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QUANTITATIVE
CHEMICAL ANALYSIS

ILLUSTRATED HANDBOOKS ON PRACTICAL CHEMISTRY

BY

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QUANTITATIVE
CHEMICAL ANALYSIS

ADAPTED FOR USE IN THE LABORATORIES OF COLLEGES AND TECHNICAL INSTITUTES

BY

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PREFACE.

THE experience derived from many years' laboratory teaching has led us to believe that the following course of Quantitative Analysis will be useful to chemical teachers and students and to analysts.

It will be seen that the scheme ordinarily adopted has not been modified to any considerable extent, but an attempt has been made to introduce recent methods and apparatus.

It has also been our endeavour to render the descriptions of methods and processes as intelligible as possible. We have accordingly carefully introduced all necessary practical details, and have illustrated the text by numerous original engravings. The book has at the same time been kept within moderate dimensions by omitting unnecessary theoretical matter, and by inserting only typical useful and well-accredited methods instead of attempting to describe all the different processes in use.

The analytical processes described in the text have been repeatedly carried out by our students, who have supplied many of the results of analysis which appear in paragraphs 940–974.

We have freely used the standard treatises, monographs and original memoirs on the subjects treated of, and have recommended the student to refer to these sources of information for further details. A list of the more important works of reference will be found in paragraph 1021.

The book is intended to supplement rather than to replace oral instruction and demonstration by the teacher; but it is confidently anticipated that it will, in a somewhat unusual degree, diminish the tutorial work of the teacher and remove the practical difficulties of the student.

The subject-matter has been arranged in eight principal Parts, which are subdivided into eighteen Sections.

Part I. deals with the various Preliminary and General Operations which are employed in analysis, such as the Use of the Balance, the Determination of certain Physical Constants, the Preparation of Substances for Analysis, the Ordinary Processes employed in Analysis, and the Preparation of Pure Substances; General Rules to be observed in Working and in the Entry of Work are also appended.

Part II. is devoted to Gravimetric Analysis. Descriptions are given of the most important Simple Gravimetric Estimations, together with others of less importance which are distinguished by being printed in smaller type. Those determinations which resemble one another have been classed together, an arrangement which has been adopted in order that unnecessary repetition in description may be avoided, and the greatest convenience in reference may be secured. The analytical methods have generally been placed in the order of their increasing difficulty.

Part III. treats of Volumetric Analysis. It commences with an account of the Measuring Vessels used for liquids and their Calibration, and of the preparation of Standard Solutions. Various processes for the Volumetric Estimation of simple substances are then described, and these are grouped in such a way as to associate those estimations which are made by means of the same solution or which depend upon similar chemical reactions.

Part IV. contains descriptions of more Complex Quantitative Estimations. Some of these are Gravimetric, others Volumetric, and others again are mixed in their character. These processes are selected as being typical. They represent in the main those which a student should carry out in order to get a useful knowledge of quantitative methods for scientific and technical purposes, and include the Analysis of Ores, of various Industrial Products, and of Water and Food, and the Examination of Oils, Fats and Waxes.

Part V. describes the processes of analysis of Organic Substances, and explains methods for the determination of Molecular Weights

Part VI. treats of Gas Analysis. It has been restricted in its scope to the more simple methods, many of which are now commonly applied to technical purposes. The omission of the more elaborate methods has been decided upon, partly because an abstract of such processes is almost useless and a full description would have added to the dimensions of the book somewhat seriously, and partly because admirable accounts of these methods are at the disposal of the student in several of the standard works referred to in paragraph 1021.

Part VII. contains certain Typical Results of Analyses. It also contains a series of Tables of Constants required for calculating percentage results from the numbers obtained by analysis, Tables of the Specific Gravity and corresponding percentage composition of diluted alcohol and of solutions of the common acids and alkalis, and tabulated characteristics of oils, fats and waxes. It concludes with Tables of Weights and Measures and of four-figure Logarithms, and some useful Memoranda.

The Atomic Weights which are given in paragraph 980 are those which

are recommended for the year 1913 by the International Committee on Atomic Weights.

Part VIII. furnishes descriptions of the Preparation of Gases, of the use of Compressed Gases, and of the Distillation of Water. It concludes with Lists and particulars of the Special Apparatus and Chemicals which are required for the processes referred to in the book, and with a list of useful Books of Reference.

An Index to the Processes of Separation contained in the text precedes the General Index.

It will be noted that the dimensions and capacities of vessels and apparatus are stated on the metric or decimal system; but the tables of metric and English equivalents, and the means of conversion given on pages 72, 525 and 526, will remove any difficulty arising from want of familiarity with the metric system which is now invariably adopted for scientific purposes.

It will also be noted that the terms *hydroxide* and *hydrate* are used indifferently for the compounds of metals with hydroxyl.

The text has again undergone a careful revision in the preparation of the tenth edition, and this has led to the elimination of errors, and the introduction of much new matter, which includes a new form of oven for drying at constant temperature; the analysis of commercial aluminium and bauxite; additional methods for the estimation of titanium in iron-ores, of phosphorus and manganese in iron and steel, and of moisture in coal; and a recent method by Bichfeldt for the detection and estimation of foreign fats in butter.

Among the many colleagues and friends who rendered us valuable assistance in bringing the book up to date, and in describing well tried and important new methods, were Dr. J. C. Crocker, Mr. W. A. Naish, A.R.S.M., and the following Fellows of the Institute of Chemistry: Messrs. E. R. Andrews, J. H. Coste, W. T. Rigby and E. T. Shelbourn.

F. C.,
J. B. C.

LONDON, *November* 1913.

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PART I.

GENERAL PROCESSES.

SECTION I.

THE CHEMICAL BALANCE. WEIGHTS AND WEIGHING.

The thick numbers inclosed in brackets in the text refer to paragraphs.

In the execution of quantitative analysis, the operation of accurate weighing requires to be constantly carried out. Hence it is essential that the student should become familiar with the use of the chemical balance, which is employed for this purpose. A convenient form of chemical balance, and the method of using it, are described below.

The Balance.

1. **The Chemical Balance** represented in Fig. 1 consists essentially of a rigid beam which is supported near to and slightly above its centre of gravity. Upon either end of the beam, and equidistant from its centre, the scale-pans are suspended.

In order to diminish the friction of the working parts at the points of support and of suspension, there are let into the beam three agate knife-edges which work upon agate planes. The beam and the pans are supported by these edges upon the planes.

When the balance is not in use, the beam is lifted from the knife-edges and is supported by a T-shaped rest; the pans are also supported.

Both the beam and the pans are usually released by the rotation of a disc with milled edge in the front of the balance-case.

