCE.—The student at first may practise on *pure* iron pyrites. We have a supply of "Rio Janeiro Pyrites" in the laboratory, which (apart from a fraction of a per cent. of chemically combined water, and a little otherwise combined oxygen) is chemically pure. The powdered substance is dried at 100°C., and analysed in this condition.

A.—ASSAY FOR SULPHUR.

In 1879, Mr. John M'Arthur, while a student in this laboratory, made a thorough critical research into methods of pyrites analysis. Of all the methods for the determination of sulphur which he tested, the following gave the best results:—

Caustic Potash Method.—Weigh out 5 grms. of pure caustic potash, free from sulphate, and 3·5 grms. of nitre, and melt these quantities in 1 cc. of water in a large silver basin.* Place 0·5 grm. of the pyrites (weighed in a preparation tube) on the surface of the mixture, stir up with a silver rod, and heat gently until the water is gone, ultimately to fusion, stirring up constantly to prevent spirting. Allow to cool, dissolve up in water, and filter off the oxide of iron; wash with hot water until the last washings are free from alkali, and acidify the solution with hydrochloric acid. Boil for a few minutes, and add excess of barium chloride. Wash the $BaSO_4$ thoroughly; ignite, and weigh. By theory, the weight of the precipitate, multiplied by ($S \div BaSO_4 =$)0·13744, gives the weight of the sulphur. But a sulphate of baryta precipitate is always liable to be impure,

---

* Or better, one made of Dittmar's alloy; 91 of Ag, 7 of Au, and 2 of Ni.

and we will take this opportunity for explaining generally what means we have for its purification. If the *barium* is the thing to be determined, the problem is easy. We need only boil the precipitate, after preliminary washing, in dilute sulphuric acid; or in more difficult cases, dissolve it in hot concentrated sulphuric acid, and, after cooling, re-precipitate it with water to obtain it in the state of purity. But if the precipitate presents itself as a form of *sulphur* to be determined, the case is more difficult. The impurities likely to be present (we speak in reference to the general case), are nitrate of baryta, chloride of barium, foreign metallic oxides, Fe_2O_3, MgO, &c. The customary mode by which one seeks to remove these is this:—The precipitate is pounded up with a rounded glass rod in the crucible, under 10 per cent. hydrochloric acid, and then heated with the acid on a water-bath for half an hour. The liquid is then diluted, allowed to settle in the crucible, the clear liquor is withdrawn with a plain (not a bulbed) pipette, and filtered through a very small filter. The precipitate is then washed twice by decantation with pure water in a similar manner. The liquid, in addition to the extracted impurities, contains some sulphate of baryta. To recover it, the liquid is evaporated in a Berlin basin to a few drops, to expel the free hydrochloric acid, and diluted with water, when the sulphate of baryta comes out as a precipitate. It is collected on the small filter, which, with its contents, is placed in the crucible over the main portion, to be dried, and ignited with it.

The *ignition* of a sulphate of baryta precipitate must not be over-done. According to experiments made in this laboratory, long-continued strong ignition in a platinum crucible produces an appreciable proportion of sulphide of barium. A quarter of an hour's exposure to a dull-red heat is sufficient to drive off all the moisture.

After determining the sulphur in pure pyrites, you may take up the case of a complex pyrites, and execute the determination in the same way.

According to Mr. M'Arthur's experiments, copper, and such small proportions of lead as are likely to be present in an iron pyrites, do not interfere with the method at all.

Combustion Method.—Before the introduction of the above method, we used to burn the pyrites in oxygen, in a boat standing in a combustion tube, collect the sulphurous and sulphuric acids formed in bromine and water (contained in a bulbed U-tube, followed by another containing iodide of potassium, to catch the bromine vapours and any stray sulphurous acid), and determine the sulphuric acid produced, working up the contents of the two U-tubes separately. The cinders, even in the absence of copper and lead, are liable to contain sulphuric acid; they must therefore be dissolved in hydrochloric acid, and the sulphuric acid in the solution determined and added on. The method is almost as exact as the caustic potash one, but more troublesome. It comes in handy when the pyrites to be analysed is contaminated largely with coally matter. But if, in such a case, the *coally matter predominates*, if, for instance, we have to deal not with pyrites proper, but with a pyritic shale or coal,

Eschka's method[*] is preferable. One part of pure carbonate of soda is mixed intimately with two parts of pure calcined magnesia. The calcined magnesia of commerce, as a rule, is contaminated with sulphuric acid; but many kinds of magnesite are quite free from sulphate, and consequently furnish a suitable magnesia on ignition. Regarding the preparation of chemically pure magnesia, *see* the Author's "Memoir" in the "Challenger" Reports, p. 16.[†]

1 grm. of finely powdered substance is mixed intimately in a platinum crucible with 1·5 grms. of the mixture, and a layer of the latter is placed on the top of the whole. The open crucible is then placed in a slanting position and heated cautiously, so that the combustion goes on at a low temperature. The mixture is then stirred up with a platinum wire, and the roasting resumed at a higher temperature until the colour shows that the oxidation is substantially at an end. To make sure of all the sulphur being in the sulphate form, the roasted mass is mixed with 0·5 to 1·0 grm. of nitrate of ammonia, and heated in the closed crucible for ten minutes. It is then lixiviated with water, and in the filtrate

---

[*] Fres. Zeitschr. for 1874, p. 344.

[†] Perhaps the sulphuric acid of the commercial article could be extracted by boiling with solution of carbonate of potash.

the sulphuric acid determined with chloride of barium. Should it be impossible to procure perfectly pure reagents, the sulphuric acid in the weight of mixed reagent used must be determined by a blank, and allowed for. A similar remark applies to the *sulphates* that may be present in the substance. Their sulphuric acid is extracted by continued boiling with carbonate of potash solution, and determined in the filtered solution.

We have made a series of attempts to adapt the Eschka method to the analysis of pyrites proper—by heating the mixture in a combustion tube in oxygen with granulated mixture in front—but failed to obtain exact results. The results were from 1–2 per cent. too low.

B.—Determination of the Metals.

(Only Iron, Copper, and Lead taken into account.)

A convenient method of *disintegration* is to heat a known weight of the pyrites in hydrogen gas to redness, which removes about half the sulphur and part of the arsenic,* and next to apply dilute sulphuric acid to the residue. All the iron dissolves as ferrous sulphate, along generally with a small quantity of copper, which is recovered by precipitation with sulphuretted hydrogen. In the filtrate from the sulphide of copper the iron may be determined by titration with permanganate, unless lime, magnesia, &c., are present and are meant to be determined, in which case the iron must, after peroxidation, be separated from the protoxides and determined, as explained in Ex. 21. The residue left undissolved by the dilute sulphuric acid is dried in the filter, and, along with the filter ash, dissolved in sulphuric and nitric acids.† The nitric acid is removed by evaporation in a Berlin basin, and the residue taken up with a little water. The lead separates out as sulphate, the copper passes into solution, and from it is precipitated by sulphuretted hydrogen. The two sulphides of copper are ignited together in hydrogen, to be converted into Cu_2S, and weighed in this form (*see* Ex. 19).

---

[*] Not the whole, according to Mr. M'Arthur's experiments.

[†] Or else the dry filter and contents together are treated with 1·5 nitric acid, and the solution is evaporated with sulphuric acid, &c.

If the sulphide of copper contains arsenic, this is generally supposed to go off with the sulphur vapour. I am not sure if this is *quite* true. In any case it is as well to re-dissolve the sulphide of copper as sulphate (*vide supra*), to separate out and weigh any sulphate of lead that may come to light, and to precipitate the copper in the filtrate by sulphocyanate of potassium and sulphurous acid, as explained in Ex. 33, p. 104. The arsenic remains in solution.

The sulphate of lead precipitate includes in general some *gangue*, and consequently cannot go direct to the balance. It is treated with warm alkaline acetate of ammonia (which dissolves the sulphate); the residual gangue is ignited and weighed. From the acetate of ammonia solution the lead is separated out by evaporating the solution to dryness in a Berlin basin, and expelling the ammonia salt; the residue is then taken up with water and a few drops of sulphuric acid, the precipitate collected on a filter, washed, ultimately with alcohol, and weighed as $PbSO_4$. Sulphate of lead becomes quite anhydrous at 110°C., and consequently can be weighed on a tared filter, previously dried at 110°C., which method is probably as exact as weighing after ignition, because it is difficult to incinerate the filter so as to ultimately have *all* the lead in the state of sulphate.

Determination of the Arsenic.—A good many years ago the author introduced in his laboratory a method for the separation of small quantities of arsenic, *given as arsenic acid*, from copper, iron, &c., which consists in this, that the *strongly hydrochloric* solution is distilled with *cuprous* chloride introduced as such, or, what is more convenient, as cuprous oxide. The arsenic passes over as $AsCl_3$. This method may be applied to an arseniferous pyrites in two ways—

(1.) The ore is disintegrated by first moistening it in a flask with 1·4 nitric acid, then adding a sufficiency of strongest (1·5) nitric acid and digesting until everything is dissolved. The liquid is then evaporated down to expel the bulk of the nitric acid. The rest is destroyed by adding fuming hydrochloric acid and re-evaporating. As soon as nitrous fumes cease to come off visibly, the residual liquid is transferred to a retort connected with a Liebig's condenser, and distilled down to near dryness;

the distillate being collected to be tested for arsenic. The residue left in the retort is now re-dissolved in the strongest hydrochloric acid, with addition of cuprous oxide, the distillation resumed, and carried on to dryness. An oil-bath is a convenient heating medium; if the liquor should "bump," this can be cured by a slow current of air or carbonic acid sent through it. The distillate is collected in water to avoid loss of hydrochloric acid gas (and possibly of chloride of arsenic). The receiving vessel must be kept cold by means of cold water. The residue in the retort is again distilled to dryness with a fresh supply of hydrochloric acid, and so on, until all the arsenic is over. From the united distillates the arsenic is precipitated (after proper dilution with water) by means of sulphuretted hydrogen. To produce a *pure* precipitate of sulphide of arsenic which can be weighed directly as As_2S_3, place the liquid in an Erlenmeyer flask, provided with a doubly perforated india-rubber cork and inlet and outlet tubes, and next pass carbonic acid through the liquid until all the dissolved air can be presumed to be expelled. Then displace the carbonic acid by sulphuretted hydrogen, and, when all the arsenic is sulphuretted, expel the excess of sulphuretted hydrogen by means of a current of (*air-free*) carbonic acid. [Sulphide of arsenic is quite appreciably soluble in sulphuretted hydrogen water]. As soon as the outgoing carbonic acid ceases to discolour lead-paper, the precipitate is collected on a weighed filter, washed with (plain) water, dried at 100°C., and weighed. $As_2S_3 \times 0{\cdot}6096 = As_2$.

(2.) After disintegration of the ore as described, and expulsion of the nitric by hydrochloric acid, the dissolved arsenic acid is reduced to arsenious by prolonged heating with aqueous sulphurous acid; the excess of the latter is then expelled, and the copper and arsenic groups are precipitated conjointly by means of sulphuretted hydrogen. The washed precipitate is dried, dissolved with the filter in fuming (1·5) nitric acid, and the solution manipulated as before. The distillation in this case becomes a neater operation.

ASSAYING FOR COPPER.

Of the numerous processes for the assaying of cupriferous pyrites (and copper ores generally) the most popular in this country is the one which Parkes long ago based upon the fact that an *ammoniacal* solution of cupric salt is readily decolorized in the cold by addition of cyanide of potassium. The point where the last trace of blue disappears is easily hit even in the presence of a precipitate of ferric hydrate. To explain the reaction we need only remember the readiness with which cupric cyanide passes into cuprous, which suggests the following equation:—

$$2CuSO_4 + 4K(NC) + (NH_4)_2O = Cu_2(NC)_2 + 2K_2SO_4 + \\ (NC)O(NH_4) + (NC)NH_4.$$

Cancel an $(NC) + K$ on both sides, and you see that 3KNC should correspond to 2Cu; yet in practice we find that the ratio varies with the quantities of ammonia-salt, ammonia, and water, and depends on the nature of the acid present. (Liebig, Fresenius, and others.) And if ferric salt* be present, more or less of the copper passes into the iron precipitate and escapes determination. Yet, from extensive experiments of Steinbeck's, it appears that good results can be obtained in the following manner:—

A known weight of the ore is disintegrated with fuming nitric acid, and, after expulsion of the bulk of the surplus nitric acid by evaporation, the rest is removed by boiling with a large excess of strong hydrochloric acid. Supposing now the weight of copper present to amount to 300 mgs. or less, the (diluted and) filtered liquor is brought up to about 400 cc., and the copper precipitated by means of a strip of platinum foil and a stick of zinc weighing about 8 grms. At a gentle heat the copper is completely precipitated in from a half to three-quarters of an hour. The copper precipitate is washed by decantation and dissolved in 8 cc. of a mixture of equal volumes of nitric acid of 1·2 specific gravity and water. After cooling, the solution is mixed with 10 cc. of a mixture of 1 volume of aqueous ammonia of 0·93 specific gravity and 2 volumes of water, diluted to 50 cc. and titrated with a solution of cyanide of potassium so adjusted

---

* There is hardly any need of pointing out to the student that ferrous salts could not reasonably be permitted to be present.

that 1 cc. corresponds to about 5 mgs. of metal. The cyanide solution must, of course, be standardized by means of a known weight of pure (electrotype) copper in a strictly empirical manner.

The presence per 100 parts of copper of even 100 parts of lead, or any quantity of zinc not exceeding five parts, does not cause any appreciable error.

The *most exact* method for the assaying of a copper ore is the electrolytic method, which was invented in 1869 by Luckow. To assay a pyrites, a known weight is disintegrated by means of fuming nitric acid, and the surplus acid chased away by evaporation. If *large* quantities of lead are present, it is better to convert the metals into (nearly neutral) sulphates by evaporation with sulphuric acid to dryness. In either case the residue is dissolved in water mixed with 20 cc. of nitric acid of 1·2 specific gravity, the solution filtered and diluted to 200 cc. The beaker should have a diameter of 8 ctms. inside and be 12 ctms. high. This liquid is electrolysed by means of the "Mansfeld" apparatus, described and figured on p. 92. For small quantities of copper a current of 0·05 to 0·07 ampère is sufficient; larger quantities of copper require, in the relative absence of iron, 0·2 to 0·3; and in the presence of considerable quantities of iron, 0·3 to 0·35 ampère.

The precipitation of the copper is completed in from five to twelve hours. The deposit is washed without breaking the current, as explained in the note on p. 101.

The great advantage of nitric over sulphuric solutions (which latter are recommended for general purposes in Ex. 32) is that any small quantities of arsenic that may be present come down only *after* the copper has been completely recovered; and that small quantities of lead go to the positive electrode as binoxide PbO_2.

Luckow's method has been adopted as the best of all known methods by the Mansfeld copper works near Eisleben, in Germany. If a sufficient number of batteries is at hand a large number of assays may be made by one analyst in a single day.

Ex. 36.—Analysis of Galena.

Native sulphide of lead, PbS; generally contaminated with iron pyrites, traces of silver, &c.

The Determination of the Sulphur can be effected by means of the fusion method described for pyrites in Ex. 35, p. 111. The aqueous extract of the fuse, containing plumbite and sulphate of alkali, is treated with carbonic acid to precipitate the lead as carbonate. The filtrate is acidified with hydrochloric acid, and the sulphuric acid precipitated by chloride of barium.

Mr. Lyall applied this method to three different portions of the same galena, and found (*a*) 13·55, (*b*) 13·57, and (*c*) 13·54 per cent. of sulphur. In case (*c*) the precipitation of the lead by carbonic acid had been omitted. Hence it would appear that this operation may be dispensed with.

Another method for the determination of the sulphur is to decompose (say 0·5 grm. of) the ore with boiling fuming hydrochloric acid (10 cc.) in a flask which communicates, on the one hand, with a Kipp supplying hydrogen, and on the other with a bulbed U-tube charged with a solution of (1 grm. of) crystallized permanganate of potash and (8 grms. of) pure caustic potash. The insertion of an inverted condenser between flask and U-tube is an improvement. (Comp. Fig. 11, p. 51.) The hydrogen enters through a stopcock pipette, the outflow end of which is inserted in the cork of the flask. After having weighed the substance into the flask, next fill the apparatus with hydrogen to expel all the air; then let in the hydrochloric acid, and boil while a very slow current of hydrogen passes through the liquid; at the end sweep out the apparatus by means of a somewhat faster current of hydrogen. The sulphuretted hydrogen evolved is oxidized by the reagents in the U-tube into sulphate with precipitation of manganite MnO_2 (K_2O or H_2O). The surplus permanganic acid is brought into the same form by addition of a few drops of alcohol and heating, the manganese filtered off, and the sulphuric acid of the filtrate determined by means of chloride of barium.

This second process ought to give only the sulphur present as PbS, or in similar forms. Any pyrites FeS_2 present should remain undecomposed. Whether this really is so has not yet been ascertained.

Determination of the Lead.—Decompose, say, half a gramme of the finely powdered substance with boiling hydrochloric acid in a Berlin basin, evaporate to dryness, dissolve the chloride of lead, &c., in boiling water and filter *hot*. Should the residue contain any pyrites or similar matter, bring this into solution by treating the washed residue with aqua regia, and add the solution to the first. The ultimate residue is ignited and weighed as gangue.

From the hot filtrate the lead is precipitated by adding an excess of sulphuric acid and, after cooling, about half a volume of 85 per cent. alcohol for every one volume of aqueous mixture. The whole is allowed to stand overnight, the sulphate of lead filtered off to be washed with first dilute and then strong alcohol. The dried precipitate is detached as completely as possible from the filter, ignited gently in a porcelain crucible, and weighed. To make sure that all the lead is really in the sulphate form, the ignited precipitate is moistened with a few drops of oil of vitriol and re-ignited, this operation being repeated until the weight is constant. The filter is moistened with a solution of nitrate of ammonia, dried, and then ignited in small instalments in a separate porcelain crucible; the ash is moistened with a drop of nitric acid and vitriol, evaporated to dryness, and ignited to be weighed as $PbSO_4$, which, of course, is added on to the principal portion. $PbSO_4 \times 0{\cdot}6829 = Pb$.

The filtrate from the sulphate of lead is evaporated over a water-bath to expel the alcohol. The liquid may contain copper, iron, lime, and magnesia, which are determined by means of the usual methods.

Determination of the Silver.—Almost all galenas contain silver, but, as a rule, the quantity of the noble metal amounts to only a minute fraction of a per cent. Yet, for an obvious reason, its exact estimation *may* be a matter of great consequence. The only reliable method is to reduce a sufficient weight of the ore to the metallic state in the *dry way*, and from the regulus obtained to eliminate the silver (and gold) by cupellation. (*See* Ex. 40.) For the reduction of a relatively pure galena (we mean an ore containing only little antimony, arsenic, iron, &c.) the following process is recommended*:—

Five grms. of finely powdered ore are mixed intimately with 50 grms. of litharge or red lead, 2 grms. of cream of tartar, and 12 grms. of carbonate of soda. The mixture is put into a smooth fire-clay crucible (about 45 mms. wide above, 30 mms. wide at the bottom, and 145 mms. deep inside), and covered with a layer of (dehydrated) common salt.

The crucible is placed in a wind furnace on a layer (10–15 ctms. deep) of glowing coke, surrounded with charcoal and heated, open, for about a quarter of an hour. The lid is then put on, more charcoal added as fuel, and the heating continued for another quarter of an hour, or until the contents are in a state of quiet fusion. [A properly constructed gas furnace may, of course, be used instead of a charcoal one.] The crucible is taken out, tapped on the floor to cause the regulus to flow into one mass, and the latter is then poured out into a conical cast-iron mould, which must stand on a *stone* floor, so that the slag can be suffered to run over. After cooling, the regulus is taken out, freed from slag with the hammer, and transferred to the cupel. If the regulus is very poor it is as well to drive off the bulk of the lead in one cupel and the rest in another. The above absolute quantities work well with relatively rich ores; of poor ores 10, 15, or 20 grms. must be taken.

It is almost impossible to procure absolutely silver-free litharge or red lead in commerce. Hence it is necessary, in general, to carry out a blank assay side by side with the assay proper, in order to find the necessary correction. The quantity of silver (or gold) contained in an ore is in this country customarily stated in *ounces troy per ton*, which, however, as easily seen, comes to the same as stating it in, for instance, *grammes per* 32 667 *grammes.*

---

* We quote from Kerl's "Metallurgische Probirkunst." Leipzig, 1882.

Ex. 37.—Silicate Analysis.

READ sections 447 and 448 in Dittmar's "Manual;" then proceed to the following exercises:—

(*a*) *Quartz*.

Finely powdered rock crystal.—A quantity of 0·4 to 0·7 grm. will be weighed out for you by the Demonstrator.* Manipulate it as follows:—

Mix in a platinum crucible with 3 grms. of mixed carbonates ($NaKCO_3$), by means of a previously heated stout platinum wire or thin glass rod; then heat, lid on, first for half an hour over an Iserlohn burner, then over a gas blow-pipe, until the mass has assumed the form of a clear liquid, free substantially from gas bells. Allow the crucible to cool down below visible redness, then cautiously dip it up to half of its height into cold water to accelerate the cooling process. Detach the fused mass from the crucible, and keep it on a watch glass. Place the crucible in a Berlin basin half full of water, and digest until what sticks to the crucible has got softened up. Then remove the crucible, put in the bulk of the fused mass, and allow to stand at a gentle heat until the whole is completely disintegrated. Now cover the basin with a concave glass plate, add hydrochloric acid in instalments until all the carbonate and silicate are decomposed, and heat until all the carbonic acid is away. Remove the glass plate, and evaporate on a water-bath to as near dryness as possible, taking care to stir at the end to prevent formation of solid crusts. Now, in order to render all the silica insoluble, keep the basin in an air-bath at 105–110°C. for an hour. Drench the contents in 20 per cent. hydrochloric acid, and allow to stand for an hour (or longer) to enable the iron and alumina to become normal chlorides; then add water, heat, and allow the silica to settle. Filter off the silica, and wash with hot water until the last washings fail to give even an opalescence with nitrate of silver. Dry the precipitated silica, detach it from the filter, incinerate

---

* *Demonstrator.*—The best method of standardizing the quartz is to disintegrate a gramme or so with fluoride of ammonium (*vide infra*) to weigh the residual sulphates as they come out, and in their hydrochloric solution to determine the SO_3 with $BaCl_2$, to obtain the oxides that were present in the quartz analysed.

the filter in a platinum spiral, and ignite precipitate and ash in a platinum crucible until constant. Observe that dry silica is a very light, mobile powder, which is easily blown away by the slightest draught of air, and that the ignited substance is highly hygroscopic.

A trace of silica passes into the filtrate, from which it can be recovered and determined by adding a known weight of iron in the form of ferric chloride, precipitating with ammonia, filtering off, igniting and weighing the precipitate. What it weighs more than the calculated Fe_2O_3 is SiO_2. The ferric chloride is easily prepared from a known weight (about 50 mgs.) of pianoforte wire, by solution in hydrochloric, and boiling with a few drops of nitric acid.

The weight of the ignited silica should be equal to that in the quartz used to within less than half a per cent.

(b) *Analysis of Felspar, or any other silicate insoluble in acids.*

Powder a few grammes very finely in an agate mortar, and keep the powder in a preparation tube. Ignite about 1 grm. in a platinum crucible to determine the water (which, in the case of felspar, will amount to very little). The residue can be utilized for the determination of the

SILICA AND BASES NOT ALKALIES.

Mix with 6 grms. of mixed alkaline carbonates $NaKCO_3$ (for 1 grm. of substance), and proceed as shown above for "Quartz." Keep the silica in a preparation tube to examine it according to Note 1.

Filtrate and Washings.—Add ammonia, drop by drop, until alkaline, then boil off the excess of ammonia in a slanting flask, filter off the precipitate (impure oxides of iron and aluminium), wash it thoroughly with hot water, separate the alumina from the rest by caustic potash and determine it, as explained in Ex. 17. If the oxide of iron precipitate is large, it must be redissolved in hydrochloric acid, and re-precipitated by caustic potash. The (alumina-free) oxide of iron (as it still contains some alkali and small quantities of lime and magnesia) is again dissolved in hydrochloric acid, precipitated with ammonia (the excess of the latter being boiled off), washed, and weighed as usual. Keep the precipitate to examine it according to Note 2.

The ammoniacal filtrate from the iron, containing part of the lime and magnesia, must be incorporated with the filtrate from the first sesquioxides precipitate. In the mixed liquor, after due concentration, the two protoxides are determined as usual.

For the determination of

The Alkalies,

apply successively Methods I. or II. and Method III.

I. *Lawrence Smith's.*—Mix 0·5 grm. of the *very* finely powdered silicate *in a mortar*, with 0·5 grm. of sal-ammoniac and 4 grms. of pure granular (precipitated) carbonate of lime; put the mixture into a platinum crucible, rinse the mortar with a little carbonate of lime, and put the rinsings on the top of the mixture in the crucible. Heat, lid on, first for half an hour over an Iserlohn burner, then for another half-hour as strongly as possible over a gas blow-pipe. The mass only sinters, yet the mineral, if it was finely enough powdered, is completely decomposed, the alkalies assuming the chloride form. Soak the crucible lid (the lid frequently has a film of sublimed alkali chloride on it) and the crucible and contents in water until the alkalies can be assumed to have gone into solution; heat, and filter. From the filtrate precipitate the lime by means of normal carbonate of ammonia at a boiling heat, filter off the carbonate of lime, evaporate to dryness, ignite the residue gently to remove the sal-ammoniac, and weigh what remains. This residue should consist of only fixed alkali chlorides, but generally it is contaminated with lime and magnesia; hence it is well to re-dissolve it in the crucible in a little water, to add a pinch of *pure* lime, and again operate as before with the slaked

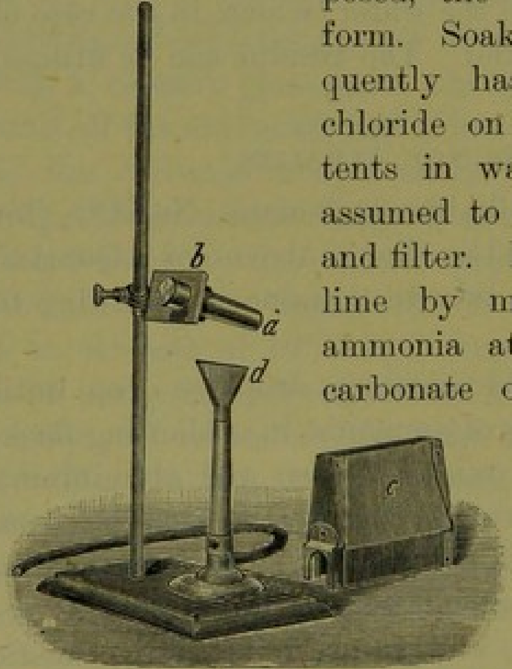


Fig. 31.

mass. The purified alkali muriates are weighed, and the potash in them is determined by chloroplatinic acid. To obtain really exact results with this method, it is necessary to use a peculiar tube-shaped crucible of Lawrence Smith's invention, in which the disintegration can be effected without loss of alkali chloride by volatilization. Fig. 31 shows the whole of Lawrence Smith's apparatus, including the heating arrangement. The crucible *a* when being heated is suspended slantingly by means of a perforated iron plate *b*, fixed vertically to the slide of the stand. The top *d* of the Bunsen is shaped so as to yield a thin but broad sheet of flame, which, during the final heating, is kept steady and rendered more effective by means of a roof-shaped chimney *c*, which is suspended at the plate *b* over the bottom part of the crucible. The part projecting from the other side of the plate remains relatively cold, so that any volatilized chloride condenses in it and is saved. The Bunsen and chimney combined gives a sufficiently intense heat; there is no need of a blow-pipe. According to Lawrence Smith, however, a little of the alkali may remain in the precipitate (as undecomposed mineral). To recover it the precipitate is dried, mixed with a little sal-ammoniac, re-ignited in the crucible, &c.

II. *Dittmar's Modification of the Baryta Process.*—Mix, say, 0·5 grm. of silicate with 3 grms. of pure hydrate of baryta ($Ba(OH)_2$ not crystals), and 0·15 grm. of anhydrous chloride of barium, and heat the mixture in a platinum crucible so constructed that an atmosphere of hydrogen can be maintained within it. An Iserlohn burner gives sufficient heat. The fuse may be worked up as in Lawrence Smith's method, but, of course, is available for a re-determination of the silica and of all the bases (except, perhaps, the lime), because the barium is easily eliminated by means of sulphuric acid. The method works very well as one of disintegration; also in this sense, that the platinum crucible remains unattacked. Whether there is really no loss of alkalies by volatilization still remains to be proved. Our experiments in this respect are not quite conclusive.

III. *Fluoride of Ammonium Method.*—Mix, say, 0·5 grm. of finely powdered silicate with 3·5 grms. of fluoride of ammonium in a platinum basin (best one with a concave lid, provided with a shielded perforation), and add a few drops of water, so that, on gentle heating, the whole assumes the form of a thin paste. Cautiously evaporate to dryness over an air-bath, stirring up with a platinum spatula, and keep the residue at a dull-red heat until vapours cease to come off. Then allow to cool, moisten the residue with a few drops of oil of vitriol, and heat again until the *free* sulphuric acid is expelled. *All these operations must be carried out in an efficient draught place.* After the mass has cooled down, dissolve it in hydrochloric acid. Take care not to completely decompose the sulphate of alumina, or else the alumina formed will not be soluble in dilute acid. There should be no residue; if there is one, it must be filtered off, and worked up with fluoride of ammonium. In the hydrochloric solution of the sulphates, all the bases can, of course, be determined by proper methods. If you care only for the alkalies, precipitate the sulphuric acid by chloride of barium; then, without filtering off the sulphate of baryta, the insoluble oxides by means of pure *(alkali-free)* baryta water (hot), and filter. From the filtrate eliminate the barium and calcium by carbonate of ammonia, and manipulate the filtrate as just explained for the Lawrence Smith method.

Notes.—1. The silica must be quite soluble in strong boiling solution of carbonate of soda. When treated with fluoride of ammonium, like a silicate, it must leave *no* residue of sulphate. If these tests do not come out right, the analysis had better be commenced anew.

2. The oxide of iron ultimately obtained always contains a little silica, which remains when the ignited precipitate is dissolved in strong hydrochloric acid. It must be collected on a filter, washed, ignited, and weighed, and allowed for. In the hydrochloric acid solution the iron may be determined titrimetrically for a check. If the weight of Fe_2O_3 as thus determined, together with that of the silica, is less than the total precipitate, the deficit must be put down as so much alumina.

Calculation of the Results.

Report your results in per cents. of the substance analysed, and then, in order to find the formula, divide each of the percentages by its formula value, and translate your analysis into a formula—

> $a\mathrm{SiO_2}$ (*i.e.*, a times 60 parts of silica) $+ b\mathrm{M'''_2O_3} + c\mathrm{M''O} + d\mathrm{R_2O}$; where $\mathrm{M'''_2O_3}$ means Al_2O_3 or Fe_2O_3, $\mathrm{M''O}$ means CaO or MgO; R_2O means K_2O or Na_2O.

Next divide all the co-efficients by a, so as to bring the formula into the form $1\mathrm{SiO_2} + b'\mathrm{M'''_2O_3} + c'\mathrm{M''O} + d'\mathrm{R_2O}$, and multiply successively by 2, 3, . . . until the factors become sufficient approximations to integers.

According to Tschermak, felspar is in general a crystal compound of three species, namely—(1) Anorthite, an ortho-silicate of the formula $(Al_2O_3.CaO).2SiO_2$; (2) albite, a sesqui-silicate $(Al_2O_3.R_2O).6SiO_2$, where R_2 is chiefly Na_2; and (3) microline, which has the same formula as albite, only R_2 is chiefly K_2. [All triclinic; orthoclase is an oblique prismatic isomer of microline.] Hence the correct way of calculating a felspar analysis is, after having found the co-efficients of the formula $a\mathrm{SiO_2} + b\mathrm{M_2O_3}$, &c., to next combine the c (CaO or MgO) with as much silica and alumina as they need to become anorthite, and to deduct these quantities $\alpha\mathrm{SiO_2}$ and $\beta\mathrm{M_2O_3}$ from the original values. The remainder $(a - \alpha)\mathrm{SiO_2} + (b - \beta)\mathrm{M_2O_3} + d\mathrm{R_2O}$ should fall in with the formula of albite.

Silicates decomposible by Hydrochloric Acid.

These we leave in the hands of the student. Most of them, however, are mixed with *undecomposible* silicates or quartz, so that what comes out as "silica" includes this admixture. To analyse such a mixture, boil it with concentrated solution of carbonate of soda, filter through a filter kept hot by a steam jacket, wash the residue, first with solution of carbonate of soda and, ultimately, with carbonate of ammonia. (With plain water a turbid filtrate is obtained). The residue is ignited, and weighed as silicate or quartz, as the case may be. In the filtrate the dissolved silica, *i.e.*, the silica of the decomposible silicate, is determined as usual.

Ex. 38.—Analysis of Chrome Iron Ore.

A.—ASSAY FOR CHROMIC OXIDE.

Preliminaries.—(1.) Procure a real average sample, which should not be too small; reduce it to a powder of about the fineness of sea sand *without rejecting any residue*, and bottle up the powder as "substance." In about 5 grms. of this "substance" determine the moisture by drying at 100°C. It usually amounts to very little, but it must be reported. The analysis proper is referred to substance dried at 100°C.

(2.) *Flux.*—Fuse together equal weights of borax-glass and the mixture $NaKCO_3$ in a platinum crucible, pour out the fuse into a platinum basin, and preserve it in a well-stoppered bottle as "chrome ore flux."

Analysis.—Reduce somewhat more than 1 grm. to an impalpable powder, dry this powder completely at 100°C., and put it into a small narrow preparation tube; cork up, and determine the exact weight of the whole, taking care to weigh also the emptied tube, so as to ascertain the exact weight of ore used. Fuse 8 grms. of flux (or 5 grms. each of the two components) in a platinum crucible of 50 cc.'s capacity over a powerful Iserlohn lamp, allow to solidify, and put on the top of the fuse the contents of the weighed preparation-tube. Heat the crucible, lid on, until the flux is quite fluid and the ore has sunk to the bottom. Now take off the lid, place the crucible slantingly on a platinum triangle, and the lid in front of it horizontally, and heat, stirring up frequently with a thick platinum wire, until all the ore is dissolved. This, unless the lamp is in first-rate condition and the gas pressure high, requires the use of the blow-pipe. Continue heating (in the presence of air, and stirring up occasionally) for about half an hour, when the chromium can be assumed to be all converted into alkaline chromate. Now allow to solidify, add 5 grms. of double carbonate $KNaCO_3$, fuse up again, and pour the fuse into a large platinum dish. Place the crucible in a basin with water, and heat until all the adhering mass is softened up; wash what sticks to the crucible into the basin, and remove the crucible. Then add the bulk of the fused mass, and allow to stand on a water-bath until the whole is completely disintegrated; then filter, and wash with hot water as long as the runnings are yellow.

The *brown precipitate* consists of basic borates and hydrates of the oxides Fe_2O_3, Al_2O_3, MgO, and often includes silica. It always contains a few mgs. of oxide of platinum, although the crucible is not visibly attacked in the fusion process. It is dissolved in hot hydrochloric or dilute sulphuric acid; the platinic oxide dissolves along with the bases; any undecomposed ore becomes visible; it is washed, ignited, and weighed. In a carefully conducted fusion it will never amount to more than 2 mgs. Such small quantities may be taken into account as containing 50–60 per cent. of chromic oxide, without serious error. Larger quantities must be disintegrated and the products added to the main quantities.

If a complete analysis be contemplated, the acid solution of the brown precipitate may be utilized for a determination of the iron. For this purpose it is treated with sulphuretted hydrogen *hot*, the mixed precipitate of sulphur and sulphide of platinum filtered off, and the iron in the filtrate titrated with permanganate or "bichrome." (*See* Ex. 18).

The yellow filtrate contains the chromium as chromate, along with chiefly borate of alkali. For the determination of the *chromium* concentrate it by evaporation to about 200 cc. Bring it to an exactly known volume or weigh it, to be able to fractionate it quantitatively.

A fraction corresponding to about 0·1 grm. of ore serves for a preliminary determination of the chromium. For this purpose the liquid is acidified strongly with dilute sulphuric acid, and then mixed with a known weight of standardized *ferrous sulphate,* sure to be more than sufficient to reduce the chromic acid to chromic oxide. 12 grms. of salt per 1 grm. of chromic oxide Cr_2O_3 are more than sufficient. The surplus ferrosum is determined by titration with standard bichrome solution (*see* Ex. 18). The determination is then repeated on a larger scale, the preliminary trial enabling one to calculate the ferrous salt, and thus to avoid immoderate excess. What is left after the preliminary test suffices for two exact titrations. The chromium is calculated as Cr_2O_3 from the ferrosum oxidized by the chromic acid. $6Fe \times 0{\cdot}4530 = Cr_2O_3$ and $Cr_2O_3 \times 2{\cdot}208 = 6Fe$.

As a matter of principle a synthetically standardized solution of bichrome ought to be taken as the fundamental standard, but bichromate of potash is not easy to obtain in a state of undoubted purity and correctness of composition.*

B.—Complete Analysis.

For a complete analysis the ore might be disintegrated as explained for the assay, but it is better to effect a special disintegration in which the addition of the extra 5 grms. of double carbonate is omitted to avoid excessive alkalinity, which brings unnecessarily large quantities of alumina and silica into the yellow solution produced from the fuse. Before going further, let us observe that even the best borax-glass of commerce usually contains silica and alumina. These do not interfere with a mere *assay*, but, in a complete analysis, must be determined by a "blank," and allowed for. Trommsdorff's "kali boricum" is generally free from these impurities, and 6·5 grms. of it, fused up with 3·5 grms. of $NaKCO_3$, give a flux equivalent to what is produced from 10 grms. of the components of the ordinary flux.

But the *kali boricum* cannot be expected to be of constant quality. I therefore propose for the future to make the flux for the complete analysis out of *pure* boric acid, $B_2O_3\ 3H_2O$ and double carbonate $NaKCO_3$. 124 parts of the acid and 163 of the carbonate should yield 174 parts of a flux equivalent to 100 of borax glass + 100 of double carbonate, *i.e.*, 200 parts of ordinary assay-flux ingredients.

Analysis of the Brown Precipitate.—Dissolve in hydrochloric acid, evaporate to complete dryness, moisten the residue with *strong* hydrochloric acid, and give the alumina and iron sufficient time to become chlorides; then dilute, filter off the *silica* and weigh it. From the filtrate eliminate the platinum by sulphuretted

---

* The most certain method is to standardize the iron salt by means of a known weight of *pure* chromic oxide, fused up with flux, &c., like a chrome ore. Pure chromic oxide can be obtained by the ignition of pure mercurous chromate produced best from pure bichromate of *ammonia*. But this method is very troublesome.

hydrogen, and, after filtration and expulsion of the dissolved sulphuretted hydrogen, re-peroxidize the iron by means of a granule of chlorate of potash. Then separate the sesquioxides (Al_2O_3 and Fe_2O_3) from the protoxides by *two* successive applications of the sal-ammoniac and ammonia process (*see* Ex. 21, p. 53). Separate the iron and alumina by caustic potash twice, according to Ex. 17, and separate and weigh the Fe_2O_3 and the Al_2O_3 as there explained. The sal-ammoniac filtrate obtained from the iron is added to those produced before. The united sal-ammoniac liquors are evaporated to complete dryness, the sal-ammoniac is chased away by calcination, and in the residue the *lime* and *magnesia* are determined by the usual methods. The solution of the calcined residue (in water and hydrochloric acid) may contain a little alumina; it is separated out by ammonia and weighed. The lime usually amounts to very little; the magnesia to a good deal.

The ignited oxide of iron must be dissolved in strong hydrochloric acid. If a residue remains, it is collected, weighed, and in the calculations allowed for as so much *silica*.

Analysis of the Yellow Filtrate.—If a whole gramme was taken for analysis, one-half of this liquor suffices for the determinations, so that the other half can be reserved for checks. Add to it *excess* of sal-ammoniac (*see* Ex. 17, second paragraph), filter off the precipitate formed, ignite, and weigh it. If the flux prescribed for complete analysis was used, the precipitate amounts to very little, and may be put down as so much *alumina*.

If the more strongly alkaline assay-flux was employed, the precipitate amounts to more, and it may be necessary to treat a finely-powdered aliquot part of the ignited precipitate with fluoride of ammonium (as in a silicate analysis, *see* p. 125), and determine the alumina in the desilicated residue by ammonia. The silica part is determined by difference.

The *filtrate* from the precipitate produced by sal-ammoniac usually contains part of the *magnesia*. It is determined by adding enough of strongest ammonia, and then applying phosphate of ammonia as usual. The *chromium* we suppose to have been determined in a separate portion by the assay-method.

The student, *for his information*, may use the reserve-half of the yellow filtrate for a determination of the chromium by means of mercurous nitrate. If the dissolved alumina was found (in the analysis of the first half) to amount to a mere trace, the yellow liquor is simply acidified with pure (N_2O_3-free) nitric acid; the precipitant added and allowed to act at water-bath heat, until the precipitate, which has at first an impure colour, has assumed the form of red crystalline $Hg_2O\ CrO_3$. If tangible quantities of alumina, &c., are present in the liquor, these must first be eliminated by means of excess of *nitrate* of ammonia (which in this case must be substituted for the chloride recommended above), and the mercurous nitrate applied to the filtrate.

The mercurous chromate is collected on a small filter and washed with a hot *very* dilute solution of the precipitant; it is then transferred, moist, to a platinum crucible (along with the filter), and ignited in a *very efficient* draught place, which is sure to carry away the poisonous mercury vapours. The residue is weighed as Cr_2O_3. A small quantity of the chromic acid, however, escapes precipitation. To recover it, eliminate, first the mercurosum as calomel, then from the filtrate the mercuricum by sulphuretted hydrogen; then boil down the filtrate to a sufficiently small volume, precipitate the chromium (now present as chromic salt) with ammonia, taking care to boil off the excess of ammonia before filtering, collect, and weigh the precipitate as Cr_2O_3.

An impure chrome ore is liable to contain

Chemically combined water.—To determine it, heat some 3–4 grms. of the "substance" (see at the beginning of the article) in a platinum boat in a combustion tube, collect the water in a tared chloride of calcium tube, and weigh. A soda-lime U-tube may be joined on to the chloride of calcium one to determine any carbonic acid that may come off.

Calculation of the Results.—We have good reasons* for assuming that all chrome iron ores contain their chromium as Cr_2O_3, while the iron in general is present, part (as a rule the greater part) as FeO, part as Fe_2O_3. Hence, in calculating results, we

---

* See Rammelsberg's Mineral Chemie.

naturally translate the data of the analysis into percentages of (SiO_2), Cr_2O_3, Al_2O_3, MgO, (CaO), and FeO, and next contrast the sum of these percentages with 100, allowing for experimental errors, the aggregate effect of which on the sum may amount to ±1 per cent. even in a good analysis. Occasionally it may amount even to a little more, but for greater definiteness in our explanations we will fix our *toleration* at ±1 per cent., and say that, if the percentages (with all the iron as FeO) add up to more than 101, some component or components must have been over-estimated, and the analysis consequently must be repeated. If the results, even with all the iron calculated as Fe_2O_3, fall short of 99, this, of course, again condemns the analysis. Hence, only the intermediate cases need be considered in the following, but we prefer to pass to an example, and assume that the results of the analysis had come out, as shown in column I. of the following table:—

	I.		II.
Chromic oxide,... ...	55·14	=	$0{\cdot}3622 \times Cr_2O_3$
Alumina, ...	5·75	=	$0{\cdot}0563 \times Al_2O_3$
Magnesia, ...	9·39	=	$0{\cdot}2327 \times MgO$
Iron (met.), ...	22·44	=	$0{\cdot}4007 \times Fe$
Oxygen, by diff., ...	7·28	=	$0{\cdot}4550 \times O$
	100·00		

A glance at column II. shows that the iron apparently is present as a mixture of xFeO and $y Fe_2O_3$, and the x and y are easily found. We have $0{\cdot}4007 \times FeO + 0{\cdot}0543 \times O = \left\{ 0{\cdot}0543 \times O + 0{\cdot}1086 FeO = 0{\cdot}0543 \times Fe_2O_3 \right\}$ *plus* $0{\cdot}2921 \times FeO$; or 8·69 of ferric oxide *plus* 21·03 of ferrous, together $= 29{\cdot}72 = 22{\cdot}44 + 7{\cdot}28$, which, of course, brings up the results to exactly 100. But as our analysis reports no components foreign to the species, we had better test it further by seeing whether it is compatible with the general formula $M_2O_3 + RO$ for the pure mineral, which, referring to 100 parts of our ore, assumes the form

$$\left\{ \begin{array}{c} 0{\cdot}4185 \times (Cr_2 \text{ or } Al_2)O_3 \\ x \times Fe_2O_3 \end{array} \right\} + \left\{ \begin{array}{c} 0{\cdot}2327 \times MgO \\ y \times FeO \end{array} \right\}$$

Obviously x and y must be so chosen that

$$0{\cdot}4185 + x = 0{\cdot}2327 + y \quad \dots \quad \dots \quad \dots \quad \text{(Eq. I.)}$$

and $$2x + y = 0{\cdot}4007 \quad \dots \quad \dots \quad \dots \quad \dots \quad \text{(Eq. II.)}$$

both subject to the third condition that the iron-oxygen demanded by the formula, which is $(3x+y)\times(O=16)$, lies between (say) $7{\cdot}28-1$ and $7{\cdot}28+1$. From Eqs. I. and II. we have

$$\begin{array}{rlr} 0{\cdot}4185+x-y &= 0{\cdot}2327, \quad \ldots \quad \ldots & \text{(I.)} \\ 2x+y &= 0{\cdot}4007, \quad \ldots \quad \ldots & \text{(II.)} \\ \hline \text{by addition,} \qquad 3x &= 0{\cdot}2149. & \end{array}$$

Whence $x=0{\cdot}07163$ and by substitution into II., $y=0{\cdot}2574$. Hence $(3x+y)=0{\cdot}4723$; and $(3x+y)16=7{\cdot}56$ which falls within our limits. To check the computation we make the additions

$$0{\cdot}4185+0{\cdot}0716=0{\cdot}4901$$
$$0{\cdot}2327+0{\cdot}2574=0{\cdot}4901;$$

(the result is as it should be) and compute

$0{\cdot}07163\times(Fe_2O_3=160)=11{\cdot}46$ per cent. of ferric oxide,
$0{\cdot}2574\ \times(FeO\ =\ 72)=18{\cdot}53$ „ ferrous „

together, ... 29·99

instead of 29·72, which brings up the results to 100·28 instead of 100.

If the analysis of an apparently pure chrome ore does not submit to this mode of manipulation, *and we have made quite sure of our analysis,* all we can do is either to calculate the FeO and Fe_2O_3 from the *analysis,* and just report the results as they stand, or, if we find it worth our while, to try and interpret the results on the basis of some reasonable hypothesis on the proximate composition of the ore. With a palpably impure ore the latter course is the only one that is open to us, if we wish to discuss the analysis mineralogically.

Unfortunately, there is no method for separating the gangue from the pure mineral, so that one could, for instance, see directly whether the silica is there as so much quartz or in some other form. From our large *toleration* for the sum of the percentages, the student must not conclude that any great error can be tolerated in the chromic oxide; *its* percentage in a good series of analyses should not be uncertain by more than ± 0·2 unit.

For an exercise in chemical arithmetic, I append the results of the analysis of a chrome ore which Mr. Cullen carried out lately under my direction:—

He found in 100 parts of ore, dried at 100°C.,

Chromic oxide, ...	52·48
Alumina, ...	6·59
Magnesia, ...	17·17
Iron, calculated as metal, ...	12·35
Silica,...	5·65
Carbonic acid, ...	0·07
Combined water, ...	1·83
Oxygen, combined with the iron, and error,	3·86
	100·00

Discuss the results arithmetically, as explained above, and see if you can interpret them as representing a mixture of *serpentine* and chrome ore, M_2O_3RO proper. The formula of serpentine is $2SiO_2\left\{2H_2O, 3MgO\right\}$

Ex. 39.—Separation of Lead and Antimony.

A.—By Means of Alkaline Sulphide.

Oxidize about 0·5 grm. of the alloy with nitric acid in a long-necked slanting flask of 200–300 cc.'s capacity, and boil off the bulk of the acid; allow to cool, dilute moderately with water, neutralize with ammonia, add 20–30 cc. of yellow sulphide of ammonium, and heat on a water-bath for half-an-hour. Decant the clear sulphide of ammonium liquid through a No. 5 filter, digest the residue with 5 cc. more of sulphide of ammonium, and wash with a warm dilute solution of the same reagent. The filtrate contains the most of the antimony as thiosalt; the precipitate, in addition to all the lead, contains a remnant of antimony, which cannot be completely removed by repeated application of sulphide of ammonium. For its recovery use the first, and then (in a second analysis) the second, of the following two methods:—

(1.) Re-dissolve the precipitate in hot hydrochloric acid, and again apply yellow sulphide of ammonium (after neutralizing with ammonia, of course) as before. The thiosalt solution is mixed with the one obtained before, and the mixture worked up as explained below. The precipitate of sulphide of lead is dried, ignited in hydrogen with sulphur until constant in weight (*see* Ex. 19), and weighed as PbS (Rose's method). $PbS \times 0.8658 = Pb$.

(2.) After having collected it on a *weighed* filter, dry the crude sulphide of lead at 100–105°C., and weigh. Detach as completely as possible from the paper, grind up in a small agate mortar, dry for ten minutes in a tared porcelain crucible, and weigh again to find what fraction of the whole precipitate has been taken. Add six times its weight of a mixture of equal weights of anhydrous carbonate of soda and sulphur; mix with a wire, and fuse very gently with lid on. Dissolve the mass in water, filter off the sulphide of lead, and treat it as explained under (1). In this case the second thiosalt solution (obtained in the fusion process) must, of course, either be worked up by itself, or else we must mix it with only a *fraction* of the sulphide of ammonium filtrate, so adjusted that it represents the same fraction of the whole as does the part of the crude sulphide of lead which passed through the fusion process.

From the thiosalt solutions the antimony is re-precipitated by acidification with dilute sulphuric acid, the mixture being allowed to stand in an open beaker at a gentle heat until the dissolved sulphuretted hydrogen is mostly gone and the liquid has cleared up. The precipitate is then collected on a filter, and washed with (plain) water. To render it weighable, dissolve it in boiling hydrochloric acid, and filter off the sulphur. Precipitate with sulphuretted hydrogen, collect on a weighed filter, wash with water, dry at 105–110°C., and weigh as Sb_2S_3, from which calculate the antimony. $Sb_2S_3 \times 0.7137 = Sb_2$. From the solution of the sulphide in hydrochloric acid onwards, operate in an atmosphere of carbonic acid, to avoid oxidation of $SbCl_3$ or H_2S, as explained on p. 116.

B.—By Means of Chlorine.

Method.—The alloy is chlorinated, and the two chlorides, $PbCl_2$ and Sb(Cl_3 and Cl_5), are separated by distillation. The *lead* chloride is in the residue.

Requirements:—(1) *A steady current of Dry Chlorine.*—This can be produced in various ways, but the handiest method for the present purpose is De Koninck's, who evolves the gas in a "Kipp" from lumps of high-class pyrolusite (MnO_2) and strong hydrochloric acid. We found it expedient to procure for this purpose special "Kipps," modified so as to stand immersion in hot water. The "manganese," of course, goes into the middle bulb (which would accommodate the marble in the case of carbonic acid), but the reaction requires to be supported by heat, which is best applied by means of a large warm water-bath, into which the "Kipp" is immersed during the operation. The gas must be dried very carefully by passing it, first, through a wash-bottle containing oil of vitriol, and then up a "tower" charged with pumice soaked in the same dehydrating liquid.*

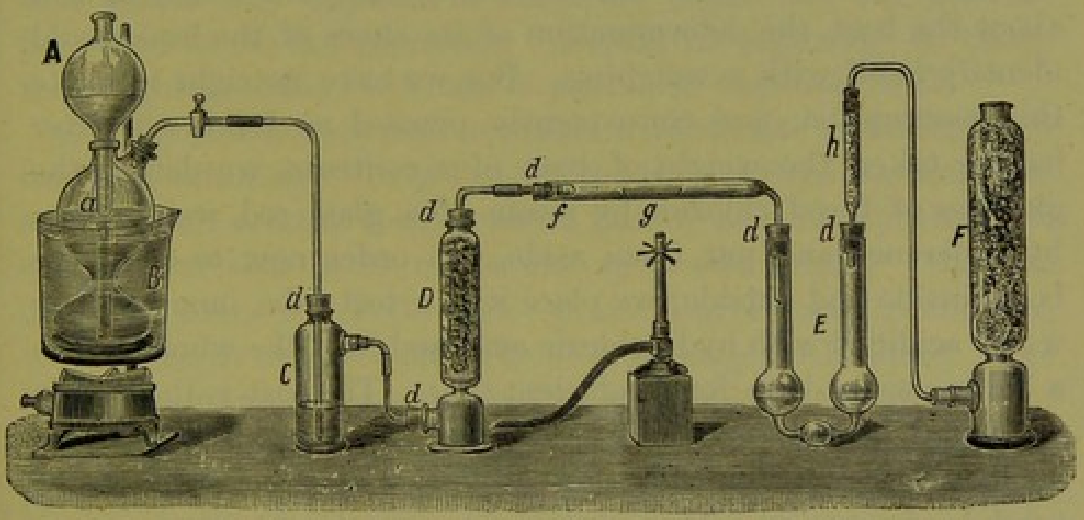


Fig. 32.