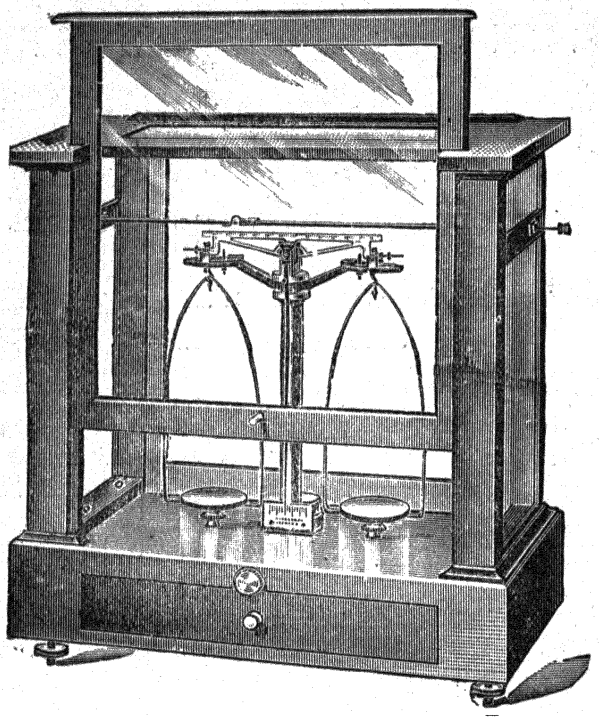
Attached to the bottom of the balance-case are three or more set-screws, which enable the balance to be adjusted to a perfectly horizontal position. This adjustment is ascertained by observing a spirit-level on the floor of the balance-case, or by a small plumb-line near the pillar.

The beam of the balance is commonly graduated in ten equal divisions, and a 10-milligram rider (6) is used for weighing fractions of milligrams.

The beam is, however, often divided differently and riders of different weights are used. The shorter the beam is the more rapid will be its swings.

Fine screws carrying small brass nuts project from the ends of the beam;

FIG. 1.



THE CHEMICAL BALANCE.

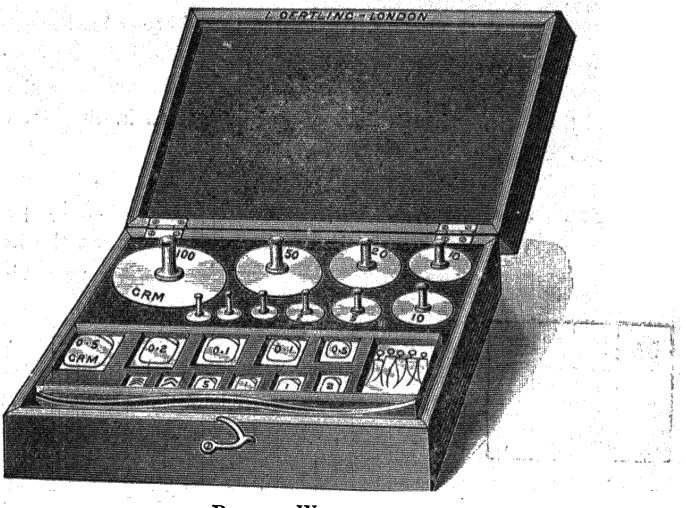
the horizontality of the unsupported beam can be secured, when necessary, by the rotation of these nuts (7).

2. **The Balance is inclosed in a Glass Case** provided with balanced sliding glass sashes at the front and the back, and with hinged side doors. This case shields the balance from dust, and hinders the access of acid fumes and of moisture. It also prevents air-currents from disturbing the scale-pans during weighing. The balance should be kept in a room which is as free as possible from acid fumes and from damp and is not subject to great changes of temperature. As a further precaution, a jar partly filled with small pieces of calcium chloride, or with pumice wetted with strong sulphuric

acid, should stand inside the balance-case. These absorbents of moisture must be renewed from time to time.

3. The Support on which the Balance rests must be free from vibration. It may consist of a slate or stone slab, resting on pillars which are let into the foundation of the building and are out of contact with the floor.

FIG. 2.



BOX OF WEIGHTS.

The slab may be more simply isolated from the vibrations of the floor by being supported by brackets firmly attached to the wall.

THE WEIGHTS.

4. The Weights, which are almost exclusively used by chemists, are those of the French or Metric System, in which the gram is taken as the unit. The convenience of this decimal system is obvious; for not only is there a simple relation between the unit of weight and the units of length and of capacity; but the different denominations in weight, being related by multiples and submultiples of ten, conform to our numerical notation, and therefore render entry and chemical calculations very easy.

The weights, from one gram upwards, are usually made of brass (Fig. 2). They are cylindrical in shape, and are provided with a narrow stem, by means of which they may be lifted. This stem is grasped by a small brass forceps,

and not by the hand. The smaller weights, from 0 5 gram downwards, are made either of platinum, or of aluminium foil or sheet. The low specific gravity of aluminium renders it possible to use a greater volume of the metal, and therefore permits of the weights being comparatively large and thick. Aluminium weights are consequently more easily handled, and are less liable to be bent or folded, than those of platinum. These smaller weights are square in shape, and usually have one corner turned up to be grasped by the forceps.

An ordinary set of weights, together with a forceps for lifting them, are shown in Fig. 2, contained in the usual velvet-lined box. The separate weights, however, differ in value in sets made by different makers, as will be seen by comparing the values of weights shown in the box with those represented in Fig. 3.

5. The Process of Weighing is much Facilitated by permanently removing the weights from the box and keeping them on the front of the floor within the balance-case. They are placed on a piece of stiff cardboard (Fig. 3), which is ruled into the same number of spaces as there are weights. Each of these spaces is covered by a weight, the value of which has been previously written within the square. Accordingly, when the weights which are requisite for counterpoising any substance have been removed from the card and placed upon the scale-pan, their value may be read off from the uncovered squares left on the card.

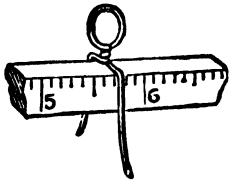
Fig 3

50	20	20	10
5	2	2	1
·5	·2	·2	·1
·05	·02	·02	·01

Card for Weights

6. The Rider is a piece of wire bent as is shown in Fig. 4. It is made either of gilded brass or of aluminium, and its form enables it to bestride the graduated beam of the balance, and to remain on whatever part of the beam it is placed. The rider is moved from one position to another by an arm which passes through the balance-case and is moved from the outside. Milligrams and fractions of milligrams are usually registered by means of the rider.

Fig. 4.



Rider on Beam.

Centigram and 12-milligram riders are in common use, but riders of other weight are also employed.

When the centigram rider is used, the beam of the balance is divided by ten main equidistant graduations, each of these spaces being further subdivided into ten. Each main division therefore corresponds to 1 milligram, and each minor division to the tenth of a milligram

When the 12 milligram rider is used, the beam is divided into twelve

main divisions, the intervening spaces being divided into tenths as before. The position of the rider is thus easily adjusted for fractions higher than 9 milligrams and lower than 11 milligrams; but in many modern balances the whole scale of ten divisions is made equally accessible to the rider.