A, *a*, chlorine-Kipp; *C*, wash-bottle, charged with vitriol; *D*, tower charged with pumice soaked in vitriol; *g*, boat containing substance, *E*, bulbed U-tube, ; *F*, tower charged with charcoal and slaked lime to absorb surplus chlorine; *d*, *d*, *d*, . . paraffined corks; *f*, thimble to prevent back-currents.

(2.) An apparatus like the one represented in Fig. 32.

The process of chlorination requires no lengthy explanation. Supposing the apparatus to be put together and the air to be expelled, regulate the heat so that the reaction progresses at a convenient rate, and at last give sufficient heat, but not more

---

* The presence in the gas of HCl is rather an advantage, because it may serve to chlorinate any adventitiously produced oxide.

than necessary, to drive the chloride of antimony out of the boat and away from the surrounding parts of the tube. Over-heating must be avoided, because chloride of lead is not by any means absolutely non-volatile. To prevent formation of a precipitate of oxychloride of antimony in the bulbs, it is as well to charge these with a solution of tartaric acid instead of with pure water.

Supposing the chlorination and distillation to have been completed, the apparatus is allowed to cool, the chlorine gas driven out of the apparatus by a current of dry air or carbonic acid, and the several products are then analysed as follows:—

(1.) *The Boat.*—It contains the greater part of the lead as a mass of fused chloride, $PbCl_2$, which often is perfectly pure. If we could be sure that there is nothing but pure $PbCl_2$ in and about the boat, the determination of its share of the lead would identify itself with a weighing. But we have no right to make this assumption, and consequently proceed as follows:—After having taken the weight of boat *plus* contents, we detach the globules of fused chloride by means of a glass rod, weigh them by difference and put them aside. In order now to clean the boat (inside and outside) we place it in a test tube, immerse it in water acidified with hydrochloric acid, and heat the whole within a boiling water-bath for a sufficient time. The boat is then taken out, dried, heated, &c., and weighed, and *this* weight noted down as the more exact tare for the calculation of the weight of the total boat-contents. The solution is neutralized with ammonia and mixed with yellow sulphide of ammonium to separate the lead from the antimony that may be present. (Compare sect. A). From the filtrate the antimony is recovered by acidification with dilute sulphuric acid.

The fused chloride which was put aside *may* include antimony. For its determination the chloride is dissolved in boiling water acidified with some hydrochloric acid, the solution evaporated to a small volume on a water-bath, and the dissolved chloride of lead allowed to crystallize out as completely as possible. The addition of a moderate proportion of hydrochloric acid increases the relative insolubility of the chloride. It is collected on a small filter and washed with small instalments of cold dilute hydrochloric acid. [For the determination of its weight it is washed

2–3 times with small quantities of absolute alcohol, dried at a gentle heat (best under the bell jar of the air-pump over oil of vitriol), and transferred to a large enough flat evaporation crucible, the part sticking to the paper being recovered by washing with hot water, as in the case of a chloroplatinate precipitate. (The alcoholic washings had better be evaporated to dryness, and any residue left be incorporated with the aqueous wash-liquors). The whole is evaporated to dryness, the residue dried at 120°C. and weighed. $PbCl_2 \times 0{\cdot}7448 = Pb$]. From the filtrate the dissolved lead is precipitated, after neutralization with ammonia, by excess of sulphide of ammonium, and filtered off. The filtrate is acidified with dilute sulphuric acid, and, if any sulphide of antimony comes out, the mixture preserved for its determination. Should no antimony be there, the weighing of the $PbCl_2$ can of course be dispensed with.

(2.) *The combustion tube* contains a sublimate including both lead and antimony. To get it out the tube is fixed slantingly in a clamp over a small beaker, and a puff of aqueous hydrochloric acid vapour sent in to render the sublimate soluble. By then distilling some water through—in successive instalments—the whole is easily washed out without producing much liquid. The lead and antimony are separated by sulphide of ammonium.

(3.) *The* U-*tube* contains the bulk of the antimony, and, in general, a little lead. The liquor is diluted, the chlorine expelled by gentle heating in an open vessel, and the two metals are precipitated conjointly by sulphuretted hydrogen. Their separation may be effected by yellow sulphide of ammonium, but this encumbers the precipitate with a mass of additional sulphur, which inconvenience can be avoided by extracting the antimony sulphide by means of warm dilute caustic potash, which, as far as this separation goes, is quite equivalent in its action to alkaline sulphide.

The process, as we see, involves in general the production of four successive mixtures of precipitated sulphide of lead and dissolved thiantimoniate. Of these, the first three may be united and allowed to settle together; the fourth (the U-tube one) is better kept by itself. But the filter which served to collect the three united sulphides of lead may be used subsequently for the filtration of the alkaline mixture from the U-tube.

Each of the three processes given in this Exercise for the separation of antimony and lead is only a special application of a more general method.

Leaving the case of section A in the hands of the student, we may define the range of the general process of chlorination by saying that it applies, in a general sense, to two *groups* of elements, including respectively—

Group A.—Sb, As, Sn, Bi, Hg, S, P, As.
Group B.—Pb, Zn, Cd, Co, Ni, Mn.

Iron belongs, so to say, to both groups.

It does not follow that the method works equally well with all combinations, nor is it necessary to specially point out that the *modus operandi* must be adapted to the special case which one may have to deal with.

Ex. 40.—Analysis of Gold and Silver Alloys by Cupellation.

HALF-A-GRAMME of alloy is put into a cupel (a small flat dish made of compressed bone-ash), along with a sufficiency of lead (*see* Note 1), and the charged cupel is then placed in a muffle previously brought up to a red heat. The two metals readily fuse up into an alloy, which at once begins to oxidize with formation of a solution of the oxide of copper, &c., in fused oxide of lead, which solution is sucked up by the porous cupel.

If a sufficiency of lead be used, the base-metallic part of the alloy is away before all the lead is oxidized. The completion of the operation is marked by an iridescence on the surface of the metallic lead caused by the extreme thinness of the last film of oxide of lead. As soon as this stage is fairly passed, the cupel is taken to the colder (front) end of the muffle, and the metal allowed to freeze very slowly so as to avoid loss by "spitting." It is then taken out and allowed to cool. The button of metal produced is cleaned with a kind of tooth-brush, and weighed. This gives the gold and silver conjointly.

To determine the *gold*, the alloy is flattened on a polished anvil with a polished hammer, then annealed, and flattened further (best with goldsmith's rollers), rolled up into a spiral ("cornet"), and then treated with 20 cc. of 1·2 nitric acid in a slanting, pear-shaped flask. When the acid ceases to act spontaneously, the liquid is boiled for about five minutes. The silver solution is then decanted off, and, to extract the rest of the silver, the boiling is resumed with stronger (1·33) acid, care being taken this time to add a charred pea, to prevent bumping, and the boiling continued for 20–30 minutes. The silver now is all dissolved; the gold remains, either in the form of a porous skeleton of the original "cornet," or as a heavy powder. It is washed with water, and then transferred to a porcelain crucible by filling the flask brimful with water and then turning it over into the crucible. With some practice it is easy to let the gold fall into the crucible without spilling any water; but the mode of doing this is more easily shown than explained in words. Pour off the water from the gold, expel the rest by gentle heating, and lastly, heat the crucible and gold to redness. The gold, as a rule, can be lifted out with a forceps, and weighed directly on the balance-pan. By deducting its weight from that of the cupelled alloy we obtain the weight of the silver. The difference between original alloy and cupelled alloy gives the base metal (copper, &c.).

Note 1.—The weight of lead required depends mainly on the weight of base metal to be withdrawn, but not entirely, as is shown by the following tables:—

I.—*Alloys of Silver and Copper, containing only very little or no Gold.*

Parts of Silver (+ Au) per 1000 of Alloy.	Lead Required for Unit of Alloy.	Lead Required for Unit of Copper.
1000	0·3	—
950	3	60
900	7	70
800	10	50
700	12	40
600	14	35
500	16	32
Less than 500	16–17	—

II.—*Alloys of Gold and Copper.*

Gold per 1000 of Alloy.	Lead Required per 1 of Alloy.
1000	1
900	10
800	16
700	22
600	24
500	26
400–100	34

Note 2.—The general rule is to add enough of lead, but to avoid an excess as far as possible, because every grm. of lead added over and above what is needful means an *avoidable* loss of silver. In any case, some of the silver escapes the balance. In the case of gold-free alloys, the loss attains its maximum for alloys containing 500–700 per mg. of silver, and then amounts to about 4·7 parts per 1000 of alloy analysed.

The gold in a well-conducted assay comes out right to within ± 0·5 parts per 1000 parts of alloy, *i.e.*, to 0·25 mg. for the 0·5 grm. of alloy analysed.

Note 3.—The process of "parting" with nitric acid succeeds only if the gold does not exceed about 25 per cent. of the whole. If it does, the requisite weight of additional silver must be added at the beginning of the cupellation, and, of course, be allowed for in the calculation. For more detailed information, *see* Jevons' articles, "Gold Assay" and "Silver Assay," in "Watt's Dictionary of Chemistry," first edition.

ELEMENTARY ANALYSIS OF COMBUSTIBLE CARBON COMPOUNDS.

Ex. 41.—Analysis of Ferrous Oxalate.

Preparation of the Substance.—Dissolve 110 grms. of ferrous sulphate in half a litre of water acidulated with a few drops of sulphuric acid, filter, add a filtered solution of 50 grms. of oxalic acid in half a litre of water, allow to stand over night, filter, and wash the precipitate with cold water until the last washings are free from sulphuric acid. Dry in an air-bath at 90° to 100°C., mix, and bottle up.

Standardization of the Salt.—The salt is said by the handbooks to be $FeC_2O_4 + 2H_2O$; but in *our preparation* at any rate, the "2" in the $2H_2O$ cannot be relied on; hence the salt had better be standardized by determining the proportion of ferric oxide which it yields on ignition in a platinum crucible. Supposing, *per* 1 *grm. of salt,* we obtain p grm. of Fe_2O_3, the iron amounts to $0{\cdot}7\ p$; the carbonic acid united with it to $88/80\ p$; hence the two conjointly to $1{\cdot}8\ p$ and the water to $1 - 1{\cdot}8\ p$.

Requirements for the Analysis.—(1) A platinum boat; (2) a combustion tube just wide enough to hold the boat; (3) absorption apparatus for water and carbonic acid, the same as used for the direct determination of carbonic acid in carbonates (Ex. 20); (4) granulated oxide of copper.

Method.—Clean out the combustion tube by drawing a tightly-fitting bunch of cotton wool, fixed to the centre of a strong string, through the tube forwards and backwards. Draw out the exit end so as to produce a strong, fairly cylindrical appendage about 80 mms. long, and of the same width as the entrance tube of the calcium chloride U-tube, and round the edge. Cut down the

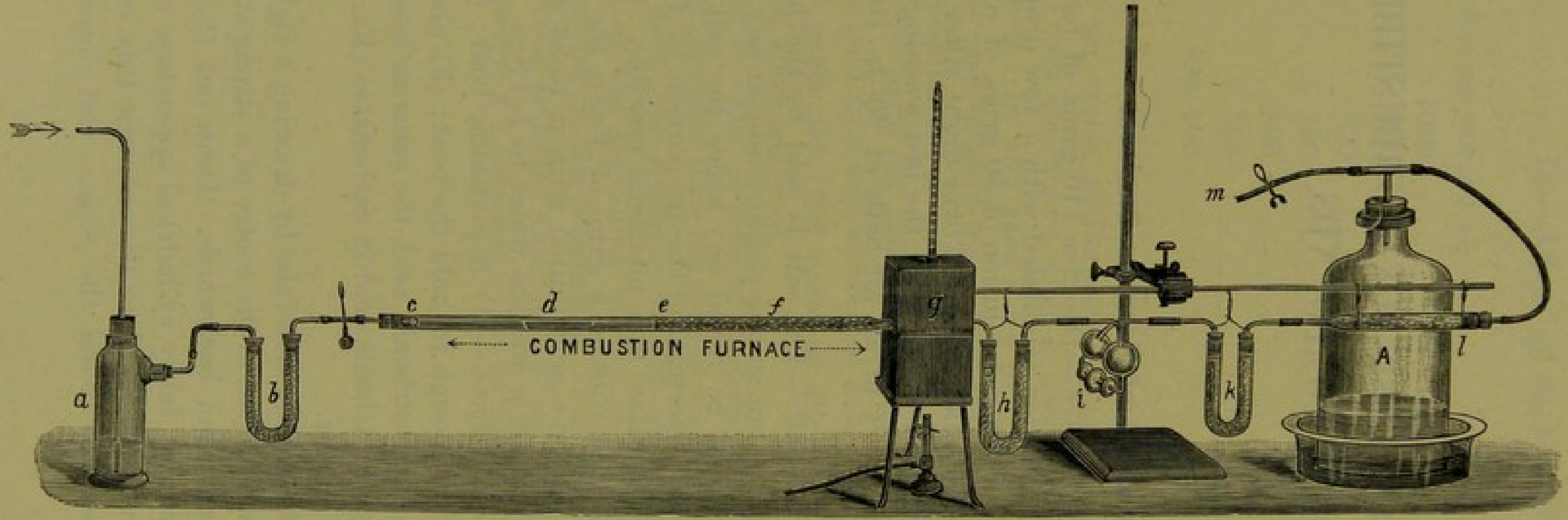


Fig. 33.

a communicates with a gas holder, charged with carbonic-acid-free air; *a*, wash-bottle charged with vitriol; *b*, chloride of calcium tube; *c*, *d*, *e*, *f*, combustion tube; *d*, platinum boat with substance; *e*, asbestos stopper; *f*, column of granulated oxide of copper; *g*, chamber to keep joint hot; *h*, tared chloride of calcium tube; *i*, tared potash bulb; *k*, tared soda-lime and chloride of calcium tube; *A*, aspirator; *l*, protection tube.

tube to a length of about 35 ctms., measuring from the shoulder of the exit end. As shown in Fig. 33, charge the tube with oxide of copper which has been previously heated strongly in pure air until free from carbonic acid, attach an india-rubber tube to the exit end, and, by means of it, a small *supplementary* chloride of calcium U-tube. The india-rubber tube is wired to the combustion tube, but not to the supplementary U-tube. Then heat the whole gradually to redness, while a slow current of chloride-of-calcium-dried air passes through the tube. After a while the flames up to a point a little to the right of *e* are turned off, but the oxide of copper is kept red hot until the outgoing air ceases to precipitate baryta water. In order now to make sure that the joint *g* (which should be maintained at a heat little short of 100°C.) is dry, tare the supplementary U-tube, attach it again for ten minutes, and weigh it. It should gain nothing, or at most half-a-mg. The drying of the joint *g* is effected within a small chamber of asbestos pasteboard, as described in Ex. 28.

The chamber stands on a thin metallic plate and is heated by a special lamp, the temperature being controlled by a thermometer.

During the above preliminaries the empty part of the combustion tube should be protected against radiant heat by means of a screen, and the time be utilized by weighing the absorption apparatus and the substance to be analysed. The latter is weighed in the tared boat, and then kept dry within a close tube made of two lipless test tubes fitting close one over the other.

Begin by attaching the absorption apparatus, taking care to wire the U-tube end of *g* this time, and *making sure of the tightness of joints generally.*

After having established, if necessary, a sufficiently low temperature in the respective parts of the tube, insert the boat with the oxalate, and at once let a slow current of air go through the apparatus. Then bring up the temperature of all the oxide of copper to redness, and next heat the empty part of the combustion tube by a single Bunsen lamp. The oxalate gets gradually heated and decomposed by radiation to some extent;

when the gas evolution becomes slack, heat the boat directly, but always cautiously, so that the gas enters the Liebig's bulbs at the rate of, at most, two bubbles per second. Finally, heat up the boat to full redness so as to insure a complete combustion.

During the combustion the current of air should be slow, but the pressure of the air, from the gas holder to a point as close to the entrance end of the combustion tube as practicable, should be *considerably higher* than what is needed to overcome the resistance of the potash. This is best attained by means of a *stopcock*, but a screw-clip on a short india-rubber connection will do. When the combustion is completed, turn on the air more fully, and keep it going until, for every one volume of empty space from *c* to the potash bulb, about three volumes of air have been utilized for sweeping out the products. Then take off the absorption apparatus, close their ends with india-rubber caps, and take them to the balance. The supplementary chloride of calcium tube is at once substituted for the working one, so as to keep the moisture out of the combustion tube, and only then the gas turned off. The tube now is ready for another analysis. Weigh the absorption apparatus, and from their gains calculate the carbonic acid and water as such in terms of 100 parts of substance. Weigh the boat containing the iron as Fe_2O_3, and, by multiplying with 0·7, find the corresponding weight of metallic iron. The three results conjointly should come up to $100 \pm 0·5$, and agree with the numbers deduced from the standardization.

Ex. 42.—Analysis of Cane Sugar or Mannite.

THE operation is the same as in the case of the preceding Exercise, with this difference that the moisture in the substance is determined separately by drying at 100°C.; or that the substance is made dry at 100°C., and analysed in this condition. It is as well also to use a somewhat longer column of oxide of copper, so as to be able to let the combustion proceed at a convenient rate; 20–25 ctms. of oxide of copper are sufficient. The percentage of carbon should agree with that demanded by the formula to ± 0·15 per cent.; the hydrogen to within ± 0·20 per cent.

Ex. 43.—Analysis of Benzoic Acid or Naphthalene.

In either case take the commercially pure substance, and purify it by resublimation.

The *modus operandi* is the same as in the preceding Exercise; only the column of oxide of copper must be 40–50 ctms. long, the combustion be conducted *very slowly*, and, at the end, the carbon concealed in the oxide of copper be burned off by means of pure oxygen. The latter, after having done its work (which is seen by the outgoing gas at the end kindling a glowing splinter of wood), is swept out by air. This is absolutely necessary, because oxygen is more soluble in caustic potash solution than air is, and the oxygen which would remain in the empty parts of the absorption tubes weighs more than its own volume of air.

Ex. 44.—The Old Method of Organic Analysis.

The student should not leave off this part of his laboratory studies without having made himself familiar with this method, because, in his practical career, it may be the only one which the apparatus at his disposal enable him to execute.

Requirements.—(1.) A combustion tube drawn out, as shown in Fig. 34. (2.) Powdered oxide of copper. (3.) Granulated oxide of copper. Each must be prepared for use by heating it to redness in a crucible, and then bottling it up while still hot in small lipless phials provided with good dry corks, or what is better, by heating it in a combustion tube like tube *a b* of Fig. 35, in a current of dry air until all the carbonic acid is proved to be away; the water then is sure to be gone.

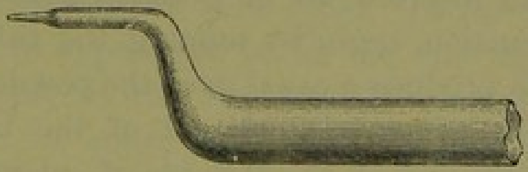


Fig. 34.

These tubes should be pretty wide, and no longer than necessary. At the end of this preliminary operation, *a* is closed with an india-rubber cap, *b* with a dry cork and a protection tube passing

FIG. 35.

through it, which is charged with soda-lime at the outside, and with calcium chloride at the inside end. (4.) A small narrow tube for the substance. (5.) A brass or copper mixing wire. (Compare p. 80).

Modus Operandi.—After having shoved a small stopper of ignited asbestos into the narrower end of the combustion tube to keep the bayonet point free of oxide of copper, put into the tube about 10 ctms. of powdered oxide of copper, then pour in about one-half of the substance to be analysed; then add another 5 ctms. of oxide of copper, and mix the oxide of copper and substance with the wire. How this is done is better shown than explained in words; it requires practice to do it well. Then put in more oxide of copper and the other half of your substance, and mix as before. Then insert an (anhydrous) asbestos stopper, and fill up the rest of the tube with granulated oxide of copper, leaving space for a terminal stopper of asbestos.

This being done, the tube is closed by means of a *dried* cork and put aside while the emptied substance tube and the absorption tubes are being weighed. A very carefully bored cork has been prepared to fit the outlet end of the combustion tube and accommodate the chloride of calcium tube, and all the time been in an air-bath at 105°C., the hole being kept from collapsing by an inserted bit of rounded glass rod. To carry out the combustion, begin by tapping the tube horizontally on a table so as to produce a canal over the powdered oxide of copper; then take the *prepared* cork out of the bath, and, after turning in the exit end of the chloride of calcium tube, insert it into the end of the combustion tube. Be sure of the absolute perfection of this joint, or the analysis will be a failure.

The potash bulbs and soda-lime U-tube are now attached, the tube is placed in the combustion furnace, and the combustion started. First heat the granulated oxide of copper, proceeding from the open end of the tube towards the other. When this plain oxide of copper is red hot, next heat the relatively pure oxide of copper at the tail, and then, gradually, the mixture, proceeding from the end nearest the opening towards the closed end. After a time the carbonic acid will cease to bubble through the potash. At this stage attach the air gasometer to the end of the bayonet point by an india-rubber tube, secure the joints, and make sure that the air is at high pressure. Now, while keeping the closed air stopcock or clip in one hand, break off the tail of the bayonet end in the india-rubber, and then admit air at the *proper rate.*

The rest requires no explanation. With solids, like sugar or mannite, very exact results should be obtained without the use of oxygen.

Ex. 45.—Analysis of Liquids.

ABSOLUTELY or relatively non-volatile liquids, such as fatty oils, high-boiling paraffins, glycerine, &c., can be treated like solids, and burned in a boat, as explained in Exs. 41–43. *Very* volatile liquids, like aldehyde, &c., demand special methods, which we do not propose to consider. Liquids of the order of alcohol, benzole, &c., are manipulated in small bulbs with long capillary necks, as represented in Fig. 36. To make such a bulb, take a tube of 7–8 mms. outer diameter, and draw it out on both sides of a selected point, so as to produce two long cylindrical appendages. One of these is fused off, and then the cylindrical converted into a spherical or ovoid bulb before the blow-pipe. To fill a bulb, heat it over a flame, so as to expel part of its air, and dip it with its open end into a supply of the liquid while cooling. More or less of the liquid will, of course, be sucked in, but a single drop within the bulb proper is sufficient to enable one to drive out all the air with the vapour of the liquid; and by re-inverting the bulb over the supply, to cause it to fill completely. But it had better be only three-fourths full. The bulb is sealed up before it goes to the balance. The combustion is conducted in a combustion tube, closed at one end, by means of granulated oxide of copper prepared for use, as shown in the last exercise. About 10 ctms. of this are introduced into the tube; the bulb is opened by cutting off about two-thirds of the tail, and both it and the cut-off part are allowed to slide down the tube and rest on the copper oxide. Should there be a stopper of liquid in the neck of the bulb, it must be driven into the bulb proper by judicious heating of the neck, the whole allowed to cool, and only then opened.

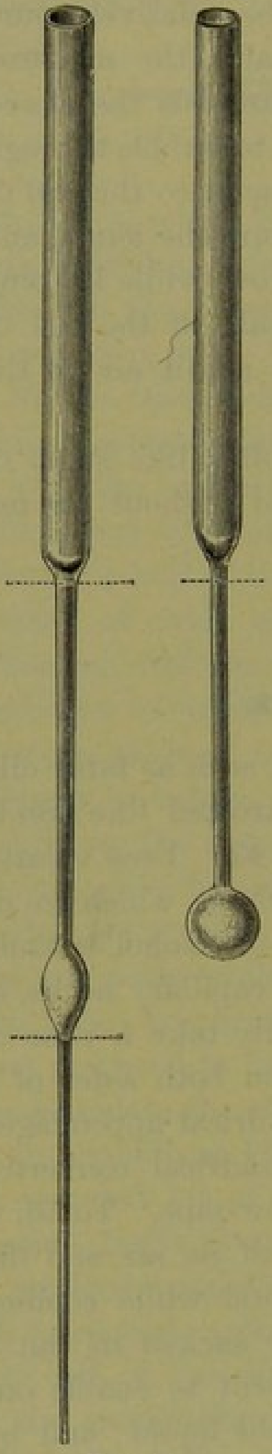


FIG. 36.

After the introduction of the bulb, the tube is filled completely with granulated oxide of copper, and, supposing the absorption apparatus to have been attached, the front part of the oxide of copper brought up to a red heat as quickly as possible. A point quite near the closed end of the tube is then heated by means of a single flame to hinder unburned vapour from getting past this point. The rest requires no explanation; any thoughtful worker will easily find out what we might say, by himself. The great difficulty, of course, is to keep a proper control over the rate of volatilization of the liquid. A couple of screens should be kept ready to be applied when and where necessary. Sometimes it is expedient to distribute the liquid in two bulbs separated by a column of oxide of copper.

Erdmann and Marchand long ago introduced a refinement upon this method, which consists in this, that the bulb is filled almost completely, so that only a part of the tail, which should be capillary, is left empty, and introduced in the sealed-up condition. After the front oxide and some of the close end have been brought up to redness, the bulb is made to burst by temporary and local application of heat. The respective part of the combustion tube should *not* lie in a gutter, but be freely suspended to admit of prompt alteration of temperature. The bulb, of course, must be almost absolutely full of liquid, so that it is burst by the steady expansion of the liquid, and not exploded by vapour-pressure. The modification certainly is an improvement, but requires considerable experimental ability for its successful application.

The combustion tube at its closed end is provided with a bayonet point, so that when all the vapour is burned, air can be driven through the tube to clear it of carbonic acid and water; or oxygen, to burn away any deposited carbon, if the liquid is richly carboniferous.

Ex. 46.—Analysis of Nitrogenous Substances.

In the combustion of a nitrogenous substance with oxygen or oxide of copper, part of the nitrogen is converted into NO, which in its turn (in oxygen) passes into N_2O_4, which latter goes, part into the water of the chloride of calcium tube, part into the potash-bulb, and makes the weight of both too high. To avoid this error, place a closely-packed spiral of copper gauze in the exit end of the combustion tube, and keep it red hot during the combustion; all the nitrogen oxides then are reduced to nitrogen. The combustion tube should be some 12 ctms. longer than usual to accommodate the copper spiral. The copper spirals are made as follows:—Heat the copper gauze in a large Bunsen flame, one part after another, so as to burn away the trace of oil which is always on it. Then cut it into strips of the breadth of 10–12 ctms., and roll up each into a closely-packed spiral, the thickness of which is such that it just goes into the combustion tube to be used. Place some half-dozen of such spirals in a combustion tube, and heat them in *pure dry* hydrogen gas until they are quite bright. Then turn off the hydrogen, and pass (air-free) carbonic acid gas over the spirals, through a T-piece inserted between the hydrogen apparatus and the tube, to expel the hydrogen. Then send a slow current of dry air over the spirals until the one nearest to the air-entrance is half-spoiled by oxidation. The rest are then sure to be free from occluded hydrogen. While keeping the half-spoiled spiral hot, allow the rest to cool in a slow current of nitrogen. After cooling, preserve the spirals in a well-corked glass tube. If a spiral has been (even thus) preserved for a long time, it must be kept in a drying chamber at 110°C. for about half an hour immediately before being used. The combustion is conducted as usual, only take care that the copper spiral is hot during the whole of the process, and if you use oxygen, see that it does not get oxidized prematurely.

Ex. 47.—Determination of Nitrogen in Organic Substances by Dumas' Method.

Method.—The substance is burned with oxide of copper in an *atmosphere of pure carbonic acid,* the nitrogen oxides are destroyed by red hot copper, and the out-going gas—carbonic acid, steam, and nitrogen—is collected over strong caustic potash solution, and measured. From the volume (V cc.), the pressure (P mms.), and the temperature (t°C.) of the gas, its weight in milligrammes is calculated.

$$W = \left(\frac{V\ P}{272{\cdot}6 + t}\right) \times 0{\cdot}45090.$$

If 50 per cent. caustic potash ley was used to collect the gas, the tension of the vapour of water can be neglected; hence, if the gas inside is brought to the atmosphere's pressure, the height of the barometer, *reduced to* 0°C., can be substituted for P. If the barometer at $t°$ stands at B_t, the equivalent height of mercury of 0° is B_o, and

$$B_o = \frac{B_t}{1 + 0{\cdot}00018\,t} = B_t\,(1 - 0{\cdot}00018\,t). \quad \text{(Practically.)}$$

Requirements.—(1.) A combustion tube, 80 ctms. long, with a bayonet point, as shown in Fig. 34. (2.) Copper spirals as above. (3.) Mixing wire. (4.) A carbonic acid apparatus, according to Kipp. To obtain *pure* gas, boil the pieces of marble in water immediately before use, and apply the air-pump after sufficient cooling so that the hidden air is sucked out through the water; on the other hand, boil a supply of hydrochloric acid (it should contain 5–7 per cent. of HCl), and allow to cool in a stoppered flask. Wash the gas with water, and then filter it through cotton wool. Keep the gas going for a considerable time before using it, so as to be sure of its containing no air. (5.) A Schiff apparatus for collecting the gas, attached to the end of the combustion tube, as shown in Fig. 37. (6.) 50 per cent. caustic potash ley (not soda) to charge the Schiff.

Modus operandi.—Charge the tube with oxide of copper and substance, as explained in Ex. 44 for the old-fashioned method of organic analysis, but put a spiral of copper into the outlet end of the tube. To the end of the bayonet point attach the exit tube of the carbonic acid apparatus; the other end communicates by a cork and quill tube inserted with the mercury joint *m* of the Schiff. An important point to attend to is that the entrance of the carbonic acid into the tube is checked by a glass stopcock or screw-clip at a point as close to the entrance end as possible. The gas-pressure up to this clip or stopcock should be considerably higher than that prevailing in the tube. Begin by sending carbonic acid through until all the air is expelled, *i.e.*, until a considerable quantity of gas evolved is completely absorbed by caustic potash. This point being reached, shut off the carbonic acid almost but not quite completely, and next heat the copper spiral to redness; then heat the plain oxide of copper in front, then the plain oxide of copper in the tail end, and, lastly, the mixture, beginning at the outward end, and progressing towards the inward one. When the evolution of gases ceases, pass a

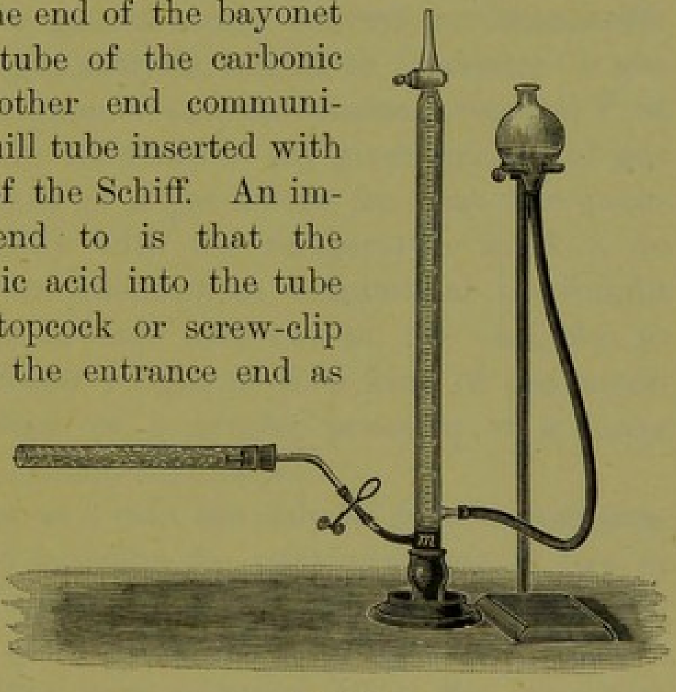


Fig. 37.

stronger current of carbonic acid through the tube until all the nitrogen can be assumed to be in the measurer. Now detach the latter from the combustion tube, shake the gas with the alkali to ensure complete absorption of the carbonic acid, and keep the apparatus in a place of *constant temperature* for about one hour, with the levels approximately adjusted. Lastly, establish exactly one atmosphere's pressure inside the nitrogen tube; take t, P, and V, and calculate.

To learn the method, begin with pure sugar, until you manage to obtain no more than, say, 0·5 cc. of nitrogen *at most* from 0·5 grm. of this substance; then pass to hippuric acid, or some other suitable example.

GAS ANALYSIS.

GENERALITIES AND THEORY.

GAS ANALYSIS, in the customary acceptance of the term, comprises only the *gas volumetric* methods for the analysis of gaseous bodies.

The mere volume of a gas, of course, conveys no information regarding its mass. In gas analysis, indeed, to " measure " a gas means to determine its volume V and its tension (pressure) P at a fixed temperature t. In reference to any given species of gas —oxygen, air, the contents of a gas-holder, &c.—the two quantities, V and P conjointly with the temperature mark t, do define the mass of a given quantum as definitely as the weight does, because, assuming in each case two of the variables to have fixed values, a greater weight of that kind of gas would demand a greater volume or a greater pressure, or a lower temperature.

Gas analysis, however, as a rule, has only to do with comparative measurements; and to define the relative masses of two or more gas quanta—I., of this kind; II., of a second kind; III., of a third, &c., it suffices to state the volumes V_1, V_2, V_3 . . which they would occupy if they were measured all at the same temperature t_0, and the same pressure P_0. This at once suggests two important questions:—1. Supposing the several bodies of gas were mixed together, would the volume V of the mixture (at t_0 and P_0) be equal to the sum $V_1 + V_2 + V_3$ . . ? 2. What is the relation between the ratios $V_1 : V_2 : V_3$ . . on the one hand, and the values P_0 and t_0 on the other?

In answering these questions, we may and will confine ourselves to the relatively limited area of combinations of temperature and pressure which occur in practical gasometry. This comes to the same as saying that pressures above, say, two atmospheres—for the vast majority of purposes the line might be drawn at one atmosphere—and temperatures below 0°C. are for us out of court. Let it also be understood that whenever we refer to a combination of t and P in a gas, this combination is tacitly assumed to be such as to keep the gas on the safe side of condensation into liquid.

On the basis of these restrictions, we will now proceed, in the first instance, to answer the second question in reference to the so-called *permanent gases, i.e.*, to the gases H_2, O_2, N_2, CO, and any mixture of two or more of them.

In a body of permanent gas, whose temperature is kept constant at t_0, the volume or the pressure may assume any value; but whenever the volume assumes a certain value V, a certain definite value P, for the pressure follows, and *vice versa*, and we always have

$$VP = \text{const.} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \text{(Boyle's Law.)}$$

The constant obviously has two denominations, inasmuch as it represents numerically both the volume at unit pressure and the pressure at unit volume (assuming for calculating purposes the law were of unrestricted applicability). It depends on the magnitude of the units chosen whether the denomination is *physically* correct; but in any case the V P for, say, a given quantum of air (there is unfortunately no name for the compound quantity), together with the given temperature t_0, defines its mass.

The relation, at a given pressure P_0, between temperature and volume is not so easily explained. We could not reasonably expect a simple relation between the *quantity* V, and the mere numerical *index* t, as read from the mercury thermometer. For our purpose, however, it is sufficient to know that, as a matter of exact experimental research the relation between t and V is the same in all permanent gases, in this sense that supposing V_1 and V_2 to be the volumes at t_1 and t_2 degrees respectively, the ratio $V_1 : V_2$ depends *only* on t_1 and t_2, and not on the *nature* of the gas. Hence, supposing we agree upon measuring temperatures by the volumes at these of a given quantum of any permanent gas (kept at a constant pressure), and call these temperature values T, we have generally $T_1 : T_2 = V_1 : V_2$ (Gay-Lussac's Law).

To find a convenient unit for these T's, let us remember that according to the concordant experiments of Rudberg, Magnus, and Regnault, all permanent gases when heated from 0°C. to 100°C. (we will call the gas thermometer readings T_0 and T_{100} respectively) expand in the ratio of very nearly 273 : 373. Hence, taking $T_0 = 273$, we have $T_{100} = 373$, or, for the two cardinal points, $T = 273 + t$, where t stands for the reading of the centigrade mercury thermometer. By a happy accident the relation holds practically for all temperatures that we need care for. (It is good practice for the student to develop the corresponding formula for the Fahrenheit scale.) The values T are called "absolute temperatures," because we have theoretical reasons for assuming that they really *measure* the respective temperatures in the sense of mathematics. By combining the two laws we have

$$\frac{VP}{T} = Q \qquad (1)$$

where Q stands for a constant number whose value depends only on the units chosen, and which obviously bears three denominations arithmetically, being the value which V, or P, or $1/T$ assumes, if in each case the other two variables are at unit value.

Let us see now how far eq. (1) applies to *non*-permanent gases. Their general behaviour may be stated thus:—As long as we keep clear of condensation into liquid the formula applies to *all* gases *approximately*, and the deviations are always in the *same sense*, namely, the same as if the respective gases, while consisting substantially of matter obeying equation (1), were contaminated with a small quantity (more or less) of a mist of the respective liquid. If we reduce the pressure from, say, P to $\frac{1}{2}$ P, or increase the temperature from T to 2 T, the volume increases to a *little more* than twice its original value, because some of the "mist" gets converted into gas.

Within the moderate range of pressures which practical gasometry discounts, the mist does not go far towards invalidating Boyle's law. It tells more strongly on Gay-Lussac's; but in reference to it, its influence can in all practical cases be reduced to practically nothing by giving the temperature a sufficiently high value. For an example, imagine a litre of saturated steam of 100°C. ($T = 373$) as it rises from water boiling under 760 mms. pressure. If heated (at 760 mms.) from 100° to say 150°, it expands into more than $\frac{373 + 50}{373}$ litres; the volume at 150° is, say, $= \frac{423}{373} + \triangle_0$ litres. And if we take away the surplus volume $\triangle_0$, and now pass from 150° to 200°, the volume increases to not $\frac{473}{423}$, but $\frac{473}{423} + \triangle_1$ litres; but $\triangle_1$ is considerably less than $\triangle_0$, and so on. From a certain high temperature onwards, the $\triangle$ becomes practically equal to *nil*; the steam in its expansion keeps pace with, for instance, its equal volume of hydrogen; and from that limit temperature upwards it follows also Boyle's law, from at least the respective pressure downwards. The student will understand now what we mean by saying that, for any gas, there is an *area of combinations* of T and P, characterized by a certain T_0 as minimum temperature, and a certain P_0 as maximum pressure, and extending on the one hand to $P = nil$, and on the other to $T = \infty$, or rather the highest value which the gas stands without suffering dissociation, within which the gas, in a practical sense at least, obeys eq. (1) in all strictness, or to use customary phraseology, is *perfectly gaseous.*

Obviously, to define a gas *quantum* numerically without reference to temperature or pressure, the right way is to bring it within its *area of perfect gaseousness,* to determine a set of simultaneous values for V, P, and T, and calculate the "Q" from these by equation (1).

But how can we ascertain the boundary lines of that area in a given case? *Practical* gasometry gives a very simple answer. If the gas is a *gas* at 0° and 760 mms., simply measure it at some convenient temperature and pressure (taking care to keep the latter down as far as expedient if you have to deal with such things as carbonic acid or sulphurous acid), and calculate the Q from the V, P, and T thus obtained from eq. (1). The same rule is applied even if the gas is contaminated with such small quantities of steam or benzole vapour, &c., as it might lick up at ordinary temperatures. Of course, in this case care must be taken to steer clear of condensation into liquid, provided the vapour belongs to the "gas to be measured." (The meaning of this clause will be made clear presently).

By proceeding in this somewhat off-hand manner, we, in general, incur the risk of quite an appreciable error; yet this error, in the generality of cases, is less, or at least not of a higher order, than that involved in the measurement of V, P, and T, by means of the ordinary laboratory instruments.

According to *Amagat*, carbonic acid from 0° upwards expands at a greater rate than air, up to about 200°, whence onwards it behaves like a perfect gas in reference to expansion caused by changes of temperature or pressure. At 760 mms., its expansion, from 0° to 200°C., is in the ratio of 1 : 1·74065. Hence, supposing we find for a quantity of carbonic acid the volume, at $T = 273°$ and $P = 760$ mms., equal to V_0, we have for the constant Q :—

(1.) By the ordinary routine mode of calculating,

$$Q' = \frac{V_0 \times 760}{273}$$

(2.) For the true Q,

$$Q = \frac{V_0 \times 1{\cdot}74065 \times 760}{473}$$

Whence $Q = 1{\cdot}0046\ Q'$.

Carbonic acid is probably the most imperfect of ordinarily occurring gases, and 0° and 760 mms. constitute about the lowest temperature and highest pressure customarily employed; hence, 0·0046 might be put down as the maximum relative error introduced by neglecting the imperfection of gases in our calculations —were it customary to measure gases in the state of *dryness;* but such is not the case.

A gas as it comes to be measured in the course of an analysis is, as a rule, *contaminated* with vapour of water, and it is the quantity of *dry* gas that is wanted. To obtain it, one way (and in the case of gases which like SO_2 or NH_3 are largely absorbed by water, the *only* way) is to remove the water by means of a suitable dehydrating agent, and measure the thus *dried* gas. But this is troublesome. With ordinary gases we always prefer another method, which is to, if necessary, add a drop of water, spread it out on the sides of the measuring tube so that the gas is *saturated* with water at the prevailing temperature, to measure the V, T, and P, and to correct the observed P by deducting the maximum tension of steam π for the respective temperature. The difference, $P-\pi$, is the tension which the gas would exhibit at that temperature T, if kept *at the observed volume* V; very *nearly, not exactly*, and the error involved in the assumption often raises the error in the calculated Q beyond 0·0046 of its value.

A special case presents itself if the *water* produced in the combustion of a gas (say, of a hydrocarbon), with oxygen over mercury, has to be measured gasometrically. We then surround the measuring tube by a glass jacket, and blow steam through the jacket, so as to raise the temperature of the gas to some value near 100°C. (which must be determined directly and exactly). If at this temperature the partial pressure of the steam is at *less* than, say, one-half of 760 mms. of mercury (the less it is the better), the hot gas, as a whole (steam *plus* excess of oxygen *plus* carbonic acid, &c.), may be assumed to be perfectly gaseous, the more readily as in such cases only a moderate degree of precision in the measurement of the pressure can be reached.

A *physical significance* for Q is easily found. A glance at eq. (1) shows $V=\frac{Q\,T}{P}$, *i.e.*, the volume of a gaseous body is proportional to the ratio $\frac{T}{P}$, the *disgregation* of the gas, as it has been called. Hence, Q may be defined as that value which V assumes whenever $\frac{T}{P}=1$, or $T=P$ numerically.

Supposing, for instance, we measure P in mms. of mercury, and T in centigrade degrees (let us at once adopt these units; they are as good as any others), $V=Q$ if

for $t =$ 0° ...... 100° ...... 200°C.
or $T =$ 273 ...... 373 ...... 473° absolute temp. &c.
$P =$ 273 ...... 373 ...... 473 mms.

But P and V in the equation are interchangeable, *i.e.*, $P=\frac{Q\,T}{V}$

Hence we may define Q as that *pressure* which the gas assumes whenever $T = V$,

if (for instance) $T = 273 \ldots 373 \ldots 473^\circ$ absolute temp. &c.,
and $V = 273 \ldots 373 \ldots 473$ units of volume.

A third definition will at once suggest itself; but we leave it on one side, because it is strained and unnatural. We prefer to explain that Q has a most important *chemical* significance.

If we define the specific gravity S of a gas as being the number which tells us what number of times the gas is heavier than its own volume of some standard gas (say H_2) of the *same disgregation*, the specific gravity, by eq. (1), is independent of the value of the disgregation chosen, and *à fortiori* of the special P and T which happen to constitute the disgregation. It consequently can depend only on the chemical constitution of the gas. It is the immortal merit of Avogadro to have divined what the dependence is. As found by him, and since confirmed by thousands of experiments, S is proportional to the molecular weight M. We always have

$$M_1 : M_2 : M_3 \ . \ \ . \ \ . = S_1 : S_2 : S_3 \ . \ \ . \ \ .$$

or generally, for given units,

$$M = \text{const. } S \quad . \ \ . \ \ . \quad (2).$$

If the Q's of a series of gaseous bodies

$$\begin{array}{ccccc} \text{I.} & & \text{II.} & & \text{III.} \\ \text{are } Q_1 & \ldots\ldots & Q_2 & \ldots\ldots & Q_3, \end{array}$$

then obviously the weights are

$$(\text{const. into})\ Q_1M_1 \quad \ldots\ldots \quad Q_2M_2 \quad \ldots\ldots \quad Q_3M_3,$$

i.e., the Q's, in a relative sense, count the molecules present in the several gases I., II., III., *&c.*

In what we have said so far in connection with Avogadro's law, we have been assuming that the several gases are chemical species, such as O_2, CO, CO_2, H_2O, &c.

But it is difficult to think that the law should *not* hold for perfect gas *mixtures* as well. So we should say, were it not proved by experience, that in the absence of chemical action, and at constant pressure and temperature, permanent gases exactly, and other gases very nearly, mix without *contraction* or *expansion*.*

The general relation between gas volume and gas weight, which is embodied in Avogadro's law on the one hand, and Regnault's determinations of absolute gas densities on the other, enables us to find a formula for the reduction of the volume of a gas in litres (or cc.'s) to its weight in grammes (or milligrammes), and *vice versa*. Of the several gas densities determined by Regnault, that for oxygen is probably the most exact. He finds that 1 litre of oxygen measured at 0°C., and a pressure equal to that exerted by a column of 760 mms. of mercury of 0°C. at sea-level and the latitude of 45°, weighs 1·429 32 grammes. As this number simply denotes the specific gravity of oxygen at 0°C., &c., referred to water of + 4° as equal to 1000, "gramme" may be taken as meaning *any unit of mass*, and litre as "the volume at 4°C. of 1000 units of mass of water." From these data we easily calculate that generally

$$\text{1 litre of gas weighs D grms.} = \left\{0{\cdot}032089\,\frac{\mathrm{P}}{273+t}\right\}\frac{\mathrm{M}}{2}, \quad \ldots \text{(eq. 3)}$$

where M stands for the molecular weight, as it is if O = 16.

For the volume of M grms. (32 grms. of oxygen, 18 grms. of steam, &c.), we have

$$\text{M grms. occupy } 62{\cdot}326 \times \frac{273+t}{\mathrm{P}} \text{ litres,} \quad \ldots \text{(eq. 4).}$$

In Glasgow the constants of eqs. 3 and 4 assume the values—

0·032 120..............................; log. = $\bar{2}$·506 776
62·267 ....; log. = 1·794 258

To be able to utilize these formulæ more directly, we must provide our gas-measuring tubes, manometers, and barometers with *true* millimetre scales, and never forget to reduce the height of a column of mercury measured manometrically to 0°C. This reduction is easy. Imagine a column of mercury h mms. high at t° C. to be contained in a cylindrical tube *inexpansible* by heat, By cooling down to 0° in this tube, it shrinks into $h_0 = \dfrac{h}{1 + kt}$

---

* It is worth while to point out that this proposition has never been *tested* experimentally in the sense in which Boyle's law has been by Regnault.

or practically $h\ (1 - k\,t)$ mms. (where k is the cubic co-efficient of expansion of mercury), but continues to exert the same pressure as before. h_0, therefore, must be substituted for the observed h. For computing without, or with four-place, logarithms, write the equation—

$$h_0 = h - h\,k\,t,$$

and compute the second term to deduct it from h. If a six-place logarithm table is at hand, it is more expeditive to work the original equation with $1 + k\,t$ in the denominator. $k = 0{\cdot}000\ 181\ 43$. [A table of the values of log. $(1 + k\ t)$ for $t = 0, 1, 2, \ . \ . \ 30°$C. is given in the Author's "Tables to Facilitate, &c.," 2nd ed., p. 26. The same book, on p. 39, gives a table (Rosetti's) for the reduction of water-weights (in grms.) to volumes (in cc.)]. In practical gas analysis we generally find it expedient to let each gas-measurer have its own unit of volume, which is most conveniently registered by stating the number of grammes of mercury of a stated temperature which corresponds to it.

One gramme of mercury (uncorrected weight; brass standards) occupies at $t°$ the volume of $13{\cdot}596^{-1} \times (1 + k\ t)$ cc.; $1 : 13{\cdot}596 = 0{\cdot}073\ 5510$; log. $= \bar{2}{\cdot}866\ 589$. [A table giving the volumes at 0°, 5°, and 30° ready calculated is found on p. 40 of the book referred to].

In practical gas analysis we rarely have occasion to reduce gas-volumes to weights. As a rule, all we care for are the relative quantities of a given series of gaseous bodies, and we may, of course, choose our own units. The natural unit for the pressures then becomes the pressure of a column of mercury 1 mm. high at the mean temperature that prevails during the series of measurements under consideration. That the temperature may have been, say, 15°C. in one case, and 16°, 17°, or 14° in another, is of no consequence practically. In the rare case when one of the measurements was made at an exceptionally high temperature, say, at 100°C., and all the rest at the temperature of the gas room, say at 15°C., the measurements involved in the one experiment at 100°C. must be corrected for the expansion of the glass and of the mercury from 15° to 100°. The linear expansion of glass is 8·3 units per million units per 1°C. Hence, if a eudiometer scale is correct at, for instance, 15°C., the real length of

1000 millimetre-divisions at 100° is greater than 1000 mms. by $(100 - 15) \times 0{\cdot}0083 = 0{\cdot}71$ mm. If a gas-measurer down to a certain mark holds V units at $t°$, its capacity at a higher temperature t' is V′.

$$V' = V \left\{1 + \delta\,(t' - t)\right\} \text{ where } \delta = 0{\cdot}000\,025.$$

The reduction of the mercury column for temperature has already been explained.

For the purposes of comparative measurement, we need only a set of *relatively* correct values for the "Q's" of the several gas-quanta concerned. Hence, of the three quantities, V, P, and T, in each set of cases, only one needs actually be *measured*. We may, for instance—

(1.) Keep T and P at constant (though unknown) values, T_0 and P_0, and measure only the values V_1, V_2, V_3, &c.; *i.e.*, for the Q's, substitute their values

$$\frac{P_0}{T_0}\left\{V_1,\ V_2,\ V_3,\ldots\ldots\ldots\ldots\ldots\ldots\right\},$$

and strike off the constant factor $\frac{P_0}{T_0}$. (The old method of gas measurement.)

(2.) Keep T and V at constant (though unknown) values, T_0 and V_0, and measure the P's; *i.e.*, substitute for the Q's their values

$$\frac{V_0}{T_0}\left\{P_1,\ P_2,\ P_3,\ldots\ldots\ldots\ldots\ldots\ldots\&c.\right\},$$

and delete the constant factor $\frac{V_0}{T_0}$. (Regnault's method.)

(3.) We may allow P and T to vary, but take care to keep the disgregation $D = T : P$ at a constant value D_0, and measure the volumes; *i.e.*, substitute for the Q's, their values

$$\frac{1}{D_0}\left\{V_1,\ V_2,\ V_3,\ldots\ldots\ldots\ldots\ldots\ldots\right\},$$

and delete the constant factor $\frac{1}{D_0}$. (Doyère's method.)

In reference to a set of gas quanta I., II., III., &c., take q_1, q_2, q_3, as representing the volumes at say $T = 400°$, and $P = 400$ mms. (or to use general terms, for any combination of a temperature and a pressure which are numerically equal to each other); take Q as having a similar meaning in reference to the substance produced by mixing I., II., III., &c., together, and we have by direct experience

$$q_1 + q_2 + q_3 + \dots\dots\dots = Q\dots\dots\dots(5),$$

whence we might deduce, were it necessary, that at *any* temperature and pressure, supposing both to be at the same values all round, the volume V of the mixture equals the sum of the volumes of the components

$$v_1 + v_2 + v_3 \dots\dots\dots = V\dots\dots\dots(6).$$

But our q's and Q bear the denomination of pressure at $V = T$ (for arithmetical purposes, say $V = 1$ and $T = 1$), hence we have for the pressures which I., II., and their mixture respectively, would exert at some temperature, T_0, if they were successively shut up in a vessel of the invariable volume V_0,

$$p_1 = \frac{q_1 T_0}{V_0} \qquad p_2 = \frac{q_2 T_0}{V_0} \qquad p_3 = \frac{q_3 T_0}{V_0}.$$

For the mixture $P = \frac{QT_0}{V_0}$, and obviously

$$\text{as } q_1 + q_2 + q_3 \dots\dots\dots\dots = Q,$$
$$p_1 + p_2 + p_3 \dots\dots\dots\dots = P\dots\dots\dots\dots(7),$$

i.e., the pressure of the mixture is equal to the sum of the partial pressures of the components.

Now, supposing all our equations from (5) to (7) correspond to the *same set* of gases, we have, for instance, for component I. and the mixture

$$(1) \qquad v_1 = \frac{q_1 T_0}{P_0} \qquad V = \frac{Q T_0}{P_0}$$

and $v_1 : V = q_1 : Q$; and

$$(2) \qquad p_1 = \frac{q_1 T'_0}{V_0}, \text{ and } P = Q\,\frac{T'_0}{V_0}{}^{*}$$

whence $p_1 : P = q_1 : Q$, or quite generally for any component

$$\frac{v}{V} = \frac{p}{P}\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(8).$$

---

[*] We add the dashes in the second case to show that the T'_0 is not necessarily the same as T_0 in case (1).

Hence, we see that the customary mode of stating the volumetric composition of, let us say, atmospheric air is susceptible of three readings; instead of saying (*a*) 100 volumes of air contain 21 volumes of oxygen and 79 of nitrogen, we may say (*b*) 21 per cent. of the pressure is oxygen pressure, and 79 is nitrogen pressure; and (*c*) 100 molecules of air contain 21 molecules O_2, and 79 molecules N_2. The statement (*b*) of the first two is obviously the more straightforward in all those cases, when one of the components at the ordinary temperature is a gas only through its association with gases properly so-called.

The student may apply what we say to the case of air saturated with vapour of water at a given temperature, and he will see what we are driving at.

From gasometry we now pass to gas analysis.

Proximate Analysis of Gas Mixtures.