Adjustment and Testing of the Balance.

The Balance should be adjusted, and its accuracy ascertained before commencing analytical work.

7. The Balance is Adjusted as follows:

The balance and its case are first made to assume a horizontal position by means of the levelling screws. This adjustment is satisfactory when the bubble of air in the circular spirit-level occupies the central position.

The scale-pans and the beam are then set free from their supports. A gentle oscillatory movement is usually imparted to the beam of the balance by the removal of its support. A slight fanning movement of the hand over one of the pans will, however, serve to start the oscillation, if necessary. The lower end of the pointer or index attached to the beam will now swing to and fro over several divisions of the ivory scale. If the pointer is found to oscillate through an equal number of divisions on each side of the zero of the scale, the balance is in adjustment.

If the spaces described by the pointer on each side of the zero of the scale are unequal, a further adjustment must be made by turning the small nut at the end of the beam, or the vane in the centre.

The observations described in paragraphs 8 and 9 are then made.

8. Delicacy or Sensitiveness of the Balance.—The speed of oscillation of the pointer is noted. The slower the oscillations the greater is the sensitiveness of the balance to small differences of weight, and *vice versâ*. If the sensitiveness of the balance is great, the rate of oscillation will be unduly slow, and the operation of weighing will become tedious.

The oscillations of the pointer become slower as the centre of gravity of the beam approaches more closely the axis of its suspension. Most balances have, attached to the central portion of the beam, a screw which carries a nut. By adjusting this nut, the distance between the centre of gravity and the suspension-axis of the beam can be varied at will. This will alter the sensitiveness or delicacy of the balance.

When a milligram weight is placed on one of the pans of an adjusted balance, and the beam is liberated, the pans should be shown to be out of equilibrium by the swings of the pointer. A delicate balance will be affected

in this way by 0·1 milligram, but for ordinary purposes it is sufficient if the balance is sensitive to 0·2 milligram.

The delicacy of the balance may be tested by placing a milligram weight on one pan, and balancing this by means of the rider on the beam upon the other side. The rider is then moved gradually along the beam until a distinct deflection of the pointer is noticed, the movement of the beam being checked by its supports while the rider is being moved.

The effect of increasing the load on the pans of an ordinary balance is to slightly diminish its sensitiveness. But when the maximum weight which the balance can carry is placed on both pans, the addition of a milligram should have nearly the same influence upon the swings of the pointer as when the pans were empty.

9. Accuracy of Construction of the Balance —If the weight of the same body is ascertained several times in succession, the balance should indicate equilibrium every time, if the contents of the pans remain unchanged. Faulty construction of the knife-edges will cause differences to appear in the successive weighings.

When each pan of the balance is loaded with equal weights—say with 50 grams—and equilibrium is secured, if necessary, by the addition of small pieces of tin-foil on one pan, the equilibrium should be maintained when the loads are changed from one pan to the other If equilibrium is not maintained when the pan-loads are exchanged, the arms of the balance are of unequal length.

Testing the Weights.

The Weights, which are to be used in analytical operations, should be tested in order to ascertain whether their relative values are correct. For most operations it is sufficient if the *relative* values of the weights are correct, and it is not essential that each weight should possess its true *absolute* value.

10. The Weights are Tested in the following way: A one-gram weight is nearly balanced with brass-clippings, and the counterpoise is finally adjusted by the addition of small pieces of tin-foil. The original gram weight is then removed and is replaced by another one-gram weight; the counterpoise must still be true. The third gram weight is tested in the same way.

The two-gram weight is then balanced against two of the one-gram weights which have been already tested; the five-gram weight is tried against the two gram and the three one-gram weights, and so on.

The fractions of the gram are then compared with one another in a similar manner, and are finally compared with the gram weight.

If the weights are correct in relation to one another, the counterpoise in all the above cases, and in all similar cases of nominally equal values, should be absolutely true. If the weights are found to be incorrect, they should be readjusted by the maker.

The Process of Weighing.

There are two methods in common use for determining the weight of a substance in air—the **Direct Method,** and the **Method of Substitution.** The result thus obtained must be corrected if the *Absolute Weight* is required.

11. Direct Weighing —In this process the substance is placed upon the left-hand scale-pan, and the counterpoising weights are placed upon the right. The weight of the substance is assumed to be equal to the weights which act as a counterpoise.

This method is expeditious and is the one in common use. Its indications are correct if the balance answers satisfactorily to the tests described in paragraphs 7–9. But if the arms of the beam are of unequal length, or if the balance is not in perfect adjustment, the true weight of the substance is not indicated by this method. This is usually of no consequence in any one series of weighings, since the *relative weights* of the different substances and not their *true weights* are required. The relative weights will be correctly given, provided the different substances are always placed upon the same scale-pan, and the condition of the balance remains unaltered between the successive weighings of the series.

12. Weighing by Substitution on any balance gives the *correct* weight of a body in air. In this method the body is counterpoised as before. It is then removed from the scale-pan, and weights are substituted for it which are in exact equilibrium with those already placed upon the other pan The weights thus substituted for the substance will represent the true weight of the substance in air, even when the balance has not previously been adjusted to equilibrium, and when the arms are not of equal length

13. Absolute Weight —Since the volume of the body weighed usually differs from that of the weights which counterpoise it, different volumes of air are displaced by the substance and by the weights Hence a body which has been counterpoised by weights in air would not usually remain in equilibrium with the same weights when the balance is in vacuo The difference between the result obtained by weighing a body in air and that obtained by weighing it in vacuo is usually so slight that it may be neglected in ordinary analytical operations.

The absolute weight of the substance in vacuo can be indirectly obtained, if necessary, in the following manner: The weight of the volume of air displaced by the weights must be subtracted from the weight of the volume of air displaced by the substance, and the number thus obtained must be added to or subtracted from the weight on the scale-pan, according as the difference is positive or negative.

Directions for Weighing.

14. The Following Rules should be attended to during the operation of weighing:

1. After the balance has been levelled (7), ascertain that the scale-pans and the floor of the balance-case are perfectly clean. If necessary, carefully cleanse these surfaces with a large camel's-hair brush, which should be kept in the balance-case for the purpose.

2. Then gently release the pans and the beam (7), and if the beam is not caused to oscillate by its release, start its motion by a fanning movement of the hand over one of the pans. The pointer must oscillate through equal spaces on each side of the zero of the scale (7).

This preliminary adjustment is unnecessary if the weight of the substance is obtained by difference or by substitution. Thus, if it is required to weigh out accurately about one gram of a powdered solid, the solid is put into a weighing bottle, or into some other convenient vessel, and the bottle and the substance are accurately weighed together About a gram of the powder is then shaken out, and the vessel is again weighed. The difference between the first and second weighings will give the weight of the powder shaken out In cases similar to this it is not necessary to attend to the previous adjustment of the beam to exact equilibrium.

3. The substance should be invariably placed on the left-hand pan, and the weights are then afterwards placed by the forceps on the right-hand pan. This ensures the convenience of putting on, changing, and removing the weights by the right hand, the beam being released from its support by the left hand.

4. The weights should be placed on the pan in systematic order. It is best to commence with a weight which is judged to be somewhat too heavy. If this is found to be the case, lower weights of the same denomination are tried in succession, until equilibrium results or the weight is somewhat too small in amount. If the weight is too small the weights of the next lower denomination should be added to it in the same systematic order. This method will be found much more expeditious than that of selecting the weights at random. The milligrams and fractions of a milligram are usually determined by the use of the rider.

5. The near approach to equipoise of the substance and the weights is judged by observing the swings of the pointer over the graduated scale. Consecutive swings to the right and to the left must finally be equal in extent.

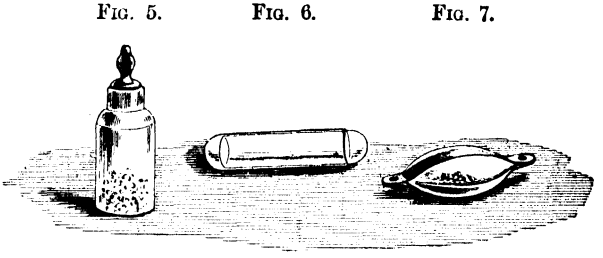
6. The balance-case should be closed while the rider is being used, and the final observation of equilibrium must be always conducted with the case closed

7. The weights must never be handled with the fingers, but should always be lifted with the forceps.

8. During the transfer of the weights, or the addition or removal of the body weighed, the motion of the beam and of the pans should invariably be arrested. This prevents the unnecessary wearing of the knife-edges by violent oscillation.

Some further precautions, which must be attended to when a body is to be weighed, will be found in paragraphs 16 and 17.

15. Entry of Weight.—As soon as a weighing is completed and an exact counterpoise has been secured, careful entry of the weight of the substance should be made in the Note-book. The best plan to secure accuracy



Vessels for Weighing.

in this entry is to write down the total value of the weights upon the pan, by noting the numbers on the uncovered spaces on the card (Fig. 4, p. 4). This entry is then checked by noting the value of each weight as it is returned to its proper position on the card.

16. A Substance should not be Placed Directly on the Scale-pan, but should, as a rule, be weighed in a suitable vessel of glass, of porcelain, or of platinum. A small crucible or evaporating basin, a clock-glass, or a watch-glass, is a suitable receptacle for a substance which is not affected by the air while it is being weighed. But hygroscopic, efflorescent, and volatile substances, and all substances which gain or lose in weight by exposure to the air, must be weighed in closed vessels, such as are represented in the above figures.

The ordinary stoppered weighing-bottle is seen in Fig. 5. A pair of watch-glasses, ground flat at their edges, and held together by a clamp of hardened brass, are represented in Fig. 7; they form a convenient receptacle for hygroscopic substances. Fig. 6 shows a pair of thin glass tubes, one of which fits closely within the other; these are often used for weighing dried folded

filter-papers. A small beaker with a suitable glass cover is usually more convenient than these tubes.

17. A Substance should never be Weighed while it is much Warmer or Colder than the Air in the Balance case, else it will appear to be lighter or heavier than it should be. This is due to two causes.

First, the hot body causes an ascending movement of air around it, and the air which flows in to take the place of that which has risen tends to raise the scale-pan; a body which is colder than the air, on the other hand, produces a downward air-current upon the pan, which tends to depress the pan.

Secondly, every substance tends to condense moisture from the air upon its surface; but the amount of moisture thus condensed diminishes as the temperature of the substance is raised, and increases as the temperature of the substance is reduced.

A body should therefore not only be at the temperature of the air, but should have been allowed to cool in a desiccator (62) if it is to give its true weight on the balance.

EXPERIMENT 1.—Carefully clean and dry the pair of watch-glasses and clamp (Fig 7), and weigh them first by the direct method and then by the method of substitution. Register the former weight in the Note-book. Cover the glasses with a dry, clean beaker, or put them into a desiccator and reserve them for future use.

Ascertain in a similar way the weights of the bottle (Fig 5) and of the tubes (Fig 6), and carefully register these weights in the Note-book. Keep the bottle and tubes covered and clean until they are required for use.

PART I.—SECTION II.

DETERMINATION OF RELATIVE DENSITY OR SPECIFIC GRAVITY, MELTING-POINT, AND BOILING-POINT.

In connection with the chemical examination of substances it is frequently necessary to determine certain of their physical properties with precision. Processes for determining Relative density or Specific gravity, Melting-point, and Boiling-point are described in this Section; the determination of vapour density will be found in paragraphs 920–928.

Relative Density, or Specific Gravity.

28. Relative Density, which is frequently called specific gravity or density, may be defined as the ratio between the weights of equal volumes of two substances, one of which is taken as the standard or unit The accepted standard for solid and liquid substances is distilled water at 4° C.

Accordingly, the relative density of a solid or liquid is obtained by dividing the weight of the substance by the weight of an equal volume of distilled water at 4° C.

It is usually more convenient to determine relative density at 15·5° C. than at 4°, and this temperature is accordingly selected for the purpose in ordinary cases.

Determination of the Density of a Solid Substance.

29. Solid Substances Heavier than, and Insoluble in, Water.— The substance is first weighed in air in the ordinary manner. It is then suspended from the beam of the balance by a fine light hair or fibre. The weight of the substance is now again taken while it is immersed in distilled water at 15·5° C., care being taken that its surface is free from adherent air-bubbles.

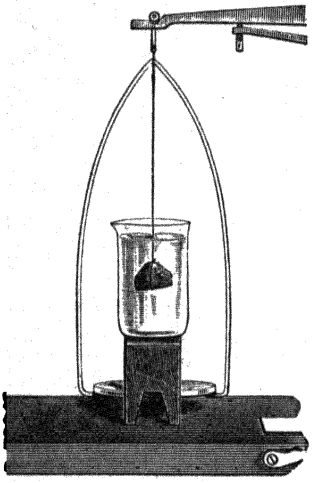
The Removal of Air-bubbles may generally be effected by applying a camel's-hair brush to the surface of the solid after it has been immersed in water In order to remove the internal air from a porous substance, however, it is necessary to immerse the substance in boiling water for some time, or to place the vessel containing the immersed substance under the receiver of an air-pump and exhaust the air.

A convenient arrangement for weighing the substance in water is shown in Fig. 8.

A small wooden bridge is placed over the left-hand scale-pan of the balance; this bridge serves as a support for a beaker of distilled water. The suspending hair or fibre is hung by a loop upon a second hook beneath the one which supports the scale-pan. The removal of the scale-pan, which would destroy the equilibrium of the balance, is thus rendered unnecessary.