For the solution of this problem we have only one direct method. Its nature is best explained by an example:—To analyse a mixture of O_2, N_2, and CO_2, we begin by measuring off a sample of the given gas (let the volume be V_0 at T_0 and P_0 of dry pressure). We then remove the carbonic acid by caustic potash, and measure the residue; *i.e.*, determine its volume V_1 at T_1 and P_1. This being done, we apply pyrogallate of potash solution (to absorb the O_2) and determine the set of values V_2, T_2, P_2, for the nitrogen. Obviously we have for the several Q's (reduced gas volumes)—

$$\text{Original gas,}\ldots\ldots\ldots\ldots\ldots\ldots = \frac{V_0P_0}{T_0} = Q_0$$

$$\text{The } N_2 \text{ and } O_2,\ldots\ldots\ldots\ldots\ldots\ldots = \frac{V_1P_1}{T_1} = Q_1$$

$$\text{The } N_2,\ldots\ldots\ldots\ldots\ldots\ldots = \frac{V_2P_2}{T_2} = Q_2$$

Hence for the percentage of

$$\text{The } CO_2,\ldots\ldots\ldots\ldots\ldots\ldots x = \frac{Q_0 - Q_1}{Q_0} \times 100,$$

$$\text{The } O_2,\ \ldots\ldots\ldots\ldots\ldots\ldots y = \frac{Q_1 - Q_2}{Q_0} \times 100,$$

$$\text{The } N_2,\ldots\ldots\ldots\ldots 100 - (x + y).$$

To show what the method can do, we will enumerate the most important of the customary reagents, and for each name the gases for which it is available as an absorbent.

1. *Water as such, or as* $Na_2SO_4.10H_2O$, absorbs HCl, HI, HBr very promptly.

2. *Dilute Sulphuric Acid* (besides acting as water) absorbs NH_3, CH_3NH_2, &c., very promptly.

3. *Caustic Potash Ley*, or strongly hydrated solid potash (a soft potash ball) absorbs all acid gases readily: CO_2, SO_2, H_2S, HCl, HBr, HI.

4. *Anhydrous* KHO acts on CO_2 only slowly. The Author has no experience about its *exact* action on other acid gases. It is used chiefly for the absorption of vapour of water, especially in the suspected presence of small remnants of acid gases. No doubt it absorbs alcohol as C_2H_5KO.

5. *Fused Chloride of Calcium* may be named here as a characteristic absorbent for water. It absorbs also alcohol.

6. *Oil of Vitriol* ($H_2SO_4 + 1/12\ H_2O$, Marignac's acid, a slight excess of water does not matter) absorbs water, alcohol, oxide of methyl, ether, propylene C_3H_6, and its higher homologues. Ethylene is absorbed only on long-continued shaking (Berthelot). Hydrogen and marsh gas are *not* absorbed.

7. *Fuming Oil of Vitriol* (SO_3 dissolved in H_2SO_4) does not absorb H_2 or CH_4, but absorbs all *olefines* C_nH_{2n} very readily. The residual gas always contains vapours of SO_3 and SO_2, which must be removed by potash before measuring.

8. *Bromine* (Br_2), in the presence of water and diffuse daylight, acts pretty much like fuming vitriol. It cannot be used over mercury, because it combines with the metal readily. The gas to be analysed is transferred to a glass-stoppered bottle over water. A sealed up bulb full of bromine is introduced, broken by shaking, and allowed to act. The liquid part of the residual bromine is then allowed to drop out into the trough, and the remaining bromine vapour absorbed by potash.

9. *Pyrogallate of Potash* (pyrogallic acid dissolved in caustic potash ley *extemp.*) absorbs oxygen largely and readily (Liebig), besides, of course, acting as KHO solution.

10. *Cuprous Chloride* dissolved in hydrochloric acid absorbs

readily; O_2, CO, C_2H_2, C_3H_4 (Berthelot); spoils the mercury badly.

11. *Cuprous Chloride* dissolved in ammonia acts like the acid form of the reagent, but absorbs besides certain hydrocarbons, including (all the ?) olefines (Berthelot); does not spoil the mercury.

12. *Chromous Sulphate* (CrO salt) solution, mixed with salammoniac and excess of ammonia, absorbs O_2, NO, C_2H_2, C_3H_4; it does *not* act on CO, C_2H_4, C_3H_6 (Berthelot).

13. *Binoxide of Manganese* (used as a compressed ball) absorbs H_2S and SO_2 (Bunsen). (Permanganate or bichromate of potash solution, mixed with sulphuric acid, no doubt acts similarly).

14. *Ferrous Sulphate*, as concentrated aqueous solution, absorbs nitric oxide largely, but the compound has a measurable tension. We may mention in passing that NO can be absorbed also, as KNO_2 and KNO_3, by the joint action of oxygen and caustic potash ley.

There is no need of our drawing up a scheme for the systematic application of these absorbents, nor is it necessary to point out that all one can attain with them is not co-extensive with the problem. There are plenty of gas mixtures which, in opposition to any chemical absorbent, behave as if they were unitary compounds. For the analysis of such gases only two methods are known; we must either effect an ultimate analysis by the "method of combustion" (*vide infra*), if possible, and from the elementary try to guess out the proximate composition, or see what we can do by means of physical absorbents. But in the case of these we must do what Bunsen has taught us, namely, apply the solvents, and interpret their effect, in the light of the laws of gas absorption.

The Law of Gas Absorption and its Applications.

Imagine v volumes of a mixture of the gas species I., II., III., to be shut up in a close vessel over h volumes of water (or alcohol or other liquid absorbent), an impervious diaphragm separating the two. As soon as the diaphragm is removed, the gas and liquid exchange molecules, and this goes on for ever; but if a constant temperature t be maintained, a point is reached sooner or later, when on both sides the changes of composition, caused by emission and reception, exactly compensate each other, so that it is the same as if the exchange had come to a stop. This point of dynamic equilibrium is reached almost instantaneously on violent shaking. The final result is that the gas space v is saturated with the vapour of the liquid, while of each of the components of the gas a quantity q is held in solution by the h volumes of liquid. This quantity q, *at a given temperature*, is in (more or less exact) accordance with the equation—

$$q = h\beta\pi \text{ .... I.}$$

where π means the partial tension of the respective component in the residue, and β is a constant, which may be defined as being the value which q assumes when $h = 1$ and $\pi = 1$ mm. The quantities q and β are, of course, of the same denomination; if q means milligrammes, β means milligrammes likewise. But we will assume q to be measured by volume at 0°C. (or $T = 273$°C.) and $P = 1$ mm., and on the basis of this assumption (with Bunsen) call β the "co-efficient of absorption."

FIG. 38.

Our equation I. has been tested experimentally only with water and, in a more limited sense, with alcohol, as a solvent; and, in reference to either, may be assumed to hold, at pressures up to about 1 atm., and temperatures from 0° to about 30°C., for all gases which, under the circumstances, do not act chemically on, or dissolve very abundantly in, the respective liquid. With a given gas species, the constant β, in general, increases when the temperature falls, or when alcohol is substituted for water. It has, in general, different values for different species of gas. Hence we at once see our way towards distinguishing a unitary gas from the isomeric mixture. Take, for instance, the case of marsh gas CH_4 as against a mixture of equal volumes of H_2 and $C_2H_6 = CH_4$ per 1 volume. With alcohol as an absorbent, the β of C_2H_6 is far greater than that for H_2. Hence, if the mixture be dissolved partially by alcohol, the residue will contain less carbon per unit volume than $\frac{1}{2}$ C_2; and similarly in similar cases.

Before going further, let us draw an obvious but important conclusion from our equation. Given a gas-mixture containing

m' volumes of species I., m'' volumes of species II., …… in unit volume; and supposing h volumes of (say) water to be shaken at a constant temperature and constant total dry pressure p, with successive (but always fresh) instalments of the mixture until absorptiometric equilibrium is established (or, mathematically speaking, supposing h volumes of water to be shaken with ∞ volumes of the mixed gas), then we have for the dissolved quantities of the several components—

$q'=hpm'\beta'$; $q''=hpm''\beta''$, &c., &c.; and for the total quantity of absorbed gas $Q=hp(m'\beta'+m''\beta''+\ldots\ldots\ldots\ldots, \&c.)$.

It is not quite so easy to calculate the composition and quantity of the gas absorbed if the h volumes of (let us say) water are shaken in a vessel of the constant capacity $(h+v)$ with v volumes of the given mixture. One thing, however, is clear beforehand: unit volume of the absorbed part of the gas will, in general, contain not m', m'', &c., volume of the components, but other quantities n', n'', &c. If r', r'', r''', &c., stand for the undissolved residues of the several components, P for the original (dry) pressure of the mixture, and p for the less (dry) pressure of the unabsorbed total residue, we have, since quite generally, $pn=\pi$ for any of the components,

$$q=h\beta(pn);$$

$$r=(np)v\frac{273}{273+t},$$

which we abbreviate into $r=(np)v_0$;

hence $$q+r=pn(v_0+\beta h);$$

but $q+r$ may be expressed in function of P and m, thus:

$$q+r=Pmv_0;$$

hence $$Pmv_0=pn(v_0+\beta h),$$

or $$\frac{n}{m}=\frac{P}{p}\cdot\frac{v_0}{v_0+\beta h}\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\text{II.}$$

or $$n=m\frac{P}{p}\cdot\frac{1}{1+\dfrac{\beta h}{v_0}}\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\text{II}a.$$

which enables one to calculate n', n'', n''', from m', m'', m''', &c.

By summing up the *special* equations represented in IIa., we have

$$n'+n''+n'''\ldots\ldots=1=\frac{P}{p}\left(\frac{m'}{1+\frac{\beta' h}{v_0}}+\frac{m''}{1+\frac{\beta'' h}{v_0}},\ \&c.\right)$$

Whence
$$\frac{P}{p}=1\div\Sigma\frac{m}{1+\frac{\beta h}{v_0}}\ldots\ldots\ldots\ldots\ldots\ldots\text{III.}$$

and by substituting this for the $\frac{P}{p}$ in eq. IIa., we have

$$n=\frac{m}{1+\frac{\beta h}{v_0}}\times\left(\Sigma\frac{m}{1+\frac{\beta h}{v_0}}\right)^{-1}\ldots\ldots\ldots\ldots\ldots\ldots\text{IV.}$$

The total quantity of dissolved gas is $Q=Pv_0-pv_0$, whence—

$$Q=v_0P\left(1-\Sigma\frac{m}{1+\frac{\beta h}{v_0}}\right)\ldots\ldots\ldots\ldots\ldots\ldots\ldots\text{V.}$$

$Q\div hp$ is what, in the case of a single gas, would be the coefficient of absorption. In the case of a mixture the quotient (which we will call the "solubility" of the gas mixture, and designate by "λ") is variable, namely—

$$\lambda=\frac{Q}{hp}=\frac{1-\Sigma\frac{m}{1+\frac{\beta h}{v_0}}}{\frac{h}{v_0}\Sigma\frac{m}{1+\frac{\beta h}{v_0}}}\ldots\ldots\ldots\ldots\ldots\ldots\ldots\text{V}a.$$

Eq. Va. affords a method for distinguishing a unitary gas from a mixture. We just determine the "solubility" λ by measuring off, at $t°$, V volumes at, say, P_0 mms. dry pressure. We then shake the gas with h volumes of, say water, and determine the residual volume v and its dry pressure p. Then we have for the pressure P which the original gas would exhibit in v volumes, the equation—

$$VP_0=vP,\text{ whence}$$
$$P=\frac{V}{v}P_0,$$

and for the solubility the equation—

$$\lambda = \frac{v_0(P-p)}{hp}.$$

We repeat the experiment at a series of values for $h:v_0$ or $h:v$, *i.e.*, with varying quantities of water at the same v.

If the gas is unitary we always find $\lambda = \beta =$ a constant number. If it is a mixture, λ will vary when $h:v$ varies. In *general* not necessarily. But in practice, it is not easy to distinguish between real and only approximate constancy in λ. Hence, supposing λ to come out practically constant, it is as well to change the solvent—say use alcohol instead of water—and see what now comes out. If the new solvent also leads to a constant λ, the unitary nature of the gas is almost proved.

Eq. [III.] shows the way to determine the composition of a mixture of two unitary gases, I. and II., if their β's are known. We shake a known quantity of the gas with a known volume of water, and determine the pressures P and p (reduced to the *volume of the unabsorbed gas-rest*) of the original gas and unabsorbed gas-rest respectively, and then have (by eq. [III.])—

$$\frac{P}{p}\left(\frac{m'}{1+\beta'\frac{h}{v_0}} + \frac{m''}{1+\beta''\frac{h}{v_0}}\right) = m' + m'' \text{..................} \quad (1),$$

$$m' + m'' = 1 \text{..} \quad (2).$$

As $\frac{P}{p}$ is known, m' and m'' can be calculated from the two equations. The easiest mode of solving them is to divide eq. 1 by m'' and solve it in respect to $\frac{m'}{m''}$, as the unknown quantity. The result, in general terms, is—

$$m' = \frac{\frac{P}{p}B' - B'B''}{\frac{P}{p}(B' - B'')}$$

where $$B = 1+\beta'\frac{h}{v_0} \text{ and } B'' = 1+\beta''\frac{h}{v_0}.$$

ULTIMATE ANALYSIS OF GASES GENERALLY.

Among the several methods which fall under this heading, only one is of sufficiently wide applicability to be worth considering in general terms. We allude to the *method of combustion*, which presumes that the gas to be analysed is in, or by addition of hydrogen or of oxygen or of either *plus knallgas** can be brought into, such a condition that the mixture, when an electric spark is sent through it, is resolved completely into one of, in general, carbonic acid, nitrogen, water, and excess of either hydrogen or oxygen, as the case may be.

Before going further, let us explain the customary mode in gas analysis of formulating the ultimate composition of a gas. Methylamine gas may serve as an example. Instead of translating the formula CH_5N into a gravimetric statement, we say—Every 1 volume of this gas contains (potentially) $\frac{1}{2}$ times 5 volumes of hydrogen, $\frac{1}{2} \times 1$ volume of nitrogen, and half-a-volume of "*carbon gas;*" meaning, what would be half-a-volume of carbon, if carbon were a gas of the formula C_2; or, to put it more realistically, "the quantity of carbon contained in 1 volume of CO_2." Avogadro's law, of course, enables us to quite directly read the volumetric composition of any chemical species in its formula, but the system is clearly extensible to gas mixtures. If, in the sequel, we speak of a gas or gas mixture as being "$(xC_2, yH_2, zO_2) + wN_2 = 1$ volume," this means that 1 volume contains w volumes of nitrogen gas, mixed with a (unitary or mixed gas) containing (potentially) x volume of "carbon gas," y of hydrogen gas, and z of oxygen gas in $(1 - w)$ volume.

For the theoretical development of the method, we will assume we had to deal with a gas mixture corresponding to *this* formula, and wanted to determine the co-efficients x, y, z, w, which constitute the volumetric elementary composition of the whole. For the determination of the carbon and the hydrogen, the general method is to measure off V† units of the gas, add a sufficiency

---

* Fulminating gas as produced by the electrolysis of water. We prefer the German word, on account of its shortness.

† Meaning what represents V volumes at the disgregation 1, or some other adopted standard disgregation. We might say "N × V molecules," where N is an arbitrary very great constant; but this would run contrary to established habits.

(S units) of oxygen to produce $V + S = V_1$ of mixture, and fire it with an electric spark. We next measure the product *cold*, to obtain its quantity (V_2 units). In order now to determine the *hydrogen*, we expose the whole to a high enough temperature to convert all the water produced into a practically perfect gas, measure the hot mixture, and then find its quantity as V_3 units. Obviously the steam amounts to $V_3 - V_2$ units, and consequently the hydrogen to $V_3 - V_2$ units likewise; whence

$$y = \frac{1}{V}(V_3 - V_2)\ldots\ldots\ldots(1).$$

Of course the result can be correct only if all the materials used (including the mercury) were perfectly dry; if knallgas was added, two-thirds of its reduced volume must be subtracted from $V_3 - V_2$ as a correction.

This method of hydrogen determination is quite generally applicable, but it is rather troublesome; hence, whenever it is possible, we prefer to calculate the hydrogen from the "*contraction*," meaning the contraction involved in the combustion, or the difference $V_1 - V_2 = $ "C." So we may, if the gas

I. Consisted entirely of hydrocarbons (including H_2 itself). The contraction being independent of the excess of oxygen added, we have (for the gas $xC_2,\ yH_2 = 1$ volume)

the equation $$xC_2,\ \underbrace{yH_2 + (2x}\ + \frac{y}{2})\,O_2 = 2x\,CO_2 + yH_2O,$$

and for the volumes, $$1 \quad (2x + \frac{y}{2}) \qquad 2x \qquad nil;$$

hence for the contraction per unit of gas,

$$c = 1 + \frac{y}{2},$$

and for the actual contraction,

$$C = Vc = V + \frac{V}{2}y,$$

whence $$y = 2\,\frac{(C - V)}{V}\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

The *carbon*, in all cases, is determined by treating the product of combustion, V_2 units, with caustic potash, and measuring the residue V''' units. We then have for the carbonic acid produced

$$K = V_2 - V''' \quad \ldots\ldots (3)$$

whence
$$x = \tfrac{1}{2}\,\frac{V_2 - V'''}{V} \quad \ldots\ldots (4)$$

II. We will now assume the gas is a mixture of hydrocarbons and free nitrogen. In this case, formula (2) may serve to calculate the hydrogen; only we must substitute for V the volume V_0 of the hydrocarbon part of the gas, to get which we must determine the nitrogen in the product of combustion, and deduct its volume $\mathfrak{N}$ from V; $V_0 = V - \mathfrak{N}$. The determination of the nitrogen is effected after absorption of the carbonic acid by analysing the residual mixture of O_2 and N_2, which may be done either by absorbing the O_2 by pyrogallate, or firing with excess of hydrogen, and measuring the contraction; one-third of it is the volume of the oxygen.

That this method of nitrogen determination applies quite generally needs hardly be pointed out. It is not quite so obvious, and yet the case, that if

III. The gas contains (besides hydrocarbons and nitrogen) even *free* oxygen in unknown quantity, the hydrocarbon *cannot* be calculated from the contraction. The only method in such a case is to remove the oxygen from the original gas by absorption with pyrogallate, and burn the residue—unless it should be known that the oxygen and nitrogen are both present only as so much *atmospheric air*. In this case, of course, the problem becomes easy of solution. [See the Author's "Tables to Facilitate," &c., 2nd edition, pp. 30 and 32]. We refer to the same book, p. 32, for the consideration of the most general case, represented in the general formula, 1 volume = $\alpha C_2, \beta H_2, \gamma O_2, \delta N_2$, for the gas to be analysed. We will only point out here that in the case of any carbon gas, which *may* contain components $C\alpha H\beta O\gamma$, the only mode of determining the hydrogen is to measure the steam produced in the combustion of the gas. To illustrate this by an example, assume the gas in one case were ethylene, C_2H_4, and in another, oxide of methyl, C_2H_6O. Both give the same proportion of CO_2, and the same contraction, and yet the second contains in every 1 volume what 1 volume of the first contains *plus* 1 volume of potential steam. If we have some knowledge of the *proximate* composition of the gas given for analysis, the problem, of course, may assume a different aspect. Supposing, for instance, we have to deal with a gas of the potential composition, $x(\alpha C_2, \beta H_2) + y CO = 1$ volume, where $(\alpha C_2, \beta H_2)$ stands for 1 volume of a unitary or complex hydrocarbon of this composition. In this case (reducing at once to unit volume of gas to simplify matters) we have, if k stands for the carbonic acid produced, and c for the contraction,

$$k = 2x\alpha + y \quad \ldots\ldots \quad \text{I.}$$
$$c = x(1 + \tfrac{1}{2}\beta) + \tfrac{1}{2}y \quad \ldots\ldots \quad \text{II.}$$
$$1 = x + y \quad \ldots\ldots \quad \text{III.}$$

i.e., we have only three equations for four unknown quantities. To be able to find these we need a fourth equation, which it may be possible to deduce from a known relation between α and β.

If, for instance, the hydrocarbon is known to be a unitary or mixed *olefine*, we have $\beta = 2\alpha$; if the hydrocarbon part is a *paraffin*, we have $\beta = 2\alpha + 1$ for a fourth equation. If β and α are known, if we know, for instance, that the hydrocarbon is pure marsh gas or pure ethylene, &c., two equations will do, say II. and III.

We are here touching upon a large question, namely, the question of the extent to which the method of combustion is available as an indirect method of *proximate analysis*.

To solve the problem in a given case, one way is to ascertain the formula for the elementary composition of the mixture, to establish equations between the α, β, γ, δ, of the formula on the one hand, and the corresponding co-efficients for the several potential components on the other, and combine these with the obvious relation

$$x' + x'' + x''' \ldots\ldots = 1,$$

where the x's stand for the perunitages of the several components. But it is evidently simpler to establish equations between the carbonic acid k obtained per unit of gas, and the sums of the portions of carbonic acid contributed, by hypothesis, by the several components, and to do the same in regard to the contraction c, the vapour of water w, the nitrogen n found, per unit of gas analysed, thus:—

$$k = k'x' + k''x'' + \ldots\ldots\ldots \quad \text{I.}$$
$$c = c'x' + c''x'' + \ldots\ldots\ldots \quad \text{II.}$$
$$w = w'x' + w''x'' + \ldots\ldots\ldots \quad \text{III.}$$
$$n = n'x' + n''x'' + \ldots\ldots\ldots \quad \text{IV.}$$
$$1 = x' + x'' + \ldots\ldots\ldots \quad \text{V.}$$

If the number of possible components does not exceed 5, we *may* be able to thus determine their perunitages x', x'', &c. Of course there may be no nitrogen, and eq. IV. as a consequence collapses. We may in addition thereto know that there is no oxygen, when eqs. II. and III. become identical, because we can calculate the hydrogen, and consequently also the vapour of water from the contraction c, and *vice versa.* In this case, only three equations, I., II., and V. (or I., III., and V.) are left, and of these again one may be lost through the existence of a known relation between k and c. We may, for instance, know that all the components are olefines, when c can be calculated from the carbonic acid k.

A similar result occurs if all the components contain the same number of hydrogen atoms, or the same number of carbon atoms per molecule. Supposing, for instance, all the components are di-carbon gases (C_2H_2, C_2H_4, C_2H_6), all the k's become equal to 2, and we have as eq. I.—

$$2 = 2x' + 2x'' + \ldots\ldots\ldots$$

which is evidently a repetition of eq. V. If all the components are of the formula C_xH_6 (ex. C_2H_6, C_3H_6, C_6H_6), we know without experiment that all the c's are $= 2{\cdot}5$, and eq. II. becomes a mere repetition of V.

For illustrations see the Author's "Tables," &c., pp. 32–34.

The following table gives the values, c, k, s_0,[*] w, and n, for a number of

---

[*] s_0 denotes the oxygen necessary and sufficient for the combustion of 1 volume of gas.

I.—*Gases Combustible by Oxygen.*

	c.	*k.*	s_0.	*w.*	*n.*
Hydrogen, H_2, ...	1·5	0	0·5	1	0
Carbonic oxide, CO, . .	0·5	1	0·5	0	0
Methyl-aldehyde, CH_2O,	1	1	1	1	0
Ammonia, NH_3,. . . .	1·25	0	0·75	1·5	0·5
Methylamine, CH_5N, . .	1·75	1	2·25	2·5	0·5
Cyanogen, N_2C_2, . . .	0	2	2	0	1
Hydrocyanic acid, NCH,	0·75	1	1·25	0·5	0·5
Marsh gas, CH_4, . . .	2	1	2	2	0
Acetylene, C_2H_2, . . .	1·5	2	2·5	1	0
Ethylene, C_2H_4,. . . .	2	2	3	2	0
Ethane, C_2H_6, ...	2·5	2	3·5	3	0
Propylene, C_3H_6, . . .	2·5	3	4·5	3	0
Propane, C_3H_8, ...	3	3	5	4	0
Oxide of methyl, C_2H_6O,.	2	2	3	3	0
Benzol, C_6H_6,.	2·5	6	7·5	3	0
Gas, $C\alpha\ H\beta = 1$ vol., . .	$1+\frac{\beta}{4}$	α	$\alpha+\frac{\beta}{4}$	$\frac{\beta}{2}$	0
Gas, $C\alpha\ H\beta\ O\gamma = 1$ vol.,	$1+\frac{\beta}{4}-\frac{\gamma}{2}$	α	$\alpha+\frac{\beta}{4}-\frac{\gamma}{2}$	$\frac{\beta}{2}$	0

II.—*Gases Combustible by Hydrogen.**

	c.	*h.*	*w.*	*n.*
Nitrous oxide, N_2O, . .	1	1	1	1
Nitric oxide, NO, † . . .	1·5	1	1	0·5

* *h* = hydrogen necessary for combustion.

† Nitric oxide does not explode with hydrogen ; it does if mixed with it and a sufficiency of N_2O, but then the result is irregular (*Bunsen*). $NO + H_2$ + sufficiency of knallgas *might* work, but we have no personal experience.

APPARATUS AND WORKING METHODS.

We propose to leave Bunsen's physical absorption method on one side, and in regard to the chemical methods, to confine ourselves to those apparatus which are constructed for the use of mercury as a trapping fluid.

Amongst the variety of such apparatus which have been invented, *Bunsen's* offer the great advantage over any of the rest, that they are cheap, easily procured, and not in any high degree liable to break.

Bunsen's Apparatus and Methods.—Apart from auxiliaries, such as a barometer, thermometer, &c., Bunsen's apparatus consists only of a mercurial trough, the longer sides of which are made of plate glass, and two kinds of graduated gas tubes, namely, *absorption tubes* for the absorptions, and *eudiometers* for the explosions.

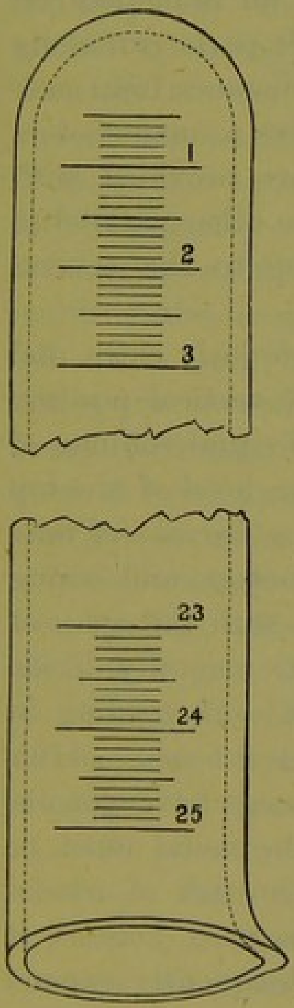


FIG. 39.

Natural size.

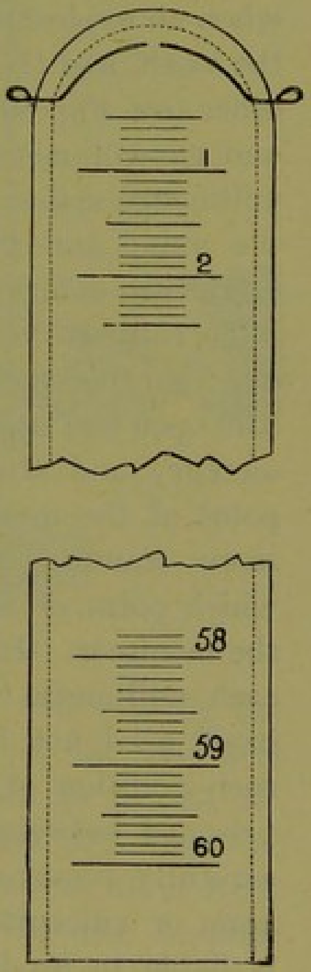


FIG. 40.

Natural size.

Before describing these and other apparatus, let us state that to be able to do justice to Bunsen's method, one must work in a special room, the atmosphere of which is not liable to any sudden change of temperature. The "gas-room" should not be heated artificially, nor be contiguous to other rooms thus heated, and its windows should face the north to avoid direct sunlight. Close to the window stands a substantial table, so constructed that any spilled mercury can be easily collected and recovered. On this table the analytical operations are conducted. Both kinds of gas tubes should be about 20 mms. wide (inside), because in narrower tubes the influence of capillarity becomes measureable. A strength of body of about 2 mms. suffices, even for the eudiometers. An absorption tube should not be more than 250 mms. long, and it should be provided with a spout (*see* Fig. 39) to facilitate the transference of its gas contents to another tube, full of mercury and standing in the same trough.

The eudiometer, for ordinary purposes, should be 400 to 600 mms. long; it must be provided with a couple of platinum wires, soldered in at opposite points near the vault. The wires without terminate in rings to append the pole ends of an induction coil when an explosion is to be effected; their inside parts run along the vault, and their ends are at about 2 mms'. distance from each other (*see* Fig. 40). To be able to use the tubes as manometers and gas-volumeters at the same time, they are provided with millimetre scales running from one end to the other parallel to the axis; and the gas volumes corresponding to the several marks are determined by *calibration*.

To calibrate a eudiometer,* we make it rigorously clean and dry; we then fix it on the table in an exactly vertical position (the open end upwards), pour in a succession of equal volumes of mercury, and after each addition ascertain the level of the top point of the meniscus by viewing it through a *horizontal* telescope, standing at a distance of some two metres, and seeing which point of the scale apparently coincides with the apex of the meniscus. It is easy, after some practice, to mentally divide each millimetre into ten equal parts, so that each reading in itself need not be uncertain by more than ± 0·1 mm. After each addition of mercury, any air-bells that may have got imprisoned between the sides of the tube and the metal must be carefully removed by means of a long, smooth stick of whalebone or vulcanite. An iron wire must *not* be used, because it is liable to produce scratches, which may subsequently expand into cracks. The most convenient mercury measurer is a short test tube, made of rather stout glass and provided with a well

---

* The word eudiometer occasionally serves as a general term for either kind of gas tube.

ground on flat lid (*see* Fig. 41). The measure is filled from out of a long-necked pipette provided with a stopcock. If, in filling the measurer, we take care that the whole of the metal, at any stage of the filling, forms *one* unbroken mass, the formation of air-bells is easily avoided. The measure is filled to overflowing, the lid pressed on to remove the outstanding hillock of metal, and the contents are then poured into the eudiometer. The capacity of the thimble should be so adjusted that each fill of mercury raises the meniscus about 20 mms. Within this short distance any decently cylindrical tube may safely be taken as being absolutely cylindrical. The unit being arbitrary, we choose it so that every millimetre of difference of level corresponds as exactly as possible to "1 *unit*" of volume. Supposing the reading, after addition of 1, 2, 3, ... n measures of mercury, to have been R_1, R_2, R_3, ... R_n, and v to be the number fixed upon as denoting the capacity of the standard measure, the eudiometer, from its close end up to R_1, R_2, R_3, ... R_n, of course holds v, $2v$, $3v$, ... nv units of volume of mercury; but obviously the gas volume required to fill it from the top *down* to R_1, R_2, ... Rn is greater by the annular space between the two menisci corresponding to the calibration and gas measurement respectively. To determine its value we fill the eudiometer with mercury up to, say, "R mms." of the scale, and then pour on a few drops of corrosive sublimate solution, which causes the miniscus to flatten out into a plane.

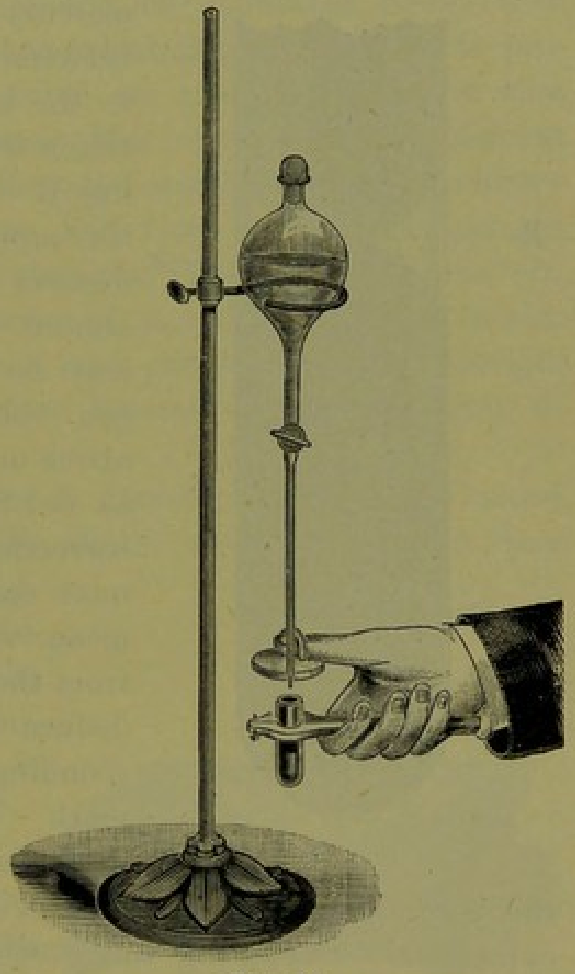


Fig. 41.

We then take the reading of this plane—let it be r (compare Fig. 42, in which the curvature of the meniscus is greatly exaggerated to make things plain). The total space up to *plane* R is obviously constant; so is the volume of the total mercury. Hence the cylinder enclosed between R and r is equal in volume to the half of the annular space between the two menisci. And supposing $R-r$ is equal to δ mms., then the annular space between the two menisci is $=2\delta$ units. As the tube is almost equally wide everywhere, δ may be taken as constant, and the gas volumes corresponding to the above mercury volumes as being equal to $(v;\ 2v;\ 3v;\ \ldots\ldots\ nv)+2\delta$. This correction having been effected, we next calculate for each interval the mean volume-value of 1 mm., and from the volume $(nv+2\delta)=$ "V" easily deduce the exact value $V\pm\epsilon$, corresponding to the nearest millimetre mark. The values of the intermediate marks are found by interpolation on the assumption that the tube within each interval is exactly cylindrical. Supposing the exact capacity down to the point "20·0 mms." is 22·78, and the average volume-value between 20 and 30 is 1·021, we compute $22{\cdot}780+1{\cdot}021$ to find the value for 21·0, we then again add on 1·021 to find the value for 22·0, and so on. We express ourselves thus because successive addition (with the constant 1·021 written at the lower edge of a slip of paper) takes less time than the corresponding series of multiplications would. During the progress of a calibration the temperature of the mercury should be kept rigorously constant, or else the values for the lower marks may become uncertain by more than one can tolerate. What we mean to point out is, that it will not do on a *dull* day to have a gas flame behind the eudiometer to enable one to read. In such a

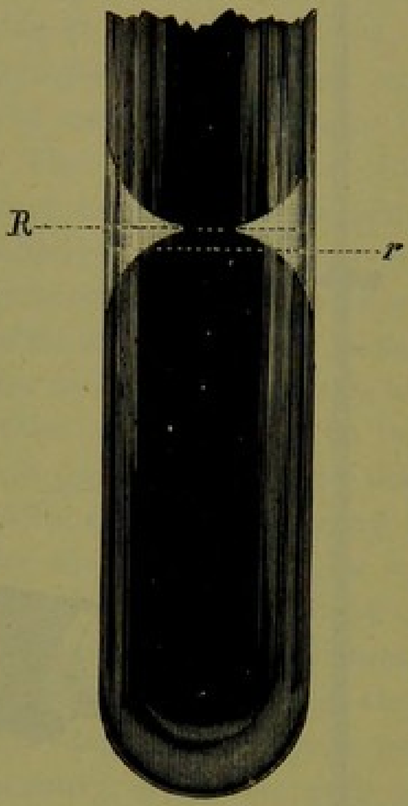


FIG. 42.

case the only correct thing to do is to keep the eudiometer immersed in a large cylinder full of water, and, during the whole of the process, to keep the temperature of this bath constant.

Each gas-measuring tube should be calibrated *twice* (with well-agreeing results) before the calculation of the table is proceeded with. In using the tubes we must never forget that each has its own unit of volume. It is expedient to supplement a calibration by ascertaining the exact weight of a fill of mercury of the prevailing temperature, and from the weight and the well-known constants to calculate the value of "1 volume" in, say, cubic centimetres or grammes of mercury of 0°C. to be able to reduce one unit to another, and gas-volume to gas-weight generally, should such reductions become necessary, as they do occasionally.

Bunsen's trough consists of a rectangular block of wood, scooped out semi-cylindrically above, and forming the base of a cistern, the sides of which are made of *plate glass*, for an obvious reason. Our figure (43) represents an improved form, in which the framework is made of iron.

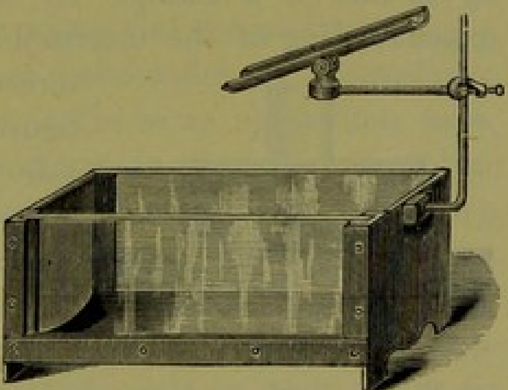


FIG. 43.

The filling of a eudiometer is effected by means of a very long funnel tube, provided with a stopcock at the end of the funnel; the funnel is used precisely in the same way as the stopcock pipette is in the charging of the standard measure. The eudiometer is charged to overflowing with mercury, the end is then firmly closed with the thumb, the eudiometer inverted in the trough, and laid down on the slanting support (*see* Fig. 43), to await the reception of the gas to be measured. If the gas to be introduced is meant to be measured moist, a drop of water is fixed to the inside of the vault of the eudiometer before pouring in the metal; the latter flattens out the drop of water, and spreads it over a considerable portion of the inner surface.

The usual mode of *preserving* a gas sample collected for analysis is to seal it up, at a pressure decidedly less than one atmosphere, in a short, cigar-shaped glass tube, provided with a short, narrow appendage at each end. To transfer the contents of such a tube to the eudiometer, one of the fused-up ends is pressed against the bottom of the trough, so as to break it off. The thus opened-up end is then brought below the end of the eudiometer in the trough, and the collecting tube subjected to a succession of jerking motions, when mercury gradually runs in, and drives the gas up into the eudiometer. Should gas-bells stick to the sides on their way up, they must be made to rise and unite with the bulk of the gas, which is done by alternately raising the eudiometer from its slanting support, and lowering it again in such a manner that the mercury inside alternately falls relatively slowly, and rises up again more quickly than it fell. Supposing the gas to be all in its proper place, the eudiometer is made exactly vertical, and fixed in this position by means of a clamp. In order now to be prepared for an exact reading of the mercury-level in the trough, a little paper screen, perforated as shown by the figure (44), is stuck in between the side of the trough and the metal, opposite the eudiometer, the thermometer suspended close to the gas space, and the barometer, if necessary, made vertical. The whole is then left to itself for half an hour or longer, to enable the gas to assume the temperature of the room. On returning to the gas-room take the necessary readings, by means of the telescope, in the following order:—(1) That of the meniscus in the tube; note it down as R. (2) That of the surface of mercury in the trough, as R_0. The paper screen enables one to effect this otherwise difficult reading with a satisfactory degree of exactitude. (3) That of the thermometer, to obtain the temperature t. (4) That of the barometer; this reading comes last, because the barometer requires to be "tapped" before being read, and this compels one to come close to the eudiometer. $R_0 - R$ gives the height of the mercury column supported in the eudiometer.

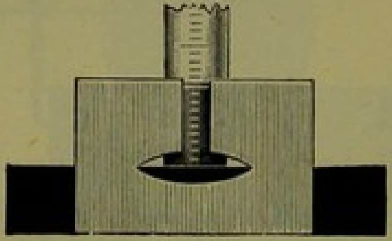


FIG. 44.

Hence, if the barometer stands at B mms., and the tension of vapour of water at t be π mms., we have for the dry pressure of the gas in mms., $P = (B + R) - (R_0 + \pi)$.

For the observed upper reading R, the calibration table gives the volume of the gas V directly, or by an easy interpolation, so that we have for the "quantity" or the "reduced volume" of gas,

$$Q = \frac{VP}{273 + t} \text{ ; for } T = P.$$

Bunsen prefers to reduce to 0°C, or $T = 273$, and 1000 mms., and accordingly calculates thus—

$$V_0 = \frac{VP}{1000\,(1 + \alpha t)}$$

where $\alpha = 1/273 = 0{\cdot}003665$. A table of the logarithms of $(1 + \alpha t)$, proceeding by tenths of a degree from $-1°$ to $+31°$C., is appended to his "Gasometrische Methoden." For the tension of vapour of water, see the Author's "Tables," p. 27. So much about Bunsen's method of gas-measurement; let us now proceed to explain how he effects the absorptions and the combustions.

Absorptions.—To be able to effect a succession of absorptions, and all the measurements involved, in the same absorption tube, Bunsen, as a rule, employs the absorbents in the form of solid or semi-solid balls, fixed to long platinum wires, by means of which they can be introduced into, or withdrawn from, the gas to be analysed.

Balls of caustic potash, chloride of calcium, and other fusible solids, are cast in a pistol-bullet mould, whose neck has been cut off. The coiled-up end of the platinum wire is held into the mould, and the molten reagent poured around it. For the treatment of a gas with an intrinsically *liquid* reagent (*e.g.*, oil of vitriol, alkaline pyrogallate solution, &c.), Bunsen fixes to one end of the wire a ball of coke or *papier-maché*, and soaks this ball with the respective reagent. To make a coke-ball, a finely-powdered mixture of 1 part of sulphur-free coal, and 2 parts of coke is pressed around the coiled-up end of the wire within a bullet-mould which has *not* been deprived of its neck, and exposed within the mould to a gradually increasing heat, terminating at redness. Should the bullet thus produced not be sufficiently solid, it is heated to about 100°, plunged into sugar syrup or coal tar, and re-ignited; this time in the open flame of the gas blow-pipe. Before using such a ball it had better be purified by treatment with, first, hot nitric, then hot hydrochloric acid, and lastly, water. The washed ball is, of course, dried and re-ignited before being soaked in, for instance, oil of vitriol.

Papier-maché balls are easily made from paper pulp prepared *extemp.* by shaking bits of filter paper with water in a bottle. They serve chiefly for pyrogallate of potash.

In introducing an absorbent ball into a gas, we must take care not to allow any air to slip in.

How long should one allow a ball to act to be sure that the respective component is completely absorbed? Unfortunately it is impossible to return a straightforward answer. The balls in general act so slowly, that it will *not* do to merely wait until the mercury ceases to rise visibly. The only certain method is to wait until one may *presume* the absorption to be completed, to measure the residue and then apply a fresh ball, and see whether there is any further contraction; and so on. Fuming sulphuric acid (as an absorbent for olefines C_nH_{2n}) acts pretty promptly; *soft* caustic potash (in absorbing CO_2) acts slowly, so does hard (dry) KHO as an absorbent for water (and CO_2).

Analysis by Combustion.—In the execution of such an analysis, a good many points have to be attended to. The following example is intended to dispose of some of these, and at the same time give a general idea of the order of operations. To determine the percentage of oxygen in, let us say, the air of the gas-room, we measure off a convenient number of units of air, then add for every 100 units of air about 75 units or so of hydrogen, and measure the mixture. A high degree of precision in the preliminary measuring off of the two gases is not necessary; yet it obviously will not do to charge the eudiometer with air down to the mark corresponding to $n \times 100$ volumes, and then to add H_2 until the mercury is down at $n \times 175$; because in the latter case the column of mercury suspended in the eudiometer is considerably shorter (and consequently the pressure of the gas higher) than it was in the first measurement. A correct method is to measure off the several gases roughly in a graduated test tube, at 1 atmosphere, and then let them up into the eudiometer.* Each of the gases, after having been introduced, must of course be "*measured*" in the sense of gasometry. This being done, the two gases must be *mixed intimately* by causing the mercury to oscillate up and down in the tube, or by closing the tube with the thumb *very firmly*, and letting the mercury run forwards and backwards. Before proceeding to the firing, the eudiometer must be closed *firmly*, by pressing it down on a properly shaped india-rubber "cork" (or actual cork coated over with a layer of vulcanized rubber), and holding it fast by means of a clamp, or the arm of a substantial stand, which arm is made to rest firmly on the top of the eudiometer, a layer of cork interposed between the two preventing breakage of the glass. The gas is now ready to be fired, for which purpose the two platinum wires are connected with the poles of a small induction coil, and the spark is made to pass through.† The effect is an almost noiseless instantaneous combustion, involving the conversion of the whole of the oxygen, and double its volume of hydrogen, into water. The very considerable shock involved is sure to send any air that may be sticking to the cork up into the eudiometer. Besides, the partial vacuum produced in the tube as a result of the explosion tends to suck in what there may be of air within, or on the top of, the cork. To avoid this error, the cork, immediately before being used, must be rubbed over with mercury and a little corrosive sublimate solution. The mercury of the trough then adheres firmly to the cork, so that the layer of air can easily be rubbed off under the mercury with the end of the finger.

In lifting the eudiometer from its cushion after the explosion, we must be careful to see that the mercury does not *rush* in, but flow in slowly, or else it may draw in a good deal of air. We will now proceed to the general treatment of the subject, and next speak of the preparation of the gaseous reagents.

Pure oxygen is easily made by heating a small quantity of pure chlorate of potash in a small bulb blown to the end of a

---

* We shall come back to this point a little further on.

† *See* Note (5) at end of volume.

hard glass tube. After the introduction of the salt the glass tube is drawn out and bent in the shape of a long narrow delivery tube. The rest calls for no explanation.

Pure hydrogen is obtained by decomposing dilute hydrochloric acid (of not more than 10 per cent.) or dilute 10 per cent. sulphuric acid with *pure* (especially arsenic-free) zinc, in the presence of platinum within a small phial, which, for obvious reasons, should just be large enough—but no larger than necessary—to prevent boiling over of the contents. The gas is passed through a narrow tube filled with fragments of caustic potash, to absorb water and sulphuretted hydrogen, and to retain droplets of liquid, and then through a narrow delivery tube into the eudiometer. Of course, all the air must be sure to be expelled before the gas is fit to be used.

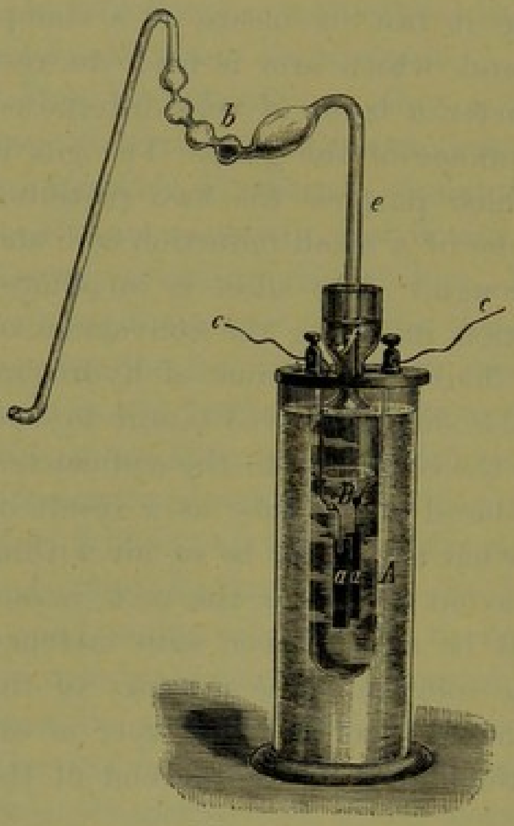


Fig. 45.

For the preparation of *knallgas* Bunsen recommends to electrolize pure oil of vitriol, (diluted to the tenfold with water) in the apparatus represented in Fig. 45. Two platinum electrodes *a a* are soldered into a cylindrical bottle of some 30 cc.'s capacity, which terminates above in a funnel into whose neck the end *e* of the delivery tube and washing bulbs is ground in. A few drops of acid poured into the funnel seals the joint absolutely. The extent to which the bottle is charged with acid is seen in the figure. The bottle is suspended in a bath of water (or alcohol, to prevent freezing in winter time). The bath has two functions: one is to prevent over-heating of the wires, the other to maintain a constant temperature, so that absorptiometric equilibrium, when once established, remains undisturbed. Oxygen being more soluble in the dilute acid than hydrogen is, the first instalments of gas contain an excess of hydrogen. Three or four Grove cells are sufficient to cause a sufficiently lively evolution of gas, and, after the gas has been going off for about 5–10 minutes, the gas which now follows can be accepted as normal. The bulbs *b* are charged with a little concentrated sulphuric acid to absorb the moisture and otherwise purify the gas. Knallgas thus prepared, even when exploded in large quantities, leaves no measurable residue. If it did, it would be of no use for gas-analytical purposes.

In order now to avoid diffuseness in the discussion of an important point, we will confine ourselves, at the outset at least, to the analysis of *gases combustible by oxygen* (H_2 and hydrocarbons), and introduce the following terms:—"Fuel" means the gas to be burned (*e.g.*, the hydrocarbon to be analysed); while "knallgas" in each case stands for the mixture of the fuel with the exact quantity of oxygen which it needs for its complete combustion. Thus: the mixture $H_2 + \frac{1}{2}O_2$ is hydrogen-knallgas; the mixture $CH_4 + 2O_2$ of 1 volume of marsh gas with 2 volumes of oxygen is CH_4-knallgas, &c.

In practice, of course, we always take care to have an excess of oxygen present; there is, however, no need in any case of a *very large* excess. The term "knallgas" includes only the calculated quantity of oxygen. Any pure knallgas, when fired with the spark at, say, ½ to 1 atmosphere's pressure, is sure *not* to miss fire; but in the case of hydrocarbons at least, the violence of the explosion may be more than the eudiometer can stand. Pure acetylene-knallgas, for instance, would shatter any eudiometer into minute fragments. To avoid such disasters we must take care to dilute our knallgas to a sufficient extent by addition of surplus oxygen (or air, which, of course, is the handiest diluent) before firing it. In practice we must go even a little beyond the safety line, because, if the temperature at the explosion is allowed to rise beyond a certain (uncertain!) point, part of the nitrogen, which in practice is always *liable* to be present, is converted into nitric acid, and the contraction becomes too high. On the other hand, we must not attenuate too much, or else the gas may miss fire or suffer only a partial combustion.

The question as to the extent to which a given kind of knallgas should be diluted before being fired, or, to speak more precisely, the question as to the degree of dilution which a given kind of knallgas must possess if its firing by a spark is to lead to a normal and safe combustion, cannot be answered in general terms. All one can say is that the required degree of dilution depends *chiefly* (not entirely) on the nature of the fuel. Supposing a certain degree to work well with ordinary knallgas ($H_2 + \frac{1}{2} O_2$); marsh gas demands a higher degree; ethylene a higher degree than marsh gas; propylene a higher degree than ethylene. Let us at once add that the required attenuation cannot by any means be calculated from the molecular formula; acetylene (-knallgas), for instance, explodes more violently than ethylene, although it contains H_2 less per molecule than, and as much carbon as, the latter gas does. In these circumstances we had better, at the outset, concentrate our attention upon one kind of fuel. We will select the case of hydrogen, and in reference to it formulate the problem thus:—Given a mixture of air and ordinary knallgas ($H_2 + \frac{1}{2} O_2$), what proportions of knallgas may it contain if its combustion in a eudiometer is to lead to a normal result?

To solve this question, Bunsen and Kolbe many years ago made an elaborate series of experiments. Starting in each case with an exactly measured volume of air, they added a graduated variety of proportions of knallgas, measured again, fired (if possible), and measured the product.

The combustion, as we see from the following table, took its normal course in experiments 1 to 5, when the percentage of knallgas lay between, say, 21 and 40, or the quantity of knallgas per 100 of air between 26 and 64; and it is reasonable to presume, with Bunsen, that the limits would be substantially the same if, for instance, oxygen instead of air were used as a diluent. It is to be observed, however, that if the hydrogen plays the part of *reagent* so that the mixture is $x(H_2 + \frac{1}{2} O_2) + yH_2 + zN_2$, the percentage of knallgas may be raised considerably beyond 40 before formation of nitric acid sets in.

Results given by Bunsen and Kolbe[*]:—

Number of Experiment.	In the Mixture as Fired.				In the Product.
	Number of units of Knallgas present per		Pressure. mm. of Mercury.	Temperature, C.	Number of units of gas per 100 of air used.
	100 units of air.	100 units of Mixture.			
0	13·45	11·86	500·6	17°·7	No explosion.
1	26·26	20·80	521·0	17°·7	100·02
2	34·66	25·74	534·4	17°·2	100·15
3	43·52	30·33	552·1	16°·3	100·07
4	51·12	33·83	571·1	16°·9	99·98
5	64·31	39·14	591·2	17°·3	99·90
6	78·76	44·06	622·5	16°·7	99·43
7	97·84	49·46	648·8	16°·8	96·92
8	228·82	69·59	648·3	6°·7[†]	89·32

Bunsen's directions regarding the application of the reaction $H_2 + \frac{1}{2} O_2 = H_2O$ generally are all based on the assumption of the general validity of the above limit values for the proportion of knallgas in the material to be burned.

But the success of an explosion, it appears to us, is determined, not so much by the percentage of knallgas present as by its *density* in the mixture to be fired; we mean the ratio of its absolute quantity to the total volume actually filled by the mixture. This ratio is conveniently *defined* by stating how many times the volume filled by the mixture is greater than that which its knallgas would occupy at 0° and 760 mms.; or, let us rather say (as we have a liberal margin to go upon), at the

---

[*] "Gasometriche Methoden," 2nd edition, pp. 72 and 73.

[†] This 6·7 is *not*, as one might suspect, a misprint. Experiment 8 was obviously made at a different time from the rest.

prevailing temperature and 760 mms. pressure. This *latter* number we will call the *attenuation* of the knallgas, and the corresponding number for the hydrogen in the knallgas the attenuation of the hydrogen.