The density of the solid is obtained by dividing the weight of the body in air, by the *loss* of weight which it sustains in water. Thus:

FIG. 8.



WEIGHING IN WATER.

If W = Weight of solid in air,
and W_1 = Weight of solid in water,
then its specific gravity $= \frac{W}{W - W_1}$.

Example.—In an actual experiment, a piece of brass weighed in air 16·765 grams, and in water 14·692 grams:

Hence its density $= \frac{16{\cdot}765}{16{\cdot}765 - 14{\cdot}692} = \frac{16{\cdot}765}{2{\cdot}073} = 8{\cdot}088.$

EXPERIMENT 2.—Determine the specific gravity of a crystal of Iceland spar, or of calc-spar, in the manner described above.

30. Solid Substances Lighter than, and Insoluble in Water.—The solid substance is weighed in air. It is then attached by means of a fine silk-thread to a solid, which is sufficiently heavy to sink the lighter body in the water. The weight of this "sinker," while it is immersed in water at 15·5° C., is determined: and the combined weights of the solid and the sinker, while they are attached to one another and immersed in water at 15·5° C., are also determined. These data will suffice for calculating the density of the substance. Thus:

If W = Weight of the substance in air,
L = Its loss of weight in water,
S = Weight of sinker in water,
C = Combined weights of substance and sinker in water,

then the density $= \frac{W}{L} = \frac{W}{W - (C - S)} = \frac{W}{W - C + S}$.

Example.—Thus a piece of paraffin-wax was found to weigh in air 18·45 grams; the weight of the sinker in water was 49 30 grams; the combined weights of the sinker and wax in water were 47 45 grams:

$$\text{Hence its density} = \frac{18{\cdot}45}{18\ 45 - 47\ 55 + 49\ 30} = \frac{18{\cdot}45}{20\ 30} = 0{\cdot}909.$$

EXPERIMENT 3.—Determine the density of a piece of paraffin-wax, using as a sinker the piece of Iceland spar, the specific gravity of which was determined in Experiment 2.

31. Solid Substances Soluble in Water.—The substance is first weighed in air. It is then weighed in a liquid in which it is insoluble. The density of this liquid must be known, and is determined, if necessary, according to the directions given in paragraph 33.

Then if W = Weight of substance in air,
W_1 = Weight of substance in the liquid,
and L = Density of the liquid;

the density of the substance in relation to the liquid is $\frac{W}{W - W_1}$

but the density of the liquid : the density of water :: L : 1

hence the density of the solid compared with water $= \frac{W}{W - W_1} \times L.$

Example.—A piece of loaf sugar was found to weigh 6·612 grams in air, and in mineral naphtha (density 0 748) its weight was found to be 3 126 grams.

$$\text{Hence its density} = \frac{6\ 612}{6{\cdot}612 - 3{\cdot}126} \times 0\ 748 = 1{\cdot}418.$$

EXPERIMENT 4.—Determine the density of a lump of sugar by weighing it first in air and then in petroleum of known specific gravity.

32. Solid Substances in the state of Powder.—Occasionally it happens that the solid substance, whose density is to be determined, is in the state of powder. In such a case a suitable bottle (Fig. 9) is weighed. The weight of distilled water at 15·5° C., which the bottle contains when it is exactly filled to the mark on the neck, is determined (34). Suppose this to be 50 grams.

FIG 9.



DENSITY BOTTLE.

The powdered solid is now introduced into the dry bottle, the whole is weighed, and the weight of the powdered solid is obtained by difference.

The bottle containing the solid is then filled to the mark with distilled water, air-bubbles inclosed in the powder are removed by heating or stirring, the liquid is brought to the temperature of 15·5° C., and the bottle and its contents are weighed again.

Now the weight of water, which is displaced from the bottle by the substance, will be the weight of a volume of water equal to the volume of the solid. This is found by taking the difference between the weight of the solid, and the excess of weight over 50 grams of the solid + water.

Hence, if W = Weight of solid,

W_1 = Weight of solid + water,

and W_2 = Weight of water which fills the bottle,

$$\text{then the density} = \frac{W}{W - (W_1 - W_2)} = \frac{W}{W + W_2 - W_1}.$$

EXAMPLE.—In determining the density of a sample of sand, a weighed bottle containing 50 grams of water was used 15 grams of sand were poured into the empty bottle The bottle was filled up to the mark with water, and the contents then weighed 59 6 grams

$$\text{Hence the density} = \frac{15}{15 + 50 - 59\,6} = \frac{15}{5\,4} = 2\,78.$$

EXPERIMENT 5.—Determine the specific gravity of a sample of silver sand, using an ordinary specific gravity bottle for the estimation.

DENSITY OF A LIQUID SUBSTANCE.

33. The Density of a Liquid is usually obtained by ascertaining directly the weights of equal volumes of the liquid and of water.

The Direct Method may be carried out as follows:

An empty bottle, or other suitable vessel, is weighed in a perfectly clean and dry state. It is then filled to a fixed level with distilled water at 15·5° C. (60° F.), and is again weighed. The difference between the two weights gives the weight of the water which fills the bottle to the level.

The clean dry bottle is then filled in a similar way with the liquid at the temperature of 15·5° C. and is weighed again. By subtracting from this weight the weight of the bottle, the weight of the liquid is obtained.

Since the volumes of water and of the liquid which have been weighed are equal, the density of the liquid is obtained by dividing the weight of the liquid by the weight of the water. Thus, if

W = Weight of vessel + water,

W_1 = Weight of vessel + liquid,

W_2 = Weight of vessel alone,

$$\text{then the density of the liquid} = \frac{W_1 - W_2}{W - W_2}.$$

The Indirect Method consists in weighing the same solid substance first in air, then in water at 15 5° C, and then in the liquid at the same temperature (29). The loss of weight in the liquid divided by the loss of weight in water will give the density of the liquid substance.

Two forms of apparatus which are used for ascertaining the density of a liquid by weighing it on the balance are the Specific Gravity Bottle (34, 35) and the Sprengel Tube (36); the use of the Hydrometer (38) dispenses with the necessity of weighing.

34. The Density or Specific Gravity Bottle (Fig. 9, p. 13) consists of a small thin glass bottle, into the neck of which an accurately ground *blown-glass* stopper is fitted. The neck is contracted below the stopper and has a mark etched upon it. The mark enables the bottle to be always charged with precisely the same volume of liquid.

This form of bottle is useful for all liquids, but more especially for volatile liquids, since the stopper prevents the escape of vapour, and consequent loss of weight, from occurring during the process of weighing.

A small separate thermometer must be inserted through the neck of the bottle when the temperature of the liquid has to be found A small light thermometer is frequently attached to the stopper The bulb of this thermometer is immersed in the liquid, and serves to give its temperature when the stopper is inserted Or the bottle may be provided with two necks, in one of which the thermometer is permanently inserted, while the other serves for filling in the liquid and is closed by the stopper.