We have calculated these attenuations for Bunsen and Kolbe's experiments, 0 – 6, and give them in the following table:—

Experiment.	Temperature t°.	Attenuation per unit volume at 760 mms.				
		and 0° C. of		and t° C. of		
		Knall gas.	H_2.	Knall gas.	H_2.	
0	17°·7	13·64	20·46	12·81	19·22	No explosion.
1 to 5	16°·3 to 17°·7	7·47 to 3·49	11·20 to 5·24	7·01 to 3·28	10·52 to 4·93	Normal results.
6	16°·7	2·94	4·41	2·77	4·16	HNO_3 produced.

In the combustion of *carburetted hydrogens* a considerable attenuation of the knallgases becomes necessary—apart from any other consideration—to prevent destruction of the eudiometer.

The following table gives, for *Marsh gas* and for *Ethylene*, the percentages of the respective knallgases and fuels which Bunsen directs us to establish in the mixture to be fired, and, in the last two columns, the corresponding *attenuations*. It shows with sufficient directness what we have to do if the gas to be burned substantially consists of, or contains approximately known proportions of, H_2, CH_4, C_2H_4, and as we have considerable latitude in fixing upon the degree of attenuation to be established, a roughly approximate knowledge of the composition of the gas to be burned is sufficient to enable one to lay down a scheme of synthesis for the mixture to be fired which keeps us in both senses on the safe side.

References to Notes.	Percentage of		Pressure in mms.	Temperature.	Attenuation referred to 1 vol. measured as 760 mms. and $t°$ of	
	Knallgas.	Fuel.			Knallgas.	Fuel.
	Marsh Gas.					
(1)	27 to 20	9 to 6·7		ordin'y	4·6 to 6·3	13·9 to 19
(2)	35	11·7	503·7	19°·2	4·3	12·9
	Ethylene.					
(3)	19·5	4·9	546·2	12°·5	7·1	28·6
	Hydrogen.					
(4)	39 to 21	26 to 14	500 to 600 mm.		3·3 to 7·0	5 to 10·5

(1) General directions given by Bunsen in his "Gasometrische Methoden," 2nd ed., p. 127. The attenuations are calculated by the writer on the assumption that the pressure of the mixture is 600 mms.

(2) Analysis quoted by Bunsen in his "Gasom. Meth.," 2nd ed., pp. 128, 129.

(3) Test analysis by Carius; p. 132 of the same book.

(4) Recapitulated from preceding tables for the convenience of the reader.

To be able to effect the synthesis directly in the eudiometer, Bunsen recommends to *virtually* provide the eudiometer with a *reduced volume* scale, in addition to the millimetre scale which it bears actually, by inverting the eudiometer full of mercury over the trough, letting a succession of equal small volumes of air—all measured off at the prevailing atmospheric pressure—rise up into the eudiometer, and noting the resulting positions of the meniscus, taking care to keep the trough-level reading approximately constant.

But it is just as easy to find the several points of the supplementary scale by calculation. Let us assume the eudiometer scale runs from an imaginary zero (a little below the top of the vault) to 500 mms. as the adopted constant trough-level reading (close to the open end). Suppose now the eudiometer is charged with a gas down to R mms.; this reading, according to the calibration table, corresponds to v volumes of gas, which v in Bunsen's system is not far removed from R itself. The corresponding volume $\mathfrak{b}$, at 760 mms. pressure is $\mathfrak{b} = v\,(760 + R - 500) \div 760$, and is easily calculated. It suffices to effect the calculation for, say, $v = 20, 50, 100, 150, 200, \ldots\ldots 500$, to be able to embody the relation between v and $\mathfrak{b}$ in a curve laid down in a system of rectangular co-ordinates, *i.e.*, on a sheet of curve-paper.* From this curve we read off the values v, for $\mathfrak{b} = 10, 20, 30, \ldots\ldots 500$, and enter them on a scale of v's in the way shown by Fig. 46.†

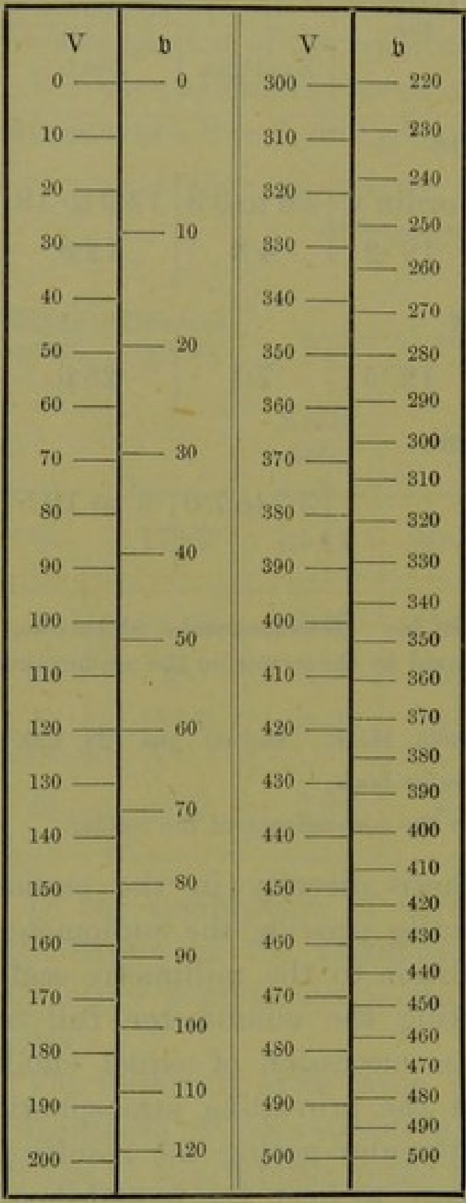


Fig. 46.

To show the way in which the double scale is meant to be used, we will assume that the gas to be burned is known to be approximately half nitrogen and half marsh gas, and fills the eudiometer down to $R = v = 100$ mms.‡ This, according to the scale, corresponds to $\mathfrak{b} = 48$, and consequently we have for the $\mathfrak{b}$'s: of marsh gas present, 24; oxygen needed, 48; mixture of substance and oxygen $48 + 48 = 96$. But $\mathfrak{b} = 96$ by the scale corresponds to $R = 170$, and down to *there* we must let in oxygen. But the gas, to afford a normal explosion, requires to be diluted down to, let us say, $24 \times 15 = 360$ volumes,

---

* To be had from Messrs. A. & K. Johnston, Geographists, Edinburgh.

† In the actual diagram, as used, the scale of "V's" should be a real millimetre scale, the scale of "$\mathfrak{b}$'s" subdivided, and both be more correctly drawn than our figure can pretend to be.

‡ We assume, for simplicity's sake, that $R = v$. Anybody will easily see his way towards constructing a scale which gives R, v, and $\mathfrak{b}$ in function of one another.

which we will assume correspond to $R = 360$ exactly. Down to this point, 360, accordingly, we must let in air.

This is our own *modus*. Bunsen would say: Add a reduced volume of air, so that the $\mathfrak{b}$ of the mixture becomes equal to so-and-so many times, say 13 times, the original $\mathfrak{b}$ of the marsh gas, which would make the $\mathfrak{b}$ of the mixture $13 \times 24 = 312$, corresponding, according to our scale, to $v = R = 373$. Of course, there is considerable latitude, or else practical gas analysis by combustion would be an impossibility.

The addition of large volumes of air to the gas to be fired detracts from the precision of the work generally, and especially from that of the determination of the nitrogen in the ultimate residue (we mean the burned gas minus carbonic acid).

Thomas [*] was the first to conceive the happy idea of effecting the necessary attenuation by mere expansion through reduction of pressure, which the kind of apparatus he used [†] readily lent itself for. Lothar Meyer and Seubert [‡] subsequently took up the same idea, and by the invention of a supplementary contrivance rendered the Bunsen eudiometer available for putting it into practice. Their apparatus is represented in Fig. 47, which requires only a few words for its explanation. As shown by the figure, the trough is pierced by two perforations in its bottom, which widen out above into cylindrical sockets for accommodating the wider ends of two india-rubber corks. The outstanding ends of the corks are fitted, one into the eudiometer, the other into the wider limb of a long Gay-Lussac-burette-like combination of tubes, which bears a millimetre scale and serves as a barometer.

The tube *g* (which should go down so far that the highest india-rubber joint below the small bulb is under the pressure of about 760 mms. of mercury, so that there is no fear of air leaking in there) serves to make the eudiometer and barometer

---

[*] "Chem. Soc. Journal." Transactions 1879, vol. xxxv., p. 213.

[†] It was a "Frankland." Described and figured in Thomas' "Memoir;" also (more briefly and without a figure) in the Author's article "Analysis" in the new edition of Watt's "Dictionary of Chemistry," vol. i., p. 243.

[‡] "Chem. Soc. Journal." Transactions 1884, vol. xlv., p. 581.

communicate with one another, and, by means of a long stout india-rubber tube, with the mercury reservoir *Q*.

To prepare the apparatus for use, the trough is emptied so far that the bottom end of the narrow limb *s* is free, the eudiometer being away meanwhile. A small quantity of water is then sucked up through *s*, and the eudiometer (moist and full of mercury) put in its place. By alternately raising and lowering the reservoir it is easy to fill the barometer completely with mercury, expel the air from it, and moisten its walls with water, so that the readings are, as they come, corrected for the tension of the vapour of water. How the apparatus is utilized for expanding a gas contained in the eudiometer is too obvious to require to be explained.

In using the apparatus as a *measurer*, Lothar Meyer and Seubert (rightly) recommend to so place the reservoir that the surface of the mercury in *B* is about at a level with the zero of the eudiometer. The gas volume then becomes nearly equal, numerically, to the difference of level between the meniscus in the eudiometer and that of the barometer, *i.e.*, equal to the dry pressure *p* of the gas; and, as a consequence, the relative error in *pv* (and consequently in the "reduced volume") is at its minimum. By means of their apparatus, Lothar Meyer and Seubert have

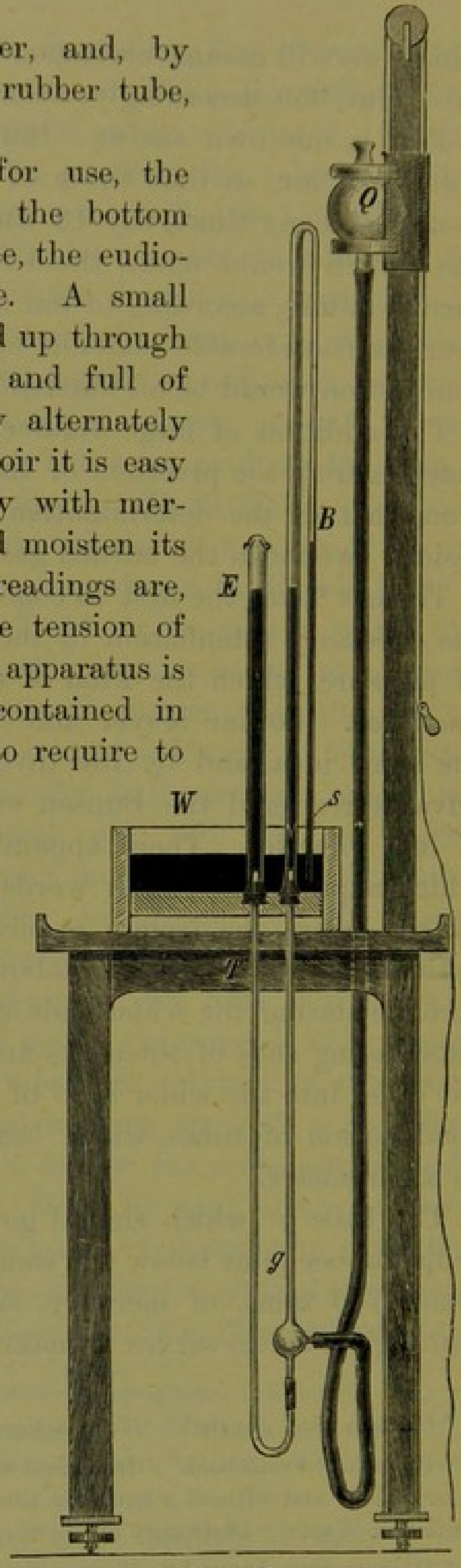


FIG. 47.

ascertained, for a series of different knallgases (1) the minimum partial pressure at which the respective knallgas, when a spark is sent through it, catches fire; and (2) a range of values of this partial pressure within which the explosion is both safe and effective. The following table gives their results in the latter respect, and besides, in so many additional columns, the corresponding partial pressures of the fuels and the attenuations of these and the knallgases:—

Formulæ of fuels and Knallgases.	Partial Pressure in mms.		Attenuation referred to unit vol. at 760 mms.	
	Knallgas.	Fuel.	Of Knallgas.	Of Fuel.
$H_2 + \frac{1}{2}O_2$	176 − 127	117 − 85	4·3 − 6	6·5 − 9
$CO + \frac{1}{2}O_2$	243 − 219	162 − 146	3·1 − 3·5	4·7 − 5·2
$CH_4 + 2O_2$	140	47	5·4	16
$C_2H_4 + 3O_2$	80 − 70	20 − 17·5	9·5 − 10·8	38 − 43
$C_2H_2 + 2{\cdot}5O_2$	50 − 40	14·3 − 11·4	15·2 − 19	53 − 66
$C_3H_6 + 4{\cdot}5O_2$	89 − 80	16 − 14·5	8·5 − 9·5	47 − 52
$C_3H_8 + 5O_2$	80	13·3	9·5	57

For the sake of more convenient comparison, we contrast the attenuations (implicity) recommended by Bunsen, with the corresponding ones of Lothar Meyer and Seubert:—

Name of Gas.	Formula.	Attenuation (per unit vol. at 760) of Gas named in Column I.	
		Bunsen.	L. M. and S.
Hydrogen, ...	H_2	4·9 − 10·5	6·5 − 9
Ord. Knallgas, . .	$H_2 + \frac{1}{2}O_2$	3·3 − 7·0	4·3 − 6
Marsh gas, ...	CH_4	13 − 19	16
Ethylene, ...	C_2H_4	29	38 − 43

With Lothar Meyer and Seubert's, or any other apparatus admitting of the method of expansion, the order of operations with a gas of unknown composition is as follows:—After having added a sufficiency of oxygen, we expand so far as to be sure to be on the safe side of the safety line, and then apply the spark. If no explosion occurs, we increase the pressure somewhat and try again, and so on until we succeed.

If no explosion occurs even at (let us say) *one* atmosphere's pressure, we must add a sufficiency of ordinary knallgas ($H_2 + \frac{1}{2}O_2$) to render the gas explosive, and fire then.

To calculate the requisite quantity of knallgas, we assume—

(1.) In the first instance, that the gas as given is substantially free of fuel of any kind. In this case an attenuation of 3·3 is sufficient. Hence, at 760 mms. pressure, we may have 1 volume of knallgas and 2·3 of diluent, or for 1 volume of diluent (given gas) 1/2·3 = 0·435 volume of knallgas. Hence, supposing the $\mathfrak{v}$ of the given gas to be = $\mathfrak{V}$, the addition of 0·435 × $\mathfrak{V}$ of knallgas should produce 1·435 $\mathfrak{V}$ of a mixture fit for explosion at 760 mms. But then

(2.) The *given* gas *may contain* some kind of knallgas which only missed fire on account of its being too largely diluted with other things. In the absence of any knowledge of the quality and quantity of this hidden knallgas, let us assume that the $\mathfrak{V}$ (reduced to 760) volumes of given gas contain (virtually) 1/10 × $\mathfrak{V}$ of ($H_2 + \frac{1}{2}O_2$). If so, the total knallgas amounts to (0·435 + 0·1) $\mathfrak{V}$ = 0·535 $\mathfrak{V}$ units, and consequently must be expanded into at least 3·3 × 0·535 $\mathfrak{V}$ = 1·765 $\mathfrak{V}$ units of actual volume by reduction of pressure before the spark is tried for the first time. Certain gas analysis apparatus (*e.g.*, Regnault's and the Author's) admit of the pressure being raised to more than one atmosphere, and thus afford an additional resource. The Author's apparatus, besides, enables one to conveniently fractionate the given gas, so that a projected scheme of operations can be rehearsed with a small sample before being applied to the bulk of the gas.

Bunsen's methods leave nothing to be desired on the score of elegance and potential precision, but they are very wasteful of time, and demand a special room for their execution.

They, moreover, almost prohibit the use of gas flames as a means of artificial illumination, a serious drawback in a city like, for instance, Glasgow, where the sun does not shine *every* day.*

The desire to avoid these inconveniences has led to the construction of quite a series of other apparatus than Bunsen's, including (as the latest arrival) one of the Author's invention,† which we will now proceed to describe, not, however, without having first stated that its leading feature is borrowed from *Doyère*,‡ in this sense, that the author, like Doyère, utilizes the *Ettling gas-pipette* as a means for the treatment of gases with *liquid* reagents, and as a means for the transference of gases generally. The gas-pipette, however, is such a useful instrument in itself that we will first of all describe it in the form which it assumed in Doyère's hands. A glance at Fig. 48 gives a sufficient idea of the construction of the instrument; there is no need of our explaining how it is used for the mere transference of gases from one tube to another, or of our defining the conditions and limits of its availability for this purpose. To explain how it is utilized for analyses by absorption, let us assume that we had measured a gas in a (sufficiently short) eudiometer, and now wished to determine, let us say, its carbonic acid by means of solution of caustic potash. For this purpose we begin by charging the pipette with mercury to the extent shown in Fig. 48. To be able to go any further we need a pneumatic trough provided with a deep well,

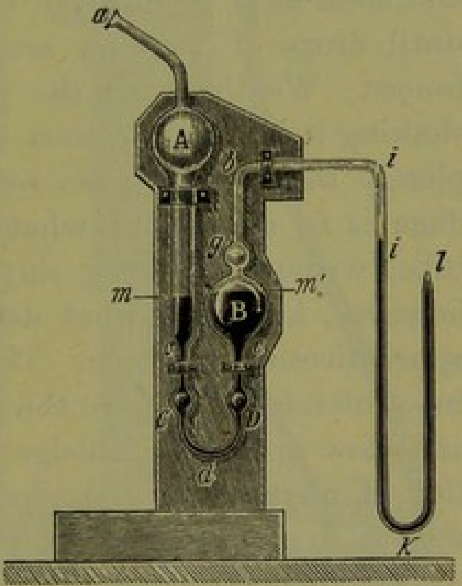


Fig. 48.

---

* A Swan-Edison electric lamp would help us over this difficulty; but it could only be thought of where an electric current of sufficient strength is always ready.

† Dittmar's "Report on the Composition of Ocean Water" (Challenger Memoirs), Part III. As these reports do not appear to be widely diffused, I will again discharge the agreeable duty of thanking my then assistant, Mr. Robert Lennox, for the great assistance he gave me in the realization of my ideas.

‡ Ann. Ch. Phys. [3], 28, p. 1.

which latter must be shaped so as to admit of the following operations:—To introduce the absorbent we immerse the U of the pipette in the well of the trough, and next blow out the air (without sending any more mercury after it than we cannot help). We then suck in a small quantity of the reagent from out of a test-tube inverted over the trough, taking care not to let any more mercury follow than necessary to seal the contents by a mercury thread, *i l*, in the U. The pipette, if not wanted immediately, may, of course, be put aside for an indefinite time, because the reagent is fully protected against the action of the atmosphere. But assuming the gas to be ready for treatment, we transfer it in its tube to the pipette trough (by means of the contrivance represented in Fig. 55, p. 205), slide the tube over the outer limb of the U, press it down so that the exit of the latter touches the top of the tube, and suck at *a* to dislodge the mercury thread, and then again until drops of mercury are seen falling into the bulb, but no *longer*. We then lift the pipette out of the trough, and, by shaking it judiciously, soon cause the carbonic acid to be completely taken up by the reagent. All that now remains to be done is to re-transfer what remains of gas to the measuring tube, without allowing any of the reagent to follow. This, however, is a somewhat delicate operation, which it takes an apprenticeship to learn. The first step is easy. We place the tube intended to receive the gas over the outer limb of the U, and blow in at *a* to dislodge the mercury thread. If the quantity of mercury in the pipette is still (substantially) what it was at first, *only part* of the gas follows. To get out the rest we lift the pipette, so that its exit becomes visible within the gas space of the eudiometer, and while maintaining this condition for the pipette, cautiously raise the eudiometer. The more the eudiometer is raised, the more energetically it "sucks" at the pipette, and (after a deal of practice) one learns to so govern the (up or down) motion of the eudiometer that, when the thread of liquid reagent begins to show itself in the outer limb of the U, he is able to make it move up or down, or stand still, as he wills. We arrest it, of course, at say 2 mms.' distance from the outflow, then re-place the pipette on the table, which at once seals the outflow by a superincumbent layer of mercury, suck at the pipette until mercury is seen to flow in, and then lift it out and place it on the table. The gas is now transferred, and is ready to be measured. Whoever tries the operations detailed will find that they are not by any means as easy as they look on paper. A little device of Mr. Buchanan's facilitates them greatly; it consists in this, that the bend at *d* is made capillary, so that any error of judgment committed does not find such immediate punishment as it would otherwise.

The writer, some years ago, finding it difficult to work the Doyère pipette, satisfactorily modified its construction in a manner shown by Fig. 49, which, however, represents an improved form of the Author's contrivance which was devised subsequently by Mr. Lennox.

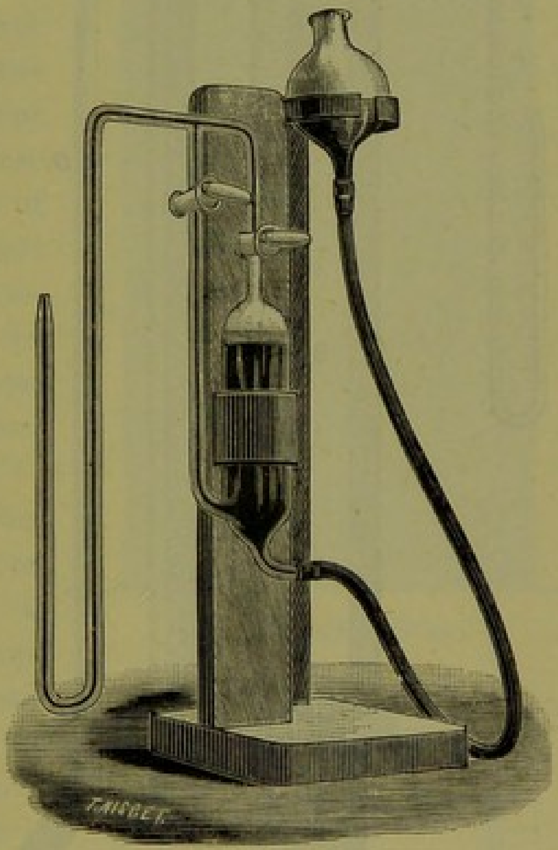


Fig. 49.

In preparing the pipette for use the first step, of course, is to fill it completely with mercury, and the second to charge it with a small quantity of the respective reagent. This is done pretty much in the same way as in the case of the original Doyère, but the moveable mercury reservoir greatly facilitates the work. Both remarks apply to the mode of introducing the gas. To blow back the gas residue into its test tube, the reservoir is raised, the stopcock of the pipette neck opened, and the gas allowed to flow on until the liquid reagent has come to about a millimetre on the safe side of the point where the side tube joins it. The principal stopcock is then closed, and that of the side tube opened to drive out the remaining thread of gas by a current of mercury.

The modified gas-pipette, combined with a measurer and exploder, and the two necessary troughs, complete the author's apparatus.

The measurer (Fig. 50) is a combination of a wide with a narrow glass tube, after the manner of Gay-Lussac's burette. As shown by the figure, it is fixed within a square water-bath, the front and back of which are made of plate glass. The back pane had better be made of ground glass, which affords a more satisfactory view of the meniscus when gas-light is used. The wide tube by its lower contracted end, and a long capillary india-rubber tube attached to it, communicates with a mercury reservoir, the support of which slides up and down at *D*. At their upper ends both tubes are provided with Geisler stopcocks. To the exit end of that of the wider tube is soldered the capillary U, characteristic of the Ettling pipette. The wide tube bears a millimetre scale; the gas volumes corresponding to the several marks are determined by gravimetric calibration. The bit of capillary tube between the stopcock and the top of the measurer joins on to the latter *quite abruptly*; the volumes are counted from the point of junction, because after the introduction of a gas the narrow canal retains its thread of mercury.

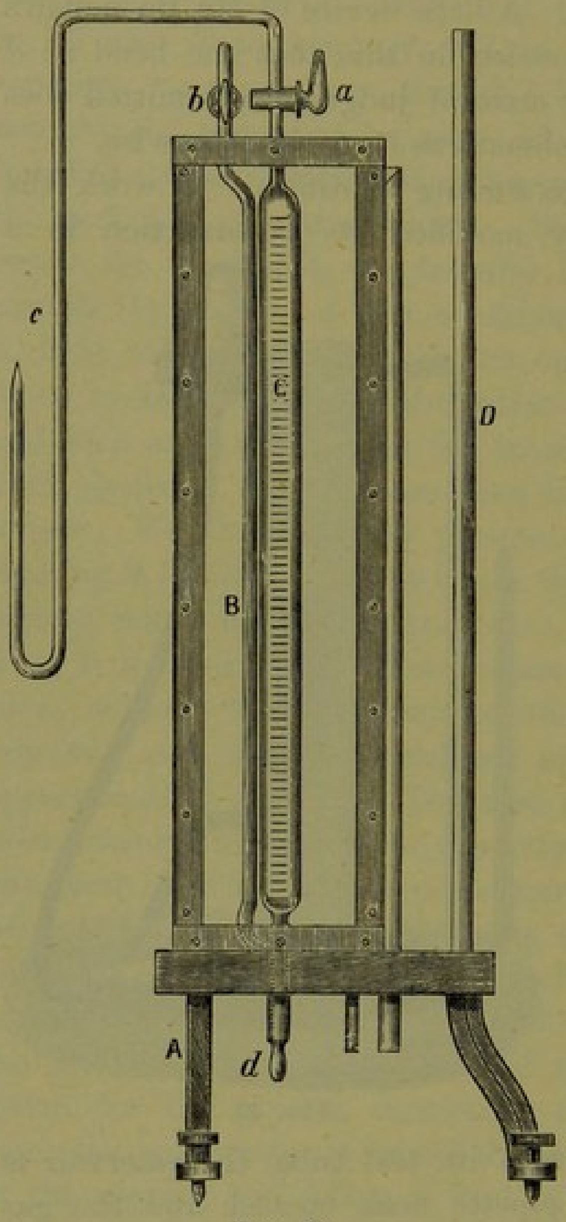


Fig. 50.

In the calibration of the measurer it is expedient to use a special (light) water-jacket, which is easily improvised out of that of a glass Liebig's condenser, but should be free of flaws and irregularities of form. More convenient than such an extemporised water-bath is a stout, four-legged stool of iron, so constructed that it supports the *ordinary* measurer's bath with safety, and raises the latter's outlet to a sufficient altitude. In a laboratory where there is a continuous supply of water direct from the street pipes, the maintenance of a constant temperature is easy. In the absence of such a water supply the temperature *must* be kept constant to within 1°C. about, somehow. The jacket being fixed over the measurer, the lower end of the latter is connected with a capillary stopcock, by means of a bit of very stout india-rubber, in such a manner that only a mere (circular) line of india-rubber is under the influence of the pressure of the mercury. The reservoir tube is slipped over the exit end of the stopcock, and raised until the metal has just got above the stopcock of the narrow side tube, which cock is now closed. More mercury is

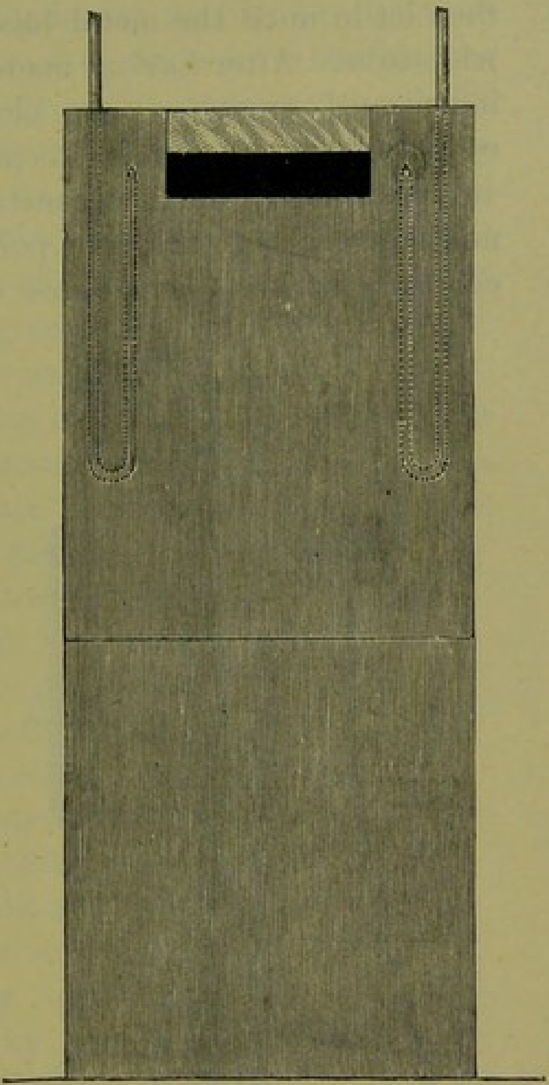


FIG. 51.—(*Side View*).

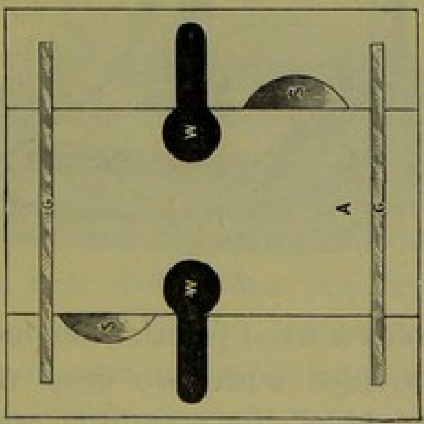


FIG. 52.—(*Top View*).

then let in until the metal has just passed the stopcock of the wide tube. After having made sure that there are no air-bells imprisoned anywhere, we close the cock below, remove the reservoir, and next, while keeping cock *b* closed, let out mercury very cautiously until the metal stands exactly at, or perhaps a millimetre above, the zero point referred to. The business of calibration then commences. We tare a convenient vessel (say a porcelain basin) on a fine balance of sufficient carrying power, run in mercury down to about 10 – 20 – 30, &c., mms., and in each case, after having taken the *exact* reading with the telescope, weigh the whole of the mercury which has been discharged so far. In a second series we check the points 15 – 25 – 35, &c., and from the two series combinedly deduce a calibration table, the volume of 1 grm. of mercury at the temperature prevailing in the bath during the calibration serving as a convenient unit; unless we prefer to so adjust the unit of volume that the numbers for the volumes agree as nearly as possible with the readings, which in the subsequent use facilitates interpolation. The calibration-table in any case, to be convenient, must proceed from millimetre to millimetre.

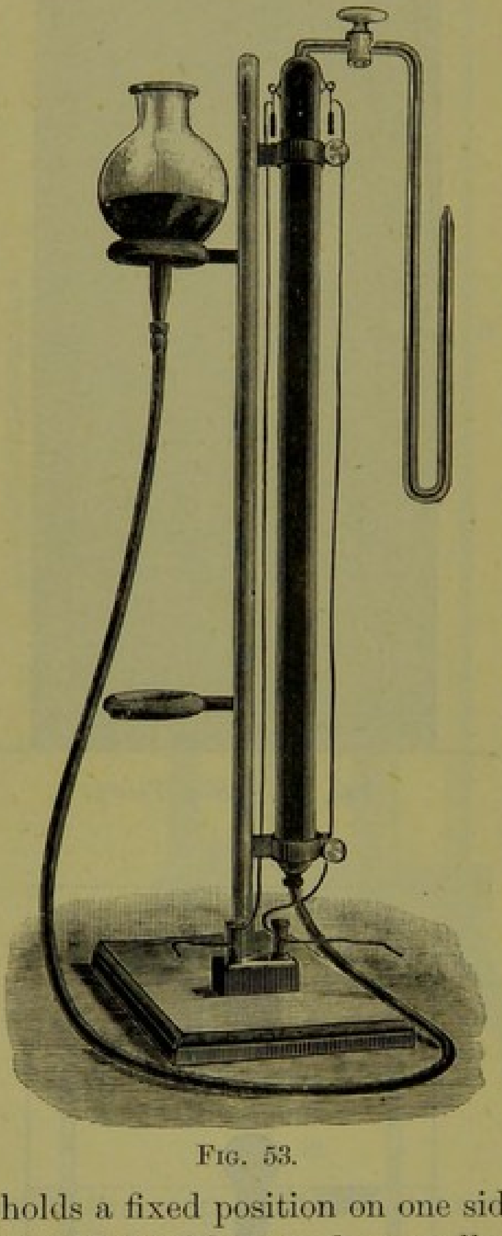


FIG. 53.

The measurer (in its bath) holds a fixed position on one side of a trough (Figs. 51 and 52) provided with two deep wells, one for the accommodation of the U of the measurer, and the other for that of the *exploder*, which stands on the other side.

The construction of the exploder is seen in Fig. 53. It must be relatively strong in the body, and so wide as to enable one to expand a gas transferred to it from the measurer to a sufficient extent before firing it. It is convenient to graduate the exploder roughly, to enable one to establish a predetermined ratio of expansion. The graduation, however, had better not be laid down on the tube, but on a slip of wood or Bristol board, which is held against the measurer when needed.

The absorber has a trough of its own.

A gas to be analysed, to be within reach of the measurer, must be contained in a short enough stout test-tube inverted over a mercury trough. Fig. 54 represents a convenient suction tube, invented by Doyère, for taking the air out of such a short gas tube while it stands over the well of the trough inverted, and thus filling it with mercury without producing any air-bells at the sides. A small portable iron trough (*see* Fig. 55) serves to convey the gas to the trough of the measurer, which we assume to have already been filled completely up to the end of the U with mercury. The cock of the side tube is kept shut until the gas has been sucked over into the measurer, which is then closed by turning its cock. The gas then is brought to very nearly the pressure of the atmosphere by placing the reservoir in the proper position. This being done, the side tube is made to communicate with the atmosphere, and the reservoir readjusted until the two mercury menisci, in the graduated and side tube respectively, are in the same horizontal plane. A horizontal "wire" in the focus of the telescope facilitates this adjustment greatly, but, as the two menisci almost touch each other, the wire is not indispensable. The gas now is at the pressure $B + b$ mms., where B stands for the height of the barometer, and b for the small excess of capillary depression in the narrow, as compared with the wide, tube. Only for absolute measurements (reduction of gas-volume to weight) needs b be known;

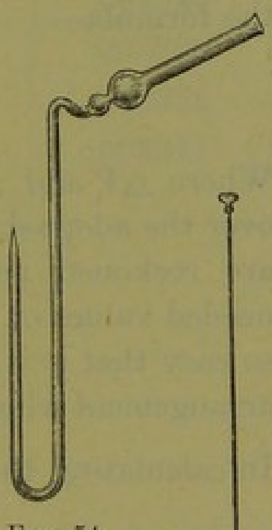


FIG. 54.

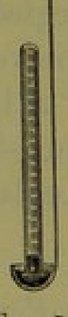


FIG. 55.

it is easily determined by letting both branches of the measurer communicate with the atmosphere and noting the difference of level. With an apparatus which served in our laboratory for a long time, b was equal to 0·6 mm. We ought to have stated before that the inside of the measurer is kept *moist*, so that the dry pressure of the gas P is $P = B + b - \pi$; where π signifies the maximum tension of vapour of water at the temperature of the gas, *i.e.*, of the bath as given by an immersed thermometer. As the pressure and temperature remain nearly constant throughout an analysis, it is *not* expedient to reduce to unit disgregation, but better to reduce to a set of convenient integer values P_0 and T_0 lying close to the observed values for P and T by means of the formula—

$$V_0 = V\left(1 + \frac{\Delta P}{P_0} - \frac{\Delta T}{T_0}\right).$$

Where ΔP and ΔT are the excesses of the observed P and T over the adopted standard values P_0 and T_0, and both increments are reckoned positive. If the reciprocals of the practically needed values of P_0 and T_0 are at hand, the calculation becomes so easy that it is not worth while to look out for any mechanical arrangement which would effect the joint correction automatically. In calculating the $\frac{\Delta P}{P_0}$ the capillary depression term b may be neglected. In many short analyses P and T are constant, so that the volumes as measured are "reduced volumes" in themselves.

All the rest of the *modus operandi* may be left in the hands of the student. For his convenience we append a table of reciprocals of practically occurring values for P_0 and T_0.

EXAMPLE.

Found.—$V = 456·3$ at $P = 762·3$ and $t = 14°·5$.

Wanted.—V_0 for 760 mms. and 15°.

Both corrections are positive.

That for ΔT is $0·5 \times ·00347 = ·00174$
" ΔP is $2·3 \times ·00132 = ·00303$

The two conjointly, ... $= ·00477$

Hence $\Delta V = ·00477 \times 456 = 2·18$, or $V_0 = 458·48$.

Reciprocals of (273 + *t*.)

t.	1:(273 + *t*).	*t*.	1:(273 + *t*.)	*t*.	1:(273 + *t*.
0	·003663	10	·003534	20	·003413
1	·003650	11	·003521	21	·003401
2	·003636	12	·003509	22	·003390
3	·003623	13	·003497	23	·003378
4	·003610	14	·003484	24	·003367
5	·003597	15	·003472	25	·003356
6	·003584	16	·003460	26	·003344
7	·003571	17	·003448	27	·003333
8	·003559	18	·003436	28	·003322
9	·003546	19	·003425	29	·003311

Reciprocals of P.

P.	1 : P.	Diff.
710	·001408	−20
720	·001389	−19
730	·001370	−19
740	·001351	−19
750	·001333	−18
760	·001316	−17
770	·001299	−17
780	·001282	−17
790	·001266	−16

EXERCISES.

Whatever kind of gas apparatus the laboratory where the student goes through his course of instruction may afford, he should begin by making himself familiar, as far as the resources of the laboratory may permit, with Bunsen's apparatus, because Bunsen's system is the only one which he could think of extemporising in his future practice as a professional chemist. Hence, the Author, although his own laboratory hardly affords *all* the facilities for doing full justice to Bunsen's method, recommends to his students the following series of exercises as an introduction to the subject:—

Ex. 1.—*Making of a Bunsen Eudiometer.*

Procure a good piece of glass tubing about 600 mms. long, 20 mms. wide inside, and of 2 mms. strength of body, which is as nearly as possible straight and cylindrical, and free of irregularities generally. By means of a pair of calibers it is easy to test a series of tubes quickly and select the best. Close the tube at one end and grind the other flat, first on a flat wet sandstone, and then on a lead plate with emery and turpentine. Then fuse in the platinum wires. To make the necessary perforations heat the respective part of the tube in the blow-pipe flame, stick on a piece of stiff platinum wire, and by means of it pull away a small portion of the glass laterally, so as to produce a very narrow capillary branch, which then cut off close to the tube. The rest is more easily explained by demonstration than in words. If you are not enough of a glass blower to solder in the wires *properly*, procure a ready-made eudiometer, but do not forget to test the wire joints thus: Fill the eudiometer with mercury completely, insert it in the trough, and repeatedly tap the bottom of the trough with it as sharply as compatible with the fragility of the instrument. If air-bells are seen to rise from the wires, the joints are leaking, and the eudiometer is useless. [Professional glass-blowers now-a-days often use a thread of a special kind of glass for, so to say, cementing in the wires, but we do not know what sort of glass it is]. Assuming now the eudiometer still requires to be graduated, empty out its mercury into a graduated cylinder (or into a tared vessel) to determine its total capacity directly (or indirectly from the weight of the metal). From the volume found, and the total length of the eudiometer in millimetres, calculate the average volume value of 1 mm. of eudiometer space. In order now to find a convenient point for the zero of the scale, pour mercury equal to 20 mms. into the eudiometer, and mark the level of the top of the meniscus by means of red ink thickened with gum. The eudiometer is supposed to have been cleaned and dried before this is done. Close the tube with a cork, or better, by means of a round stick of wood fixed in its open end as a handle, heat it in its entire extent to beyond the fusing point of wax, and then paint it all over with wax kept molten in a basin, and allow the wax to freeze, taking care to turn the tube round frequently to prevent one-sided accumulation of the wax. After having thus produced a thin uniform coating of wax on the tube, scratch in a millimetre scale, so that the glass is laid bare at the intended marks, taking care that the 20-stroke coincides with the red ink mark made (which is quite distincty visible through the wax); number the scale from the close end downwards, and etch it in with hydrofluoric acid. Gaseous H F gives the more satisfactory scales, the liquid acid is the more convenient agent.* The scale needs not be etched in very deeply, because it is always read with a telescope which magnifies considerably; but this being so, the figures must be very small and stand close to the general scale, each on its projecting centimetre stroke.

For the construction of the scale a screw-engine, so contrived that every revolution of the wheel advances the cutting tool by exactly one or one-half of a millimetre, is by far the most satisfactory apparatus. But such engines are very expensive, and for the mere making of millimetre scales Bunsen's copying engine (if provided with a really correct standard scale) is almost as good. A drawing of it is in Bunsen's book, p. 28 of the second edition; but its construction can be made clear enough by a verbal description. Imagine a table about 2 metres

---

* Both are dangerous substances, which require to be handled cautiously. Ask the Demonstrator to instruct you.

long with a flat semi-circular, or better, roof-shaped gutter running from one end to the other. In this gutter the eudiometer to be graduated is fixed at the right, the standard scale (which is etched pretty deeply into a hard glass tube of about the diameter of a eudiometer, and should have a range of about 800 mms.) at the left end. Both tubes are held fast by means of strips of strong sheet brass screwed to the table, so that their outer edge, which must be exactly rectilinear, is in the middle line of the respective tube. The ruler for the standard scale is a plain straight edge; that for the eudiometer is provided with notches constituting a half-centimetre scale, every second notch being a little longer than the preceding one. The tubes being fixed, an exact copy of the standard scale is produced on the eudiometer by means of a long beam compass. While one foot is made to slide along the straight edge of the standard from mark to mark, the other foot (governed by the right hand) serves to scratch the marks into the wax coating. The standard-foot of the compass should have the shape of a strong but sharply pointed needle, the other that of a hatchet with an oblique edge which *cuts* in the marks *through* the wax instead of scraping them off as a needle would.

To convert his copying into a real dividing engine, good enough for making burette scales or the scales of gas tubes divided into cc., &c., Bunsen has added to it a glass plate bearing a system of etched-in lines so laid down that they all (virtually) pass through the apex of an isosceles triangle, whose base they divide into (say 22) equal parts of convenient length.

The writer has modified the Bunsen dividing engine in the following points:—

The system of lines is on an exactly rectangular plate of plate glass, and so arranged that they constitute a rectangular triangle and divide the lesser cathete of this triangle into 50 or 100 equal parts. The glass plate, when used, lies between two brass rails fixed on the engine table, a brass spring attached to one side of the glass plate causing the other to lie flat against its guiding rail. At a convenient place a flat thin ruler with a bevelled edge goes across the plate from rail to rail; it is held fast by two thumbscrews, in such a way, however, as to admit of slight alterations in the adjustment of the edge in reference to the system of lines. The undivided cathete of the triangle is parallel to the brass guiding rail against which the glass plate is being pressed by the spring. Along it runs a scale of equal parts, so adjusted and figured that it gives the exact length of one degree of the scale produced by the intersection of the bevelled edge with the system of lines. To divide a given length into, say, 10 equal parts, measure it out in millimetres, and divide by 10 to find the exact place where the bevelled edge must go across the system to produce degrees of the intended length. The beam compass is constructed so that, while one foot is fixed, the other can be made to slide forwards and backwards; the final adjustment being effected by means of a micrometer screw governing the respective part. Such beam compasses are to be had in commerce.

The apparatus, to be quite convenient, must be provided with a *number* of glass plates, whose systems of lines overlap and supplement one another. One of the glass plates may bear a plain millimetre scale for the making of millimetre scales, but for the graduation of eudiometers or barometers the original Bunsen contrivance is better.

Let us now return to our subject. The millimetre scale being completed, we proceed to the calibration of our instrument.

Ex. 2.—*Calibration of the Eudiometer.*

In regard to this operation we have little to add to what we said on pp. 180–183.

The thimble for measuring off the equal instalments of mercury is easily made. A sufficient length of stout tubing is closed at one end, a quantity of mercury equal to about 20 mms. of eudiometer space poured in, and the tube cut off at a level with the top of the meniscus. It is then ground down so as to hold very nearly the predetermined quantity of mercury, and fit the ground glass lid *without rocking*. Of course, there is no need of a separate thimble for each eudiometer, but it is useful, in addition to the ordinary ("20 volume") thimble, to have a second which holds *exactly* five times the weight of mercury. The larger thimble enables one to find the points corresponding to 100, 200,......500 volumes promptly and more exactly than would be possible with the smaller one. This being done, a second calibration is made with the small thimble, and the results are discounted for the *subdivision* of the 100-volume intervals. The details of the calculation will easily be found out by the student on a little reflection.

Ex. 3.—*Preparation of a Reduced Volume Scale for the Eudiometer* (*see* pp. 193 and 194).

Our dividing engine enables one to graduate the scale with ease and exactitude.

Ex. 4.—*Making and Calibration of a Bunsen Absorption Tube* (*see* p. 179).

The student, after having made the two gas-tubes, may utilize them for carrying out the first of the following exercises in gas analysis *repeatedly* until he has learned to work them properly. This being done, *our own* students pass to the use of our apparatus.

Ex. 5.—*Calibration of the Measurer in the Author's Apparatus.*

We keep a stock of ready-graduated measurers, so that each student can have one of his own, but he must do the calibration himself. (For the *modus operandi*, *see* pp. 202 and 203).

Gas Analysis.

We presume our own apparatus to be used.

Ex. 6.—*Analysis of a Mixture of Air and Carbonic Acid.*

Fill the measurer about one-third full of pure air, and measure this air exactly; then add some pure carbonic acid, and measure again. In the gas mixture thus produced determine the carbonic acid by absorption with caustic potash solution, in the pipette, and, in the residual air, the oxygen by explosion with hydrogen, as explained above. Compare the percentages found with those demanded by the synthesis. Atmospheric air contains 21·0 per cent. by volume of oxygen.

Ex. 7.—*Analysis of a Mixture of Carbonic Oxide and Carbonic Acid.*

Prepare some of the mixture $CO + CO_2 = 2$ volumes by decomposing oxalic acid with oil of vitriol in a small flask, and analyse the gas thus:—(1) Absorption of the CO_2 by potash, and measuring of the residue; (2) Combustion of the residue with oxygen; (3) Determination of the CO_2 produced in (2), after addition of a measured volume of air to enable one to measure any residue. The theoretical composition is seen in the formula.

Ex. 8.—*Analysis of Marsh Gas.*

To obtain pure marsh gas heat a mixture of 1 part of anhydrous acetate of soda and 4 parts of soda-lime in a combustion tube,* and purify the gas by passing it first through a small U-tube or wash-bottle (either had better have *glass* joints only) charged with bromine, and thence through a U-tube charged with pumice soaked in caustic soda solution. After having expelled the air collect what follows in a mercury gas-holder, and preserve it therein for analysis.

Analyse the gas by combustion, taking care that the mixture to be fired is at about 15 times the volume which the CH_4 in it would occupy at 760 mms., or else you may shatter your exploder.

Calculate the volumes of "carbon vapour" and hydrogen gas per unit volume, and see if the results agree with "CH_4."

Ex. 9.—*Analysis of Ethylene.*

The best method of preparing pure ethylene is Mitscherlich's. It consists in passing vapour of *pure* 85 per cent. alcohol (not of

---

* C. A. Brinley recommends to dissolve 750 grms. of caustic soda and 750 grms. of acetate of soda in 800 cc. of water, and add 1250 grms. of coarsely powdered quick-lime. The mixture is cautiously evaporated into dryness in an iron basin, then powdered coarsely and heated in an iron flask or in a combustion tube. Yield, 125 litres.

methylated spirit) through boiling vitriol so diluted with water that it boils at 165°C.* To free the gas from ether and alcohol vapour, pass it through (1) an empty bottle kept cold in ice, and (2) oil of vitriol. Collect the gas, in the first instance, over boiled-out water alkalinized strongly with KHO in a small Pisani gas-holder. From it transfer it without too much loss of time to a mercury gas-holder or distribute it in tubes trapped by mercury. To make quite sure of the absence of ether and other foreign vapours, treat a quantity in a pipette with ordinary vitriol. Of the gas thus finally purified pass a quantity into the measurer, measure it exactly, and dilute it with air to an exactly known (say twice its original) volume. Analyse this mixture thus:—

(1.) Determine in a portion the ethylene by absorption in fuming oil of vitriol. The kind of crystalline, partly hydrated SO_3, which was referred to in the exercise on Kjeldahl's method, p. 83, is well adapted for the purpose. A measured volume of the gas is transferred to a plain tube of suitable dimensions, and treated therein with a coke-ball soaked in the reagent.

The residual gas (air) is sucked into a pipette charged with caustic potash, to be freed from SO_3 and SO_2 vapours. It is thence transferred to a clean tube, and from it to the measurer.

(2.) After having thus determined the percentage of C_2H_4 in the mixture, and thus indirectly that of the real C_2H_4 in the ethylene used,† measure off a small quantity of the same mixture and subject it to the process of combustion with oxygen.

Take *great* care that the mixture to be fired is at the proper *attenuation*. According to our experience, an expansion into 30 volumes (volume of real C_2H_4 at $760 = 1$) is sufficient.

As long as you are comparatively inexperienced in this operation, better arrange matters so that if the exploder itself should explode you are personally safe.

Determine the contraction and the carbonic acid produced, and in the residue, after absorption of the latter, the oxygen left unburned to obtain the nitrogen.

Compare all your results with the corresponding values

---

* Bulb of the thermometer in the *liquid*.

† With Mitscherlich's method it is not easy to obtain a gas which is quite free of air.

demanded by the synthesis as supplemented by the proximate analysis.

Ex. 10.—*Analysis of a Mixture of* H_2, CO, CH_4, *and* N_2.

Pure carbonic oxide is easily prepared by decomposing a formate with *(not fully)* concentrated sulphuric acid, or else from the $CO + CO_2$ produced from oxalic acid, by removal of the CO_2 in a gas-pipette; nitrogen, by passing purified (CO_2 and H_2O free) air over red-hot metallic copper. From supplies of the pure gases kept shut up over *mercury*, prepare a mixture of them by exact quantitative synthesis, and then analyse the mixture by combustion. The "*attenuation*" for the mixture to be exploded is calculated from the synthesis; if you were quite ignorant of the quantitative composition of your gas, you would naturally try the spark first at the attenuation 15, and then, if necessary, proceed to less volumes. From the values (C, K, $\mathfrak{N}$) found, and the relation $x' + x'' + x''' + x'''' = 1$, calculate these per-unitages, and compare them with those demanded by the synthesis.

Ex. 11.—*Extraction of the Absorbed Gases from a Water, and their Determination.*[*]

Substance.—To obtain a suitable water to operate upon, prepare a supply of perfectly pure water by "torturing" ordinary distilled water with strongly alkaline permanganate, boiling off the ammonia and re-distilling. Place one or two litres of such water in a glass-stoppered bottle of about twice the capacity, and shake it violently with some 20 successive fills of the bottle of (always fresh) normal atmospheric air,[†] taking care to maintain, as nearly as possible, a constant temperature, which is best done by means of a large water bath kept at the temperature of the laboratory, into which bath the bottle is immersed for a sufficient time whenever the contents, when tested with a thermometer

---

[*] We refer to only such waters as derive their gas contents from the normal atmosphere; natural strong absorptions of CO_2, for instance, such as Apollinaris water, &c., demand special methods.

[†] We mean *not* the air of the laboratory.

immersed in them, show a tendency to get too warm. The air is sucked from the open atmosphere through a glass tube passing through a perforation in the window frame into a pair of suction bellows, and thence blown into the air-space of the bottle. At the end of the absorption, note the temperature of the water operated upon and the height of the barometer. For the

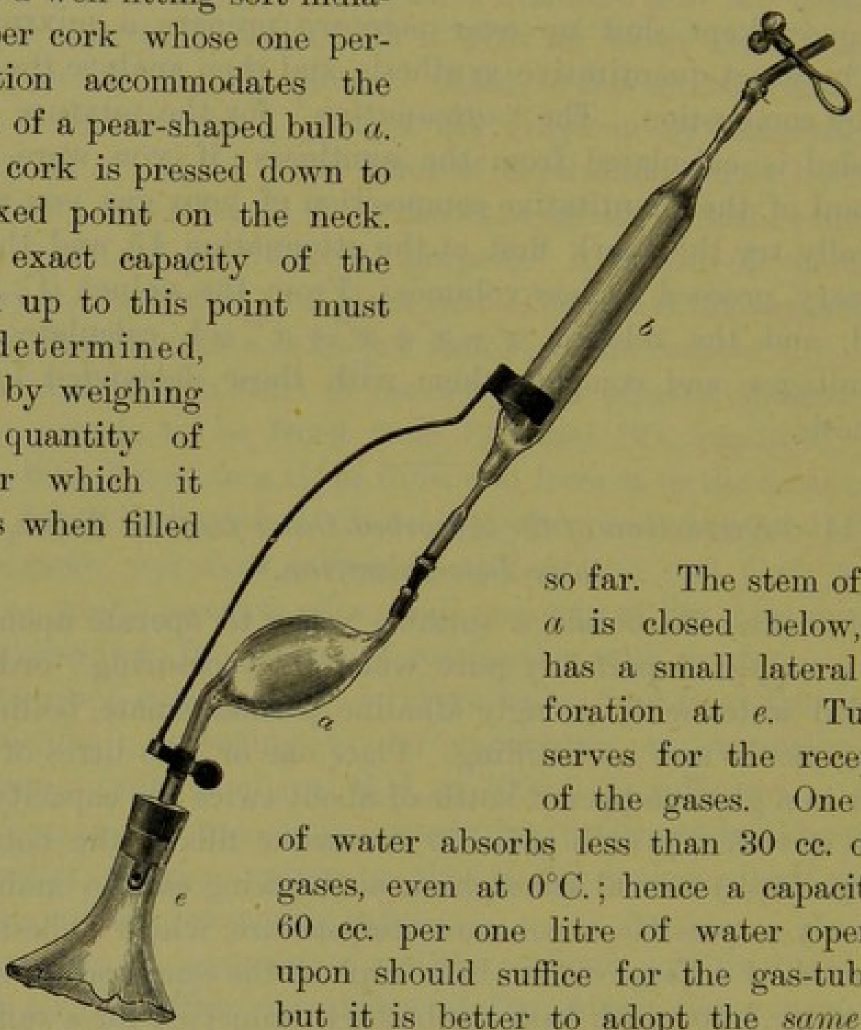


Fig. 56.

Extraction of the gases, Bunsen's method, as modified by Jacobsen, is the best. Jacobsen's apparatus is represented in Fig. 56. A is a globular flask of 700–800 cc.'s capacity, provided with a well-fitting soft india-rubber cork whose one perforation accommodates the stem of a pear-shaped bulb *a*. The cork is pressed down to a fixed point on the neck. The exact capacity of the flask up to this point must be determined, best by weighing the quantity of water which it holds when filled so far. The stem of bulb *a* is closed below, but has a small lateral perforation at *e*. Tube *b* serves for the reception of the gases. One litre of water absorbs less than 30 cc. of air gases, even at 0°C.; hence a capacity of 60 cc. per one litre of water operated upon should suffice for the gas-tube *b*; but it is better to adopt the *same size* (60 cc. about) for a flask of 700–800 cc.'s capacity, as supposed to be represented in the figure. The order of operations is as follows:—The flask is filled with the water to be analysed through a very wide funnel tube, which goes down to its bottom. The water is poured in cautiously so as to avoid the formation of gas-bells, and, when the flask is full, an additional 200 cc. or so are poured in by the funnel and allowed to run over the edge of the flask. The flask having been thus charged to overflowing, the cork is screwed in down to that fixed point, and the stem of the pear-shaped bulb (which has previously been charged with a little pure water) pressed into the perforation of the cork, in such a way, however, that the lateral perforation is *within* the cork. The gas-tube *b* is now joined on by means of a good india-rubber tube secured with wire, and then the air is expelled from the bulbs by heating the water in *a* to boiling and keeping up the ebullition until the air can be assumed to be all away. The bit of india-rubber tube at the end of *b* is now closed with a clip, the lamp withdrawn, and the end of *b* sealed up. The stem of bulb *a* is now pushed down so that the perforation is within the water, and the flask then placed in a heated water-bath, to expel the gases. As there is a strong vacuum in the flask at first, the boiling commences far below 100°C., and as the whole of the gas of the water at 760 mms. pressure would fill less than half the space at its disposal, as long as the gas tube remains sufficiently cool* there is no fear of the pressure within rising beyond that of the atmosphere even at the end. The whole of the operation, indeed, can be conducted without ever raising the temperature of the bath to 100°C.

After 1–2 hours' boiling the gases can be assumed to be expelled, and the next step is to drive the whole of them into bulb *b* and shut them up there. With some practice it is easy, at the end of the operation, to almost completely fill bulb *a* with hot water, so that little gas is *there*. The stem of *a* is then drawn up so as to bring the lateral perforation within the cork,† and the top stratum of water in *a* kept boiling for a while so as to drive the gases into *b*, which is then closed by pinching the indiarubber tube which connects it with *a* — the lamp, of course, being removed immediately after. Should a little water have gathered in *b*, this is easily let down into *a*

---

* This condition almost takes care of itself.

† If a naked flame is used instead of a water-bath, this flame of course must be removed immediately afterwards.

by cautiously opening the screw clip at the joint for a few moments, until the water is just sucked down.

The gas tube is now detached, and its lower end sealed up to bring the gas into a condition in which it may be preserved unchanged for any time. For its

Measurement it is transferred first to a plain tube in Bunsen's trough (*see* p. 183). It is then sucked into the measurer and measured. The results are reduced to cc., measured dry at 0° and 760 mms. pressure, and referred finally to 1000 cc. of water analysed.

For the reduction to 0° Bunsen's table of the logarithms of $(1+at)$ comes in handy; if it is not at hand calculate thus:—

$$\frac{V(P-\pi)}{(273+t)} \times \left\{ \frac{273}{760} = 0{\cdot}359\ 211 \right\}$$
$$\text{Log. } 0{\cdot}359211 = 0{\cdot}555\ 349 - 1,$$

or, to put it into an easily remembered form: reduce to 1000 mms. pressure and 359°·2* absolute temperature.

Analysis.—The carbonic acid is absorbed by solution of caustic potash in the pipette, and determined by re-measuring the residue. The latter is divided into two parts for *two* determinations of the oxygen by explosion with hydrogen. In calculating the latter, remember that water-air contains some 33 per cent. of oxygen, not 21, as ordinary air does. For 100 volumes of gas to be analysed add some 80 volumes of hydrogen, and as the knallgas is certainly less than 3×40 volumes, but not much less, an expansion into $3{\cdot}3 \times 120 = 400$ volumes before firing will work well.

Finally, compare your results, for the absolute composition of the air, in 1000 cc. of water analysed, with the values calculated from the co-efficients of absorption and the barometric pressure at the saturation of the water with air, and the law of gas absorption. The proportion of carbonic acid in ordinary air (as taken from, for instance, a Glasgow street) may rise to 0·05 per cent. by volume instead of the normal value of 0·03; but this does not disturb the percentages of oxygen and nitrogen in the carbonic acid free part of the absorbed air. Consult Dittmar's "Tables to facilitate," &c., 2nd edition, pp. 41–43.

---

* 359 = number of degrees in the circle *minus* 1, for mnemonic purposes.

PROMISCUOUS EXERCISES IN APPLIED ANALYSIS.

1.—Analysis of a Sea Water.*

Preliminary Note.—The results of a sea water analysis should be given in two ways, namely: (1) in reference to 1000 grms. of the sea water; and (2) in reference to 100 grms. of chlorine, meaning total halogen, determined titrimetrically by silver, and calculated as chlorine. The several samples of sea water required for the determinations should be measured off in pipettes, but weighed exactly immediately afterwards. The *weight* of the sample enters the final calculation. In the sequel, "Take *n* cc." means, *weigh* out a quantity equal to *n* cc., by pipette measurement.

CHLORINE.

Memoir, p. 4.

I. For an approximation, Mohr's method is very convenient. *Requirements:*—(1) Neutral silver solution, prepared by dissolving 17 grms. of pure fused nitrate of silver in water, and diluting to 1000 cc. (2) A solution of chromate of potash K_2CrO_4, containing 5 grms. of the salt per 100 cc.

To analyse a sea water, take 5 cc., add a few drops of chromate solution, and then, from the burette, nitrate of silver solution until the red colour of chromate of silver, which appears transitorily from the first, becomes permanent on stirring. Every 1 cc. of solution used indicates $1/10$ $Cl = 3{\cdot}545$ mgs. of chlorine, very nearly. A far more exact result is obtained if the silver

---

* Mostly abridged from Dittmar's Report on the Composition of Ocean Water, in "Report on the Scientific Results of the voyage of H.M.S. *Challenger*," by Sir C. Wyville Thomson, Knt., F.R.S., &c., and John Murray, F.R.S.E.; "Physics and Chemistry," vol. i. To be referred to as "Memoir,"

solution is standardized empirically with a sea water whose chlorine has been previously determined with high precision, and the rule be followed in both the standardization and analyses to maintain constant ratios between the total silver solution used on the one hand, and the total volume of sea water and reagents at the end, and also the volume of chromate added as an indicator, on the other. That a certain depth of redness must be adhered to, as indicating the "end" of the reaction, stands to reason. Taking S as a symbol for the volume of total silver solution required, and M as that of the final volume of the mixture, the relation $M = 1{\cdot}25\ S$ can be maintained in all cases by addition of water; of course, M needs not to be measured with high precision.

II. *Exact method* (Volhard's modified). *Requirements*:—(1) Perfectly pure chloride of potassium. Prepare pure perchlorate, and heat the salt in a platinum basin until the oxygen is apparently gone. Then fuse the residue in a platinum crucible, and keep it in fusion until every trace of oxygen is sure to be away. The salt then may contain a little surplus alkali. Therefore, dissolve the fuse in water, add a few drops of pure hydrochloric acid, and evaporate in platinum (or Berlin porcelain, which is almost as good) to perfect dryness. Next, keep the dry salt in a crucible, close to but below its fusing-point, until the water may be presumed to be expelled. Now, powder the salt coarsely, and resume heating until the weight is constant. Preserve the salt in a good preparation-tube or bottle; but before having kept it long, prepare from it a

(2) *Standard solution of Chloride of Potassium*, by dissolving $1/10\ KCl = 7{\cdot}459$ grms. in a tared litre-flask in water, and diluting to 1000 cc., thus:—After having added about 0·9 of the water, mix by rotating, then fill up to the mark, determine the *exact weight* of the solution, and only then mix by shaking. Note down that $1/10$ KCl grms. = for instance, 1006·3 grms.* = (by intention to) 1000 cc.

(3) *A Solution of Nitrate of Silver*, containing, as nearly as possible, $1/10\ Ag = 10{\cdot}793$ grms. of silver per 1000 cc., besides about 20 cc. of free nitric acid of 1·4 spec. grav. (See below.)

---

* We mean the weight of the "1 litre" of solution, as found.

(4) *A Weaker Solution of Nitrate of Silver*, containing 1/100 Ag = 1·0793 grms. of silver (and 2 cc. of 1·4 nitric acid) per litre. If an exactly standardized supply of solution (3) is not at hand, this solution is best made by direct synthesis from weighed pure silver.

(5) *A Weak Solution of Sulphocyanate of Ammonium*, containing 1/100 NCS grms. per litre in this sense, that, under the circumstances which prevail when it is used, it just saturates solution (4) volume for volume. This point must, of course, be made sure of by repeated direct trials.

(6) *Solution of Iron Alum.*—50 grms. of iron-ammonia-alum, 20 cc. of 60 per cent. sulphuric acid, and enough of water to produce about 1 lit. of solution.

Note.—Make sure that neither silver solution contains *nitrous* acid, and that both the sulphocyanate and the iron alum are free from chloride. To test the sulphocyanate, precipitate a sample completely with nitrate of silver, wash the precipitate by decantation, and heat it (in a draught place) with concentrated sulphuric acid and a little water until the visible reaction is at an end. Then allow to cool, and pour into much water. If chlorine is present, a milky opalescence will appear.

The Standard Silver Solution.—Its preparation is easy. We dissolve 1/10 $AgNO_3$ = 17 grms. of pure fused nitrate in water, add 20 cc. of 1·4 nitric acid, and dilute to 1 litre. Or else we dissolve 1/10 Ag grms. of metallic silver in 29 cc. of 1·4 nitric acid, previously diluted to double its volume, and dilute to 1000 cc. As the solution must be standardized with the chloride of potassium solution in any case, *absolutely* pure nitrate or metal need not be used. To determine the exact titre both by weight and by volume, tare a 200 cc. phial, and weigh into it, first, 50 cc. of the standard chloride of potassium, and then 50 cc. + an additional 1 cc.—all exactly measured—of the silver solution; shake violently, and allow the mixture to stand in the dark until the precipitate has settled so completely that (practically) the whole of the supernatant liquor can be decanted off clear into a beaker.* Do so, and determine the small remnant of

---

* A little reflection will show whether or not it is worth while to allow for the dissolved silver remaining in the phial as part of a moist precipitate.

dissolved silver by adding 5 cc. of iron alum, and then weak sulphocyanate out of a burette until the mixture becomes distinctly red. With the help of the weak silver solution determine the end point several times by to-and-fro titration, and take the mean of the last 3–4 results, which ought to agree with their mean to within 1/20 cc. If everything was well done, far less excess of silver solution than 1 cc. will be sufficient to make sure of the existence of a remnant of dissolved silver at the end, so that, in a second and third trial with 50 cc. of KCl, 50·1 cc. of strong silver or 50 cc. of strong *plus* 1 cc. of the centesimal solution will do.

Should it be the case that the first few drops of sulphocyanate strike a red tint, do not take it for granted that you have hit the point, but add a measured sufficiency of the weak silver solution, pour the whole back into the phial, shake up, allow it to settle, &c. The volumes of added reagents must, of course, be noted down and allowed for in the calculation.

From the mean of a number of well-agreeing experiments, calculate the *volume-titre* and the *weight-titre* thus:—Supposing 50 cc. of chloride solution to have required 50 cc. of silver and 3·2 cc. of weak NCS solution, the excess of silver obviously is = 0·32 cc. of strong solution, and 49·68 cc. of silver solution are equivalent to 50 cc. of chloride solution = by intention to 50 × 1/10 Cl mgs. It is better, however, to base the calculation upon the *dry* KCl as calculated from the weight of the 50 cc. and the weight of 1 litre of chloride solution as ascertained in its preparation. But the silver solution itself is intended to be measured by *weight* in the analyses. To calculate the *weight-titre* we reduce the 0·32 cc. of excess of strong silver solution found in the titration to weight by multiplying by 1·024 (which is a good enough approximation to the specific gravity; in the present case this produces practically no change), deduct the result from the weight of silver solution used, and put down the rest (call it S grms.) as representing the equivalent to the C grms. of real chloride of potassium used as 50 cc. of solution. We then have

C grms. of chloride of potassium = S grms. of silver solution.

$$\therefore 7{\cdot}459 \quad \text{,,} \qquad \text{,,} \quad = \frac{S \times 7{\cdot}459}{C} = W.$$

Note down that W grms. of silver (=to so-and-so many cc. as calculated before) precipitate 1/10 Cl=3·545 grms. of chlorine. (W comes to about 1025.)

For the analysis of a sea water, determine the chlorine first in 5 cc. by method I. (Mohr's) as an approximation, then twice in 10 cc. (weighed) by method II. in its gravimetric form. The burette serves only to measure out the proper quantum of silver solution as calculated from the preliminary analysis. Report in terms of 1000 parts by *weight* of sea water analysed.

Appendix.—If a large number of sea waters has to be analysed for chlorine, it is convenient to prepare the (strong) silver solution on a large scale, not merely to save trouble, but chiefly to avoid the loss of precision necessarily involved in the successive use of different standard solutions in different analyses. The method of preparation we used in the course of the "Challenger" research was as follows:—A supply of the purest nitrate of silver was reduced to powder, mixed, and standardized by keeping a known weight of about 10 grms. of salt in a tared crucible near its fusing point, then fusing, allowing to cool, and weighing the dry residue. From the result it was easy to calculate the quantity required for (let us say) 40 litres of solution. But such a large volume as 40 litres is difficult to measure *in toto*, and the volume of water (or rather very dilute nitric acid, 20 cc. of 1·4 acid per litre) required cannot be calculated. A near guess at the required volume, however, is easily made. Supposing the salt (weighing about 680 grms.) to be dissolved in 39 lit. of solvent, the solution produced will amount to 39 lit. + about 680 ÷ 4·35 = 156 cc., say 39·16 lit., so 0·84 lit. of solvent should complete the 40 lit. To be on the safe side we add only (say) 0·4 lit., and after having mixed the whole by blowing (dust-free) air through it, proceed to analyse a measured small volume somehow. As "tenth-normal" sulphocyanate is always at hand, the simplest method is to apply Volhard's method (*see* Ex. 13) to, say, 50 cc.; but, to obtain the highest precision, it is better to measure the sulphocyanate by *weight*, which is done by delivering it from a kind of ungraduated Mohr's burette, made out of a *wide* glass tube, so that the burette becomes short enough to be suspended from, and tared on, a fine balance. The solution is standardized expressly with, say, ½ grm. of directly weighed metallic silver, which gives its titre per 1 grm., and then applied to the silver solution in hand. Supposing we find that the silver solution contains 1·017 times the intended weight of silver per litre, our 40 litres (or what it may be now, say V lit.) have to be diluted to 1·017 × V by addition of 0·017 V of water, or better, say 0.015 V to keep on the safe side. The final correction is made on the basis of a series of titrations with 50 cc. (weighed) of standard chloride of potassium solution by our method II., as above described.

Lime and Magnesia.

Memoir, p. 32.

Weigh out 500 cc. of sea water, add 15 cc. of 20 per cent. hydrochloric acid, and boil for fifteen minutes to expel the carbonic acid. Then allow to cool, supersaturate the acid by addition of 100 cc. 10 per cent. of ammonia, then add 180 cc. of oxalate of ammonia (1 cc. = 11·2 mgs. of CaO), and allow to stand cold over two nights. Then filter off the precipitate, wash it first with cold, then with hot, water, dry, and ignite. This precipitate, apart from any remnant of carbonic acid, contains about 9 per cent. of impurities, chiefly soda, also magnesia. To purify the crude lime, slake it in a beaker with water, add 5 cc. of hydrochloric acid, boil away the carbonic acid, allow to cool, add ammonia drop by drop until alkaline, and then boil off the excess of ammonia to bring down the sesquioxides, which collect, wash hot, re-dissolve in 2 cc. of hydrochloric acid, and re-precipitate by ammonia, boiling off the excess of the latter as before. Filter off the precipitate (it amounts to 1–2 mgs.), and to the united filtrates add 20 cc. of ammonia and 40 cc. of oxalate of ammonia, to re-precipitate the lime in the cold. Allow to stand over night, then heat the mixture on a water-bath, filter off the oxalate, and ignite it in a small platinum crucible as usual, using the blow-pipe for finishing, until the weight is rigorously constant.

To determine the *magnesia*, mix all the lime filtrates and wash-waters, and weigh them on a large precision balance. Take about one-tenth of the whole, weigh it, add 20 cc. of 10 per cent. ammonia and 12 cc. of phosphate of ammonia

(1 cc. = 20 mgs. of MgO), and allow to stand for at least twelve hours. Filter off the phosphate of ammonia and magnesia, wash it with 3 per cent. ammonia, dry, ignite, and weigh. The most exact mode of manipulating the filter is, after removal of the bulk of the precipitate, to re-place it in the funnel and dissolve off the adhering precipitate by means of the least sufficient quantity of dilute acetic, strengthened by a little nitric acid, to evaporate filtrate and wash-water in a tared crucible to dryness, and ignite the residue. The bulk of the precipitate is then added, ignited till constant, and weighed.

The Potash.

Memoir, pp. 12 and 234.

Since the completion of the "Challenger" analyses, the Author, conjointly with Mr. John M'Arthur, has made an extensive critical research in the Finkener method of potash determination, and on the basis of this work we now recommend the following form of the Finkener process for the analysis of sea water (or similar) salts.

Take 100 cc. of sea water, add a volume of standardized sulphuric acid equivalent by calculation to the chlorine, as determined, for instance, by Mohr's method (supposing 10 cc. of sea water had required 60 cc. of silver solution containing 60 × Ag/10 mgs., 100 cc. obviously demand 60 × 40 mgs. of sulphuric acid calculated as SO_3), and double the calculated volume of chloroplatinic acid solution (*i.e.*, for normal sea water 200 mgs. of platinum Pt). Evaporate on a water-bath—towards the end with constant stirring—to a very small volume, and stir diligently while this cools down to prevent formation of large crystals. Then add 30 cc. of absolute alcohol, and, after half an hour's standing, 15 cc. of absolute ether.* Mix well, and allow to stand, best on a glass plate under a small bell-jar with ground edges, for two hours. (According to our experience, with potash salts generally, five minutes' standing with the alcohol and about half an hour's with it and the ether should suffice, but we have so far not had occasion to apply this modification to *sea water* at all extensively). Filter off, and wash with ether-alcohol as

---

* Make sure that both the ether and alcohol are free from ammonia.

usual (*see* Ex. 15, p. 27). The precipitate always includes some foreign chloroplatinates. To remove these, give the salts a final wash with plain ether, and allow the remnant of this to dry off in the air; then re-dissolve in hot water, again evaporate to a very small volume, and re-precipitate with ether-alcohol as before. The thus purified precipitate is washed, freed from at least the *ether* by drying at a gentle heat, transferred with 150 cc. of hot water to an Erlenmeyer flask of 400–500 cc. capacity, and the platinum precipitated by hydrogen, as explained in Ex. 15.

According to our experiments, the weight of platinum obtained if multiplied by 0·751 gives, *in cases like the present*, a close approximation to the weight of potassium sought, calculated as KCl; hence the factor 0·4744 gives the potash K_2O. (The factor $K_2O : Pt$ calculated from the present atomic weights ($Pt = 194·8$; $O = 16$) is 0·48386).

TOTAL (BASES AS) SULPHATES.

Memoir, p. 17.

Weigh out 20 cc. of sea water, add a quantity of standard 20 per cent. sulphuric acid *barely* equivalent to the chlorine (see "Potash"), and evaporate to dryness in a flat platinum crucible of about 25 cc. capacity, provided with a perforated lid and a shield under the perforation, as represented by Fig. 57. The evaporation is conducted on an air bath, with the lid off, until the residue is nearly dry. In order now to expel the remnant of volatiles, put on the perforated lid, and a large piece of platinum foil over the latter, and let a large Bunsen flame play down on the foil so that the mass is heated chiefly from above. Towards the end the heat from below may be increased. When visible vapours have ceased to come off, heat the still covered crucible over a naked flame to redness for a time, allow to cool, and weigh. Then moisten with a *little* of the acid and water so that a small excess of sulphuric acid is sure to be present, evaporate, ignite again, and weigh this residue. If vapours of SO_3 were seen to go off, the chlorine is sure to be all away, and all that is necessary is to finish by repeated ignition until the weight is constant.

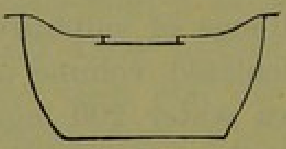


FIG. 57.

Take care not to use an excessive heat; on the other hand, make sure that the aqueous solution of the residue is neutral to litmus. From the "total sulphates," subtract the lime, magnesia, and potash, all calculated as sulphates; the rest gives the sulphate of soda, and thus the soda independently of the determination of the chlorine, sulphuric acid, and carbonic acid.

After having thus determined the principal components, check your results by expressing the bases and the acids found per 1000 parts as multiples of Cl_2, SO_3, Na_2O, K_2O, CaO, MgO respectively, and balance the number of base-equivalents against that of the acid-equivalents. There should be a *small* excess of base, some 0·001 × R_2O, about per 1000 parts of sea water.

THE CARBONIC ACID.

Memoir, p. 107.

Method. — From 1 lit. of sea water the carbonic acid is eliminated by boiling with excess of sulphuric acid in a flask under an inverted condenser, and collected in a vacuous vessel previously charged with a measured (excessive) volume of standard baryta-water. The excess of unprecipitated baryta left is determined by titration with standard hydrochloric acid, and from the results the carbonic acid is calculated.

The *apparatus* is represented in Fig. 58. *C* is a Pisani gas-holder containing air free of carbonic acid (only one of the two bottles is shown in the figure). To prepare it, almost empty one bottle into the other, clip the connecting india-rubber tube, drop a stick of caustic potash into the small remnant of water left, put on your hand, or the india-rubber cork with glass rods instead of the tubes in the perforations, and shake vigorously for two or three minutes. All the carbonic acid is absorbed. The rest follows from the inscriptions on the figure.

Reagents—1. *Decinormal Hydrochloric Acid.*—Distil *pure* acid of 1·1 spec. grav., collecting only the middle portion, which is free from carbonic and sulphurous acids, &c., on the one hand, and ammonia on the other. Dilute it to a strength convenient for its acidimetric analysis (with standard alkali), and from the thus standardized acid prepare one which contains, say, 1·01 times 1/10 HCl grms. per litre. Determine its exact strength by silver, exactly as shown under "Chlorine," method II.; make it as exactly as possible volumetrically decinormal, and record both the *volume-titre* and the *weight-titre*.

2. *Decinormal Baryta Water.*—15·75 grms. of pure $Ba(OH)_2 + 8H_2O$ should give 1 litre of decinormal solution. To allow for the carbonate, dissolve $n \times 17$ grms. in hot (distilled) water, filter, and dilute with boiled-out water to about n litres in a large bolthead. To determine the strength of the solution, measure off from a burette, say, 30 cc. of the acid, add a few drops of turmeric tincture, and then run in (from another burette protected by a soda-lime tube) the baryta solution until the liquid becomes brown; then again, drop by drop of the acid until the liquid just becomes clear light yellow. After the result of such tests, dilute

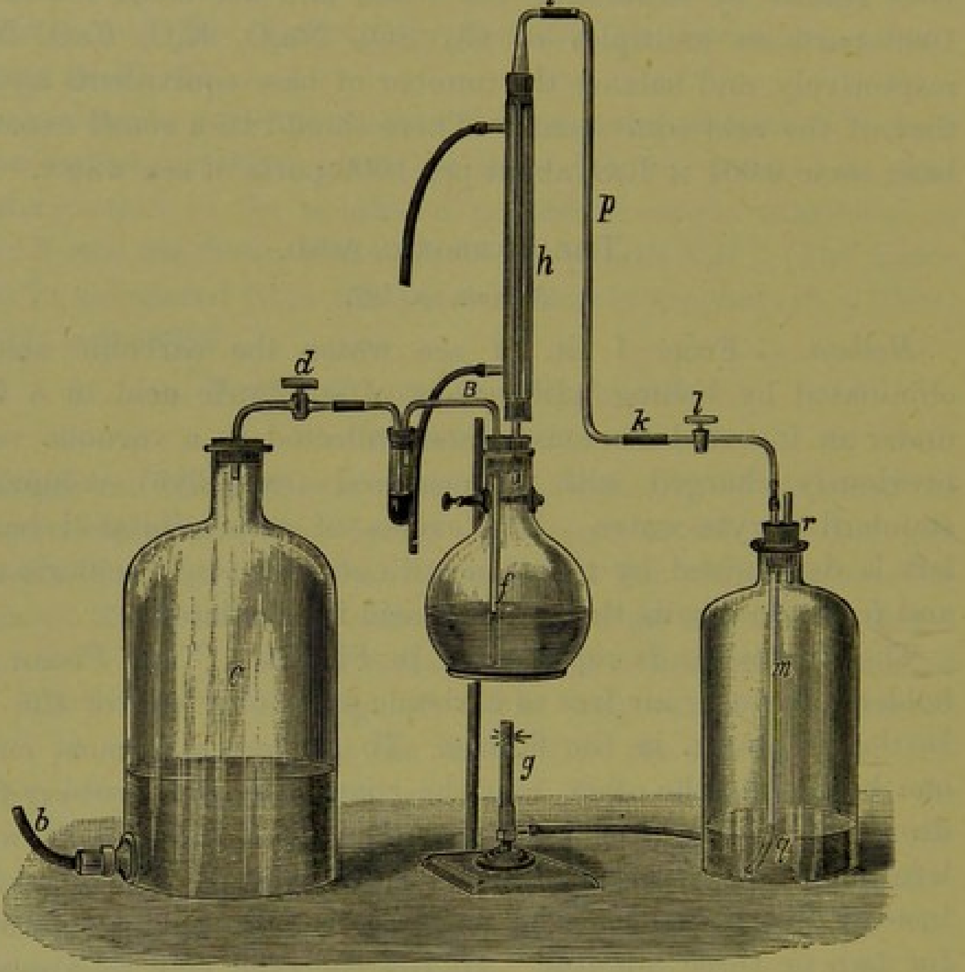


FIG. 58.

Between *d* and B, mercury trap ; *f*, decomposition flask ; *h*, inverted condenser ; *b*, india-rubber tube ; *r*, india-rubber cork ; *m*, vacuum flask ; *q*, baryta-water.

the baryta so that it contains about 1·01 times as much baryta per litre as it is intended to. Then transfer the solution to Winchesters; the one to be used more directly must be provided with a syphon with a Mohr's clip at the end, and with a protecting soda-lime tube. Allow the solution to clear up completely in this Winchester, and then determine its titre *finally* by *weighing* out, say, 100 cc. of the acid, and thus indirectly the exact weight of real acid, HCl, present in the 100 cc. according to the weight-titre, and titrating as before. But the bulk of the baryta had better be measured in a pipette. The best kind of pipette for this purpose is one constructed on Stas' principle (*see* Fig. 59). The pipette delivers a known volume (50 to 60 cc.) when completely filled from below to overflowing, and then allowed to run out spontaneously, the last drop being removed as far as possible by short contact of the lower end with the wet side of the receiving vessel. The last instalment of acid and baryta are added from burettes graduated so that they give the tenths directly, and that 0·02 cc. is very plainly visible.

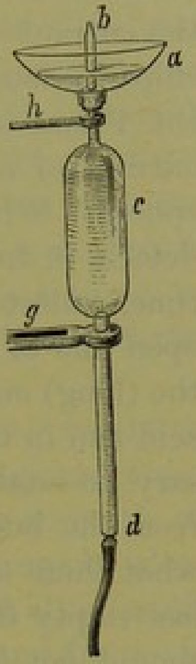


FIG. 59.

The Analysis.—To obtain a really exact result we must operate upon a *whole litre* of sea water, which may be presumed, in general, to contain less than 110 mgs. $= 5 \times \frac{1}{2}CO_2$ mgs. (per litre), corresponding to less than 50 cc. of the baryta water. But we must start with a decided excess, so that the Stas' pipette had better be adjusted to about 60 cc. To prepare the vacuum flask, wash it first with some ordinary baryta water, and then with water. Then exhaust it at the air-pump,* and fill it with (purified) air from out of the Pisani. It is now ready to receive its baryta water, and be evacuated for the analysis. The sea water is measured into the flask with the least amount of shaking, then mixed with 5 cc. of 20 per cent. sulphuric acid (which is ample), and immediately connected with the condenser, and through the latter with the vacuum flask, the stopcock of which

---

* When you exhaust a flask for the first time, it is as well to place it within a box, or wrap it up in a towel, and see that it does not collapse. Bolt-heads sometimes are very thin in the body. Bottles as a rule stand better.

is turned on cautiously, so as to establish a slow current of air. The contents are now brought up to the boil, and kept boiling for about twenty minutes, when all the carbonic acid can be assumed to be eliminated. The liquid then is allowed to cool; the current of air is made a little faster, and continued until it stops by itself. During the whole of the process the pressure in the Pisani should be a little short of that which produces a current of air when the pressure in the flask is at one atmosphere. When the vacuum is undone, close the vacuum flask, detach it from the apparatus, and by making it rotate for a time, collect all the stray carbonic acid in the baryta. Then open one of the two perforations, run in some turmeric, insert the (long) outlet tube of the hydrochloric acid burette, and let acid run in until the alkaline reaction is almost gone. If necessary, re-establish a decidedly alkaline reaction by adding baryta from the burette. Now, close the flask again, and again collect what there may be of liberated carbonic acid in the flask. At last empty the contents into a tared Erlenmeyer or phial, which should not be larger than necessary; put on a good cork, and allow the mixture to stand until the precipitate has settled. Weigh the mixture to $\pm$ 0·1 grm., pour off as much as possible of the clear liquor, determine its weight, and finish your titration by the zig-zag mode.

The calculation requires no explanation.

Do not rely on the constancy of the titre of the *baryta;* it diminishes gradually, all protection tubes notwithstanding.

Note.—Before operating on the sea water, rehearse the method with 1 litre of boiled-out distilled water, *plus* a suitable weight of pure carbonate of soda.

ALKALINITY.

Memoir, p. 106.

All sea water is *alkaline*, in this sense that the sulphuric and hydrochloric acids do not quite suffice to neutralize the bases. The surplus base is present as a mixture of carbonate R_2CO_3 and bicarbonate $RHCO_3$, and therefore, for calculating purposes, can be represented as consisting of $xR_2CO_3 + yCO_2$; *i.e.*, so much normal carbonate *plus* so much "loose carbonic acid." "Alkalinity," in a quantitative sense, is customarily defined as meaning the weight of carbonic acid present in the normal-carbonate part of the carbonate. It is referred customarily either to 1 litre of sea water or to 100 parts of total salts or to 100 parts of *chlorine*. For its determination Tornoe has given the following method:—

Requirements.—(1.) A dilute hydrochloric acid so standardized that 1 cc. contains 1/22 HCl mgs., and consequently corresponds to 1 mg. of carbonic acid (CO_2). 22 cc. of such acid contain 1 mg. equivalent of hydrochloric acid, or as much as 10 cc. of the decinormal acid. (*See* "Carbonic Acid.") Hence, ten volumes of the latter diluted with water to 22 volumes or 454·5 cc. (better the *weight* of decinormal acid containing by silver titration 45·45 × HCl mgs.), diluted to 1000 cc., gives standard acid of the required strength.

(2.) *A Solution of Pure Carbonic Acid-free Potash,* exactly or nearly equivalent to the acid, volume by volume, prepared from recently causticised pure alkali. To determine the strength of the alkali take, say, 40 cc. of the acid, add a few drops of alcoholic *aurine* solution, heat in a Berlin basin, and add alkali until the *violet* colour appears and remains. Use the to-and-fro mode of titration, and from the mean of the last 3–4 results (which should agree very closely) calculate that 1 cc. of alkali $= k$ cc. of the acid, *i.e.*, corresponds to k mgs. of CO_2.

To analyse a sea water, measure off 250 cc. in a Berlin (or silver or platinum) basin; glass is not safe. Add an excess of the acid and aurine, boil for fifteen minutes to expel all the carbonic acid, and titrate back with alkali, using the to-and-fro method.

Note.—Ordinary good lime water is stronger than the above standard alkali, and could probably be substituted for it without loss of precision. The greater basilousness of the potash is no advantage, because the end-reaction in any case is brought about by the magnesia of the sea water.

If there is enough of sea water, take 500 cc. of it for the analysis, and use *decinormal* hydrochloric acid and (standardized) lime water as reagents.

TOTAL SALTS.—*Tornoe's Method.*

Memoir, p. 40.

Evaporate 30–40 cc. of sea water to dryness in a large (tared) porcelain crucible, provided with a good lid, over a water-bath.

Then put on the lid, and heat over a Bunsen for about five minutes, allow to cool in an exsiccator, and weigh. The weight, however, requires a correction, because, in the last stages of the evaporation, and especially in the ignition, part of the chloride of magnesium (by the action of water) becomes magnesia. To determine this magnesia, dissolve the residue in water (in a Berlin basin) along with a sufficiency of decinormal hydrochloric acid, add aurine, heat to boiling, and titrate back with standardized lime water or alkali. Supposing the magnesia was found equivalent to 31 cc. of decinormal acid, deduct the small volume corresponding to the original alkalinity, which will bring down the number to, let us say, 30 cc.; then the magnesia produced in the dehydration amounts to

$m = 30 \times 1/20 \times MgO$ mgs., and the original chloride to
$c = 30 \times 1/20 \times MgCl_2$ mgs.; hence we have to add
$1{\cdot}5 \times (MgCl_2 - MgO) = 1{\cdot}5 \times (Cl_2 - O)$ mgs., or
$1{\cdot}5 \times 54{\cdot}9 = 82{\cdot}4$ mgs. to obtain the *total salts, exclusive of all carbonic acid.* The result affords a valuable check for the sum total of SO_3, $(Cl_2 - O)$, and bases as determined separately.

Note.—It still remains to be ascertained how much of the hydrochloric acid which goes off in the dehydration is *hydrobromic acid.*

THE BROMINE.

Memoir, pp. 98 and 239.

Weigh out 1 kilogrm. of sea water, and add four hundredths of the quantity of decinormal (acid) silver solution, which, according to the chlorine determination, would bring down all the halogen.* Shake vigorously in a Florence flask or clear-coloured bottle, allow to settle in the dark, syphon off the liquor as clear as possible, and to it add the same volume of silver solution as you used for the first precipitation. The two precipitates are wrought separately, but in the same manner. Wash by decantation with water, and collect the washings in a wide-necked bolthead. They are allowed to stand until the small turbidity has settled completely. The supernatant liquor is then

---

* There is, of course, no need of wasting precisely standardized silver for this. 17 grms. of fused nitrate + 20 cc. of 1·4 nitric acid dissolved to 1 litre will do.

syphoned off clear, the precipitate from the washings collected on a filter, and treated like an ordinary chloride of silver precipitate; to be weighed as AgCl.

The principal precipitate is transferred to a Berlin basin, and dried over a water-bath in the dark. The dried precipitate is then transferred to a large porcelain boat which has been previously tared within, and along with a piece of combustion tubing about two inches longer than the boat itself. Within the tube the dehydration of the haloid is effected by embedding it in magnesia in the gutter of a short combustion furnace, and cautiously heating it to fusion in a current of dry air. After cooling, the outside of the tube is cleaned of adhering magnesia and weighed. The tube is then re-placed in the magnesia bed over the furnace, and the haloid fused and kept at fusion heat in a current of dry chlorine until the bromine appears to be away. The gas is then turned off, the chlorine displaced by dry air, and the (cold) tube weighed again. The chlorination is repeated until the weight of the resulting chloride is constant. There must be no cork at the combustion tube; the chlorine (and air) are led in by a bit of drawn out combustion tubing, the wide end of which *almost* fits into the combustion tube like a piston. As there is no surplus pressure to overcome, the joint needs not be air tight. From the loss which the haloid suffered in the chlorination, the bromine is calculated. As AgBr yields AgCl, every (Br − Cl) parts of loss correspond to Br parts of bromine.

$$(\mathrm{Br}-\mathrm{Cl})\times 1{\cdot}79675=\mathrm{Br} \text{ and } (\mathrm{Br}-\mathrm{Cl})\times 4{\cdot}2225=\mathrm{AgBr}.$$

As in a given haloid precipitate the loss involved in the chlorination (l) is proportional to the ultimately obtained chloride of silver (c), it is easy to see how we allow for the small weight of stray haloid filtered off and weighed as chloride. Obviously (its weight) $\times \frac{l}{c}$ is the correction to be added on to the loss suffered by the bulk of the precipitate.

After having determined the bromine, we are in a position to calculate the *true* chlorine from the *chlorine* determined, as shown in the first section. As we determined the chlorine by titration, the number of gramme equivalents of chlorine found, *minus* the number of grm. equivalents of bromine found, per kilo., gives the true chlorine.

AVERAGE COMPOSITION OF OCEAN-WATER SALTS.

Memoir, pp. 137 and 138; also pp. 203 and 204.

	Per 100 parts of Total Salts.	Per 100 of Halogen calculated as Chlorine.	
	Dittmar.	Dittmar.	Forchhammer.
Chlorine, ...	55·292 *	99·848	Not determined.
Bromine, ...	0.1884	0·3402	Not determined.
Sulphuric Acid, SO_3, . .	6·410	11·576	11·88
Carbonic Acid, CO_2, . .	0·152	0·2742	Not determined.
Lime, CaO, ...	1·676	3·026	2·93
Magnesia, MgO, ...	6·209	11·212	11·03
Potash, K_2O, ...	1·332	2·405	1·93
Soda, Na_2O, ...	41·234	74·462	Not determined.
(Basic Oxygen equivalent to the Halogens), . .	(–12·493)	...	...
TOTAL SALTS, . . .	100·000	180·584	181·1

---

* Equal conjointly to 55·376 parts of chlorine, which accordingly is the percentage of "halogen reckoned as chlorine" in the *real* total solids.

Combining acids and bases, we have (Dittmar)—

Chloride of Sodium, ...	77·758
Chloride of Magnesium, ...	10·878
Sulphate of Magnesium, ...	4·737
Sulphate of Lime, ...	3·600
Sulphate of Potash, ...	2·465
Bromide of Magnesium, ...	0·217
Carbonate of Lime, ...	0·345
Total Salts, ...	100·000

In the open ocean the quantities of bromine, sulphuric acid, magnesia, potash, and soda, per 100 of chlorine, are almost constant; that of the lime is subject to slight, that of the carbonic acid to very tangible, variation. The loose carbonic acid (not reported in this table) is eminently variable.

The weight of salts per kilo. varies from about 33·7 to 37·6 grms. The following

Table gives the specific gravity of sea water at 15·56°C. = 60°F. (*water of* 4°C. = 1000); *and the weight of* "Chlorine," *in grammes per litre: in function of the weight of* "Chlorine," *in grammes per kilogramme*:—

"Chlorine" grms. per		Diff.	Specific Gravity.	Diff.
Kilo.	Litre.			
17·0	17·386		1022·68	
17·5	17·909	·523	23·38	·70
18·0	18·433	·524	24·07	·69
18·5	18·958	·525	24·76	·69
19·0	19·484	·526	25·46	·70
19·5	20·010	·526	26·15	·69
20·0	20·536	·526	26·85	·70
20·5	21·064	·528	27·54	·69
21·0	21·593	·529	28·24	·70

Abridged from tables in *Memoir*, p. 81.

2.—Stassfurth Potash Salts.

(Commercial chloride of potassium, kainite, carnallite, &c.)

MAKE a standard substance-solution containing, say, 20 grms. of substance in 200 cc., but standardized by weight as well as by volume for greater precision in the fractionations. The insolubles are collected on a filter, ignited, and weighed, if necessary.

For the Determination of the Potash, we recommend the following two methods:—

1.—Tatlock's Method.

Mr. Tatlock's method, according to extensive critical experiments carried out by the Author and Mr. M'Arthur, gives very exact results with, at least, anything containing no less than about 30 per cent. of potash, calculated as KCl, but it does so only if carried out *exactly* as prescribed by the inventor, and given in Ex. 15, p. 25. For the student's convenience, we re-state the essential points, assuming 1 grm. of substance to be under analysis (although 0·5 to 0·6 grm. is ample)—

(1.) Dilute to about 50 cc., add (a few drops of hydrochloric acid and) platinum solution containing 2·5 grms. of platinum (whatever the percentage of potash may be), and evaporate to a magma.

(2.) After cooling, digest for an hour with 5 cc. of 5 per cent. chloroplatinic acid solution,* which will produce some 6 cc. of a 17 per cent. solution.

(3.) Then continue as directed in Ex. 15.

Dry the chloroplatinate at 100°, and multiply with 0·30627 to find the chloride of potassium. This factor is based on our numerous test analyses; the factor 0·30707, calculated from (Seubert's) Pt = 194·8, does not afford quite so close an approximation.

2.—Our own Form of Finkener's Method.

In regard to it we refer to the section on "Potash" under "Sea Water," p. 225. The abbreviated mode of digesting with ether-alcohol there referred to may confidently be applied. The washed salt-mixture ($R_2SO_4 + xPtCl_6K_2$) must be *re-crystallized.* The thus purified salt-mixture is dissolved in hot water (about 200 cc. per gramme of chloroplatinate), the platinum reduced out by hydrogen, and weighed. According to our standard trials, the weight multiplied by 0·76084 gives the corresponding weight of chloride of potassium. The factor 0·76571, calculated from Pt = 194·8, affords a less close approximation.

For a complete analysis, supplement the above by determinations of magnesia, sulphuric acid, and a gravimetric chlorine

---

* Meaning a solution containing 5 grms. of Pt in 100 cc.

in so many separate portions, and by the following two determinations:—

(1.) *Total Salts*, by Tornoe's method. (*See* p. 231). This gives the *water* by difference.

(2.) *Soda*, by difference from (1) and the rest of the determinations; or else by the total sulphate method given for sea water.

For a more *direct* determination of the soda, the best method probably would be to first eliminate the potash as far as possible by the Tatlock method, and then work up the filtrates as follows:—Beginning with the alcoholic liquors, distill off the alcohol, then add the aqueous filtrates and washings, and reduce out, and filter off, the platinum; evaporate the filtrate to dryness, after addition of a little more sulphuric acid than necessary to convert the bases into sulphates. Finkenerize these, and, without stopping to re-crystallize, treat the salt-mixture ($R_2SO_4 + xPtCl_6K_2$) with saturated solution of sal-ammoniac, as shown in Ex. 15, p. 29. The residue may serve for the determination of the small quantity of potash which escaped the Tatlock method of precipitation.* The soda is in the sal-ammoniac solution; it is recovered by evaporation to dryness and ignition. Convert the residue into neutral sulphates. Weigh these, dissolve them in water, filter off any small residue that may be left (to weigh it and deduct it as a correction), and in the filtrate determine the magnesia, which calculate as $MgSO_4$. The soda is found by subtracting this weight from that of the two sulphates weighed before.

Should *lime* be present, it is best determined in the "total sulphates" by dissolving in water and precipitating judiciously with *alcohol*.

The precipitate is allowed to settle, collected, washed with dilute alcohol, then re-dissolved in water and a little hydro-

---

* For this purpose, the best method is to reduce the precipitate with hydrogen, either in the wet or in the dry way (*see* p. 28), to filter off the platinum, evaporate the filtrate to dryness, and ignite the residue ($KCl + xNH_4Cl$) gently to remove the ammonia salt. The residue is dissolved, evaporated as far as possible on a water-bath with excess of chloroplatinic acid, and the residue washed, first with 80 per cent. (by volume) alcohol, and lastly with strong alcohol. The chloroplatinate is dried at 100–110°, and weighed.—(*Fresenius' modus*).

chloric acid, the lime precipitated as oxalate, and weighed ultimately as CaO. In this case the filtrates from the lime-precipitates serve for the magnesia.

3.—Cast-iron.

FOR most of the determinations the iron must be in the form of fine borings or filings. These are liable to contain *oil*, which must be extracted with boiling ether (under an inverted condenser). The ether-washed residue is dried at 100°C., and preserved in a preparation tube.

THE TOTAL CARBON

can be determined by burning a known weight of the very finely divided substance with oxide of copper in a current of oxygen and weighing the (dried) carbonic acid. (*See* "Organic Analysis.") This method, however, is little used, because the comminution of the substance is almost impossible without risk of contamination. In practice, the only way is to first eliminate the iron in some way not involving loss of carbon as carburetted hydrogen, and then to determine the carbon in the carbonaceous residue.

Methods for the Preparation of the Carbon Residue.

(1.) *Cupric Chloride method.*—340 grms. of crystallized cupric chloride and 214 of sal-ammoniac, or 554 grms. of the double salt $CuCl_2, 2NH_4Cl + 2H_2O$, are dissolved in 1850 grms. of water. 2–5 grms. of the substance are digested in the solution—20 to 25 cc. of solution for every 1 grm. of substance—until complete disintegration is effected. The residue consists of carbonaceous matter and metallic copper. To extract the latter, add hydrochloric acid and more copper-ammonium chloride, and digest until all the copper is dissolved; then filter off on an *asbestos filter* constructed as follows:—Stop up the neck of an ordinary funnel with glass wool, and then pour on a suspension of fine asbestos fibres in water so as to produce a bed of the latter, and wash as long as any fibres are seen to go through. The asbestos must be prepared by heating it in a current of very *moist* air to remove all its fluorine. The crude carbon is collected on the filter and washed until all the *chlorine* is away. It is then dried, and thus got ready for combustion.

(2.) *Weyl's method* offers the advantage of being applicable directly to compact iron. An Argand lamp cylinder, tied over at one end with bladder or vegetable parchment, is suspended within a beaker, and both are charged to the same height with dilute hydrochloric acid. A piece of the substance in the form of rod, 10–15 grms., is fastened in a forceps provided with long platinum ends, which in its turn is connected with the positive (platinum) pole of a single Grove cell. The negative pole is in electric connection with a piece of platinum foil immersed in the acid of the beaker. The connections being made, the iron is plunged into the acid of the cylinder as far as possible without wetting the points of contact between forceps and substance. By properly adjusting the distance between the two terminals, so regulate the current that only *ferrous* salt is produced. After some hours the whole of the immersed iron is dissolved. The remaining piece of iron is cleaned from adhering carbon, washed, dried, and weighed to obtain the weight of the disintegrated part by difference. The crude carbon is filtered off and washed as before for the determination of the real carbon contained in it.

Determination of the Real Carbon in the Crude.

(1.) One method is to place it in a platinum boat, to burn it in a current of oxygen with granulated oxide of copper in front, and weigh the carbonic acid as in organic analysis. Although the water is not weighed, it must be removed by calcium chloride as usual. To provide against vitiation of the results by sulphurous acid, put some binoxide of lead in the *bend* of the calcium chloride tube, and separate it from either column of the latter by stoppers of cotton or glass wool. The combustion tube need not be quite so long as would be necessary in an organic analysis.

(2.) *Ullgren's method* (modified). The principle of this method is to oxidize the carbon by means of a mixture of chromic acid and semi-concentrated sulphuric acid, and weigh the carbonic acid, directly or indirectly. Our *modus operandi* is to effect the oxidation within a slanting Florence flask of 250 cc.'s capacity, provided with a ground-in inlet tube, in a current of carbonic-acid-free air; to send the air, carbonic acid, and vapours through an upright condenser, and then through a U-tube charged with pumice moistened with a solution of red chromate of potash. The thus purified carbonic acid is collected in an evacuated flask charged with the necessary volume of standard baryta. (*See* "Carbonic Acid" under "Sea Water.") For every grm. of iron 4 grms. of crystallized chromic acid and 40 cc. of vitriol diluted with 20 cc. of water are used. If the carbon contains a remnant of chlorine, add some sulphate of silver in crystals to retain the chlorine as chloride of silver. Instead of the vacuum-method, the ordinary gravimetric *modus*—drying of the gas by calcium chloride, and collecting it in caustic potash solution and soda lime (*see* Ex. 20)—may be employed.

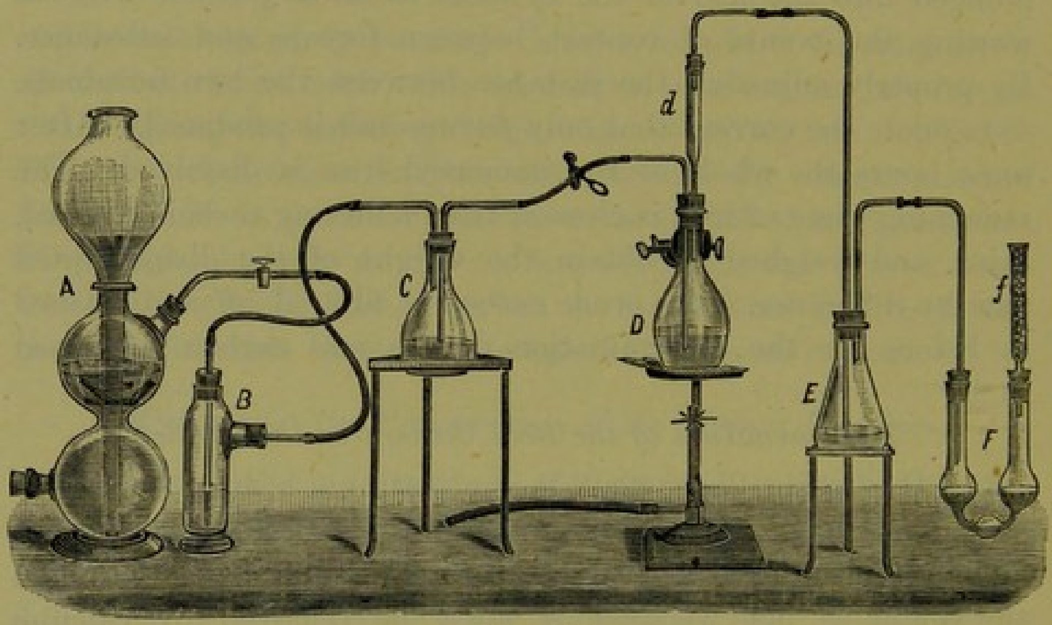


Fig. 60.

Apparatus for the Determination of the Sulphur.

To determine the Graphite separately, digest a fresh portion of the substance in hydrochloric acid as long as any gas comes off, collect the crude carbon on an asbestos filter; wash successively with (1) hot water, (2) hot caustic potash solution, (3) alcohol, (4) ether (M. Buchner); dry the residual graphite, and determine it by combustion in oxygen as carbonic acid.

The Sulphur.

Fresenius' method.—The substance is dissolved in hydrochloric acid, the sulphuretted hydrogen produced oxidized into sulphuric acid, and determined as sulphate of baryta.

Two flasks, one of 300–400 cc.'s capacity, and a smaller one, are so rigged up and connected with a "Kipp" delivering *pure* hydrogen, and with one another, that one is at liberty to pass the hydrogen right through the apparatus, or, by means of it, to force a liquid contained in the lesser flask into the larger. (*See* Fig. 60).

The former is charged with hydrochloric acid of 20 per cent., the latter with a known weight (some 10 grms.) of the substance. By its outlet it communicates with a system of apparatus containing the absorbent and oxidant for the sulphuretted hydrogen. We have the choice among many agents. Fresenius himself recommends a solution of bromine in hydrochloric acid; we prefer alkaline permanganate. Our figure gives the corresponding form of the apparatus. In any case the first step is to fill the apparatus completely with *pure* hydrogen. Then some acid is sent over on the iron, so as to cause a moderate gas evolution, and this operation is repeated until the iron is completely disintegrated and all the sulphuretted hydrogen driven into the oxidant. Supposing alkaline permanganate to have been used, dilute the liquor, add a few drops of alcohol, and heat to reduce the Mn_2O_7 to MnO_2, which filter off and wash to obtain a filtrate which contains the sulphur in the form of sulphate, so that it can be weighed as $BaSO_4$. In any case it is an improvement to insert an inverted condenser between the decomposition flask and the U-tube containing the oxidant. The insoluble residue in the flask *may* contain a remnant of sulphur in some form. To recover it, Eschka's method or the caustic potash and nitre method, both given under "Pyrites" (pp. 113 and 111), may be used.