Before the bottle is used, it is thoroughly cleansed with distilled water, then dried in the steam-oven, and is accurately weighed when it is cold. A more rapid method of drying the bottle consists in rinsing it out with alcohol, then with ether, and then placing it in the steam-oven.

The process of drying by either method may be accelerated by sucking out the vapour by means of a glass tube which is passed down to the bottom of the bottle.

In making *very accurate* determinations of the density of a liquid, it should be remembered that immediately after the bottle has been heated or cooled its capacity is slightly altered The normal capacity is only restored after the bottle has remained at the ordinary temperature for some hours.

The bottle must now be filled to the mark with distilled water which has been brough to the temperature of 15·5° C. in a separate vessel. This is conveniently effected by filling the bottle with distilled water, the temperature of which has not been first adjusted, and then placing it in a bath of water which is kept at 15·5° C.

If the temperature of the water in the bath is above the standard temperature, it may be reduced by means of ice, or by dissolving in it a few crystals of sodium thiosulphate or of ammonium chloride.

As soon as the distilled water in the bottle has assumed the standard temperature, which will take from twenty to thirty minutes, the excess of liquid is removed by a pipette, until the meniscus (246) just touches the

mark. The dry stopper is then inserted, and the bottle is quickly but carefully dried with a clean dry cloth. The bottle and its contents are then weighed.

The difference between the weights of the bottle, when filled and when empty, gives the weight of the water at 15·5° C. which it contains when it is exactly filled up to the mark. This weight must be carefully entered in the Note-book.

The weight of the bottle and of the water which fills it to the mark must be redetermined from time to time, since the bottle decreases slightly in weight with use and its capacity may also undergo some change

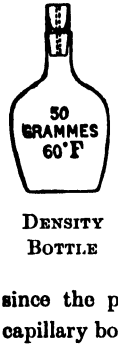
A precisely similar series of operations is now carried out with the liquid whose specific gravity is to be found. The weight of the liquid which fills the bottle to the mark is thus determined. By dividing this weight by the weight of the equal volume of water, already obtained, the density of the liquid is found.

Example.—In the estimation of the density of a sample of methylated spirit, a 50-gram specific gravity bottle weighed, when empty, 24 5655 grams. When filled with distilled water at 15 5° C it weighed 74 5445 grams; and when filled with methylated spirit at 15 5° C it weighed 65 9260 grams:

$$\text{Hence the density} = \frac{65\ 9260 - 24\ 5655}{74\ 5445 - 24\ 5655} = \frac{41\ 3605}{49\ 9790} = 0\ 8275.$$

35. Another Form of Specific Gravity Bottle which is suitable for non-volatile liquids is shown in Fig. 10. The neck of this bottle is fitted with a *perforated* stopper. The perforation enables the bottle to be precisely filled with the liquid, with the entire exclusion of air-bubbles.

Fig. 10.



Density Bottle

After the bottle has been filled with liquid, and the liquid has been brought to the requisite temperature (34), the stopper is dropped into the neck: the liquid will then *entirely fill* the bottle and the perforation in the stopper, a small quantity overflowing from the perforation. The bottle is then wiped dry and weighed.

A cloth may be used for wiping the surface of the bottle; but the top of the stopper should be wiped by the dry hand, since the porous cloth would absorb some of the liquid contained in the capillary bore of the stopper, and lower the level of the liquid.

This form of bottle may give less accurate results than that described in paragraph 24, since the insertion of the stopper with different degrees of pressure will cause the capacity of the bottle to vary.

36. The Sprengel Tube is more readily used than the ordinary specific gravity bottle for taking the specific gravity of a liquid at a temperature differing from that of the atmosphere.

As is shown in Fig. 11 it consists of a broad vessel into which two thick-walled capillary tubes are fused. The two capillary tubes are drawn out to slightly tapering ends, and are bent at right angles, as is shown at *a*, *b*, and a mark is lightly scratched on the tube (*b*).

The ends of the capillary tubes are ground to fit small ground glass caps; these are used for covering the ends, as is shown in the figure, and they prevent the evaporation of a volatile liquid after it has been introduced into the tube. The use of the modified form (37) often enables the caps to be dispensed with.

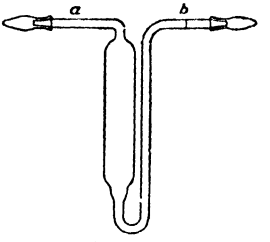


FIG. 11.
SPRENGEL TUBE.

The weight of the empty tube is ascertained after it has been thoroughly cleansed and dried.

The caps are then removed, and the tube is filled with distilled water by immersing the unmarked end (*a*) in water, and applying suction at the other end (*b*). The water should reach some distance beyond the mark on the tube (*b*). The tube and its contents are then brought to 15·5° C., or to a higher temperature if necessary, by hanging the broad part of the tube in a beaker of water which is at the requisite temperature (Figs. 12, 13).

The distilled water should still reach the mark on the narrow tube (*b*). If it extends beyond this mark, some water is sucked out by pressing a piece of filter-paper gently against the pointed extremity (*a*): as soon as the liquid exactly reaches the mark, the filter-paper is withdrawn. The tube, which is now exactly filled to the mark, is removed from the water, the caps are replaced, and the whole is carefully dried and weighed.

The tube is then emptied and dried, and is exactly filled to the mark, in the way already described, with the liquid whose density is required. It is then weighed.

The calculation of the density is made in the same way as from the weighings with the bottle (34).

Example—Thus, in determining the density of petroleum-ether, the tube, when empty, was found to weigh 10·5005 grams; when filled with water its weight was 16·659 grams; and when filled with petroleum-ether its weight was 14·471 grams

$$\text{Hence the density} = \frac{14.471 - 10.5005}{16.659 - 10.5005} = \frac{3.9705}{6.1585} = 0.6448.$$

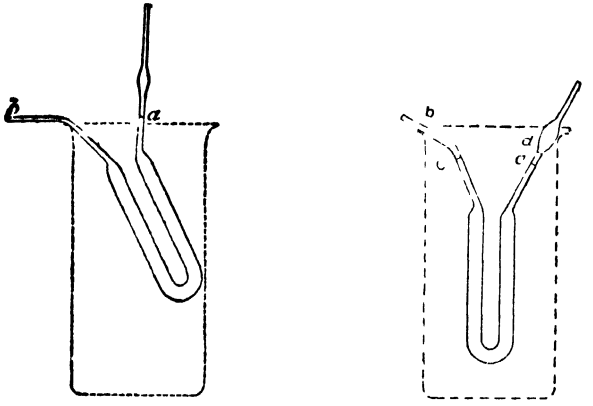
EXPERIMENT 6.—Determine the density of a sample of petroleum by the specific gravity bottle, and control the determination by means of the Sprengel tube.