As the sulphur in pig-iron never amounts to much, it is essential to make sure of the freedom of the reagents from sulphur. Even with apparently pure reagents it is as well to make a blank experiment, which differs from the analysis only in this, that pure (sulphur free) iron wire is substituted for the cast-iron to be analysed.

For the following determinations, it is necessary in general to operate upon a solution which contains none of those "organic" compounds which are produced when carboniferous iron is dissolved in acids. The general method is as follows:—A convenient weight, say 5 grms. of substance, is dissolved in a flask by gradual addition of 60 cc. of nitric acid of 1·2 spec. grav., applying heat only at the end. The liquor is evaporated to a small volume in a Berlin basin; 5 grms. of nitrate of ammonia are then added, the whole evaporated to dryness over a sand bath, and the residue heated first in the sand bath and then over a direct flame until the organic matter can be assumed to be volatilized or destroyed. A muffle, kept at a dull-red heat, may be used with advantage. Small quantities are transferred, as far as possible mechanically, to a platinum crucible and ignited in it. The crude oxide of iron thus obtained is dissolved by prolonged digestion in strong hydrochloric acid, and the excess of acid removed by evaporation, as far as possible without producing insoluble basic salt on subsequent dilution with water. The diluted solution is filtered. When we speak in the sequel of "carbon-free oxide" or chloride, we refer to the above operations.

THE PHOSPHORUS.

5 grms. of substance are converted into carbon-free chloride, which is next, after suitable dilution, reduced by sulphuretted hydrogen or by sulphite of soda (*see* p. 36). In the former case the sulphur precipitate is filtered off. In order now to bring down the phosphoric acid, add first, if necessary, a small quantity of pure ferric chloride,* and to the *cold* solution, which should be diluted to about 1 litre, carbonate of soda solution drop by drop, until a tangible brown precipitate ($FePO_4 + xFe_2O_3$) has been produced. The precipitate is allowed to settle in a well-stoppered flask, then filtered off promptly, and washed 2–3 times with cold water. It is then dissolved in hot, dilute nitric acid, the solution being run into the flask to dissolve what of the precipitate adheres to its sides. Should a residue remain,

---

* As a rule, and unless very special precautions are taken to prevent it, enough of ferricum is formed spontaneously.

dissolve it in strong hydrochloric acid, evaporate the solution by itself to near dryness, add nitric acid, and evaporate again to remove the chlorine, and then unite the two liquors. From the nitric solution, the phosphoric acid is precipitated by molybdenum (*see* Ex. 16, p. 31). In precipitating the molybdenum from the acid solution of the crude PO_4MgNH_4 with sulphuretted hydrogen, apply the gas hot, and let it act for a sufficient time to make sure of the *arsenic* (if present) being eliminated.*

Mr. Riley † (a well-known specialist in iron analyses) prefers the following method:—After having (by a procedure similar in principle to the above) concentrated the phosphoric acid in a ferric oxide precipitate containing about 3 decigrms. of iron, he dissolves this precipitate in hydrochloric acid, evaporates to about 15 cc., and next adds 13 grms. of solid citric acid. He then neutralizes the solution with ammonia, adds 20–30 drops of magnesia mixture, and enough of strongest (0·88) ammonia to make the mixture very strongly ammoniacal. The total volume at this stage should be about 50 cc. On standing over night, the mixture deposits star-shaped crystals at the sides of the beaker and on the rod; these are broken up with the rod, and the mixture allowed to stand over a second night, when the phosphoric acid is supposed to be all in the precipitate, which is manipulated as usual. If the pyrophosphate should be black from an admixture of charcoal, this is set right by heating it with some fuming nitric acid and re-igniting. "It is always free of iron" (and of surplus magnesia from citrate ?) In most of the test analyses which Riley produces, the pyrophosphate (after having been weighed) was redissolved in strong hydrochloric acid,‡ a small crystal of citric acid added, the precipitate reproduced by adding excess of ammonia and allowing to stand over two nights as before, collected, ignited, and weighed. The

---

* For a *determination* of the *arsenic*, it is better to distil a special quantity of carbon-free oxide with strong hydrochloric acid and cuprous chloride, and determine the arsenic in the distillate as As_2S_3. (*See* p. 115).

† "Chem. Soc. Journal," 1878. Transactions, p. 104.

‡ Is this sufficient to convert the pyrophosphate into ortho-acid? We may say, in passing, that Riley used ignited pyrophosphate of magnesia as a standard substance in his trials.

difference in weight between the crude and purified pyrophosphate never amounted to much.

THE MANGANESE.

For relatively large percentages of manganese (in spiegel-eisen or ferro-manganese),

Volhard's method works well. It is founded upon the precipitation $Mn_2O_7 + 3MnO = 5MnO_2$, which, under certain conditions, takes place when a feebly acid solution of manganous sulphate or nitrate* is mixed in the heat with one of permanganate of potash. A quantity of the iron, containing from 3–5 decigrms. of manganese, is made into carbon-free ferric chloride, and this converted into sulphate by evaporating down with oil of vitriol until thick vapours of the latter are seen to go off. This sulphate is dissolved in water in a graduated flask, diluted to about 500 cc. for every grm. of iron, and the iron is precipitated by addition of a milk of oxide of zinc *in the cold*. The mixture is then diluted to the mark and filtered through a dry filter. In an aliquot part of the filtrate (conveniently 200 cc.), the manganese is determined by first acidifying it with a few drops of nitric acid, and then adding, at a boiling heat, permanganate of potash out of a burette until there is a slight excess of reagent, seen by the rose colour which the liquid shows when the precipitate settles.

From the above equation it will be easily understood that a permanganate solution, which, in the ordinary iron process, peroxidizes 10FeO, precipitates in Volhard's 3MnO mgs.; so that in this sense 1 mg. of ferrosum corresponds to 0·3803 mg. of MnO or 0·2946 of metallic manganese. The presence of zinc in the liquid is essential, because in its absence a compound of $MnO_2 \, x \, MnO$, instead of $MnO_2 \, x \, ZnO$, goes down.

For the determination of *small* quantities of manganese, the safest method no doubt is to *begin* at least by a gravimetric method of separation, which yields the manganese by itself in a solid form. The acetate of ammonia method is as good a one as could be used. Starting from the "ferric chloride" solution, first boil to reduce the manganese to manganous salt, then allow to

---

* With chloride the reaction is irregular.

cool, dilute to about 500 cc. per grm. of iron, and next neutralize cautiously with ammonia, avoiding the formation of a permanent precipitate. Then add enough of acetate of ammonia, heat to ebullition (but do *not* boil for any length of time), filter hot, and wash with hot, very dilute acetate of ammonia. The manganese is in the filtrate, and can be precipitated by ammonia and colourless sulphide of ammonium (in a corked Erlenmeyer). If it amounts to very little it is more exact to evaporate all the filtrate to dryness, to burn away the ammonia salts, re-dissolve the residue in a little water and hydrochloric acid, and precipitate the manganese from the solution by sulphide of ammonium, or (hot) with carbonate of soda. The sulphide of manganese precipitate, when heated with sulphur in hydrogen, becomes weighable MnS. (For *modus operandi, see* pp. 42 and 43). The carbonate on ignition leaves Mn_3O_4.

By way of appendix, we give

Pattinson's method.—Principle:—If a mixed solution of ferric and manganous chlorides, which contains at least 1 part of iron for 2 parts of manganese, is mixed with bromine water or bleaching powder solution, heated to 60–70°C., and then mixed with carbonate of lime, it gives a precipitate containing the iron as Fe_2O_3 and the manganese as MnO_2. A quantity of substance containing 0·1 to 0·15 grm. of manganese is made into carbon-free ferric chloride solution. This is neutralized (cold) by gradually added carbonate of lime, and the dark-red liquor re-acidified with a few drops of hydrochloric acid. 60 cc. of a clear bleaching powder solution,* and hot water to bring up the temperature to 60–70°C. are now added, and the precipitation is then effected by addition of 1·5 grms. of carbonate of lime. The mixture is stirred as long as carbonic acid goes off, and then allowed to settle. Should the supernatant liquor exhibit a red colour of permanganate, this is reduced by addition of a drop or two of alcohol. The precipitate is filtered off and washed with warm water until every trace of chlorine or hypochlorous acid is gone. It is then transferred with its filter to a beaker and dissolved in a strongly sulphuric solution of a known

---

* 15 grms. of good bleach dissolved in cold water to 1 lit. and filtered.

weight of ferrous sulphate (use the standardized salt of Ex. 18), preferably in an atmosphere of carbonic acid. The remnant of ferrosum is then determined by titration. From the weight of ferrosum oxidized, the MnO_2 is calculated as manganese. Pattinson prefers the bichrome process. He uses a measured volume of an only approximately standardized solution of ordinary pure ferrous sulphate, and determines the strength of an equal volume by putting in a filter similar to the one used, and then titrating with bichrome. Supposing the iron solution and filter which acted upon the MnO_2 requires less bichrome than the original combination by n cc., then n cc. contains as much available oxygen as the MnO_2 to be measured. Supposing 1 cc. of the bichrome $= 56$ decimgs. of iron $=$ Fe decimgs., the oxygen amounts to $n \times \frac{1}{2}O$ corresponding to $\frac{1}{2}n \times MnO_2$ or to $\frac{1}{2}nMn$ decimgs. of metallic manganese, *i.e.*, if we begin by calculating the ferrosum corresponding to those n cc., every 1 part of such iron corresponds to $27{\cdot}5 \div 56 = 0{\cdot}49107$ parts of manganese.

Pattinson's method would adapt itself well to the determination of the manganese in a small precipitate of sulphide or carbonate of manganese obtained in a separation.

The Silicon.

The carbon-free oxide contains all the silicon of the iron as silica. Fuse it with (at first moist) caustic potash and nitre in a silver dish, dissolve in water, transfer to a Berlin basin, add hydrochloric acid, &c. The silica must be tested for titanic acid. If titanium be present, mix a known weight of the crude silica with fluoride of ammonium, add a drop of water (in platinum), then a few drops of sulphuric acid, evaporate to dryness and ignite (in a good draught place). The silicon goes off as fluoride; the titanic acid remains, and is weighed. (*See* Finkener, Quant. part, p. 694.)

A method for the direct and exhaustive determination of the titanium was given by Drown and Shimer (Fres. Quant., 6th edition German, vol. ii., p. 440).

The Iron and Foreign Metals.

Convert a known weight of substance into carbon-free oxide and analyse it like a mineral, paying due regard to the great predominance of iron. For the determination of the iron itself the best method probably is to reduce a quantity of oxide corresponding to an exactly known weight of substance in hydrogen (in a boat standing in a combustion tube), to allow to cool in carbonic acid, dissolve the metallic iron in *n* cc. (measured) of dilute sulphuric acid in the absence of air, dilute to V cc. and titrate with permanganate. Supposing the analysis to bring out *p* mgs. of iron, dissolve *p* mgs. of pure iron in *n* cc. of the dilute sulphuric acid used, dilute to V cc., titrate again, and calculate on the basis of this special standardization.

DETERMINATION OF THE SILICA, &C., PRESENT AS SLAG.

For this determination we have no really satisfactory method. Wöhler recommends to volatilize (from a weighed sample contained in a porcelain boat standing in a combustion tube) the iron by means of a current of perfectly dry and *air*-free chlorine at a red heat, and analyse the residue. For this purpose it is first treated with water to remove the bulk of the chlorides; from the residue the carbon is then burned away in oxygen, and the ash and chloride liquor are analysed conjointly.

STEEL AND WROUGHT IRON

are analysed like cast iron; only, as the quantities of carbon, phosphorus, &c., are far less, we must work in a larger scale, and correct our results by *blanks* whenever the absolute purity of the reagents is not proved quite directly. The iron in this case is best determined by difference.

For the determination of the *carbon* in a steel, Eggertz has invented a *colorimetric method*, for the execution of which it is necessary to have a supply of a steel in which the percentage of carbon has been determined with high precision. The nearer this percentage comes to that of the steel to be analysed the better.

Dissolve 1 grm. each of the standard steel and of the substance respectively in 10 cc. of pure nitric acid of 1·2 at a gentle heat as far as possible; decant off the acid, and treat the residue with other 5 cc. of acid, and filter the liquor if necessary. Procure two test tubes of 15–16 mms. diameter, which are as nearly as possible equally wide; on one make a diamond mark corresponding to, say, 20 cc.; on the other make a mark at the same height. Pour each of the two liquors into its test tube, and dilute it up to the mark. Both solutions are *brown*, the more intensely so the greater the quantity of carbon present per unit volume. One is in general darker than the other. Take the darker solution, and, by cautious addition of successive instalments of water, tone it down, so that when compared (at the same height of liquid) with the other the two colours are identical. Both solutions now contain the same amount of carbon per unit volume. Hence all that is required to enable one to arrive at the result is to measure the two solutions in graduated tubes. Supposing the standard solution amounts to 30 cc., and contains (by standard analysis) 2 mgs. of carbon, while the substance solution measures 20 cc., then 1 cc. of either contains 2/30 mgs. of carbon; and the carbon in the 20 cc. of substance solution is $2 \times 20 \div 30 = 1{\cdot}33$ mgs.

4.—Superphosphate of Lime.

I. *The Soluble Phosphoric Acid.*—The proportion of P_2O_5 which passes into solution on treatment with cold water depends on the way in which the solution is prepared. A committee of German agricultural chemists* experimented on the matter and fixed upon the following method:—

Twenty grms. of substance are rubbed up in a mortar with cold water (*without grinding*), and the mixture is washed into a 1000 cc. flask with as much cold water as permits of mixing by rotatory motion. The whole is allowed to stand for two hours (with frequent agitation), filled up to the mark, and passed through a dry filter. In an aliquot part of the filtrate the soluble phosphoric acid is determined by one or other of the following processes:—

(1) *The Molybdenum Process* (*see* Ex. 16, p. 31).—This works in all cases and gives good results.

---

* Fresenius' "Zeitschrift" for 1880, p. 244.

(2) *The Oxalate Process.*—The solution is alkalinized *cold* with ammonia and the precipitated phosphate re-dissolved as far as possible, in cold acetic acid. If a residue remains (PO_4Al or PO_4Fe), it is filtered off and washed (cold), dissolved in HNO_3, and its P_2O_5 determined by molybdenum. From the acetate filtrate, the lime is precipitated by adding (a calculated) excess of oxalate of ammonia in the cold and then heating on a water bath until the oxalate has settled. [The precipitate is ignited, and weighed as CaO; it generally contains a little phosphoric acid, which in an exact analysis must be determined with molybdate, and allowed for.] From the filtrate the magnesia is precipitated by means of ammonia, and, in the filtrate from the magnesia precipitate, the phosphoric acid by magnesia mixture. The phosphoric acid, of course, is calculated from the *sum* of these two precipitates.

(3) *Titration with Uranium.*—(1) 38 grms. of acetate of uranium* are dissolved in water with 5 cc. of glacial acetic acid and diluted to one litre. 1 cc. = about 5 mgs. of P_2O_5. (2) 100 grms. of crystallized acetate of soda are dissolved in water, mixed with 100 cc. of acetic acid of 30 per cent. (or 30 grms. of glacial) and diluted to 1 litre.

For the exact standardization of the uranium solution, *mono-potassic phosphate* recommends itself on account of the facility with which it can be obtained pure. (It is PO_4KH_2 without crystal water, and stands 150°C. without any of the chemically combined water going off; on ignition it leaves metaphosphate KPO_3, so that we have two easy and exact modes of standardization); but in the present case it is better to use an *analysed* supply of, say di-calcic phosphate, or, better, (analysed) mono-calcic phosphate. In either case, the quantity containing 5 grms. of P_2O_5 is dissolved in water, *plus* the least sufficiency of nitric acid, and diluted to 1000 cc. To standardize the uranium, measure off from a burette, say, 30 cc. of the uranium solution, and add 6 cc. of the acetate solution. Then heat the liquid to 90–100°, and at this temperature add, from another burette, of the standard phosphate until a drop of the mixture, when it is

---

* Or nitrate, but acetate is preferable.

placed on a porcelain plate and a very little powdered ferrocyanide of potassium put in its centre, ceases to give the red-brown coloration characteristic of uranium. Find the end point repeatedly by to-and-fro titration (always taking the point of disappearance of the end reaction as the end point), and from the mean result calculate the number of mgs. of P_2O_5 which 1 cc. of uranium is equivalent to. Also note down the volume of uranium equal to 1 cc. of phosphate.

For the analysis, measure off an aliquot part of the solution, add enough of caustic soda to cause an incipient precipitate, and re-acidify with acetic acid,* add 1 cc. of acetate for every 5 cc. of uranium presumably required, and titrate at 90–100° with uranium, until a drop, when tested with prussiate, gives a red brown colour. From this preliminary analysis, calculate the volume (V cc.) of substance solution equivalent to, say, 25 cc. of uranium, and for an exact determination measure off 25 cc. of uranium first, and add 5 cc. of acetate of soda. On the other hand, measure off a volume V' of substance solution presumably *insufficient* to precipitate all the uranium, though as near V as it can safely be made, add caustic soda and acidify with acetic acid, add it to the uranium, keep at 90–100° for some time, and finish with *standard* phosphate. Or else take, say, more than V cc. of substance solution, prepare it with soda and acetic acid, and dilute to a convenient multiple of its original volume, say to $\frac{5}{4}$ths. Put the solution into a burette, and with it titrate the 25 cc. of uranium. If the phosphate is free from alumina and iron, and care be taken to establish as nearly as possible the same conditions in the analysis as prevailed in the standardization (*i.e.*, if the quantities of acetate, P_2O_5, &c., per unit volume of final titration-mixture are nearly the same on both sides), the results are pretty fair.

II.—*The Insoluble Phosphoric Acid* can be determined in two ways:—

(1.) Dissolve a fresh quantity of substance in nitric acid—any residue left is dissolved in hydrochloric acid, the solution evapo-

---

* If a precipitate insoluble in acetic acid is left, this consists of phosphate of alumina and iron and *its* P_2O_5 remains undetermined, unless it is filtered off and wrought with molybdenum.

rated down and the remnant of chlorine expelled by repeated evaporation with nitric acid—dilute, filter and precipitate with molybdate. This gives the total phosphoric acid directly and the insoluble by difference.

(2.) Take the residue left on the filter in the preparation of the substance solution, and wash it two or three times with small quantities of cold water, best with the help of the filter-pump. Then wash the precipitate off the filter, dissolve it as above, and determine the phosphoric acid by molybdate. The second method, although open to obvious objections, is the better one in practice.

III.—*Sulphuric Acid, Lime, Magnesia, &c.*—It has been explained above how the lime and magnesia in the substance-solution are determined incidentally.

The Chlorine is determined in a separate portion as AgCl.

The Sulphuric Acid is determined in another separate portion as $BaSO_4$. In the filtrate from the sulphate of baryta,

The Alkalies may be determined by precipitating the magnesia, phosphoric acid, &c., by excess of *pure* milk of lime in the heat. Addition of some ferric chloride at the end brings down the phosphoric acid more exhaustively, and facilitates filtration. The mixture is filtered hot, and from the filtrate the lime and baryta are precipitated by carbonate of ammonia in the heat. The filtrate from the carbonates is evaporated to dryness, and from the dry residue the ammonium salts are burned off. The residue should consist of alkaline chlorides, but it is never pure. Dissolve it in water, filter off any residue, and convert into sulphates, which weigh. Dissolve the sulphates in water (if a residue of sulphate of lime or baryta remains, filter it off and weigh it), and determine the potash by Finkener's method. The soda (which is of no great importance) is found by difference.

Ammonia, if present, is eliminated by distillation with caustic soda, and determined in the distillate.

The total Nitrogen is estimated by combustion with soda lime, or by Kjeldahl's process.

For a *complete* analysis, the insoluble residue obtained in the making of the substance solution is analysed like a phosphorite. But such an analysis is never required in practice; it is sufficient, in addition to the phosphoric acid and perhaps the lime, to determine the *sand*, meaning the part insoluble in acids.

5.—Guano.

The moisture is supposed to go off at 100°C., but at this temperature guano loses a considerable amount of ammonia, which must be caught and determined, to be deducted from the loss of weight suffered by the substance. A large silver condenser (a silver tube about 2 ctms. wide, enclosed in a metal jacket)* affords a convenient heating apparatus. It is fixed horizontally, and a boat charged with 2–3 grms. of guano placed in its centre. A Varrentrapp and Will bulb, or bulbed U-tube, charged with a sufficient known volume of standard acid is attached to one end of the silver tube, the other communicating with a perspirator supplying a slow current of dry air. As soon as all the connections are made, steam is blown through the jacket, and the water and ammonia sent through the absorber, until the weight of the residue is constant.

Total Fixed Components.—A known weight (say 2 grms.) is charred in a tared platinum crucible, and at last incinerated at the lowest sufficient temperature. Addition of a known weight of pure ferric oxide promotes the combustion. To reconvert the caustic lime, which may have been formed, into carbonate, evaporate some carbonate of ammonia over the crude ash and heat to *dull* redness; repeat the operation until the weight is constant. The ash is *not* available for the determination of the phosphoric acid, because pyrophosphate may have been produced in the calcination.

The Phosphoric Acid.—To 1–2 grms. of the substance add a sufficiency of hot, saturated baryta water (prepared ex temp. over the substance from crystals and water), evaporate to dryness, and *char* completely. Next extract what is soluble in dilute nitric acid. To the washed charcoal add again some baryta, incinerate, and dissolve the ash in dilute nitric acid.

---

* Such condensers were introduced some years ago by Professor Crum Brown; we find them very useful for distillations of ammonia-free water, acetic acid, &c.

Mix the two nitric solutions, and in an aliquot part determine the phosphoric acid by molybdenum. The solution suffices for a number of determinations.

The Sulphuric Acid might be determined in the insoluble part of the baryta residue. But it is better to prepare a fresh quantity of char, and subsequently ash, without baryta, to extract the sulphates with dilute hydrochloric acid, and determine them with barium chloride in an aliquot part of the solution.

Another serves for the *Lime and Magnesia*, which can be determined as explained under "Superphosphate," which, if sesquioxides are relatively absent, and some carbonate of soda was added in the charring and incineration, affords an additional determination of the phosphoric acid.

The Alkalies.—Char a known weight with baryta (as for phosphoric acid) and a little barium chloride, and from the char extract what will dissolve in water. Incinerate the charcoal with a little more of the barytic reagents, and lixiviate the ash with water. From the united liquors the barium is precipitated by carbonate of ammonia, and from the filtrate the alkalies are recovered, as chlorides, by evaporation to dryness and calcination. The chlorides are made into sulphates, and the potash is determined by Finkener's method.

The Chlorine.—Char a known weight of substance with a little baryta, extract with cold dilute nitric acid, and precipitate with nitrate of silver.

The Carbonic Acid (if present) is best liberated with dilute sulphuric acid, and determined *directly*. (*See* Ex. 20).

The Ammonia can be determined by distilling the substance with magnesia-milk * out of a flask connected with a Liebig's condenser. The distillate is run into the midst of a quantity of standard acid contained in a beaker, and determined by titration. (*See* p. 84). (Boussingault). Schlœsing mixes the guano with milk of lime in a flat dish, places this over another flat dish containing measured standard acid standing on a ground glass plate. A well-fitting bell-jar, which, of course, has been got

---

* Distillation with caustic soda will not do, because this liberates ammonia from the nitrogenous organic components.

quite ready and greased beforehand, is put over the whole, and the apparatus left to itself for 48 hours. The ammonia is then all in the acid.

The total Nitrogen, in the absence of nitrates, is best determined by Kjeldahl's method; in their presence, by Dumas' method (*see* Exs. 30 and 47.)

The Nitric Acid by Schlœsing's method. (*See* Ex. 31).

Uric and Oxalic Acids.—Boil a known weight with carbonate of potash solution, filter, and wash. Both acids go into solution as potash salts. To precipitate the *uric* acid, acidify with hydrochloric acid, and allow to stand for 24 hours; collect the precipitate on a weighed filter dried at 100°C., wash with *small* instalments of cold water, dry at 100°C., and weigh. (Method used in Urine analysis.) The oxalic acid is in the filtrate. Supersaturate with ammonia, add acetate of calcium and allow to stand until the precipitate has settled completely. Decant through a filter and digest the precipitate with dilute acetic acid. The precipitate now is impure oxalate of calcium. Perhaps weighing it as such would afford a sufficient approximation; but it is probably better to place it in a flask along with some *pure* binoxide of manganese, conveniently made from sulphate by precipitation with permanganate, to decompose by added sulphuric acid, and weigh the carbonic acid evolved (directly). (Not tried yet.) Some chemists recommend to apply this method direct to the guano. In this case we must, of course, allow for the carbonic acid of the carbonates.

For the separate determination of the soluble parts treat, say, 10 grms. of substance with about 200 cc. of cold water, collect what remains on a weighed filter dried at 100°C., and wash with small instalments of cold water. The residue is dried at 100°C. and weighed. With regard to the analysis of the two parts we have nothing to add to what the student will readily find out by himself, except perhaps the remark that all the alkalies—at least, practically—pass into the solution.

Note regarding the incinerations.—Mixtures of phosphates and charcoal are apt to attack platinum vessels. Hydrate of baryta is sure to attack them very perceptibly. Porcelain (in the case of baryta or alkali being used) may yield up silica.

Vessels of Dittmar's silver alloy (*see* foot-note, p. 111) will probably work best.

6.—Milk.

The methods to be given are invented for *fresh* milk, which is still perfectly sweet. Before measuring off a sample for a determination, agitate the milk to make sure that the fat is uniformly diffused. It is advisable—in hot weather it is necessary—to start all the determinations at the same time.

Total Solids.—A requirement for this and the following determination is *purified sand.* A supply of fine white sea-sand is digested with strong hydrochloric acid, then washed with abundance of water to remove the dissolved parts and the light dust, and at last ignited in a platinum basin. A platinum crucible of 30 cc. is charged with such sand up to about one-third of its height, the sand moistened with water, and then dried again at 100°C. until constant in weight. 2 cc. of the milk are then dropped on the sand, so as to wet it as uniformly as possible, and the whole is re-weighed (lid on) to determine the weight of the added milk. The crucible is then kept (open) in a drying chamber at 100°C. until the weight is constant. This gives the percentages of total solids and water.

The Fat.—10 cc. of the milk (weighed) are poured on 20 grms. of sand contained in a flat Berlin basin, and over it evaporated to dryness with continual agitation with a glass or porcelain spatula to prevent formation of lumps. The residue is dried fully by keeping it for a time in a drying chamber at 100°C., and then transferred to a dry flask of about 200 cc.'s capacity. What sticks to the basin is removed by softening it up with a little water, and evaporating the liquid to dryness over an additional small quantity of sand. In order now to extract the fat, the united sandy residues are boiled with 50–60 cc. of *anhydrous* ether under an inverted Liebig's condenser, the contents allowed to cool and filtered into a tared, short-necked flask of about 100 cc.'s capacity, and from out of it subjected to distillation to recover the ether, which is used for a repetition of the extraction. The ether recovered this time (with more ether, if necessary) is used for washing the sand (cold) until the last runnings are free from fat, which is ascertained by allowing a few drops to evaporate on a watch-glass, and rubbing the residue against the watch-glass with the little finger. The least trace of fat then becomes visible as a coating on the glass. The fat solution is deprived of as much of its ether as possible by distillation, and the bulk of the rest is next removed by heating the flask on a water-bath (in the open laboratory) and blowing air through it from time to time.* At last the flask is kept at 100° in a chamber (its vapour being sucked out from time to time) until its weight is constant. Should the (molten) fat not be quite clear, it must be dissolved in absolute ether, filtered into another tared dry flask, and in it brought to dryness.

The above method may be modified as follows to save time without much loss of exactitude:—Place the dry sand-residue in a phial of, say, 150 cc.'s capacity, tare the whole on a balance, add 100 cc. of ether, stop up well, and allow to stand for some hours, with occasional agitation. Then allow to settle completely. Weigh the *whole*, decant part of the ethereal solution into a tared fat flask, *and, by weighing what remains*, ascertain the weight of ethereal liquid poured out. Determine the fat contained in the fraction, which incidently gives the weight of the solvent, which is associated with the fat. Supposing the fat amounts to n mgs., the ether associated therewith to p grms., the whole of the ether present in the original sand mixture just before fractionating to P grms., then the total fat is $x = \frac{n \times P}{p}$.

The total ash might be determined in the residue from the total solids, but it is better to evaporate a fresh quantity of milk (say 5 cc.) to dryness in a porcelain crucible without sand, and incinerate at the *lowest* sufficient temperature.

Albumenoids and Sugar.

These are best determined by Ritthausen's method.

Requirements.—(1) A standard solution of sulphate of copper,

---

* If the flask were placed in the drying chamber as it comes off the condenser, an explosive atmosphere might be formed within the chamber.

containing 63·5 grms. of $CuSO_4$ $5H_2O$ per litre; (2) A solution of caustic potash equivalent to (1), volume for volume, in the sense of the equation, $CuSO_4 + 2KHO = Cu(OH)_2 + K_2SO_4$. There is no need of *high* precision in either standardization.

10 cc. of the milk are weighed out, diluted to 200 cc. with water, and mixed first with 5 cc. of the copper solution, and then with a volume of the caustic potash so adjusted that a small trace of the copper remains dissolved in a slightly acid liquid; 0·7 × 5 cc. will, as a rule, be sufficient. The whole of the albumenoids and the fat are now in the precipitate in combination (or association) with cupric hydrate. The precipitate is collected on a weighed filter, and washed successively with (1) water, until the sugar is out; (2) alcohol of 85 per cent. by weight; (3) absolute alcohol; (4) ether, until all the fat is removed; (5) again absolute alcohol, to remove the ether.* [The filtrate and aqueous part of the washings are mixed and preserved for the determination of the sugar]. The precipitate is dried, first over oil of vitriol, in the cold, then at 125°C. until its weight is constant. It is then ignited (the filter being incinerated separately), and lastly heated in contact with air until constant in weight. This weight, when deducted from that of the dried albumenate of copper, gives the weight of the *albumenoids* probably with as high a degree of precision as can be attained by any direct gravimetric method for their determination. A higher degree of *constancy* in the results is obtained by determining the total nitrogen by Kjeldahl's method in, say, 10 cc. of milk; 1 part of nitrogen corresponds to 6·452 parts of milk albumenoids (Ritthausen). Yet Ritthausen's process is invaluable as furnishing a very convenient material for the determination of the milk sugar.

THE SUGAR.

The aqueous filtrate from the albumenate of copper is diluted to a known volume, and next small aliquot parts are devoted to the approximate determination of the volume of Fehling's solution (*see* Note 2), which a given volume of the liquor is capable

---

* Ritthausen utilizes the alcoholic and ethereal washings for a determination of the fat. We prefer the sand method.

of reducing (with formation of a red precipitate of cuprous oxide). A quantity corresponding to 1–2 grms. of milk is now mixed with about 1½ times the volume of Fehling's solution which it is capable of reducing, the mixture heated to boiling, and kept hot on a water-bath until the cuprous oxide has settled. The precipitate is then collected on a filter, washed with hot water, dissolved in an excess of an acid solution of iron alum, the solution cooled down promptly in the absence of air (best in carbonic acid), and titrated with standard permanganate diluted so as to correspond to about 5·6 mgs. of iron per cc. From the results the weight of the milk-sugar is calculated. $2Fe = 1 \times O = Cu_2O$ *exactly*, and one part of cuprous oxide, by *experience*, corresponds to *about* 0·6756 parts of milk-sugar ($C_{12}H_{22}O_{11}\ H_2O$); ∴ 1 mg. of iron = 0·860 mg. of milk-sugar. To obtain an *exact* result, repeat the analysis, and at the same time carry out a parallel experiment with a known weight of *pure* milk-sugar equal to the quantity to be determined according to the preliminary analysis, taking care to let both processes and titrations go on under *precisely the same conditions*. The experiment with pure sugar affords the factor for the reduction of the number of cc. of permanganate used to mgs. of sugar under operation.

Note 1.—Commercial milk is very frequently adulterated with added water, or by removal of part of the fat (as cream). As the composition of even genuine milk is subject to great variation, such adulteration cannot, in general, be proved with certainty. But it is easy on the other hand to ascertain what proportions of water and fat would have to be added, or taken away from, a standard milk of assumed fixed composition to produce a given kind of milk. All that is necessary is to determine the fat and the solids not fat, and to refer the results on both sides to one part of *solids not fat; i.e.*, of that component which, in the presumed manipulation, would remain constant in an absolute sense. To explain this by an example, let us adopt what Mr. Wanklyn puts down as the average composition of genuine milk as our standard, and then contrast the numbers with the results in a given analysis of suspected milk:—

	Wanklyn's Standard.	Suspected Milk (say)
Fat,	3·2	3·18
Solids not fat,	9·3	8·43
Water,	87·5	88·39
	100·0	100·00

Reducing to 1 part of *solids not fat*, we have

	Solids not fat.	Fat.	Water.	Milk.
Standard,	1	0·344	9·409	10·753
Suspected,	1	0·377	10·483	11·860
Additions to 10·753 of Standard reqd.	0	+0·033	+1·074	

Note 2.—Fehling's solution is best made ex temp. from the following two solutions:—(1) 34·65 grms. of crystallized sulphate of copper are dissolved in water, and made up to 1 litre. 1 cc. = 5 mgs. of *glucose* (not milk-sugar, or even inverted milk-sugar); (2) 173 grms. of Rochelle salts and 70 grms. of caustic soda (sticks) are dissolved to 1 litre. Equal volumes of the two mixed together constitute "Fehling's solution" (of half the customary strength).

7.—Soap.

Substance.—In the analysis of any impure substance the first point to be attended to is to prepare a good *average* sample; in the case of a soap we have to contend with the additional difficulty that in a given sample it is difficult to keep the percentage of water constant for any time. The best course is (from a homogeneous sample) to at once weigh out all the portions of substance required for the several determinations on so many watch-glasses, and note down their weights.

Water.

Dry, say, 3–5 grms. at 105°–110°C. until constant.

Impurities.

While the drying process progresses, treat a weighed sample with boiling strong alcohol in a flask. A pure soap (meaning a soap containing only alkali salts of fatty acids and perhaps glycerine) dissolves completely; any admixture of alkali carbonate, sulphate, silicate, or gelatine (which occurs occasionally) remains behind. Collect the insolubles, if any, on a weighed filter, wash with alcohol, dry at 100°C. till constant, and weigh. If the insolubles amount to anything considerable, devote one such precipitate to a qualitative analysis. We now proceed on the assumption that the soap was practically soluble without residue in hot alcohol. Where this assumption does not hold, the first step in each of the following determinations is to dissolve the respective sample in hot alcohol, filter, and evaporate away the alcohol if necessary. The solution obtained is treated as prescribed.

Fatty Acid.

Dissolve, say, 5 grms. of the soap in a tared Erlenmeyer flask in 100 cc. of water, and add a sufficient volume of standard sulphuric acid out of a burette, to produce a decidedly acid solution. Then heat on a water-bath until the fatty acid has gone to the top as a clear oil, leaving a clear aqueous liquid below. Then allow to cool, when the fatty acid in many cases will become solid or semi-solid, and filter the aqueous part through a *wet* filter. Re-melt the fatty acid in hot water, with frequent agitation, to give the soluble parts a chance of going out, again allow to cool, and filter as before. Continue this with smaller and smaller instalments of water, until the last water is neutral to litmus and gives no precipitate with barium chloride. Take care that the bulk of the fatty acid remains in the Erlenmeyer, and only very little goes on the filter. This small quantity is recovered by drying the filter at 100°C. (a test tube serves to support the funnel, so that any fatty acid that runs out collects in it), dissolved in hot alcohol, and added to the bulk of the fatty acid in the flask. The fatty acid is then dried at 100°C. until constant, and weighed. The fatty acid is customarily calculated as hydrate, *i.e.*, it is stated in the report that 100 parts of soap gave so-and-so many parts of fatty acid ($C_nH_{2n}O_2$, or $C_nH_{2n-2}O_2$) as weighed; the alkali combined with the acid into soap as Na_2O or K_2O. But $2C_nH_{2n}O_2$ combine with Na_2O into

$2(C_nH_{2n-1}O_2)Na + H_2O$; hence the sum of the several percentages must be corrected by subtracting $H_2O = 18$ grms. for every Na_2O or K_2O grms. of alkali, present as neutral soap in 100 grms. of substance* *(vide infra).* The calculation cannot be based upon the weight of the fatty acid, because its molecular weight is unknown.

The Total Alkali is determined in the aqueous filtrate and washings obtained in the determination of the fatty acid by titrating in the heat with standard alkali. The result, when corrected for the *surplus alkali,* gives the datum required for the combined water ($\frac{1}{2}H_2O$ per molecule) in the fatty acid.

The Surplus Alkali used to be determined by dissolving the soap in water, then salting it out, and determining the alkali in the salt liquor produced. But the process has been proved by Wright and Thompson † to be erroneous, because even a neutral soap, when thus treated, yields free alkali by hydrolysis.

Wright and Thompson recommend the following process:—A known weight of soap is dried, and then boiled with a sufficiency of strong or, better, absolute alcohol. The filtrate is titrated with alcoholic acid or alkali,‡ using phenol-phthalein as an indicator. In the residue on the filter the alkali present as carbonate is titrated as usual. The two alkalinities added together (algebraically in equivalents) give the alkalinity of the soap.

THE ALKALI SALTS GENERALLY.

The chlorine (present as chloride of potassium or sodium) can be determined in an aliquot part of the sulphuric liquor obtained in the preparation of the fatty acid.

For the sulphuric acid, potash, and soda, decompose a special portion of the soap with hydrochloric acid, and use aliquot parts of the aqueous solution for (1) sulphuric acid, and (2) potash and soda. The alkalies are recovered in the first instance as (in general impure) chlorides; these are converted into and weighed as sulphates, and in them the potash is determined by Finkener's

---

* This comes to the same as saying that in adding up percentages the fatty acid must be calculated as anhydride.

† "Soc. of Chem. Ind. Journ.," 1885, p. 634.

‡ As the solution may contain free fatty acid in lieu of alkali.

method. Observe that most "soda" soaps contain more or less of potash.

A shorter but less exact method is this:—Char a known weight of the soap in a platinum crucible, and extract the char with water. Then incinerate the charcoal at the lowest sufficient temperature, treat the ash with water, add the solution to the first, and analyse the mixture; an insoluble residue usually consists of lime.

The incineration method is always adopted when we have to deal with a soap contaminated with *silicate.*

THE GLYCERINE.

To determine it dissolve the soap in water, decompose with a slight excess of sulphuric acid, remove the fatty acid, which wash with the least sufficient quantity of water. Neutralize the aqueous liquor with carbonate of potash, and evaporate on a merely simmering water-bath to a syrup. Exhaust this syrup with absolute alcohol to obtain (a residue of sulphates and) a solution of impure glycerine. Evaporate away the alcohol, dissolve the residual glycerine in a mixture of two volumes of absolute alcohol and one volume of ether, filter, evaporate to dryness, dry at 100°C., without insisting upon constancy of weight, as glycerine is volatile, and weigh. A more exact method probably is to oxidize the glycerine in the solution with alkaline permanganate, and determine the oxalic acid produced.* In this case it is better to eliminate the fatty acid by *hydrochloric acid.* The aqueous filtrate from the fatty acid is neutralized with caustic potash and mixed with caustic potash, 5 grms. of solid alkali per 0·25 grm. of glycerine present. Powdered permanganate of potash is now gradually added until the solution is permanently pink at a boiling heat, which is maintained for half an hour. The excess of reagent is then decomposed by cautious addition of sulphurous acid or sulphite of soda, and the precipitate of peroxide of manganese filtered off. The solution is acidified by acetic acid, and the oxalic acid precipitated by acetate of calcium in the heat. The precipitated oxalate is

---

* Fox and Wanklyn, "Chem. News," 1886, I., p. 15.

collected on a filter and washed with hot water. It might be dried at 100°C., and weighed (as $C_2O_4Ca + H_2O$ Fresenius), or ignited and weighed as CaO. Fox and Wanklyn, however, prefer to titrate the oxalic acid with permanganate. For this purpose dissolve in the minimum of pure (nitrous acid free) dilute nitric acid, add water and dilute sulphuric acid, and then standard permanganate from the burette, until the liquid is permanently pink. $2Fe = 1 \times O = C_2O_4H_2$. According to Fox and Wanklyn, $C_3H_8O_3 + O_6 = C_2H_2O_4 + CO_2 + 3H_2O$.

RESIN.

Many cheap soaps are made from a mixture of resin and fat, instead of pure fat. Resin is substantially a mixture of acid anhydrides of high molecular weights; ordinary colophony consists chiefly of the anhydride of abietinic acid, $C_{44}H_{62}O_5 . H_2$. In the process of saponification, the resin anhydrides are converted into their alkali salts, which latter, on decomposition with acids, yield a precipitate consisting of the (hydrated) acids. Hence, were our process of analysis applied to a resinous soap, the resin acid would go with the fatty acid, and be weighed as such. Even the mere detection of resin in a soap is not easy. Barfoed,* who investigated the matter, has given the following, amongst other, methods:—

(1.)—*Detection of Resin in a fatty acid, containing much Stearic and Palmitic, beside little or no Oleic.*—The acid-mixture is dissolved in warm alcohol of 70 per cent. (by volume), and the solution allowed to stand, cold, for 24 hours. The fatty acids separate out almost completely as a crystalline precipitate; the resin acids remain dissolved. The resin is isolated by evaporation, or by addition of water and some hydrochloric acid, and shaking, with judicious application of heat. By repeatedly boiling the resin precipitate with water, it becomes more compact and easier of identification. It is contaminated in general with some oleic acid, but not to the extent of veiling its characteristic properties.

(2.)—*If Oleic Acid is present in quantity*, the following method is used:—The acid mixture is saponified at 100°C. with

---

* Fres. Zeitschrift, for 1875, p. 20.

very dilute caustic *soda* (10 per cent. solution diluted with about seven times its volume of water), an immoderate excess of alkali being avoided.*

The soap solution is evaporated to complete dryness, the dried soap powdered finely, and dried completely at 100°C. It is then treated for a few hours with *absolute* alcohol (5–10 cc. per 1 grm. of soap) in a *close* bottle at about 80°C.† The mixture is now allowed to cool (when some fat-soap separates out), and, after having made sure that no noteworthy quantity of the alcohol has been lost, 5 cc. of *absolute* ether are added for every 1 cc. of alcohol. This produces a voluminous precipitate of previously dissolved fat-soap, which, after 24–48 hours' standing, has settled completely so as to leave a clear liquid above itself. An aliquot part of the clear liquor is then measured off and evaporated to dryness, the residual resin soap dissolved in water, and the resin acid precipitated by hydrochloric acid. After 24 hours' standing the precipitate is collected on a weighed filter, washed first with cold and then with warm water until all the hydrochloric acid is removed, dried at 100°C. for 5–6 hours, and weighed. The fatty acid might be found by difference. Barfoed, however, prefers to operate upon two portions of the dry soap weighed out at the same time, and to use one for the resin as explained, and the other for the determination of the total acid (fatty and resinous), so as to obtain the ratio of the two quantities independently of the weight of the original substance.

In calculating the results, 1 grm. of resin (abietinic, &c., anhydride) may be taken as corresponding to 1·03 grms. of resin acid as it is weighed on the filter (Barfoed). If the resin is given as part of a *soda* soap, the second method is liable to an obvious simplification; we must make sure, however, of the absence of potash and glycerine.

Thomas S. Gladding‡ has given a method founded upon the

---

* Alcoholic soda, used conjointly with phenolphthalein as an indicator, would work better.

† Alcohol boils at 78°C. No doubt, an open flask attached to an inverted condenser and heated in a water-bath would work as well without danger.

‡ "Chem. News" for 1882, I. (vol. xlv.), p. 159. Taken from "American Chem. Journal," vol. iii., No. 6.

presumption (confirmed by him experimentally) that resinate of silver is soluble, while the silver salts of the ordinary fatty acids are insoluble, in ether. We refer to the memoir cited.

8.—Butter.

TOTAL FAT AND NON-FAT.

10–20 GRMS. of substance are weighed out in an Erlenmeyer flask, and dehydrated by heating on a water-bath, and occasional addition of absolute alcohol. The water soon goes so far that none of it remains in a visible form. The rest is expelled in a drying chamber at 100°C. This gives the percentage of *water*.

To determine the

Curd and Salt, the product is passed through a *dried* and weighed filter, by means of a hot-water funnel (the filtered pure fat being put aside for further tests), and the fat adhering to the filter removed by placing the funnel in an ordinary stand, trapping its outlet end with mercury contained in a narrow beaker (or bit of a test tube standing in a beaker), and then filling the filter to the edge with anhydrous ether. A concave glass plate is placed on the funnel to prevent loss by evaporation. After some time, the fat is completely dissolved; the solution then is allowed to run off, and the residue washed completely with ether. The (uncovered) funnel is allowed to stand in a warm place in the open laboratory until the bulk of the ether is gone (*see* footnote, p. 256), and the filter and contents are then dried at 100°C. until their weight is constant. This gives the curd and salt. The latter is extracted and determined by evaporating to dryness, and weighing of the dehydrated residue, or indirectly, by titration with silver by Mohr's method.

FOREIGN FAT.

Of the many methods invented for the determination of foreign fats in butter,

Reichert's is the easiest and best. The butter is dehydrated and filtered (*see* above), and of the fused fat, 3 cc. are measured off in a graduated pipette, and weighed, to be saponified with

1 grm. of caustic potash, and 20 cc. of ordinary alcohol on a water-bath. The alcohol is then *completely* removed by evaporation, the residue dissolved in 50 cc. of water, transferred to a distillation flask, and mixed (cold) with "20 cc. of sulphuric acid, prepared by diluting 1 volume of oil of vitriol with 10 volumes of water." No doubt far less acid will do. As 56 mgs. of *pure* KHO neutralize 1 cc. of normal sulphuric acid, 1 grm. neutralizes 17·8 cc. of normal acid; hence 25 cc. of normal acid, *i.e.*, 25 × 49 mgs. of H_2SO_4, are ample. The flask is attached to a Liebig's condenser, a slow current of air passed through the liquid, and the latter distilled, the distillate being filtered into a graduated tube. When 10–20 cc. are over, the distillate is poured back, the distillation resumed, and kept on steadily until exactly 50 cc. of distillate are produced. The (filtered) distillate is titrated with decinormal caustic soda (1 cc. = 1/10 NaOH = 4 mgs.), litmus being used as an indicator. According to Reichert, the number of cc. of decinormal alkali neutralized is—

For genuine butter,........................	14·0 ± 0·45
„ lard (pig's),..............................	0·3
„ ox fat,..	0·25
„ coco-nut fat,..............................	3·70

Excluding the last named fat, we have for a mixture containing x grm. of butter and $1 - x$ grm. of ordinary fat in 1 gramme: Alkali required by calculation $= x \times 14 + (1 - x)\, 0{\cdot}3 = V$, which symbol shall stand for the cc. of alkali used in the analysis of the mixture. Hence, $x = \dfrac{V - 0{\cdot}3}{13{\cdot}7 \pm 0{\cdot}5}$ or, to be on the safe side, in pronouncing judgment on a suspected butter, say, $x = \dfrac{V - 0{\cdot}3}{13}$ according to which formula, fat requiring 13·3 cc. (to 14·45) is genuine. It is easily seen that a mixture of x of butter and $1 - x$ of coco-nut oil requires these 13·3 cc. if $x = 0{\cdot}93$. As the method is purely empirical, rehearse it (before actual use) with (1) pure butter, made by yourself out of cream (by shaking a supply in a wide-necked bottle, &c.); and (2) say suet, and adhere to the "letter of the law" in all the trials. [For further information on methods of butter analysis generally, *see* "Dammer, Illustrirtes Lexikon der Verfälschungen" (Leipzig); p. 152].

RANCIDITY.

Rancid butter contains free acid which can be determined by dissolving, say, 10 grms. of the filtered dehydrated butter in 30 cc. or q. s. of ether, adding phenol-phthaleine, and titrating with decinormal alcoholic alkali in the cold, taking care to stop when the liquid, by addition of the last drop and stirring, becomes violet throughout, for however short a time. On standing, the violet colour disappears through saponification of the fat by the excess of alkali. The result is conveniently reported, as so much *butyric acid*, $C_4H_8O_2$.

9.—Assaying of Tanning Materials.

THESE materials owe their availability for tanning to the presence in them of some kind of "tannin." All "tannins" agree in the following properties:—(1) They are solids, soluble in water, and exhibiting feebly acid properties; (2) the solution of the potash or soda salts absorbs oxygen from the air with great avidity, and formation of dark-coloured soluble compounds; (3) they precipitate gelatine from its solution; (4) they are precipitated from their aqueous solutions by animal raw hide with formation of "leather;" (5) they strike a dark-blue or green colour with solution of ferroso-ferric salt, preferably the acetate; (6) when dissolved in water and mixed with a sufficiency of sulphuric acid they are readily oxidized in the cold by addition of permanganate of potash.

Upon the propositions (4) and (6) Löwenthal has founded a method for the determination of the "tannin" in sumach, hemlock* extract, gall nuts, oak bark, &c., which we will now proceed to describe, assuming, for fixing ideas, that we had to deal with *sumach*.

ASSAYING OF SUMACH.

Sumach consists of the dried shoots and leaves of *rhus coriaria*. The commercial article usually has the form of a powder. 7 grms. of the air-dry powder are extracted three times with boiling-

---

* An American tree, belonging to the order of *Coniferæ*.

hot water on a water-bath; the mixed extracts are filtered and diluted to 1 litre, so that 1 cc. corresponds to 7 mgs. of substance.

Reagents Required.

(1.) *A solution of Permanganate of Potash,* so adjusted that 1 cc. oxidizes about 1·8 to 2·0 mgs. of ferrosum. According to Neubauer's experiments with gallo-tannin, 1 grm. of ferrosum corresponds to 0·7423 grm. of tannin; hence 1 grm. of tannin corresponds to 1÷0·7423 = 1·3471 grms. of ferrosum. Hence, supposing the permanganate to be so adjusted that 1 lit. = 2·021 grms. of ferrosum (= 1·140 grms. crystals of $KMnO_4$ by calculation), 1 cc. of such solution would correspond to exactly 1·5 mgs. of tannin. Neubauer's factor does not necessarily hold for other tannins,* hence the most rational mode of reporting would be to state that 100 grms. of sumach contain tannin equivalent to so and so many grammes of ferrosum (in reference to oxidation by permanganate). This, however, is not customary; and, as the general practice is to report per cents. of "tannin," we will adopt Neubauer's factor as if it held for the tannin in question.

(2.) *A solution of Indigo Carmine* (sulphindylate of soda) in water, acidulated with sulphuric acid, which contains in every litre 60 cc. of oil of vitriol and so much of the pigment that the solution requires very nearly its own volume of permanganate for oxidation. With a certain kind of very superior indigo-carmine, which we have in the laboratory, this means about 12–13 grms. of carmine. All carmines, of course, are not of the same strength.

(3.) *Hide Shavings.*—Raw ox hide as obtainable from any tanner is deprived of its hair by moistening the hairy side with dilute caustic soda, and then plucking off the hair. The unhaired hide is washed with abundance of water, and next steeped in ordinary alcohol for about two days to take out part of the water. The treatment with alcohol is repeated, absolute alcohol being used at the end to obtain a water-free hide, which is dried over sulphuric acid at the ordinary tem-

---

* It indeed is highly questionable whether it is correct for gallo-tannin itself.

perature. The thus dehydrated hide has all the properties of leather.* It shows no tendency to putrefy, even if kept in the air, and not even, it appears, if moistened, and then allowed to dry in the air. By means of a sharp plane it is easily reduced to shavings. It may be comminuted also by means of a rasp; but the heat evolution in this case is so considerable that the raspings become appreciably singed. The shavings are preserved in a bottle.

Modus operandi.—Observe that the process to be described is a purely empirical one, and in its execution nothing must be taken for granted except the proposition that the volume of permanganate required to oxidize, say, unit weight of a certain kind of tannin under given conditions is constant *as long as the conditions remain the same,* including even the rate at which the permanganate is dropped into the solution to be oxidized. We assume that the permanganate solution has been standardized exactly with ferrosum, and that the indigo solution has been approximately adjusted to the intended strength.

(1.) Measure out 20 cc. of indigo, add 1 litre of water and 10 cc. of 60 per. cent. sulphuric acid; mix in a round-bottomed, short-necked flask ("bolt-head"), and drop in permanganate with constant agitation until the mixture becomes *golden-yellow,* free from all admixture of green. Repeat this several times, and take the mean of the last 4–5 titrations, which ought to agree to within ±0·1 cc. of permanganate.

(2.) After a preliminary titration of the sumach extract, measure off exactly a volume corresponding to about 10 cc. of permanganate, add 20 cc. of indigo, 1 litre of water, 10 cc. of 60 per cent. sulphuric acid, and titrate again. Deduct the permanganate corresponding to the indigo according to (1), and put down the balance as corresponding to the *permanganate reducers in the sumach.* This titration also must be done several times; the results are not quite so constant as in the case of unmixed indigo.

---

* This process was invented by the author some years ago, and proposed for the preparation of costly skins, such as tiger skins, which stand the expense of alcohol.

(3.) Measure off five times as much sumach solution as you used in titration (2), and for every 10 cc. of permanganate which this would require weigh out 1 grm. of hide shavings, which, if our directions were followed, means 5 grms. of the latter. Place the hide in a flask, add a volume of water equal to the sumach solution, wait until the hide is softened up; then add the sumach solution, and allow to stand overnight so as to give the hide time to imbibe the tannin. Then filter through a dry filter, measure out a volume equal to twice the volume of sumach solution used in titration (2) (*i.e.*, corresponding to the weight of sumach titrated), and titrate with permanganate under the exact conditions which prevailed in titration (2).

(4.) The nett permanganate used this time corresponds to the gallic and other permanganate reducers, *not* tannin. It is deducted from the nett permanganate used in titration (2) as a correction. The difference is calculated into "tannin" by Neubauer's factor. An example may serve to make the mode of calculation, &c., clear. The substance worked upon was genuine sumach of first quality. 7·003 grms. of sumach were exhausted with water, and the extract diluted to 1 litre.

1 cc. of permanganate by standardization against pure ferrous sulphate was found to correspond to 1·855 mgs. of iron. 20 cc. of indigo solution required 19·53 cc. of permanganate. 7·7 cc. of sumach extract + 20 cc. of indigo, in presence of 10 cc. of 60 per cent. sulphuric acid and 1 litre of water, required, as the mean of several titrations, 29·63 cc. of permanganate. Deducting 19·53 cc. for the indigo, we have 10·10 cc.

Treatment with Hide.—5 grms. of hide were moistened with 38·1 cc. of water, 38·1 cc. of sumach extract were added, and the mixture allowed to stand. After standing over night 15·4 cc. of the filtered solution (as the mean of two numbers) required 1·22 cc. $KMnO_4$ (corrected for indigo).

Hence permanganate, corrected for gallic acid, &c., $= 10·10 - 1·22 = 8·88$ cc. Now $8·88 \times 1·855 = 16·47$ mgs. of iron $= 0·7423 \times 16·47 = 12·23$ mgs. of tannin, according to the factor. 7·7 cc. of extract $= 53·9$ mgs. of sumach; therefore percentage of tannin $= 22·69$.

10.—Partial Analysis of Tea.

PROCURE a good average sample, mix it well, and keep it bottled up.

The Water.—Weigh out 2–3 grms. of the sample between watch-glasses, and heat in an air-bath to 105–110°C. until the weight is constant.

The Theine may be determined either in the original substance or in the aqueous extract from it.

In the former case 2·5 grms. of the finely-powdered leaves are mixed with 0·5 grm. of ignited magnesia. The mixture is transferred to a shallow porcelain basin, about 30 cc. of water are added, and the whole is evaporated on a simmering water-bath, on constant stirring, until the mass has almost but not completely dried up. If the evaporation be carried too far, there is a danger of some of the theine being lost by volatilization. The mass is then scraped out by means of a metal spatula, and transferred to a dry, conical flask of about 150 cc.'s capacity. 50 cc. of chloroform are added, the flask is connected with a small, inverted condenser, and the extraction of the theine effected by heating the flask and contents in a water-bath. After about a quarter of an hour's heating the flask is cooled down, detached from the condenser, and the extract decanted through a filter made of loose paper into a small, tared, conical flask. The chloroform is then distilled off and used for a second extraction of the residue. After three treatments in this way the theine is extracted as far as possible. The chloroform is finally distilled off, the residue dried at 105°C. and weighed once, merely for a check, as "*crude theine.*" It is largely contaminated with resinous matter, which is removed by treatment with boiling water and filtration. The solution of theine is evaporated to dryness in a tared platinum or porcelain crucible, dried at 105°C., and weighed.

When the aqueous extract of the tea is used for the determination of the theine, the total amount of residue is much smaller than in the case just mentioned, and the extraction with chloroform is much more quickly and easily effected. Another advantage is that the theine obtained from the first contains only a small, unweighable quantity of resinous matter (insoluble in hot water). For the execution of this modification 2 grms. of the tea (unpowdered) are extracted several times with boiling water, each instalment of water being allowed a sufficient time to act, and the flask in which the extraction is carried out being kept on a water-bath. The extract is evaporated with magnesia as before, the theine extracted repeatedly from the residue by chloroform, dried, and weighed.

Mr. John M'Arthur, in each of two tea analyses, I. and II., applied the two modifications of the method to the same sample, and obtained the following percentages of theine:—

	I.	II.
From the leaves,....................................	3·80	4·00
From the infusion,................................	3·73	4·20

The Tannin.—7 grms. of original tea are extracted several times with boiling water, the solution is filtered, and diluted to 1 litre. In the extract the tannin is determined exactly as described under "Assaying of Sumach," the treatment with hide not being forgotten. The end-point of the reaction is, as a rule, more difficult to determine exactly than in the case of sumach; a number of titrations must be carried out in order to eliminate the irregular errors as far as possible.

11.—Analysis of Wood Spirit.

Wood spirit consists mainly of methyl-alcohol $CH_3\ OH$, acetone $CO\ (CH_3)_2$, and water; besides these, there are a host of minor components, of which acetate of methyl, $CH_3.COOCH_3$ and di-methyl-acetal $CH_3-CH\left\{\begin{matrix}O\ CH_3\\ O\ CH_3\end{matrix}\right.$ are best known.

When we speak of the "analysis" of a wood spirit, we generally mean the determination of the methyl-alcohol present as such, or, potentially, as acetate of methyl, and of the acetone.

In the examination of what pretends to be *pure* methyl-alcohol, *e.g.*, the kind of alcohol sold for the making of aniline colours or for the use of chemists, it is expedient to begin with qualitative tests to prove, if possible, the absence of certain impurities. Pure methyl-alcohol has only a very faint and *not* unpleasant smell. It mixes with water in all proportions without formation of a milky mixture. 1 cc. when mixed with 2 cc. of concentrated oil of vitriol gives a colourless, or almost colourless, mixture. 1 cc. when mixed with 5 cc. of water, and then one drop of bromine water, gives a yellow liquid; if the colour of the bromine disappears, this indicates the presence of allyl-alcohol $C_3H_5\,OH$. For the detection of acetone we may use the method given below in a quantitative form. In regard to ethyl-alcohol see the next exercise.

Supposing qualitative tests for impurities to have given negative results, or only proved the presence of traces of the respective substances, a determination of the *vapour-density* by Gay-Lussac's method—volatilization of a known weight over mercury in a graduated tube, and measurement of the volume, temperature, and pressure of the vapour—affords an excellent test for impurities generally; because, apart from water (which we will assume to be absent), of all components of wood spirit methyl-alcohol has the lowest vapour-density.

Given a mixture of volatile substances, I., II., III.........., containing p_1 grms. of component I., p_2 of component II., &c., and we have obviously for each of these—

$$p=\left(\frac{p}{\mathrm{M}}\right)\times\mathrm{M},$$

where M is the molecular weight, *i.e.*, p grms. represent p/M gramme-molecules, and consequently at any fixed upon disgregation, *e.g.*, that corresponding to 100°C. and 500 mms. pressure for the vapour-volume of the component under consideration—

$$\frac{p}{\mathrm{M}}\times\mathrm{C}\ \text{litres},$$

where C is a constant as long as the disgregation remains the same. Hence, we have for the vapour-volume of 1 grm. of our mixture at standard disgregation—

$$\left\{\frac{p_1}{\mathrm{M}_1}+\frac{p_2}{\mathrm{M}_2}+\frac{p_3}{\mathrm{M}_3}\cdots\cdots\cdots\frac{p_2}{\mathrm{M}_2}\right\}\mathrm{C}\ \text{litres}.$$

But $H_2 = 2$ grms. of hydrogen occupy C litres likewise; hence, the specific gravity of the mixed vapour on the hydrogen-scale is—

$$S = 1 \div 2\left(\frac{p_1}{M_1} + \frac{p_2}{M_2} + \frac{p_3}{M_3}\right)$$

Example:—The given liquid consists of 0·8 grm. of methyl-alcohol and 0·2 grm. of water. In this case we have—

$$S = 1 \div 2\left(\frac{0{\cdot}8}{32} + \frac{0{\cdot}2}{18}\right)$$

The divisor computed is 0·07222, and its reciprocal, *i.e.*, S = 13·85.

In this *particular* case, however—*i.e.*, if we know that, substantially speaking, *water* is the only impurity present—we need not go to the trouble of determining the vapour density; the specific gravity of the liquid, taken at, say, 15°56C. (= 60°F.), or at 0°C., gives us all we want, with the help of the alcoholometric table appended to the end of this article.

For the determination of the specific gravity of a liquid like methyl-alcohol the Westphal balance is a handy instrument; but more exact results can be obtained by means of a cylindrical narrow-necked specific-gravity bottle provided with either one mark, or a calibrated millimetre scale, at the narrow neck, and with a well-fitting stopper for the funnel-shaped appendage in which the neck terminates; because with such a bottle volatilization is easily prevented by inserting the stopper, and a pre-determined fixed temperature established by means of a water-bath.

In the examination of a *wood spirit* more especially, the determination of the *boiling-point* curve comes in as a useful preliminary. To effect it, place 100 cc. of the spirit in a fractionating flask of about 1·7 times the capacity, and attach the flask to a Liebig's condenser, after having fixed a thermometer in its neck, so that the bulb is fairly below the lower edge of the side tube. Then distil the contents over a naked flame at the lowest rate compatible with the condition that the thermometer bulb is always immersed in fully saturated vapour, and at regular short intervals note down the reading of the thermometer and the corresponding volume, v, of total distillate obtained at that stage. Thus—

$v =$	0	5 cc.	10 cc.	....	90 cc.	95 cc.
$t =$ (say)	64°0	64°0	64°1	....	66°	67°1

As methyl-alcohol has quite a characteristic tendency to *bump* on distillation, it is necessary to prevent this somehow. The best method is to send a *very slow* but continuous current of air or hydrogen through the boiling liquid, but this means a relatively complex apparatus. More convenient expedients are to put some fragments of an alloy of tin and (little) sodium into the liquid, or, in the absence of this alloy, a few pieces of the stem of a clay tobacco pipe.

Supposing the distillation to be completed, lay down the v's as abscissæ and the t's as ordinates in a system of rectangular co-ordinates (*i.e.*, on a sheet of "curve-paper," as sold by Messrs. W. & J. K. Johnston, Geographers, Edinburgh), and draw a continuous curve, so that it takes in the t's as nearly as possible, to obtain the *boiling-point curve.*

Before going further, we will give a brief statement of the physical characters of the principal components of wood spirit.

Methyl-alcohol.—The specific gravity ${}_4S_t$, meaning the sp. gr. at $t°$ referred to water of 4°C. as standard and taken as $=1$ is as follows *:—

$t =$	0	5°	10°	15°	15°56	20°
${}_4S_t =$	·81015	·80557	·80098	·79640	·79589	·79181

Boiling point under 760 mms. pressure = 64·°96, say 65°; 29 mms. of difference of pressure corresponds to 1° of difference in the boiling point, or from about $760-30$ to $760+30$ mms., 1 mm. of increment in pressure corresponds to 0°0345 in the boiling point.

Acetone.—A colourless liquid possessing a strong fragrant smell, and mixing with water in all proportions. Extractable from its aqueous solution, if not too dilute, by addition of dry carbonate of potash as an upper layer. ${}_4S_0 =$ ·81858, T. E. Thorpe.

---

[*] According to an investigation by Dittmar and Charles A. Fawsitt communicated to the Roy. Soc., Edin., in 1887.

According to H. Kopp, S_0 = ·8144; $S_{13\cdot9}$ = ·7995. Boiling point, 56°53 at 760 mms. (Thorpe).

Acetate of Methyl.—A colourless mobile liquid of a strong agreeable smell. According to H. Kopp, S_0 = ·9562; boiling point, 56°53 at 760 mms.

According to experiments made in our laboratory by Mr. James Robson (on a hot summer day), 100 volumes of water dissolve 35·8 volumes of the ester; or 1 volume of the latter requires 2·8 volumes of water for its solution.

The *Ethyl-ester*, according to Mr. Robson's experiments, requires 11·7 times its volume of water.

Di-Methyl-Acetal.—A colourless liquid possessing a peculiar ethereal smell. According to Krämer and Grodzki (Ber. d. Deutsch. Chem. Ges. for 1876, p. 1930), S_{15} = ·8554; boiling point, 63·°2 to 64·°8 at 760 mms. Soluble in 15 parts of water.

Determination of the Methyl-Alcohol.

For this determination Krell, some years ago, invented a convenient method, the principle of which is to convert the methyl of the alcohol into iodide and to measure, *i.e.*, to indirectly weigh, the latter. The method was subsequently modified by Krämer and Grodzki. In the following we reproduce the directions given by the latter in his article on methyl-alcohol in *Dammer's Handwörterbuch der Verfälschungen*:—

15 grms. of biniodide of phosphorus are placed in a flask of 30 cc. capacity connected with an inverted condenser, and 5 cc. of the alcohol to be analysed are gradually dropped on the iodide through the condenser while the flask is being kept cold in a water-bath. This being done, 5 cc. of a solution of 1 part of iodine in 1 part of aqueous hydriodic acid of 1·7 specific gravity are added, and the whole is digested at a gentle heat for a quarter of an hour. The condenser is then turned downwards, and the water-bath heated up to cause the iodide of methyl formed to distil over. It is collected in a tube, graduated into tenths of a cc., under water. When the iodide is over, as far as possible practically, the aqueous (upper) layer in the tube is made up to 15 cc. by addition of more water, shaken with the (heavy) iodide and the latter allowed to settle, to be measured as it

stands. According to Krämer and Grodzki's standard trials 5 cc. of pure methyl-alcohol give 7·45 cc. of iodide instead of the 7·8 cc. required by theory and the known specific gravity of the iodide. The method, however, valuable as it is, is invested with numerous errors, which defy all calculation. Hence, to give reliable results, it must be wrought in a strictly empirical style, and this includes that, instead of relying on Krämer and Grodzki's results, we had better prepare perfectly pure methyl-alcohol ourselves, work 5 cc. of it in *the apparatus meant to be used*, and determine our own constant.

According to Grodzki (l.c.), a methyl-alcohol, to be fit for aniline-colour making, should yield at least 7·3 cc. of (crude) iodide.

If acetate of methyl is present, a quantity of iodide of methyl is produced from it which is almost exactly the same as if the ester in the course of the process were decomposed into acetic acid and methyl-alcohol, and the latter acted on by the hydriodic acid as if it had been there as such from the first. This, however, is no reproach to the method, because acetate of methyl, being so readily saponified by alkalies, is really worth its equivalent of methyl-alcohol. If a separate determination

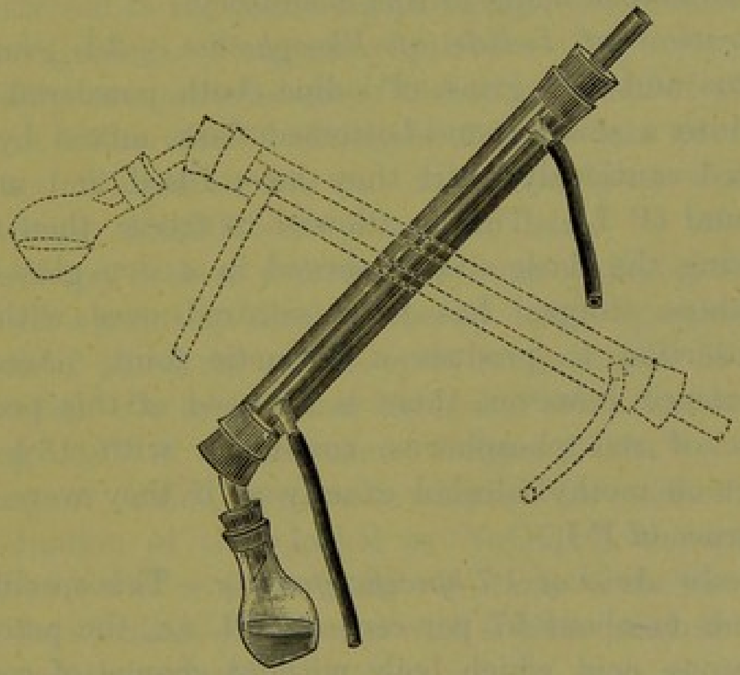


FIG. 61.

be desired, heat a known quantity of the spirit with a sufficient measured volume of standard caustic soda in a closed bottle to 100° for a sufficient time, *i.e.*, until all the acetate is decomposed into alcohol and soda-salt; then allow to cool, and determine the excess of caustic soda left by titration with standard acid (and alkali). Every NaOH part of soda neutralized corresponds to CH_3, $COOCH_3$ parts of methyl-acetate = CH_4O parts of methyl-alcohol. The presence of acetone or di-methyl-acetal produces appreciable (positive) errors; but we cannot afford here to discuss the matter any further, and must refer to Krämer and Grodzki's original memoir (cited under *Di-Methyl-Acetal*). *See* also Bardy and Bordet Comptes Rendus 88, 236.

The distillation apparatus must be so constructed that the condenser can be turned either upwards or downwards without undoing any joint. Fig. 61 represents the apparatus which we are in the habit of using in this laboratory.

Preparation of Iodide of Phosphorus.—3·1 grms. of *red* phosphorus and 25·4 grms. of iodine (both powdered and *dry*) are put into a small round-bottomed flask, mixed by shaking, and heated cautiously until they have fused and united into a compound ($P\ I_2$). This is allowed to freeze, then taken out by breaking the flask and preserved in a *dry* glass-stoppered bottle, whose stopper has been smeared over with vaseline before insertion to produce a hermetic joint. According to our experience, however, there is no need of this preparation; 1·6 grms. of red phosphorus, conjointly with 13·4 grms. of iodine, act on methyl-alcohol exactly as if they were combined into 15 grms. of $P\ I_2$.

Hydriodic Acid of 1·7 *specific gravity.*—This specific gravity corresponds to about 57 per cent. of HI, *i.e.*, the percentage of that aqueous acid which boils without change of composition at 127°C. For its preparation the most convenient method is the following:—Dissolve 5 grms. of iodine and 10 grms. of iodide of potassium in 20 grms. of water in a mortar, and add other 80 grms. of water. Through the brown liquid thus produced pass sulphuretted hydrogen until the liquid is decolorized, *i.e.*, until the reaction $H_2S + I_2 = 2HI + S$ is accomplished. Then dissolve an additional quantity of iodine in the liquid, again decolorize by means of sulphuretted hydrogen, and so go on until a fresh instalment of iodine added refuses to be decolorized by sulphuretted hydrogen, which will be the case *before* the liquid is quite up to the desired percentage of HI. When that point is reached heat gently to cause the sulphur to coagulate and the dissolved sulphuretted hydrogen to escape, and filter off the sulphur. Then add the necessary supplementary iodine and enough of red phosphorus to convert it into hydriodic acid, and distil the mixture, taking care to change the receiver as soon as the boiling point has become constant at (or very near) 127°C.

DETERMINATION OF THE ACETONE.

An important determination, because the presence of more than 0·5 per cent. of acetone in a given methyl-alcohol unfits it for the purposes of the aniline-colour maker (Grodzki). The method described in the following paragraph was worked out by Krämer and Grodzki. Reagents required:—

1. *A doubly-normal solution of iodine* in iodide of potassium. 25·4 grms. of iodine and 50 of iodide of potassium are dissolved in water and diluted to 100 cc. 2. *A doubly-normal caustic soda* containing $2NaOH = 80$ grms. per litre. 3. *Alcohol-free ether.* Ordinary ether, according to our experience, can be made almost absolutely alcohol-free by long digestion with a large excess of powdered caustic soda in the cold. If required at short notice, the crude ether is boiled with the reagent at the "wrong end" of a condenser. Copper flasks,* as sold for the making of coffee, are well adapted for either purpose. After elimination of the alcohol as $NaOC_2H_5$, the mixture is distilled from out of a water-bath. To remove the last remnant of alcohol the distillate is tortured with sodium under an inverted condenser and then distilled.

To analyse a wood spirit, mix 1 cc. of it with 10 cc. of the caustic soda in a graduated test tube; then add gradually 5 cc. of the iodine solution. Iodoform is produced, sometimes visibly, by the reaction—

$$\underset{\text{Acetone.}}{CO(CH_3)_2} + 3I_2 + 3NaOH = \underset{\text{Acetic Acid.}}{(CO.CH_3)OH} + 3NaI + 2H_2O + \underset{\text{Iodoform.}}{CHI_3}$$

---

* Glass flasks, being attacked by the alkali, are not safe.

$CO(CH_3)_2=58$; $CHI_3=394$; hence 1 grm. of iodoform produced indicates 0·1472 grm. of acetone.

To extract the iodoform shake the mixture with 10 cc. of ether, allow the ethereal solution to rise, measure off an aliquot part of it, let it evaporate spontaneously on a tared watch-glass, and weigh the iodoform after having kept it for a while over concentrated sulphuric acid, without, however, aiming at constancy of weight, which is unattainable on account of the appreciable volatility of the compound. The iodoform obtained is liable to be contaminated with non-volatile matter. To determine it, volatilize the (weighed) product at a gentle heat, weigh the residue, and deduct it as a correction. In calculating the whole of the iodoform present from the part weighed multiply with the ratio of the volume of the *ethereal layer* (*not* that of the total ether taken) to the volume of ethereal solution measured off for evaporation.

The following table is extracted from the Memoir, quoted in the foot-note on p. 275. It is based on duplicate determinations of the specific gravities at 0°, about 10° and about 20° of pure methyl-alcohol, and of aqueous alcohols of 5, 10, 20, 30, 40, 50, 60, 70, 80, 90, 95 per cent. derived from it by gravimetric synthesis. The methyl-alcohol used was proved to be free of acetone; it suffered no diminution in specific gravity on re-distillation over anhydrous sulphate of copper; its vapour-density was practically equal to 16. The values S given by the table are probably correct to ±0·0001; they are sure not to be out by more than ±0·0002. As stated in the heading, they are taken in reference to water of 4° as = 100000. To find the specific gravities in reference to water of any other temperature $t°$ as a standard, divide with the specific gravity $({}_4W_t)$ of water at $t°$. Taking the weight of one volume of water of 4° as = 1, that of one volume of water at $t°$ is ${}_4W_t=1-\epsilon$. For

$t =$ 4°	0°	15°	15·°56
$\epsilon =$ nil	·000 129	·000 840	·000 928

and generally,

$${}_tS={}_4S\,(1+\epsilon)$$

with sufficient exactitude.

DITTMAR AND FAWSITT'S TABLE OF THE SPECIFIC GRAVITIES OF AQUEOUS METHYL-ALCOHOLS AT 0° AND AT 15·°56C.; WATER OF + 4° = 100000.

I.—From 0 to 30 per cent. of CH_4O.

$${}_4S_0 - {}_4S_t = a\,t + b\,t^2$$

Percentage.	Sp. Gravity at 0°C.	Diff.	a	b	Sp. Gravity at 15·°56C.	Diff.
0	999 87		− 6·0	+ ·705	999 07	
1	998 06	− 181	5·4	·694	997 29	− 178
2	996 31	175	4·8	·681	995 54	175
3	994 62	169	3·9	·670	993 82	172
4	992 99	163	3·0	·659	992 14	168
5	991 42	157	− 2·2	·648	990 48	166
6	989 90	152	1·2	·634	988 93	155
7	988 43	147	0·2	·621	987 26	167
8	987 01	142	+ 0·9	·609	985 69	157
9	985 63	138	2·1	·596	984 14	155
10	984 29	134	+ 3·3	·581	982 62	152
11	982 99	130	4·8	·569	981 11	151
12	981 71	128	6·2	·552	979 62	149
13	980 48	123	7·8	·536	978 14	148
14	979 26	122	9·5	·519	976 68	146
15	978 06	120	+ 11·0	·500	975 23	145
16	976 89	117	12·5	·480	973 79	144
17	975 73	116	14·5	·461	972 35	144
18	974 59	114	16·2	·440	970 93	142
19	973 46	113	18·3	·420	969 50	143
20	972 33	113	+ 20·0	·398	968 08	142
21	971 20	113	22·2	·373	966 66	142
22	970 07	113	24·3	·350	965 24	142
23	968 94	113	26·4	·321	963 81	143
24	967 80	114	29·0	·291	962 38	143
25	966 65	115	+ 31·3	·261	960 93	145
26	965 49	116	33·8	·230	959 49	144
27	964 30	119	36·0	·191	958 02	147
28	963 10	120	38·8	·151	956 55	147
29	961 87	123	41·1	·106	955 06	149
30	960 57	130	44·0	·063	953 55	151

II.—From 30 to 100 per cent.

$_4S_0 - {}_4S_t = a\,t.$

Percentage.	Specific Gravity at 0°C.	Diff.	a	Specific Gravity at 15·°56C.	Diff.
30	960 57	− 130	+ 44·36	953 67	
31	959 21	136	45·66	952 11	− 156
32	957 83	138	46·93	950 53	158
33	956 43	140	48·17	948 94	159
34	955 00	143	49·39	947 32	162
35	953 54	146	50·58	945 67	165
36	952 04	150	51·75	943 99	168
37	950 51	153	52·89	942 28	171
38	948 95	156	54·01	940 55	173
39	947 34	161	55·10	938 77	178
40	945 71	163	56·16	936 97	180
41	944 00	171	57·20	935 10	187
42	942 39	161	58·22	933 35	175
43	940 76	163	59·20	931 55	180
44	939 11	165	60·17	929 75	180
45	937 44	167	61·10	927 93	182
46	935 75	169	62·01	926 10	183
47	934 03	172	62·90	924 24	186
48	932 29	174	63·76	922 37	187
49	930 52	177	64·60	920 47	190
50	928 73	179	65·41	918 55	192
51	926 91	182	66·19	916 61	194
52	925 07	184	66·95	914 65	196
53	923 20	187	67·68	912 67	198
54	921 30	190	68·39	910 66	201
55	919 38	192	69·07	908 63	203
56	917 42	196	69·72	906 57	206
57	915 44	198	70·35	904 50	207
58	913 43	201	70·96	902 39	211
59	911 39	204	71·54	900 26	213
60	909 17	222	71·96	897 98	228
61	907 06	211	72·37	895 80	218
62	904 92	214	72·91	893 58	222
63	902 76	216	73·45	891 33	225
64	900 56	220	73·98	889 05	228

II.—From 30 to 100 per cent.—*Continued.*

Percentage.	Specific Gravity at 0°C.	Diff.	a	Specific Gravity at 15·°56C.	Diff.
65	898 35	- 221	74·51	886 76	- 229
66	896 11	224	75·05	884 43	233
67	893 84	227	75·57	882 08	235
68	891 54	230	76·10	879 70	238
69	889 22	232	76·62	877 14	256
70	886 87	235	77·14	874 87	227
71	884 70	230	77·66	872 62	225
72	882 37	233	78·18	870 21	241
73	880 03	234	78·69	867 79	242
74	877 67	236	79·20	865 35	244
75	875 30	237	79·71	862 90	245
76	872 90	240	80·22	860 42	248
77	870 49	241	80·72	857 93	249
78	868 06	243	81·23	855 42	251
79	865 61	245	81·73	852 90	252
80	863 14	247	82·22	850 35	255
81	860 66	248	82·72	847 79	256
82	858 16	250	83·21	845 21	258
83	855 64	252	83·70	842 62	259
84	853 10	254	84·19	840 01	261
85	850 55	255	84·67	837 38	263
86	847 98	257	85·16	834 73	265
87	845 39	259	85·64	832 07	266
88	842 78	261	86·12	829 38	269
89	840 15	263	86·59	826 68	270
90	837 51	264	87·07	823 96	272
91	834 85	266	87·54	821 23	273
92	832 18	267	88·01	818 49	274
93	829 48	270	88·48	815 72	277
94	826 77	271	88·94	812 93	279
95	824 04	273	89·40	810 13	280
96	821 29	275	89·86	807 31	282
97	818 53	276	90·32	804 48	283
98	815 76	277	90·78	801 64	284
99	812 95	281	91·23	798 76	288
100	810 15	280	91·68	795 89	287

12.—Determination of Ethyl-Alcohol.

For the determination of the percentage of real, in a substantially pure aqueous, alcohol, we need only determine its specific gravity at a definite convenient temperature, and by means of one of the tables, based on standard experiments, which have been drawn up, translate the result into the corresponding percentage. The following table has been calculated by the author from Mendelejeff's famous experiments,* not quite directly though, but in this way:—

Landolt and Börnstein's Physikalische Tabellen include a table (on their p. 151) which, proceeding from per cent. to per cent., gives the specific gravities, ${}_{15}S_{15}$, of aqueous alcohols to five decimal places. According to its heading, the table has been drawn up by the "*Kaiserliche Normal-Aichungs-Commission*," and is "*basirt auf den von Mendelejeff berechneten Formeln.*" From this table I have calculated the percentages corresponding to the specific gravities ·999, ·998, ·997, ... ·794 to originally three decimals by simple interpolation. Hence, apart from the errors introduced by neglecting second differences and cancelling the third decimals of the percentages, the specific gravities given in column 1 of our table as functions of the stated percentages should be as exact as the original table is. To check my computations I calculated the specific gravities for all integer percentages backward from my table, again by simple interpolation, and, comparing them with those in the original table in Landolt's book, found that—

The difference *nil* occurred 51 times,
„ ±1 „ 44 „
„ ±2 „ 5 „
Water = 100000,

which showed, incidentally, that our table, in point of arithmetical precision, is practically at a level with the one in Landolt and Börnstein's book.

The third column gives the differences of the consecutive p's to facilitate interpolation; column 4 gives the reciprocals of

---

* Poggendorff's Annalen, vol. cxxxviii, pp. 103 and 230.

these differences to facilitate backwards interpolation. Each of such a couple of differences belongs to the interval between the p or S, which it stands on a line with, and the next *preceding* entry. The numbers given in column 5 as $\triangle S$ for 1° of change of temperature belong to the respective values S or p individually.

These values $\triangle S/\triangle t$ were calculated from two tables included in Mendelejeff's Memoir, which give the specific gravities ${}_{4}S$ referred to water of 4° at 0°, 10°, 20°, and 30°, one for all integer percentages from 5 to 5, as found virtually by direct experiment; the other for all integer percentages from 10 to 10, as calculated by means of interpolation formulæ. From the respective entries it was easy to calculate the values $({}_{15}S_{10}-{}_{15}S_{20})\div 10$ for 5, 10, 15, &c., per cent. alcohol, and these values I adopted as approximations to *any* $\triangle S/\triangle t$ from $t=10$ to $t=20$, for the respective p. To form an idea of the degree of approximation afforded by these values, I used them for calculating the specific gravities ${}_{15}S_{15}$ from the values ${}_{15}S_{10}$ as given (virtually) in Mendelejeff's Memoir, and compared them with the entries in the table in Landolt's book, which had served me for the calculation of the entries p in my table. The differences ranged as follows:—

For $p=$	100 to 50	45	15	35, 30, 25, 20, 10, 5
	-5 to $+1$	$+10$	-15	$+6$ to -9 units.

Water = 100000 units.

This may not do full justice to Mendelejeff's work, but it surely suffices for all practical purposes. Relying chiefly on the data of Mendelejeff's *calculated* table, I found the values $\triangle S/\triangle t$ for all the specific gravities given in my table under S by graphic interpolation, and entered them in column 5. In the table the specific gravities are referred to water of 15·°.

1. To find the specific gravity ${}_{4}S$ referred to *water* of 4°C. from ${}_{15}S$, calculate thus—

$${}_{4}S={}_{15}S(1-0{\cdot}000\,840).$$

2. To find the specific gravity referred to water of 15°·56C. = 60°F. calculate thus—

$${}_{15\cdot56}S={}_{15}S(1+0{\cdot}000\,088).$$

TABLE GIVING THE RELATION IN AQUEOUS ETHYL-ALCOHOL BETWEEN SPECIFIC GRAVITY AT 15°C. ON THE ONE HAND AND THE PERCENTAGE BY WEIGHT OF REAL ALCOHOL, OR THE SPECIFIC GRAVITY AT ANY TEMPERATURE FROM 10° TO 20°, ON THE OTHER.

Calculated after Mendelejeff's Determinations, by W. Dittmar.

Water of 15°C. = 1000.

Spec. Grav. at 15·° $_{15}S_{15}$.	Percentage. p.	Δp for ΔS = 1.	Diff. in Spec. Grav. for		Spec. Grav. at 15.° $_{15}S_{15}$.	Percentage. p.	Δp for ΔS = 1.	Diff. in Spec. Grav. for	
			Δp = 1.	Δt=1°.				Δp = 1.	Δt=1°.
1000	0·00			0·144	975	17·25	·84	1·19	·330
999	0·53	·53	1·89	·146	974	18·08	·83	1·20	·348
998	1·06	·53	1·89	·147	973	18·91	·83	1·20	·367
997	1·61	·55	1·82	·150	972	19·73	·82	1·22	·387
996	2·16	·55	1·82	·152	971	20·54	·81	1·23	·405
995	2·73	·57	1·75	·154	970	21·35	·81	1·23	·421
994	3·30	·57	1·75	·157	969	22·13	·78	1·28	·434
993	3·91	·61	1·64	·161	968	22·89	·76	1·32	·450
992	4·51	·60	1·67	·166	967	23·65	·76	1·32	·466
991	5·12	·61	1·64	·170	966	24.39	·74	1·35	·480
990	5·77	·65	1·54	·174	965	25·13	·74	1·35	·496
989	6·43	·66	1·52	·180	964	25·84	·71	1·41	·510
988	7·09	·66	1·52	·186	963	26·53	·69	1·45	·522
987	7·78	·69	1·45	·192	962	27·23	·70	1·43	·535
986	8·49	·71	1·41	·199	961	27·90	·67	1·49	·548
985	9·20	·71	1·41	·206	960	28·55	·65	1·54	·560
984	9·96	·76	1·32	·214	959	29·21	·66	1·52	·570
983	10·72	·76	1·32	·223	958	29·84	·63	1·59	·581
982	11·50	·78	1·28	·231	957	30·46	·62	1·61	·593
981	12·28	·78	1·28	·242	956	31·09	·63	1·59	·604
980	13·10	·82	1·22	·254	955	31·69	·60	1·67	·614
979	13·92	·82	1·22	·267	954	32·30	·61	1·64	·623
978	14·74	·82	1·22	·281	953	32·88	·58	1·72	·632
977	15·58	·84	1·19	·296	952	33·45	·57	1·75	·641
976	16·41	·83	1·20	·311	951	34·03	·58	1·72	·650

Spec. Grav. at 15·° $_{15}S_{15}$.	Percentage. p.	Δ p for Δ S = 1.	Diff. in Spec. Grav. for		Spec. Grav. at 15·° $_{15}S_{15}$.	Percentage. p.	Δ p for Δ S = 1.	Diff. in Spec. Grav. for	
			Δ p = 1.	Δ t = 1°.				Δ p = 1.	Δ t = 1°.
950	34·59	·56	1·79	·657	915	51·68	·45	2·22	·800
949	35·15	·56	1·79	·666	914	52·13	·45	2·22	·801
948	35·70	·55	1·82	·673	913	52·58	·45	2·22	·802
947	36·25	·55	1·82	·680	912	53·02	·44	2·27	·803
946	36·78	·53	1·89	·687	911	53·47	·45	2·22	·804
945	37·31	·53	1·89	·694	910	53·91	·44	2·27	·806
944	37·84	·53	1·89	·700	909	54·35	·44	2·27	·807
943	38·36	·52	1·92	·707	908	54·80	·45	2·22	·808
942	38·88	·52	1·92	·712	907	55·24	·44	2·27	·809
941	39·39	·51	1·96	·718	906	55·68	·44	2·27	·810
940	39·90	·51	1·96	·723	905	56·12	·44	2·27	·811
939	40·40	·50	2·00	·727	904	56·56	·44	2·27	·812
938	40·90	·50	2·00	·733	903	57·00	·44	2·27	·813
937	41·40	·50	2·00	·737	902	57·43	·43	2·33	·813
936	41·89	·49	2·04	·741	901	57·87	·44	2·27	·813
935	42·38	·49	2·04	·746	900	58·31	·44	2·27	·814
934	42·86	·48	2·08	·750	899	58·74	·43	2·33	·815
933	43·35	·49	2·04	·753	898	59·18	·44	2·27	·816
932	43·83	·48	2·08	·756	897	59·61	·43	2·33	·817
931	44·30	·47	2·13	·760	896	60·05	·44	2·27	·817
930	44·78	·48	2·08	·763	895	60·48	·43	2·33	·817
929	45·25	·47	2·13	·767	894	60·91	·43	2·33	·818
928	45·73	·48	2·08	·770	893	61·35	·44	2·27	·819
927	46·20	·47	2·13	·773	892	61·78	·43	2·33	·819
926	46·66	·46	2·17	·774	891	62·21	·43	2·33	·820
925	47·13	·47	2·13	·778	890	62·64	·43	2·33	·820
924	47·59	·46	2·17	·781	889	63·07	·43	2·33	·820
923	48·05	·46	2·17	·783	888	63·50	·43	2·33	·820
922	48·51	·46	2·17	·786	887	63·93	·43	2·33	·821
921	48·96	·45	2·22	·788	886	64·36	·43	2·33	·822
920	49·42	·46	2·17	·790	885	64·79	·43	2·33	·822
919	49·88	·46	2·17	·792	884	65·21	·42	2·38	·823
918	50·33	·45	2·22	·794	883	65·64	·43	2·33	·824
917	50·78	·45	2·22	·796	882	66·07	·43	2·33	·825
916	51·23	·45	2·22	·798	881	66·49	·42	2·38	·826

Spec. Grav. at 15·° ${}_{15}S_{15}$.	Percentage. p.	Δp for $\Delta S =$ 1.	Diff. in Spec. Grav. for		Spec. Grav. at 15·° ${}_{15}S_{15}$.	Percentage. p.	Δp for $\Delta S =$ 1.	Diff. in Spec. Grav. for	
			$\Delta p =$ 1.	$\Delta t = 1$·°				$\Delta p =$ 1.	$\Delta t = 1$·°
880	66·92	·43	2·33	·825	845	81·46	·40	2·50	·854
879	67·34	·42	2·38	·826	844	81·86	·40	2·50	·855
878	67·77	·43	2·33	·826	843	82·26	·40	2·50	·856
877	68·20	·43	2·33	·827	842	82·66	·40	2·50	·857
876	68·62	·42	2·38	·828	841	83·06	·40	2·50	·858
875	69·04	·42	2·38	·829	840	83·46	·40	2·50	·859
874	69·46	·42	2·38	·830	839	83·86	·40	2·50	·860
873	69·88	·42	2·38	·830	838	84·26	·40	2·50	·860
872	70·30	·42	2·38	·830	837	84·65	·39	2·56	·860
871	70·73	·43	2·33	·831	836	85·05	·40	2·50	·861
870	71·15	·42	2·38	·832	835	85·44	·39	2·56	·862
869	71·57	·42	2·38	·833	834	85·83	·39	2·56	·862
868	71·99	·42	2·38	·834	833	86·22	·39	2·56	·862
867	72·40	·41	2·44	·835	832	86·61	·39	2·56	·863
866	72·82	·42	2·38	·836	831	87·00	·39	2·56	·863
865	73·24	·42	2·38	·836	830	87·38	·38	2·63	·864
864	73·66	·42	2·38	·837	829	87·77	·39	2·56	·865
863	74·08	·42	2·38	·838	828	88·15	·38	2·63	·865
862	74·49	·41	2·44	·839	827	88·53	·38	2·63	·865
861	74·90	·41	2·44	·840	826	88.91	·38	2·63	·865
860	75·32	·42	2·38	·840	825	89.29	·38	2·63	·865
859	75·73	·41	2·44	·840	824	89·67	·38	2·63	·866
858	76·15	·42	2·38	·841	823	90·05	·38	2·63	·866
857	76·56	·41	2·44	·842	822	90·42	·37	2·70	·866
856	76·97	·41	2·44	·842	821	90·79	·37	2·70	·866
855	77·38	·41	2·44	·844	820	91·16	·37	2·70	·865
854	77·79	·41	2·44	·845	819	91·53	·37	2·70	·864
853	78·21	·42	2·38	·846	818	91·89	·36	2·78	·864
852	78·62	·41	2·44	·847	817	92·26	·37	2·70	·863
851	79·02	·40	2·50	·848	816	92·62	·36	2·78	·862
850	79·43	·41	2·44	·848	815	92·98	·36	2·78	·862
849	79·84	·41	2·44	·849	814	93·34	·36	2·78	·861
848	80·24	·40	2·50	·850	813	93·70	·36	2·78	·861
847	80·65	·41	2·44	·852	812	94·05	·35	2·86	·860
846	81·06	·41	2·44	·853	811	94·41	·36	2·78	·859

Spec. Grav. at 15·° $_{15}S_{15}$.	Percentage. p.	Δp for ΔS = 1.	Diff. in Spec. Grav. for		Spec. Grav. at 15·° $_{15}S_{15}$.	Percentage. p.	Δp for ΔS = 1.	Diff. in Spec. Grav. for	
			Δp = 1.	Δt = 1·°				Δp = 1.	Δt = 1·°
810	94·76	·35	2·86	·859	800	98·16	·33	3·03	·850
809	95·11	·35	2·86	·859	799	98·49	·33	3·03	·849
808	95·45	·34	2·94	·858	798	98·81	·32	3·13	·848
807	95·80	·35	2·86	·857	797	99·14	·33	3·03	·847
806	96·15	·35	2·86	·856	796	99·46	·32	3·13	·846
805	96·48	·33	3·03	·856	795	99·78	·32	3·13	·845
804	96·82	·34	2·94	·855	794	100·10	·32	3·13	·844
803	97·16	·34	2·94	·854	**794·32**	**100**			
802	97·49	·33	3·03	·852					
801	97·83	·34	2·94	·851					

Referring to water of 4°C. as = 100000, the specific gravity $_4S_t$ of absolute alcohol, according to Mendelejeff, is

$$_4S_t = 80\ 625 - 83{\cdot}4t - 0{\cdot}029t^2\ ;$$

hence (by Mendelejeff's computation) we have for the

Specific Gravities of Absolute Alcohol—

t	0°	5°	10°	15°	20°	25°	30°
$_4S_t$	806 25	802 07	797 88	793 67	789 45	785 22	780 96

The degree of relative exactitude which we reach in the determination of alcohol by the specific gravity method depends, of course, on the degree of exactitude with which we determined the specific gravity, and on the *strength* of the *alcohol solution operated upon.*

Supposing, for instance, in one case, we operate upon a 1 per cent., and in a second upon a 50 per cent. alcohol, and our experimental specific gravities are right to within ±0·0001. *i.e.*, 0·1 by our table, then the uncertainty in the first case is 0·053 per cent. per 1 per cent., *i.e.*, about 1/20 of the value to be determined.

In the second case it is only 0·046 per cent. absolutely, *i.e.*, 0·046 ÷ 50 = ·00092 of the value to be determined.

Hence, if the given solution is weak, it is expedient to strengthen it by fractional distillation, to, for instance, drive all the alcohol contained in 200 grms. of given solution into, say, 20 grms., and then to determine the specific gravity of the strong liquor.

Distillation as a preliminary to specific gravity determination is indispensable if the given liquor contains (non-volatile) dissolved solids.

In the analysis of *undistilled alcoholic beverages* (wine, beer, &c.), we must not forget that these in general contain free acetic and other volatile acids which, if allowed to pass into the distillate, would raise its specific gravity. This source of error is avoided by alkalinizing the liquor with caustic soda before distilling it. The distillate then obtained, however, is liable to contain ammonia, which, if present, must be removed by redistillation after addition of a slight excess of (preferably phosphoric) acid. In the case of liquors rich in *carbonic acid,* it is best to begin by eliminating the greater part of this component by shaking the liquor repeatedly with, always renewed, air in a flask of sufficient capacity.

Apparatus.—For most purposes a fractionating flask attached to a small Liebig's condenser works well enough. There is in general no need of any refined means for preventing volatilization of alcohol from the distillate formed; but it is necessary to have a suitable adapter at the outflow end of the condenser so that the distillate as it comes over has not to fall through more than, say, a height of 1–2 mms. of air before it unites with what is already over. The receiver must be tared before use so that the weight of distillate obtained can be determined without transvasation. How far must the distillation be pushed to be sure that all the alcohol is in the distillate? In answer to this question let us say, first of all, that *cæt. par.* the efficiency of the process as a method of separation is the greater the more slowly the distillation is made to progress, or the greater the proportion of the vapour which suffers condensation before it reaches the condenser tube. With beer, cider, Rhine wine, or claret if one distils at a moderate rate, there is no need of more than one-half to two-thirds of the liquid being drawn over. But it is better in any case to strengthen one's judgment by fixing a good thermometer in the neck of the flask (as explained under "Wood Spirit," in the section on the boiling-point curve) and to continue distilling for a while *after* the thermometer has reached the point which it would show with pure water boiling in the *same apparatus*.*

In the case of liquids very poor in alcohol we must work on a relatively large scale, and, if necessary, strengthen the first distillate by re-distillation. With such liquids it is as well to, from the first, use a distillation apparatus so constructed that a *very considerable portion* of the vapour is *made* to condense before the rest gets over the hill. Of the multitude of *dephlegmators* invented Hempel's is the simplest, and it is as efficient as any other not based upon the use of liquid baths kept at prescribed temperatures. It consists of a (sufficiently) long, narrow tube (provided near its upper end with a soldered-in side tube, like the neck of a fractionating flask, and drawn out into a narrower appendage below so that it can be fixed in the cork of the distillation flask), which is filled with pea-sized glass beads up to near the side tube. The upper open end serves for the insertion of a thermometer. For the

Determination of minute quantities of alcohol in aqueous liquors (such as, for instance, pass into the urine after the imbibing of alcohol), chemical methods must be resorted to. For the mere detection of the alcohol a good method is to first concentrate the alcohol by distillation in, say, a Hempel apparatus, and then to apply the iodoform test, as described for acetone under "Wood Spirit" (p. 279). Whether the method as there given would afford reliable *quantitative* results has not yet been ascertained. Supposing it does, every CHI_3 parts of iodoform correspond to C_2H_6O parts of alcohol, because one of the two carbon groups in $CH_3.CH_2OH$ becomes formic acid. Perhaps the following adaptation of Wanklyn and Chapman's

Method of limited oxidation would give reliable results. After a preliminary distillation, boil an aliquot part of the distillate

---

* This point must be determined beforehand, and quite directly.

with a known sufficient volume of a standard solution of bichromate of potash and the corresponding quantity of standardized sulphuric acid ($4H_2SO_4$ for $1K_2Cr_2O_7$) in a flask under an inverted condenser until all the alcohol can be assumed to be oxydized into acetic acid:—

$$C_2H_6O + 2O = H_2O + C_2H_4O_2.$$

Hence $$1K_2Cr_2O_7 = 3 \times O = 3/2C_2H_6O.$$

In the resulting green liquid the residual chromic acid is determined by adding a properly adjusted known excessive weight of standardized ferrous sulphate (*see* p. 34), and then titrating back with standard bichrome solution, using ferricyanide of potassium as a drop-indicator for ferrosum. From the quantity of chromate reduced, the alcohol is calculated according to the above equation.

According to J. C. Thresh,* small quantities of alcohol contained in an aqueous liquor can be detected by subjecting it to distillation (if necessary), and then distilling the distillate with a little chromic acid. The distillate now formed contains aldehyde, and consequently, when boiled for a time with caustic potash, and allowed to stand for a few hours, assumes a yellow colour. In this way as little as 0·02 per cent. of alcohol can be detected.

SEPARATION OF ETHYL AND METHYL ALCOHOL.

The word "separation" in our heading must be taken in the sense of side-by-side determination, because a method of real separation is not known. It certainly cannot be effected by fractional distillation. Some years ago the Author had occasion to inquire into this matter, and for this purpose worked out an approximate indirect method of quantitative separation, which is based upon the facts that the *iodides* of the two alcohols can be separated fairly well by fractional distillation, and that methyl-iodide has a higher specific gravity than the ethyl compound. 20 cc. each of pure ethyl-alcohol, pure methyl-alcohol, and of the alcohol mixture under analysis are converted separately into iodides thus:—

---

* Pharm. Journ. and Trans. [3], ix., p. 408. Not having this journal at hand, we quote from Jahresbericht for 1878, p. 1074.

20 cc. of the alcohol are poured on 30 grms. of iodine, contained in a small flask kept cool by a water-bath, and 4 grms. of red phosphorus are then added in small instalments. The mixture is distilled by means of a water-bath, the distillate washed, *first* with water (to avoid formation of iodoform), then with aqueous caustic soda, and then again with water, to be dried by addition of fused chloride of calcium, and distilled. The specific gravities of the three iodides are determined side by side of one another at the same temperature. In an analysis thus made the following results were obtained (by Mr. James Robson):—

	Pure CH_3I.	Pure C_2H_5I.	Mixture.
S = Spec. grav. at 18°0,…	2·2882	1·9426	1·9975
$1 \div S$, … …	0·43703	0·51477	0·50063
Percentages of $CH_3I = p =$	100	0	18·2

The percentage was calculated on the assumption that the two iodides mix without contraction or expansion, *i.e.*, thus:—

$$0{\cdot}43703p + 0{\cdot}51477(100 - p) = \frac{100}{\text{S of mixture.}}$$

That assumption, it is true, is not proved to be correct, but we are pretty safe in presuming that the specific gravity of any mixture of the two iodides lies between those of the two components. Hence the result will always be right in a qualitative, and probably afford at least a rough approximation to the truth in the quantitative, sense. Besides, if we have to deal with a doubtful case, it is open to us to prepare the respective iodide in a large scale and fractionate it by distillation under a bead tower. By this refinement even a small admixture of methyl-alcohol to ethyl-alcohol can be detected with certainty and *vice versa.*

The *degree* of ease with which the two iodides part on distillation (as compared with the alcohols) may be seen from the following experiments:—

20 cc. of iodide of ethyl, boiling at 73°·3 to 73°·4, and 1 cc. of iodide of methyl, boiling (under the same circumstances) at 42°·5 to 43°·5, were mixed by Mr. Cullen and distilled from out of a Hempel (bead-tower) apparatus. The boiling point ranged as follows:—

Volume over, in cc.,	0	1	2·5	3	Almost all.
Boiling point, ...	67°	70°	71°	71°	73°

The methyl compound obviously accumulated in the earlier fractions, so that, supposing the experiment had been made on a larger scale, the specific gravity of, say, the first tenth of the distillate, would have left no doubt about the *presence* of methyl-alcohol at any rate.

By way of contrast let us state shortly what we observed in the fractionation of a mixture of the two alcohols, which was carried out by Mr. Robson.

360 cc. of a high-class spirit of wine of 92·5 per cent. by weight were mixed with 40 cc. of pure methyl-alcohol from Kahlbaum in Berlin. 380 cc. of the mixture were distilled under a bead tower, and thus divided into five fractions:—

Fraction,	I.	II.	III.	IV.	V.
Boiling point,*	72°–76°	76°·4–76°·9	76°·9	75°–77°	77°·3
Volume,	20	260	20	48	22·5 cc.

Portions of Fractions I. and V. and of the original mixture (it was it whose iodide figured in the above statement beside the pure ethers) were made into iodides, and the specific gravities of all determined side by side with those of the two pure ethers. The percentages of CH_3I in the respective iodides were as follows:—

	Orig. Mixture.	Fr. I.	Fr. V.
Percentage, ...	18·2	28·2	4·0

It is not worth while to reduce these numbers to percentages of methyl-alcohol in the corresponding liquids analysed. The numbers as they stand show that although the two alcohols when distilled together tend to separate in accordance with their boiling points, the actual separation does not amount to much; even the first twentieth of distillate (as iodide) contained only 28, and the last twentieth still contained 4 per cent. of the methyl compound.

The above experiences were gathered incidentally in the course of an experimental critique of a method for the detection of

---

* Uncorrected.

methyl-alcohol in ethyl-alcohol, which was invented in 1876 by Riche and Bardy.

Riche and Bardy's method (*Comptes Rendus* for 1876*) is as follows:—10 cc. of the alcohol, previously rectified over carbonate of potash if necessary, are placed in a small distillation flask with 15 grms. of iodine, and 2 grms. of red phosphorus are added gradually, while the flask is kept immersed in a cold water-bath to prevent loss of alkyl-iodide.† The mixture is distilled by means of a water-bath, and the iodide collected under 30 cc. of water. The iodide is separated from the aqueous part and transferred to a small flask containing 5 cc. of aniline, with which it unites readily into hydriodates of alkyl-anilines. Should the reaction become too violent, it must be moderated by immersion of the flask into cold water, to be subsequently supported by gentle heating. After an hour's standing the (solid) product is dissolved in water, any excess of either co-reagent boiled off, and the solution, after cooling, decomposed by addition of an excess of caustic potash or soda. The alkyl-aniline separates as an oil, which, if it does not rise by itself, can be made to rise by adding some solid caustic alkali to increase the specified gravity of the mother-liquor. By adding some water or alkali ley it is driven up into the neck of the flask, and allowed to clear up there. 1 cc. of the oil is incorporated with 10 grms. of a mixture made of 100 parts of sand, 2 of common salt, and 3 of nitrate of copper, the mixture placed in a test tube, and in it kept at 90°C. for 8–10 hours by means of a water-bath. The product is lixiviated with instalments of warm alcohol so as to produce 100 cc. of filtrate. This latter is always intensely coloured; but while pure ethyl-alcohol yields a dark brownish-red colour, free of all admixture of violet, if methyl-alcohol was present the tincture exhibits a more or less pronounced *violet* colour. With 2·5 per cent. of methyl-alcohol the shade of violet is very distinct. To detect minor quantities, 5 cc. of the tincture are diluted with water to 100 cc., and 5 cc. of this solution

---

* Not having this periodical at hand (I am writing in the country), I quote from Allan, "Commercial Organic Analysis," 2nd ed., vol. i., p. 51.

† Alkyl, a generic term for methyl, ethyl, &c.

(corresponding to 0·25 cc. of tincture) are diluted with 400 cc. of water in a porcelain basin, to be heated to near boiling and used for the dyeing of a bit of white merino-wool cloth (about 10 by 10 ctms.), which must be free of sulphurous acid. The cloth is kept in the liquor at water-bath heat for about half an hour. It is then taken out, washed with water, and dried. If the alcohol under analysis was pure, the cloth remains white, but if it was contaminated with methyl-alcohol, the cloth exhibits a more or less intense violet colour.