37. A Useful Modification of the Sprengel Tube is shown in Figs 12, 13 It is especially convenient for dealing with volatile liquids and for taking the specific gravity of a liquid at a temperature much lower or higher than that of the air

The narrow tubes in which the U-tube terminates are bent into directions at right angles to one another, but each of them forms an obtuse angle with the limb of the U-tube The tube (*a*), upon which the mark is made for registering the constant volume, is expanded into a bulb just beyond the mark; this bulb allows expansion of the liquid to take place by rise of temperature, without loss of the liquid occurring by overflow from the end of the tube The tube (*b*) must be drawn out to a tapering end to prevent the liquid from receding from its end.

In using the apparatus, the liquid is sucked in until it fills the tube and part of the bulb, and is then brought to the desired temperature in the usual way by

FIG. 12. FIG. 13.



MODIFIED SPRENGEL TUBE

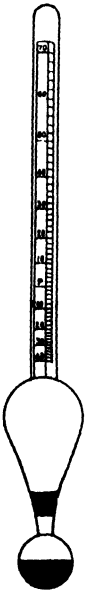
immersion in water The volume of the liquid is finally adjusted to the mark by holding the apparatus with the capillary (*b*) horizontal (Fig 12), and sucking out the liquid by applying filter-paper to (*b*) until the liquid descends to the mark (*a*). As soon as the apparatus is placed in an erect position (Fig 13), the liquid sinks to (*c*) in the capillary (*b*), and ascends to (*d*) in the other capillary The liquid is thus withdrawn from the ends of the capillary tubes, and is therefore protected against loss during the process of weighing

38. The Hydrometer furnishes a rapid means of taking the density of a liquid substance, and dispenses altogether with the process of weighing. It is a glass or metal float (Fig. 14), which is weighted below so as to cause it to assume a vertical position when it is placed in the liquid whose specific gravity is to be determined. The stem is so graduated that the number which is level with the surface of the liquid, when the hydrometer is floating freely shows the specific gravity of the liquid. The temperature of the liquid must

be adjusted to the temperature at which the hydrometer has been graduated, which is usually 15·5° C.

The accuracy of the graduation may be ascertained by floating the hydrometer in liquids, the densities of which have been determined by accurate weighing (34-37).

Fig. 14



Hydrometer.

Melting-point of a Solid Substance.

The Determination of the Melting-point of a Solid Substance.—Three methods are described in the succeeding paragraphs. The first two are alike in principle and are the methods usually adopted. The third method is useful in special cases.

39. First Method.—The substance is placed in a thin-walled glass tube, which is about 1 mm. in diameter, and is sealed at one end (Fig. 15). Such tubes are readily made by softening a thin-walled narrow test-tube in the Bunsen flame and drawing it out until it is reduced to the required diameter. The long tube thus produced is cut into tubes 5 cm. in length, each of which is then closed at one end by fusion in the flame.

The open end of one of these tubes is dipped into the finely powdered substance in a watch-glass, so as to take up some of the powder. The tube is then held mouth upwards and tapped gently with a small spatula until the powder is shaken down to the bottom. These operations are repeated until about 1 cm. of the tube is filled.

The tube is then attached to the stem of a delicate thermometer, just above the bulb, by binding it by thread or fine wire (Fig. 15); or a little rubber ring, snipped off some small rubber tubing, may be slipped over the upper end of the tube and the thermometer stem. It is necessary that the tube enclosing the substance should be in actual contact with the glass of the thermometer bulb.

The thermometer and tube are now placed in a beaker containing a liquid which has a higher boiling-point than the melting-point of the solid (Fig. 16), the upper portion of the tube being allowed to project slightly above the surface of the liquid. If the bath consists of strong sulphuric acid the tube need not be fastened to the stem of the thermometer, as it will be caused to cling to it by the action of the thin intervening film of acid.

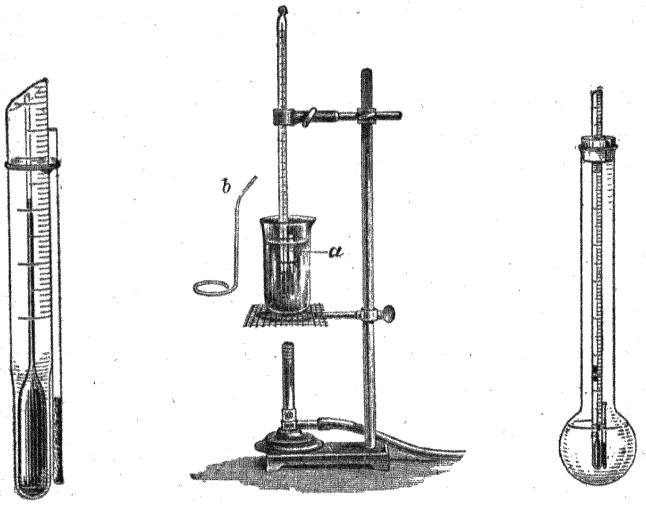
The beaker is then heated until the solid substance melts, and the temperature of its liquefaction is accurately noted by the thermometer. It is

necessary that the rise of temperature should be very gradual when the melting-point is nearly approached.

During the process of heating, the contents of the bath should be constantly mixed by the movement up and down of a stirrer, which is made of bent glass rod or of stout wire in the shape shown at (*b*) in Fig. 16; or the mixture may be effected by a slow stream of air-bubbles which are made to pass up through the liquid from the bottom of the beaker. It is necessary to secure in this way a uniform temperature throughout the mass of the liquid during the determination.

The stirring may be dispensed with if the thermometer bulb and substance

FIG. 15. FIG. 16. FIG. 17.



MELTING-POINT APPARATUS.

are immersed in a boiling-tube containing liquid, which is itself surrounded by the liquid in the beaker or flask which serves as the outer bath.

The thermometer and tube are then removed and are allowed to cool; and the process of fusion is repeated with a *new tube containing a fresh sample* of the substance, since refusion often takes place at a lower temperature than the first melting. The mean temperature obtained from several experiments, made on different samples of the substance, will give the melting-point of the solid.

If the Mercury-thread of the Thermometer extends above the surface of the liquid when the melting-point is read off, a correction must be applied for the contraction due to the cooling of the mercury.

The following formula will give the correction to be added:

$$N(T - t) \times 0{\cdot}000156.$$

Here N stands for the number of degrees on the thermometer stem which are not heated by the liquid, T is the temperature indicated by the thermometer, t is the temperature taken by placing the bulb of a second thermometer midway between the surface of the liquid and the top of the mercurial column, and 0 000156 is the apparent coefficient of expansion of mercury in glass.

In the case of certain fats and of some other substances, the exact point of liquefaction is seen with difficulty. It is then preferable to use a narrow tube open at both ends, but the tube must be heated in a liquid which does not act upon the substance in any way.