When the present writer, some years ago, applied this method to a number of samples of spirit of wine, suspected to be adulterated with small proportions of methylated spirit, he observed no violet tinge in the alcoholic tinctures of the pigments produced, but the merino test gave, in all cases, distinctly positive results. This, in a sense, was satisfactory; but when we proceeded to test-experiments with spirits of undoubted genuineness and methylated alcohols prepared from such spirits by addition of measured proportions of pure methyl-alcohol, we obtained puzzling results. Even with the pure spirits the merino cloth in most cases (not always) exhibited a distinct colour similar to that yielded by mixtures containing about half a per cent. of added methyl-alcohol. With mixtures containing 2 per cent. of methyl-alcohol or more there was no difficulty; the colours obtained from these could not have been misinterpreted. With the assistance of Messrs. John M'Arthur, Arch. Kling, William Cullen, and James Robson, I tried hard to discover the cause of the irregularities referred to, and found, as a matter of high probability at least, that they were owing to the presence in the spirits of traces of higher alcohols. Special experiments made with really pure aniline showed that they were not caused by any impurity in the commercially "pure" aniline used in the majority of the trials. The following description of the form of the method which we ultimately adopted shows indirectly how the difficulty was overcome:—

To test a (strong) spirit of wine for methyl-alcohol, convert at least 40 or 60 cc. (the more the better) into iodide by means of the proportions of iodine and red phosphorus recommended by Riche and Bardy (*vide supra*), but wash the iodide, first with water,[*] then with dilute caustic soda, and lastly again with water; dry it with granulated fused chloride of calcium, and re-distil it. For a preliminary test, measure off 4 to 6 cc. of this iodide into a small tared flask, weigh it, add for every *gramme* of iodide 0·58 cc.[†] of pure aniline, and heat the mixture under an inverted condenser by means of a water-bath for a few minutes; then allow to stand for an hour in the cold. Dissolve the solid product in water, boil off any excess of aniline or iodide, allow to cool, eliminate the alkyl-aniline, oxidize 1 cc. of it, from the product produce 100 cc. of alcoholic tincture, and dilute 5 cc. of the tincture to 100 cc. with water. Run 5 cc. of this dilute solution into 400 cc. of boiling hot water contained in a Berlin basin, which place on a full-going water-bath. Immerse a square decimetre of previously washed white merino cloth in the hot liquor for five minutes; then take out the cloth, add other 5 cc. of the dilute colour solution, mix well, re-place the cloth in it, and continue heating for half an hour. Then take out the cloth, wash it with water, and dry it.

Of the various cases that may present themselves, only one needs be considered here. We will assume that the colour taken on by the merino is that feeble shade, which may or may not be owing to the presence of methyl-alcohol in the original spirit. Assuming as a hypothesis that it is, proceed to concentrate your "methyl" by a series of fractional distillations of the bulk of our alkyl-iodide. Supposing you had operated upon 50 cc. of spirit. In this case the yield of iodide will amount to some 40 cc., of which we will assume that 32 cc. are still at your disposal. Distil these out of a small Hempel apparatus, and collect the first 16 cc.; then distil these 16 cc. and collect the first 8 cc., and from these 8 cc. again extract the most volatile 4 cc. Convert these into alkyl-aniline, &c., &c., as above explained. If the colour obtained in the preliminary test really owed its origin to methyl, the proportion of methyl in these 4 cc. is now about the eight-fold of what it was in the

---

[*] To prevent formation of iodoform.

[†] A little more than the quantity demanded by eq. $C_2H_5I+C_6H_5NH_2=HI.N(C_6H_5).(C_2H_5).H$. Whether *only* mono-ethyl-aniline salt is produced is another question which we do not propose to consider.

original iodide, and far more intense violet colour will come out. If it was owing to some irregularity, say in the process of oxidation or to some impurity in the aniline, the doubtful shade in the preliminary test will reappear. If it was owing to the presence of propyl, amyl, &c., the cloth will take on no colour at all except perhaps a faint shade of grey, with no violet tinge in it. A large number of critical experiments with genuine spirits and mixtures of such with known proportions of methyl-alcohol (some of the trials were carried out with 140 cc. of spirit) enables us to affirm that the second case only rarely presents itself. As a rule, a non-methylated spirit, in its thrice distilled iodide, yields no colour; while a spirit containing as little as a fourth of a per cent. of methyl-alcohol furnishes a decidedly violet cloth.

Wanklyn and Chapman's method of limited oxidation includes a number of methods for testing a spirit for an admixture of methyl-alcohol. The one that suggests itself most forcibly is based upon the (assumed) fact that, in their general process of oxidation, ethyl-alcohol yields only acetic acid; while methyl-alcohol yields carbonic acid (and water) as final products. To test this method, Mr. M'Arthur made a number of trials in the following manner:—

An oxidizing solution was prepared by dissolving 98·2 = $1/3K_2Cr_2O_7$ grms. of bichromate of potash in water, adding 210 grms. of a 62·3 per cent. vitriol = 130·7 grms. of real H_2SO_4, and diluting to 1 litre, to obtain a solution of which 1 cc. = 16 mgs. of available oxygen. (To be referred to as "bichrome mixture"). To test a spirit, 1 grm. of it was mixed with 60 cc. of bichrome mixture in a small flask provided with an inverted condenser, the upper end of which communicated with a bulbed U-tube charged a known volume of standard baryta water, and the mixture boiled until the oxidation was apparently completed. A slow current of carbonic-acid-free air served to sweep the stagnant carbonic acid into the barytic reagent. The carbonic acid was determined by titrating the excess of baryta left as $Ba(OH)_2$. (*See* p. 229.) The following analyses may be quoted:—

(1.) 1 grm. of a high-class *spiritus vini* of 85 per cent. (by weight) yielded 10·3 mgs. of carbonic acid.

(2.) 1 grm. of a mixture of 95 volumes of the same spirit, with 5 cc. of pure methyl-alcohol, gave 47·9 mgs.

(3.) 250 cc. of a suspected *spiritus vini* was distilled under a bead tower and the first 50 cc. collected; these were again distilled in the same manner and 10 cc. drawn over. Of these 10 cc. 1 grm. was operated on as before. The carbonic acid obtained amounted to 12·2 mgs.

Of these analyses No. 1 is the most important for us here; it clearly shows that even genuine *spiritus vini* yields a larger proportion of carbonic acid than could be accounted for by the presence of traces of (non-normal) higher alcohols. Hence the method is *not* available for the detection of small quantities of methyl-alcohol.

Another method which readily suggests itself is to aim at the production of *formic acid* from the methyl-alcohol, and test for it by means of nitrate of silver. To test this method (which was recommended by J. T. Miller), Mr. M'Arthur mixed 3·5 cc. of the above *spiritus vini* with 25 cc. of bichrome mixture and 2 cc. of water, allowed to stand a quarter of an hour, and distilled off 25 cc. The distillate was alkalinized with carbonate of soda and next boiled down to 10 cc. to eliminate the aldehyde (C_2H_4O) produced. The residue was acidified with acetic acid, filtered, mixed with a solution of 0·1 grm. of nitrate of silver in 3 cc. of water, and boiled. Only a faint dark turbidity was produced.

3·5 cc. of the 5 per cent. methylated alcohol used for the above experiment (2), when treated in the same manner, yielded a strong precipitate of metallic silver.

This method, as we see, is more reliable than the carbonic acid one. But after all, Wanklyn and Chapman's general process, it appears to us, should lend itself better for the

Detection of Ethyl-alcohol in Methyl-alcohol

than for the solution of the inverse problem. To detect an admixture of ethyl to methyl-alcohol, all that is required is to boil a known weight of the suspected alcohol with a sufficient excess of bichrome mixture under an inverted condenser, or, what is better, to keep the mixture of alcohol and reagent in a close vessel* at 100° for a sufficient time and distil the resulting liquid to dryness, best from out of a retort immersed in a sperm-oil bath and connected with a Liebig's condenser. To prevent "bumping" put a few fragments of clay tobacco-pipe into the retort, or, what is better, let a slow current of air bubble through the distilling mixture. The residue is re-dissolved in a little water and again distilled to dryness to recover a remnant of acetic acid. The united distillates are titrated with baryta water to ascertain the weight of acetic acid produced. For a check add a few drops of surplus baryta to the neutralized liquid, evaporate to dryness over a water-bath, re-dissolve in a little water, filter off the carbonate of baryta produced, evaporate the filtrate to dryness, dry the acetate at 110° until constant, and weigh it. Then determine the percentage of baryta by igniting the acetate and weighing the carbonate.

We have not yet had occasion to try this method in real earnest. In applying it to a suspected methyl-alcohol one must not forget that acetone, if present, yields acetic acid as well as ethyl-alcohol does; $C_2H_4O_2$ parts per $CO(CH_3)_2$ parts of the ketone; as one of the two methyl groups burns into carbonic acid and water.

Berthelot recommends to heat the suspected methyl-alcohol with concentrated sulphuric acid, as if one intended to prepare oxide of methyl gas from it. This ether is readily absorbed by *ordinary* oil of vitriol, which does not act very promptly on the *ethylene* produced from the ethyl-alcohol. The residual ethylene is identified as bromide $C_2H_4Br_2$ or by gas analysis. In regard to this method also we have no personal experience. The same remark applies to the methods which now follow.

Riche and Bardy use a method which is founded upon the formation of aldehyde from the ethyl-alcohol. Its most characteristic feature, however, is the peculiar manner in which they identify the aldehyde. *Special Reagents:*—(1) A solution of thiosulphate of soda of 1·29 specific gravity. (2) A solution of

---

* A sealed-up tube, if not too full and at all carefully prepared, is not likely to burst. A "pressure bottle," meaning a bottle whose stopper is held down in some way or other, is less safe; it must be tied up in a strong linen bag while being heated in its water-bath to avoid accidents.

permanganate of potash of 1·028 specific gravity.* (3) A solution of 0·02 grm. of rose-aniline in a litre of water.

4 cc. of the liquid under examination are mixed with 6 cc. of concentrated sulphuric acid and 10 cc. of water (with the view, we presume, of fixing part of the methyl-alcohol as methyl-sulphuric acid), and the mixture is distilled, 8 to 10 cc. being drawn over and run into 10 cc. of water. This liquid is mixed with 5 cc. of sulphuric acid and 10 cc. of the permanganate solution, and the mixture is allowed to stand for ten minutes. 4 cc. of the thiosulphate solution and 4 cc. of the rose-aniline solution are then added. In the absence of ethyl-alcohol the mixture is yellowish-white; in its presence it becomes more or less intensely violet. Acetone, formic acid, and isopropyl-alcohol give no similar reaction.

Upon the observation of A. W. Hofmann's that iodide of methyl is far more readily attacked by *ammonia* (with formation of chiefly iodide of tetra-methyl-ammonium) than ethyl-iodide is, *Tiemann* some years ago based a method for the separation of the two ethers, or rather alcohol-radicals, which worked well in his hands. Hence, a good method for detecting methyl in ethyl-alcohol probably would be to first convert the given alcohol into iodide, and next to concentrate the *ethyl* in a small fraction of the whole by a series of fractional distillations. The concentrated iodide (say the least volatile 1/8 or 1/16) is treated in Tiemann's way,† *i.e.*, digested with aqueous ammonia at the ordinary temperature for 6–8 hours. The methyl-iodide now has assumed, at least substantially, the form of solution of iodide of tetramethyl-ammonium, and is easily removed by sucking off the aqueous layer. The residual iodide is washed, dried, distilled, and identified as (pure or impure) C_2H_5I by its specific gravity and boiling point.

---

* Why define the strengths of these solutions by their specific gravities, instead of simply stating the weight of dry reagent per litre?

† Kindly communicated to the Author by Professor Tiemann in a private letter.

NOTES.

Note (1) on Exs. 1 to 3.—*On the Theory of the Balance.*

The study of this subject may (and, indeed, had better be) postponed until the student has become quite familiar with the instrument by its practical use. The following notes are intended to supplement what he may find in his text-books on mechanics or physics:—

Imagine a fine Oertling balance, in which the knife-edges, bearings, and suspension arrangements are ideally perfect. Imagine the left side to be charged with P grms. and the right side with P grms. likewise (including the weights of the pans, &c.), and it is clear at once that the dis-arrested beam can remain at rest only in *one* position, because the conjoint effect of the weight W_0 of the beam and the charges P and P is the same as if they were all concentrated in a fixed point C, which lies below the axis of rotation in a line passing through this axis and standing perpendicular on the plane of the two end edges. If disturbed in that position, the beam vibrates about it as a pendulum. Imagine now a small overweight Δ to be added on, say, the right side; the effect is that the common centre of gravity of the system shifts from C to a point C′ lying a little to the right of C; the balance, to gain what is now its position of rest, must turn through an angle α, which *cœt. par.* is the greater the greater Δ. If the three axes lie in exactly the same plane, the angle of deviation α is independent of the magnitude of the charges P and P, because these conjointly act like *one* point equal to P + P in the axis of rotation. If this axis lies above the plane of the end-edges, angle α for a given Δ is the less the greater P; and if the plane of the end-edges lies above the axis of rotation, the angle α for a given Δ is the greater the greater P. As easily shown with the help of a little algebra—

$$tg\,\alpha = \frac{\Delta l}{W_0 s_0 \pm 2Ph}$$

where l is the arm-length of the balance (which we have tacitly assumed to be exactly the same on both sides), s_0 the distance of the centre of gravity of the empty beam from the axis of rotation, and h the distance of the axis of rotation from the plane of the terminal edges. The + in the denominator corresponds to the case when the axis of rotation lies above the plane of the end-edges; the − to the opposite case. Taking J as designating the length of the needle, measured from the axis of rotation to the zero of the scale, in degrees of the scale (which runs horizontal and is divided into degrees of equal length, say, into millimetres), and n the number of degrees through which the needle moves in describing the angle α, we have—

$$\frac{n}{\Delta} = \text{“E”} = \frac{l\,\mathrm{J}}{\mathrm{W}_0 s_0 \pm 2\mathrm{P}h}$$

The value which E assumes when the milligramme is taken as the unit of weight we will call the "sensibility" (*German Empfindlichkeit*) of the balance.

By means of the *gravity-bob* (without which no balance is complete) we can give s_0 any value however small that we could reasonably care for; hence we can give to E, *i.e.*, to the deviation per milligramme of overcharge, any value we like; we can render E so great as to make the deviation corresponding to even 0·001 mgs. distinctly visible! In other words, there is no limit to the potential precision of a balance—if it is absolutely perfect. But no balance is; the knife-edges are no absolutely straight rigid lines, the bearings no absolutely rigid planes, &c., and as a necessary consequence the position of rest, instead of being absolutely constant, is anywhere within a small angle $\pm\beta$. This indifference-angle is the greater the greater the sensibility, but for a given charge (P, P) its weight-value π is constant, and it is obviously of no use to increase the sensibility beyond the value which renders that angle $\pm\beta$ just visible and no more. With a really good balance it would, as a rule, be a mistake even to go so far, for a number of reasons, of which we will content ourselves with naming one which is perhaps less obvious to a beginner than some of the rest.

The time of vibration t of a balance is the same as that of a mathematical pendulum, the length R of which equals the momentum inertiæ of the (charged) beam divided by its momentum staticum; hence, if R_0 is the length of the second pendulum, we have

$$t^2 = 1'' \times \frac{\mathrm{R}}{\mathrm{R}_0}$$

But the momentum of inertia of the charged beam is

$$l^2(k\mathrm{W}_0{}^* + 2\mathrm{P});$$

the momentum staticum stands before us in the denominator of the formula for E. Hence the time of vibration is the greater the heavier and the longer the beam, and it increases rapidly with the charge P. Any student who is at all familiar with this chapter in mechanics will easily see that we are right in concluding that for a given balance, charged with a given P on both sides, the time of vibration is proportional to the square root of the sensibility, or, in symbols, that

$$t^2 = \text{const. E}.$$

By increasing the sensibility to the 4, 9, 16 fold, we increase the time of vibration to the 2, 3, 4 fold.

---

* k is a numerical factor which depends on the shape of the beam; with the customary beam form it is very near 1/3.

To the student who has gone through Exs. 1 to 3 with a fine balance constructed for heavy charges, the practical bearings of this need not be explained.

If we screw down the bob so far that the time of vibration assumes the small value that would just suffice for exact readings of the excursions of the needle, the decimilligramme (as an overweight) ceases to be visible, even with the longest needle one could reasonably use. But this difficulty can be overcome easily by optical means.

The Author some years ago[*] devised an arrangement, which was executed for him by Mr. Oertling, and has since done him excellent service. It consists of a narrow ivory scale, divided into very small degrees, which is fixed slantingly (at about the angle at which you hold a book for convenient reading) to a point near the lower end of the needle, and a (feebly magnifying) microscope fixed to the pillar of the balance, which microscope is provided with one vertical wire in its focus, and pervades the central (fixed) part of the front pane of the balance-case to enable one to read while the case is shut. The ordinary scale which does duty as usual, if required, is divided conveniently into millimetres, the micro-scale into degrees, each of which has the angular value of 0·1 degree of the principal scale. The apparent motion of the "wire" in the microscope on the micro-scale is in the same sense as that of the real motion of the needle on the ordinary scale below, which provides against blunders in the ±. The microscope, to be more than an illusion, must be very steady, and for this reason *be fixed* to the *pillar* of the stand of the balance. It adds about £3 to the cost of the instrument.

A cheaper arrangement is the following:—The micro-scale, divided conveniently into fifth-millimetres, is fixed slantingly to the *pillar*, and the needle at the corresponding part is shaped thus $[^{a}_{b}$; a hair, by means of capillary perforations at a and b, is stretched out between a and b so that it is parallel to the surface of the micro-scale, and at only 0·2 to 0·5 mm.'s distance from it. A (short) terrestrial telescope, fixed in the central (fixed) part of the front pane of the balance-case, serves for reading. The telescope needs not be very steady, as the hair is so close to the scale. The object-glass is a single lens, which, under the circumstances, produces an image within the tube which is rather less in size than the scale itself; the eye-piece is a feebly magnifying compound microscope, which magnifies this image as far as necessary for a distinct reading of tenths of degrees. I have applied this arrangement to one of my balances and found it to work very well; but it is not equal to the one described before.

Whoever uses the method of *vibration* in its exact form (Ex. 2) prefers, of course, to so place the centre of gravity of the beam that 1° of deviation corresponds to *exactly* 1, 0·5, 0·2 mgs., &c., to avoid computation. The Author many years ago contrived for the purpose an *auxiliary gravity-bob*, which is fixed to the upper end of the needle by

---

[*] Zeitschrift für Instrumentenkunde. February number of 1882.

mere friction so that it can easily be moved up and down. The respective part of the needle has the shape of a triangular prism, which turns one of its sides towards the observer. This side is divided into millimetres. With a hectogramme-balance the auxiliary bob needs not weigh more than 2–3 grms. Supposing the upper edge of the bob to be y mms. away from its highest position, and we have for the weight-value of 1° of deviation, *i.e.*, for $\frac{1}{E}$ the equation—

$$E^{-1} = (E^{-1})_0 + ay,$$

where $(E^{-1})_0$ and a are constants, easily determined by ascertaining the value E^{-1}, first at $y = 0$, and then when y is at its maximum value.

For further information, *see* the Author's Memoirs—*Ueber die Waage des Chemikers, Zeitschrift für Instrumentenkunde*, Oct., 1881; also his article "Balance," in the new edition of the *Encyclopædia Britannica.*

Note (2) to Ex. 10, p. 13.

The table referred to on the last line of p. 13 was intended originally to be nothing more than an extract from Kolb's well-known table; but it subsequently struck me that it would be better to base it on determinations of our own. I accordingly caused Mr. Archibald Kling to carry out the following experiments:—

A perfectly pure hydrochloric acid of about 1·11 specific gravity was made from pure materials with great care, and put aside well-stoppered as "acid A." The exact percentage in A was determined by diluting a known weight with water to a weight so adjusted that the solution lent itself for the application of our gravimetric modification of Volhard's method. (*See* p. 220.) By means of it it was ascertained that acid A contained 22·525 per cent. of HCl. From acid A two more dilute acids were derived by gravimetric synthesis, which were intended to contain about 20 per cent. and 18 per cent. of HCl respectively; but through a blunder in the calculation of the proportions of water to be added, the percentages came out as follows:—

In A, as stated,	22·525
In B, by synthesis,	18·172
In C, by synthesis,	16·983

and, unfortunately, the calculations of these two latter numbers were made only after all the specific gravity work had been completed. Nor could Mr. Kling have checked the percentages of B and C by direct analyses without delaying the publication of the book. But from Kolb's table it is quite evident that the relation between percentage p and specific gravity S is governed by an almost linear function; besides, I know Mr. Kling's work to be sound, and his results for S and p fall in so well with the formulæ which I deduced from them, that I have little hesitation in giving the following table based on his work, feeling sure that it is, at the worst, more than at a par in point of precision with any of the tables given in the handbooks of chemistry.

The specific gravities were determined by means of two test-tube-shaped specific gravity bottles, provided with capillary necks bearing etched-in (calibrated) millimetre-scales. The temperatures were established, and kept constant, by means of a large water-bath. The bottles had a capacity of about 20 cc., and 1 mm. of the scale corresponded to a little less than 0·01 cc.; one fill of the bottle enabled one to determine the specific gravity at three temperatures, namely, at 8–10°, then 15°, and lastly 20° (about), by combining the scale readings and the one weighing. After weighing the bottle and contents, the last temperature was re-established, the liquid in the neck brought down to near 0 mm., the bottle and contents weighed again, and thus a fourth determination effected. For each acid two such series of observations were made, one with bottle I., the other with bottle II.

From the observational results I calculated the following table by means of equations of the form—

$$(1)\quad S_t = S_0 - a\,t;\ \text{where } a = a_0 \pm b\,p$$

$$(2)\quad p = c + (S_{15} - 1)d,$$

which were found to do sufficient justice to the observations. All the specific gravities must be understood to be referred to water of 15°C. as = 1. Reduction to the vacuum omitted.

Table for finding the Percentage p of HCl from the Specific Gravity ${}_{15}S$ at 10° to 20°.

${}_{15}S_{15}$.	p.	Δp.	For $\Delta t = 1°$, $\Delta S =$	${}_{15}S_{15}$.	p.	Δp.	For $\Delta t = 1°$, $\Delta S =$
			(0·0001 ×)				(0·0001 ×)
1·085	16·96		3·0	1·100	19·85	·19	3·5
1·086	17·16	·20	3·0	1·101	20·04	·19	3·6
1·087	17·35	·19	3·0	1·102	20·24	·20	3·6
1·088	17·54	·19	3·1	1·103	20·43	·19	3·6
1·089	17·73	·19	3·1	1·104	20·62	·19	3·7
1·090	17·93	·20	3·2	1·105	20·81	·19	3·7
1·091	18·12	·19	3·2	1·106	21·01	·20	3·8
1·092	18·31	·19	3·2	1·107	21·20	·19	3·8
1·093	18·50	·19	3·3	1·108	21·39	·19	3·8
1·094	18·70	·20	3·3	1·109	21·58	·19	3·9
1·095	18·89	·19	3·3	1·110	21·78	·20	3·9
1·096	19·08	·19	3·4	1·111	21·97	·19	3·9
1·097	19·27	·19	3·4	1·112	22·16	·19	4·0
1·098	19·47	·20	3·5	1·113	22·35	·19	4·0
1·099	19·66	·19	3·5	1·114	22·55	·20	4·1

To form an estimate of the degree of precision attained by Mr. Kling in his work, I deduced from each of his 24 determinations of specific gravities ${}_{15}S_t$, and the t's, the percentage p of the respective acid by means of the table, and compared it with the p_0 found by analysis of A, or synthesis from A. The results were as follows:—

Acid A.—$\pm(p-p_0)$ varies from ·005 to ·04; mean of the 8 values $=\cdot028$, corresponding to $\pm\Delta S=\cdot00014$.

Acid B.—$\pm(p-p_0)$ varies from ·02 to ·10; mean of the 8 values $=\cdot049$, corresponding to $\pm\Delta S=\cdot00024$.

Acid C.—The individual values Δp were: $+\cdot01$; $+\cdot03$; $-\cdot04$; $-\cdot05$; $+\cdot06$; $-\cdot12$; $-\cdot16$; $-\cdot21$; general mean $=\cdot085$, corresponding to $\pm\Delta S=\cdot00042$. Series C obviously includes at least three bad determinations. As soon as I found this, I based my constants chiefly on series A and B, and I believe that the table (from 22·5 to 18 per cent., and for each kind of acid from about 8° to 20°) may be relied on as being correct, as a table for finding the p for a given ${}_{15}S_t$, to within $\pm 0\cdot04$ per cent. of HCl, and as a table for finding the S for a given p to within $\pm\cdot0002$.

The Author's *differential method* of specific gravity determination may here be referred to as coming in useful occasionally in the preparation of standard solutions. Its requirements are:—(1) A test-tube-shaped specific gravity bottle, which should not hold less than 30 cc., and must be provided with a well ground in, narrowly perforated, glass stopper. (2) A cylinder large enough for the bottle (1) being freely suspended within a liquid contained in the cylinder. (3) A precision balance so arranged that a thing to be weighed can be suspended from one of the pans below the table. (Regnault's arrangement). The cylinder is charged with liquid I. after this has been brought to the temperature of the balance-room; the specific gravity bottle, charged with the same liquid, is suspended within the mass of liquid in the cylinder by means of a fine platinum wire, hooked on to the balance-pan, and its tare taken in grammes as soon as it has assumed a constant value. The bottle is now taken out, emptied, charged to almost overflowing with liquid II., and next kept plunged into liquid I. up to the neck to assume the temperature of I. The stopper is then put on, the overflowing liquid wiped off quickly with filter paper, and the bottle suspended within I. to be weighed again, care being taken to wait until the balance gives constant readings, and to see that the temperature remains constant throughout. Supposing the bottle holds V grms. of water at $t°$, and the second tare is, say, *greater* than the first by Δ, then, designating the two specific gravities (${}_tS_t$) by S′ and S″, we have—

$$S''-S'=\frac{\Delta}{V}$$

with a degree of precision which is not easily reached by any other known method.

NOTE (3) to EXS. 14 and 15.

As shown by the Author,* the two double salts $MgSO_4.K_2SO_4 + 6H_2O$ and $FeSO_4.K_2SO_4 + 6H_2O$, when dissolved in at least *hot* water, suffer partial decomposition into the two component sulphates. At his request Messrs. James Robson and Andrew Hodge have tried, by means of systematic synthetical experiments, to ascertain the conditions under which a solution of the two sulphates ($FeSO_4$ and K_2SO_4, or $MgSO_4$ and K_2SO_4) deposits pure crystals of the respective double salt on cooling. The case of the magnesia salt was taken in hand by Mr. Robson. According to his experiments, a solution of $n \times K_2SO_4$ grms. of sulphate of potash and n, or $1·1\ n$, or $1·2\ n$ times $MgSO_4$ in a quantity of hot water, insufficient for holding the double salt in solution after cooling, when allowed to cool, deposits in general, besides a crop of double-salt crystals, more or less of a sandy mass of small crystals of sulphate of potash, which stick chiefly to the lower faces of the large crystals of the double salt. The proportion of solid sulphate of potash produced is the less the greater the excess of magnesia salt used. The following, it appears, is an infallible recipe for obtaining unmixed crystals of the double salt $MgK_2S_2O_8 + 6H_2O$:—

87·15 grms. of pure powdered sulphate of potash and 153·45 grms. of sulphate of magnesia ($7H_2O$ salt) are dissolved in 350 grms. of hot water; the solution is filtered into a perfectly clean flask, made up to 640 grms., and allowed to stand under a stopper of cotton wool thrust into the neck until the temperature has fallen to about 60°C. without deposition of crystals. The liquor is then transferred to a glass basin, covered up and allowed to stand overnight. The next morning one finds a crop of transparent crystals, which are quite free of all visible admixture of free sulphate of potash. Two analyses of crystals produced in this manner gave the following results:—

	I.	II.	Mean.	Theory.
Water, ...	26·90	26·78	26·84	26·82
Sulphuric Acid,......	39·60	39·83	39·71	39·75
Magnesia, ...	10·26	10·03	10·14	10·02
Potash, ...		not determined.		23·40
				100·00

Mr. Hodge's results with the iron salt are quite analogous. It takes about 1·25 to 1·3 times $FeSO_4$ per 1 K_2SO_4 in a hot solution to obtain cooling crystals of the double salt which are not contaminated with free sulphate of potash. To obtain pure crystals dissolve 29 grms. of sulphate of potash (powdered) and 56 grms. of pure ferrous sulphate ($FeSO_4 + 7H_2O$) in 100 grms. of hot water, acidulated with 0·5 cc. of 20 per cent. sulphuric acid to prevent precipitation of ferric compounds, and proceed otherwise as directed above in regard to the magnesia salt. The crop of crystals obtained is mechanically pure, and gives the right

---

* Proceedings of the Royal Society of Edinburgh for 1886-7.

percentage of iron on titration with permanganate. In the case of either double-salt, however, should a crust of suspicious-looking small crystals come out (beside normal looking ones), sift these off after drying. The case of the double sulphate of copper and ammonia (the subject of Ex. 19) still requires to be looked into. From our present incidental experience it appears that the salt made from a solution of the calculated proportions of the two sulphates as prescribed in the exercise is normal and unmixed.

We may state on this occasion what Mr. Hodge has found out in experiments on potash alum. 100 grms. of pure potash alum were re-crystallized from hot water, the mother liquor evaporated down, allowed to deposit its crystals, the second mother liquor treated similarly and so on until the ultimate mother liquor was so far reduced that it just sufficed for duplicate determinations of the potash (by Finkener's method) and of the alumina (by precipitation with sulphide of ammonium). The ratio of potash to alumina was the same in the ultimate mother liquor as it was in the original alum. But this does not prove that the alum is not decomposed by water. A cold saturated solution was placed in a battery cell, which was immersed up to near its edge in pure water, and the latter renewed from day to day. After about a week's standing the liquor of the cell was analysed for potash and alumina, and the latter found to predominate *largely* over the former. This confirms an old experiment of Graham's, who showed that if alum solution diffuses into pure water (quite directly) the potash salt wanders up faster than the alumina salt does.

NOTE (4) to Ex. 24, p. 63.

In the determination of the carbonic acid in a bleaching powder, a mere bulb-tube charged with stannous chloride does not suffice for the absorption of the chlorine; it must be followed by a U-tube charged with pumice soaked in the stannous solution.

NOTE (5) to Ex. 26, p. 74.

The method for the separation of nickel and cobalt from iron given in the foot-note was introduced by Schwarzen*berg*.

NOTE (6) to Ex. 34.

Since the above section of the book was written, Mr. Frank Lyall has, at my request, carried out a number of experiments for seeing to what extent the Dirvell-Clark method is available as a means of bringing pure cobalt (given, say, as double nitrite of cobalticum and potassium) into a weighable form. To obtain pure metallic cobalt a supply of Fischer's salt was made into oxalate, the latter into metal, the metal into chloride, the chloride into purpureo-chloride. This last was re-crystallized and reduced in hydrogen to obtain pure metallic cobalt, and from this a standard solution of chloride was made synthetically. For each test analysis a known weight of standard solution was boiled down to have it as strong as possible, and expel the dissolved air which otherwise (after addition of ammonia) gives rise to the formation of cobaltic compounds.* To the boiling-hot mixture ammonia is added in successive instalments until the precipitate, which is first blue and amorphous, has assumed the characteristic crystalline form and violet colour of the double salt PO_4CoNH_4. This is allowed to settle (which it does very quickly), filtered off, and washed with small instalments of cold water, but no longer than necessary, as the precipitate is not quite insoluble in water. Three determinations were made, with the following results :—

Metal taken.	Weight p of ignited precipitate. $P_2O_5 2CoO$.	Weight of metal found $= p \times 0{\cdot}404$.	Error.	Volume of filtrate and washings.
(1)......·2285	·5635	·2277	– ·0008	135 cc.
(2)......·0914	·2248	·0908	– ·0006	95 cc.
(3)......·0485	·1188	·0481	– ·0004	70 cc.

The filtrates from (1) and (2) were mixed with sulphide of ammonium, heated, allowed to stand, and the (slight) precipitate collected, roasted, and weighed as CoSxOy. Its weight in the case of (1) was 1·3 mgs.; in the case of (2) it was 1 mg.

From these experiments it appears that, although the method involves a slight loss, it may be used as a supplement to the nitrite method, namely, for bringing the cobalt of the "Fischer's salt" into a weighable form. All that is necessary is to dissolve the yellow salt in hot hydrochloric acid, evaporate to dryness (to render any silica insoluble) to dissolve the residual chlorides in a little acidulated water, filter, and apply the phosphate process as explained. Special experiments showed that the proportion of phosphate recommended by Clark (five parts of solid $PO_4(NH_4)_2H$ for one of cobalt metal) works well.

NOTE (7).—*On Platinum Solution and Platinum Residues.*

The best material for the making of platinum solution is pure spongy platinum, which is to be had from Messrs. Johnson, Matthey & Co., but, of course, costs more than the ordinary metal. The customary mode of converting the metal into *platinum chloride*, *i.e.*, chloroplatinic acid

---

* Dr. Clark recommends to boil the solution with HCl "to convert any meta- or pyro- into ortho-phosphate." There surely is no occasion for this, as the P_2O_5 is added in the ortho-form.

$PtCl_6H_2$[*] solution is to heat with aqua regia (3 volumes of hydrochloric acid of 1·1 and 1 volume of nitric of 1·2) until the metal is dissolved. The solution is evaporated as far as possible on a water-bath, and then re-evaporated with added hydrochloric acid to destroy the remnant of nitric acid. The residue contains more or less of the nitroso-compound $PtCl_6(NO)_2$. To remove it the residue is taken up with water, and the solution re-evaporated; the N of the compound goes off as N_2O_3 $[PtCl_6(NO)_2 + 2HO.H = 2NO.OH + PtCl_6H_2]$. But the N_2O_3 by the action of the water is converted partly into nitric acid, which remains, and it reproduces nitroso-compound; to destroy it the evaporation with hydrochloric acid must be repeated and supplemented by one with water. It is questionable whether all the nitroso-compound can be thus destroyed.

Mr. M'Arthur and the Author, in the course of a research on the combining constant of platinum in the chloroplatinates,[†] came to adopt the following method:—The platinum is placed in a large glass-stoppered colourless bottle (for 20 grms. of metal or less a litre bottle is of convenient size), a quantity of hydrochloric acid of 1·1 is poured on it, and the bottle then filled with well washed chlorine gas by displacement, and closed. In the course of 12–24 hours the chlorine is mostly, if not all, absorbed with formation of $PtCl_6H_2$. The bottle is then refilled with chlorine and allowed to stand until the chlorine is gone, the bottle again refilled with the gas, and so on until all the platinum is dissolved. The "chlorine Kipps" referred to on page 137 came in useful here. With one of these at hand the method is not so troublesome as it appears at first sight. Of course it is not a method for making platinum solution *ex temp.*; but in a properly regulated laboratory the reagent rarely needs be made on short notice. The solution produced is evaporated on a water-bath, the residue is re-evaporated with water, and the chloroplatinic acid thus obtained dissolved in water and diluted to a convenient volume, say to 20 cc. per gramme of metal, to produce "5 per cent." solution.

Pure chloroplatinic acid solution is intensely, but clear, yellow; it is free of all tinge of brown. If there is such a tinge, this indicates the presence of iridium or platinous chloride.

To make pure platinum out of broken-down crucibles, &c., the best laboratory method is Schneider's. It is as follows:—The crude metal is dissolved in aqua regia (if any black powdery residue remains, which obstinately refuses to dissolve, it may be put aside as iridium), the solution evaporated as far as possible on a water-bath, and the residue re-dissolved in water. The solution is neutralized with pure carbonate of soda,[‡] the carbonic acid driven off, and the solution (of $PtCl_6Na_2$)

---

[*] It is remarkable that to this day a considerable minority of chemists are under the impression that what goes as platinum chloride is $PtCl_4$. Even the most neutral solution preparable contains $PtCl_4.H_2Cl_2$, and the H_2Cl_2 cannot be removed by evaporation on a *water-bath* at any rate.

[†] Communicated to the Roy. Soc., Ed., in the summer of 1887.

[‡] Trammsdorff's "purissimum" crystals of $Na_2CO_3 + 10H_2O$, are very pure.

mixed with a quantity of pure caustic soda, which had better be made expressly from pure crystals of carbonate in a nickel basin. The solution is kept at a boiling heat for an hour or longer, and a strong alkaline reaction kept up by occasional additions of caustic soda. The effect is that, while the platinum retains the chloroplatinate form, the iridium and other foreign platinum metals are reduced to lower chlorides (Ir_2Cl_6; $PdCl_2$, &c.), with formation of hypochlorite of soda, which latter must be reduced by addition of a little alcohol in the heat. (My impression is that this last operation might well be omitted; but I have so far always carried it out, as it gives little trouble.)

After the reduction of the hypochlorite, the liquid is acidified strongly with hydrochloric acid, which often leads to the formation of a green insoluble iridium compound, any precipitate filtered off, and the platinum of the filtrate precipitated by adding pure powdered sal-ammoniac until the mother liquor consists of a saturated solution of this salt. After some hours' standing all the platinum is down as chloroplatinate of ammonia. This is filtered off, washed first with concentrated sal-ammoniac solution, then once or twice with small quantities of water, and lastly with alcohol. It is then dried and ignited cautiously in a porcelain crucible, best in small instalments, because the heating of a *large* porcelain crucible is an inconvenient operation. The residual spongy metal is placed in a basin and washed very thoroughly with, first hot water to extract any trace of fixed alkali chloride, then boiling hydrochloric acid (which always dissolves a trace of platinum), and lastly again with water. The residual metal is re-ignited, and is now ready to be used as *pure metal.*

WORKING UP OF PLATINUM RESIDUES.

These may be classified as shown in the following:—

1. *Spongy metal*, as obtained in the Finkener method, or from $PtCl_6(NH_4)_2$, in nitrogen determinations. This kind may be allowed to take care of itself. We would only remind the student that small proportions of impurities, such as may well be neglected in an analysis, cannot be tolerated in a material intended to be used for making *pure* solution.

2. *Solid chloroplatinates* of potassium, ammonium, &c., as obtained analytically. These are reduced with *carefully purified* hydrogen either in the dry way or in the wet way, explained in Ex. 15, p. 28. The powdery metal obtained is carefully and exhaustively washed, and ignited in porcelain.

3. *Alcoholic and Ethereal Filtrates.*—These are subjected to distillation by means of a water-bath until all the ether and the bulk of the alcohol is over. The residual aqueous liquid is united with what there may be of

4. *Aqueous Filtrates.*—These are best reduced with hydrogen in the wet way, &c. (*See* 2.)

5. Small quantities of platinum diffused throughout a large volume of aqueous liquid can be precipitated with zinc as platinum black,

which is washed with acid and then water. As the product is liable to be contaminated with lead (from the zinc), it must be dissolved in aqua regia, the surplus acid expelled by evaporation, the residue re-dissolved, and the solution mixed with sulphuric acid to precipitate the lead if present. The $PbSO_4$ is allowed to settle, filtered off, and the platinum of the filtrate precipitated by means of sal-ammoniac, or as metal by hydrogen in the wet way.

The following method of Mr. Tatlock's may be quoted here as coming in useful in many cases:—Given an impure solution of chloroplatinic acid (*i.e.*, a solution free of iridium, &c., but contaminated with ordinary metals), precipitate the platinum as such by adding caustic soda and alcohol, and boiling. Whether the platinum thus obtained is pure or not depends, of course, on the nature of the impurities present. The method, no doubt, is valuable as a first step in recovering platinum from impure solutions of all kinds.

NOTE (8).—*Determination of the Sulphuric Acid in Sea Water.*

(Forgotten to be inserted on p. 224 after section on "Chlorine.")

Weigh out 100 cc. of the sea water, add 25 cc. of a chloride of barium solution containing $0{\cdot}25 \times BaCl_2$ grms. per litre and 10 cc. of 20 per cent. hydrochloric acid. Heat the mixture on a water-bath for a time, and allow to stand over night; decant the clear liquor through a small Swedish filter, previously washed with hydrochloric acid, wash the precipitate, first by decanting filtration with hot water acidulated with hydrochloric acid, and then with plain hot water on the filter. Dry the precipitate, detach it from the filter, incinerate the latter by itself in a platinum spiral, add the ash to the precipitate, ignite in a small platinum crucible—not too strongly or too long (*see* p. 112)—and weigh. $BaSO_4 \times 0{\cdot}34323 = SO_3$.

To make quite sure of the purity of the reagents, make a blank analysis with 100 cc. of pure water and the exact volumes of reagents prescribed. If a (small) precipitate is formed on standing over night, collect it on a filter of the same kind as used in the analysis, incinerate the filter and contents in a tared platinum crucible, and deduct the weight of the ash from that of the sulphate of baryta precipitate obtained in the analysis as a correction.

NOTE (9).

The adjoining figure represents a new kind of glass two-way cock, which was introduced lately by Messrs. Greiner and Friedrich, of Stültzerbach, Germany. Its application in combustions and other analytical operations is obvious.

INDEX.

PAGE

A

Acetate method for separation of sesquioxides and protoxides 53
Acetate of methyl, properties - 276
Acetone, properties - - - 275
—— determination - - - 279
Albumenoids in milk - - - 256
Alcohol, absolute; specific gravities at 0° – 30° - - - - - 289
—— aqueous; specific gravities (table) - - - 286-289
—— detection of traces - - 291
—— determination in liquors 284-290
—— separation from methyl-alcohol 292
—— detection in methyl-alcohol 299-301
Alkali, free and combined, in soap 261
Alkalies in silicates - - - 124
Alkalimetry - - - - - - 46
Alkalinity of sea water - - 230
Alumina, separation from iron - 33
Amagat, experiments on carbonic acid - - - - - - 159
Ammonia in its salts—
Determination - - - 43
do. Kreusler's apparatus 84
Ammonia in guano - - 252, 253
Ammonium, chloroplatinate; manipulation - - - - - 44
Antimonious acid, determination by iodine - - - - 59
Antimony, separation from lead 135-140
Arsenic, determination in pyrites - 115
Arsenious acid, determination with iodine - - - - - 58
—— determination as sulphide - 116

B

Balance, theory of the - - - 302
—— Dittmar's improvements 304-305
Barium, determination - - - 18
—— chloride; analysis - - -17-20
—— sulphate; purification - - 112
Bichrome method of iron determination - - - - - 37
Biniodide of phosphorus, preparation 278
Bleaching powder, analysis - -60-67
—— Assay for oxygen - - - 61

PAGE

Bleaching powder, Duflos' gravimetric method - - - 62
—— Titrimetric methods - -60-62
—— Gas-volumetric method - - 64
Boiling-point curve - - - 274
Brass, analysis - - - 101-104
Bromine, determination in sea water - - - - - 232
Bunsen's gas apparatus - - 179-193
Butter, analysis - - - 265-267

C

Calcium, separation from phosphoric acid - - - - 30
—— determination in sea water - 224
—— separation from iron and manganese - - - - 52
Carbon, determination—
In cast-iron - - 238-240
In organic substances - 143-152
In steel - - - - 247
Carbonates, analysis - - -47-52
Carbonic acid in sea water - 227-230
Cast-iron, analysis - - 238-248
Chloracetic acid, a reagent - - 105
Chloride of platinum, preparation 310
—— potassium, preparation - - 220
Chlorides, determination of chlorine
—— gravimetric method - - 17
—— titrimetric method (Mohr's) - 219
—— do. (Volhard's) 21, 220
—— combination of gravimetric and titrimetric method - - 21
Chlorination, method of metal analysis - - - 136-140
Chlorine, active; in bleaching powder - - - -60-67
—— as chlorate and total in bleach 63
Chlorine, gas; generation of - - 137
Chrome iron ore; analysis - 128-135
—— do. assay - - 128
—— do. calculation of results - - - 132-135
Cobalt, determination as phosphate 309
—— separation from nickel - 106-111
—— separation of small quantities from iron (foot-note) - - 74

PAGE
Copper, determination as sulphide 42
—— do. as sulphocyanate - - - - 104
—— determination by electrolysis 100
—— do. by titrimetric methods—
By cyanide of potassium - 117
By iodine - - - - 75
—— separation from nickel - - 104
—— do. from zinc 101-102, 104
Copper-voltameter - - - 97
Cupellation - - - - 140-142

D

Di-methyl-acetal, properties - - 276
Dittmar's apparatus for gas analysis - - - 201-207
—— silver alloy (note) - - - 111
Doyère's gas-pipette - - - 199
Dumas' method of nitrogen determination - - - - 152

E

Electrolysis, quantitative - 91-101
Electrolytic apparatus - - 92-93
Ethylene, analysis - - - 213
Eudiometer, Bunsen's - - 179, 208
—— calibration of - - 180, 211

F

Fat in milk - - - - - 255
—— foreign in butter - - - 265
Fatty acid, in soap - - - 260
Felspar, analysis - - - 122-127
—— do. calculation - - 126
Ferricum, direct determination - 39
—— reduction to ferrosum - - 36
Ferrosum, standard sulphate of - 34
Filter-ashes, determination - - 16
Finkener's method of potash determination - - 26, 225, 236
Fluoride of ammonium in silicate analysis - - - - 125
Foreign fat in butter - - - 265
Fulminating gas, apparatus for - 188

G

Galena, analysis - - - 119-121
—— extraction of silver from - 120
Galvanometer - - - - 95
Gas absorption, physical; theory 168-172
Gas analysis—
Exercises - - - 208-218
Theory - - - 155-178
—— Bunsen's apparatus and methods - - - - 179

PAGE
Gas analysis—
—— Lothar Meyer and Seubert's apparatus and method - 195
—— Dittmar's methods - 201-207
—— Doyère's method by absorbents 199
Gases—
Disgregation - - - 160
Extraction from waters 215-218
Proximate analysis - 166-168
Relation of weight and volume 162
Ultimate analysis - 173-178
—— combustible—
Table giving combustion constants per unit - - 178
Their analysis, necessary attenuation before firing 190-198
Gasometry, volumetric; theory of 155-166
Gas-volumetric analysis, example - 64
German silver, analysis - 104-111
Glycerine, determination in soap - 262
Gold and silver alloys, analysis by cupellation - - - 140-142
Greiner and Friedrich's new stopcock - - - - - - 313
Guano, analysis - - - 252-255

H

Haen, De; titrimetric determination of copper - - - 75
Hydriodic acid, preparation - - 278
Hydrochloric acids, specific gravity of aqueous - - - 305-307
—— standard - - - 13, 21
Hydrogen, determination in organic substances - - - 143-152

I

Iodides of ethyl and methyl, their specific gravities, etc. - - 293
Iodide of phosphorus, preparation 278
Iodine, pure; preparation - - 56
—— standard solution, preparation and applications - - 56-60
Iron, cast; analysis - - 238-248
—— gravimetric determination - 23
—— titrimetric determination 34-42
—— separation from alumina - 33
—— separation from manganese and calcium - - 52-55
—— traces in nickel, determination 105

J

Jacobsen's apparatus for extracting the gases from a water - 216

K

Kjeldahl's method of nitrogen determination - - 83-85

PAGE
Knallgas apparatus - - - - 188
Kreusler's apparatus for Schlœsing's method - - - - - 88
—— for ammonia distillation - 84

L

Lead in galena, determination - 120
—— separation from other metals as sulphate - - 101, 104, 120
—— separation from antimony 135-140
Liebig's potash bulbs, manipulation of - - - - - 50
Lime, determination in sea water - 224
—— separation from phosphoric acid 30
Limited oxidation method of analysis - - - - - 298-300
Liquids, their combustion with oxide of copper - - - 149
—— volumetric apparatus for 10-12
—— determination of specific gravity 12
Lothar, Meyer, and Seubert's gas analysis apparatus - - 195
Lunge's vitrometer - - - 90

M

Magnesia, determination - - 24
—— determination in sea-water - 224
Manganese, native oxides; analysis 67-75
—— native oxides, their assay for active oxygen—
  Bunsen's method - - 70
  Fresenius and Will's - - 68
  Permanganate methods - 69
—— determination of traces of nickel and cobalt - - 74
—— separation from iron and calcium - - - - 52-55
—— titrimetric determination—
  Pattinson's method - - 245
  Volhard's method - - 244
Manometer, to test gas evolution apparatus - - - - - 44
Marsh gas, analysis - - - 213
Measuring flask, graduation - - 11
Measurement of liquids by volume 10-12
Methyl-alcohol, determination of - 276
—— detection in spiritus vini 295-299
—— properties - - - - 275
—— aqueous, specific gravities and percentages (table) - 281-283
Milk, analysis - - - 255-258
—— do. calculation - - 258

N

Nickel, electrolytic determination 100
—— separation from cobalt - 106-111
—— separation from much iron (foot-note) - - - - 74

PAGE
Nitrates and nitrites, their analysis—
  By Schlœsing's method - 85
  By Walter Crum's method - 89
Nitrogen in organic substances, determination—
  By Dumas' method - - 152
  By Kjeldahl's method 83-85
  By Varrentrapp and Will's method - - 79-83
Nitrometer, Lunge's - - - 90

O

Organic analysis, ultimate - 143-154
Oxalate of iron, preparation and analysis - - - - 143
Oxalic acid in guano - - - 254

P

Permanganate method of iron determination - - - 34
Phosphate of lime, analysis - 30-32
Phosphoric acid, separation from lime - - - - - - 31
—— determination by molybdate - 31
—— titration with uranyl-acetate 249
Phosphorus in cast-iron - - 242
Pipettes, graduation of - - - 12
Platinum, preparation of solution and recovery from residues 310
Potash, determination by chloroplatinic acid—
  Finkener's method 26, 225, 236
  Tatlock's method - 25, 236
  Fresenius' (foot note) - - 237
Potash, separation from iron - 23
Precipitates, weighing of, on tared filters - - - - - 45
Pyrites, analysis - - - 111-118

R

Rancidity of butter, determination 267
Reciprocals of $273+t$ and 710 to 790 207
Reduced volumes scale for eudiometer - - - - 193-194
Reporting of analysis - - - 19
Resin in soap - - - - 263
Rheostats - - - - 98-99
Riche & Bardy's test for methyl-alcohol - - - 295-298
—— test for ethyl-alcohol - - 300
Rose's mode of manipulating heavy metallic sulphides - - 43

S

Salts, total; in sea water - - 231
Schlœsing's method - - - 85

PAGE
Sea water, analysis - - 219-235
—— composition - - - - 234
—— chlorine and specific gravity - 235
Silica, amorphous; separation from quartz, etc. - - - 127
Silicates, analysis - - - 122-127
Silicon in cast-iron - - - 246
Silver, determination; gravimetric 20
—— determination; titrimetric - 20
—— extraction from galena - - 120
—— and gold alloys, analysis by cupellation - - - 140-142
Slag in cast-iron - - - - 247
Soap, analysis - - - 259-265
Spathic iron ore, analysis - 55-56
Specific gravity of liquids—
  Determination of - 12-13, 274
  do. change of standard 280, 289
  do. the author's differential method - - - 307
Specific gravity tables for—
  Aqueous ethyl-alcohol 286-289
  do. hydrochloric acid - 306
  do. methyl-alcohol 281-283
Standard solutions, adjustment - 13
—— do. preparation of large supplies - - - 223
Stas' pipette - - - - - 229
Stassfurth salts, analysis - 235-238
Steel, analysis - - - - 247
Sugar in milk - - - - 257
Sulphate of baryta, purification - 112
—— of copper and ammonia, analysis - - - 42-47
—— of iron and potash, analysis 22-24
—— do. do. preparation 308
—— of magnesia and potash, analysis - - - 24-32
—— of magnesia and potash, preparation - - - 308
Sulphuric acid, determination - 22
—— do. do. in sea water - - - - 313
Sulphurous acid, determination with iodine - - - - 59
Sumach, assay of - - - - 267
Superphosphate of lime, analysis 248-252

T PAGE

Tanning materials, assaying of - 267
Tatlock's method of potash, determination - - - 25, 236
Tea, determination of tannin and theine - - - - - 271
Thiosulphuric acid, determination by iodine - - - - 59
Total bases in sea water, as sulphates 226

U

Uranyl acetate, for phosphoric acid determinations - - - 249
Uric acid in guano - - - 254

V

Voltameter (knallgas) - - - 188
—— (copper) - - - - 97
Volumetric apparatus for liquids 10-12

W

Walter Crum's method for determining nitrous and nitric acid - - - - - - 89
Water, determination by direct method - - - 76-79
Water gases, extraction - - 215
Weighing, routine method - - 1
—— method of vibration - - 3
—— absolute - - - 5
—— reduction to vacuum - - 8
—— of pre-determined quantities of liquids - - - - 10
Wood spirit, analysis - - 272-283
—— do. components - 275-276
—— do. determination of acetone - - - 279
—— do. examination for ethyl-alcohol - - 299-301

Z

Zinc, determination by electrolysis 102
—— separation from copper - 102-104
—— do. from iron, nickel, cobalt, manganese, by chloracetic acid - - - - 105

William Hodge & Co., Printers, Glasgow.

OTHER WORKS BY THE SAME AUTHOR.

I.—Report on the Composition of Ocean Water:

Part of "The Physics and Chemistry of the Voyage of H.M.S. *Challenger.*" Part I. Printed for Her Majesty's Stationery Office. Sold by Adam and Charles Black, and Douglas & Foulis, Edinburgh; and others. 1884.

II.—A Manual of Qualitative Chemical Analysis:

Douglas & Foulis, Edinburgh, 1876. TABLES belonging thereto, same publishers, 1877.

III.—Analytical Chemistry:

A Series of Laboratory Exercises, constituting an Elementary Course of Qualitative Analysis. W. & R. Chambers, Edinburgh; 2nd edition; 1886.

IV.—Tables to facilitate Chemical Calculations:

Printed for the Author by James Maclehose & Sons. Sold by Williams & Norgate, London.