If any difficulty is experienced in introducing the substance into this open tube, the fine end of the tube may be inserted into the melted substance. A small quantity will enter by capillary attraction. This is allowed to cool and solidify, and the tube is then attached to the thermometer and immersed in the bath. The moment of liquefaction of the substance is indicated by its ascent in the tube. The temperature of the thermometer is noted when this movement is seen to occur.

It should be borne in mind that many substances, more especially the animal fats, show a lower melting-point when the process of fusion is repeated; but in such cases the normal melting-point is usually regained after the substance has remained in the solid state for some hours.

EXPERIMENT 7.—Determine the melting-point of a sample of paraffin-wax by the above methods, using a beaker containing water for the bath

40. Second Method.—A modified form of vessel for determining melting-points is shown in Fig. 17. It is made by blowing a bulb at the end of a piece of wide glass tube, and should be about 15 cm. in length with a diameter of about 3 cm and with a bulb about 5 cm in diameter.

This bulb is nearly filled with concentrated sulphuric acid. The bulb of the thermometer is then dipped into the acid, and the tube containing the substance is placed alongside the bulb and in close contact with it, as was described in paragraph 39.

This thermometer bulb and tube are now dipped into the acid (Fig. 17), the upper part of the tube remaining above the surface of the liquid, when the small tube will adhere to the thermometer by the surface-tension of the acid film. The stem of the thermometer is held in position by means of a cork inserted in the mouth of the large tube, the cork having a groove cut in its edge to permit air to escape as it is expanded by heat.

When all is properly adjusted, heat is gradually applied to the bulb and the melting-point is observed. The process is repeated and the results dealt with as has been already described (39).

The discoloration of the acid after continued use may be removed by dropping in a crystal of potassium nitrate.

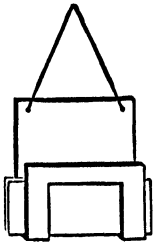
EXPERIMENT 8.—Determine the melting-point of sulphur or of benzoic acid in the apparatus shown in Fig 17, using strong sulphuric acid as the bath.

41. **Third Method.**—The substance, in the form of powder, of minute crystals, or of thin slices, is held between two microscopical cover-glasses This makes the exact time of fusion very evident, since the film of substance, which is more or less opaque before it is melted, becomes suddenly transparent when it fuses The large heating surface which is exposed, relatively to the amount of substance used, also causes the indication to be very sharp.

The method of procedure is as follows:

A thin square microscope "cover-glass" is cut into halves, a small quantity of the substance is placed between these glasses and is caused to assume a very thin layer by gently pressing and sliding the glasses between the fingers.

FIG. 18.



MELTING-POINT APPARATUS.

The glasses are then fastened to a platinum-foil holder of the shape shown in Fig 18 The holder may be made by suitably folding the foil and then cutting out a square piece with a pair of scissors If necessary, the holder and the glasses may be more firmly bound together by means of thin platinum wire

The whole is now suspended, in contact with the bulb of a thermometer, in a wide test-tube. The test-tube serves as an air-bath and is immersed nearly up to its mouth in a bath of sulphuric acid or other suitable liquid The temperature of the liquid is gradually raised until the film suddenly becomes transparent, and the temperature is then immediately read upon the thermometer

In order to prevent undue convection of air, it is well to insert a plug of cotton-wool in the neck of the test-tube.

The cover-glasses may be used as long as they remain unbroken.

The method gives uniform results and is especially suitable for the determination of the melting-points of waxes and of fats These substances need not be previously melted and cooled as is necessary when the first method (39) is employed.

BOILING-POINT OF A LIQUID SUBSTANCE.

The Boiling-point of a Pure Liquid is always the same when the liquid is boiling under the same pressure and similar conditions. This constancy of boiling-point is frequently made use of to ascertain the purity of a liquid, as well as to detect its nature.

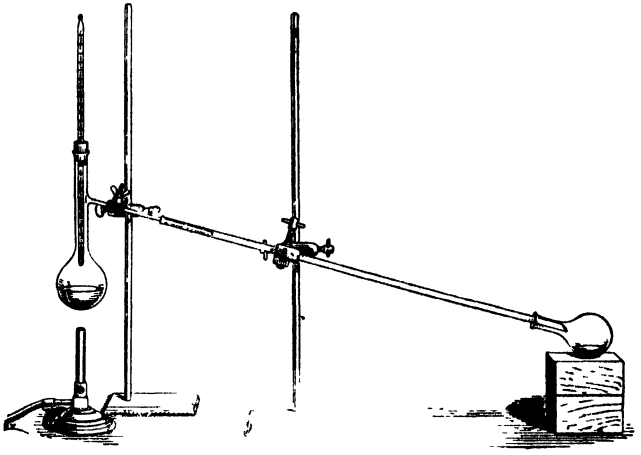
Three methods are described for determining the boiling-point, by ascertaining the temperature of the vapour produced by the liquid when the vapour pressure is equal to that of the atmosphere. The first is the one commonly employed. The other methods are resorted to when only a small quantity of the liquid is available.

42. First Method.—The liquid is placed in a flask (Fig. 19), the neck of which is provided with a delivery-tube at the side. The neck is closed by a perforated cork, through which a thermometer passes. The bulb of the thermometer should be fixed just above the surface of the liquid.

Heat is gradually applied until the liquid boils, the side tube serving to carry away the vapour which is produced. The bulb and part of the stem of the thermometer are thus constantly surrounded by the vapour of the boiling liquid.

If the boiling-point of the liquid is above 120° C., an air condenser,

FIG. 19.



BOILING-POINT APPARATUS.

consisting of a long glass tube slipped over the side tube of the flask, will suffice for condensing the vapour. This arrangement is shown in Fig. 19. If the boiling-point is below 120°, a Liebig's or other form of cold water condenser (**1016**) should be used.

As soon as the reading of the thermometer remains constant above the surface of the boiling liquid, the temperature is registered as the boiling-point of the liquid.

This reading will, however, require correction by the formula given in paragraph **39**, if the upper part of the thread of mercury in the thermometer is cooled by extending above the cork.

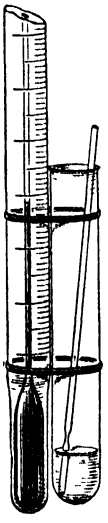
It should be remembered that any considerable difference in the atmospheric pressure will cause an appreciable variation in the boiling-point. It will therefore be necessary either to arrange a means for adjusting the pressure within the flask, if the atmospheric pressure varies much from 760 mm. of mercury; or, as an alternative, to specify the barometric pressure read

during the time of taking the boiling-point. Thus, if the boiling-point observed is 62° C. and the barometric pressure is 760 mm., it may be entered 62° C. /760 mm.

A rough correction may be applied, if necessary, on the assumption that an increase or diminution of 20 mm. in the atmospheric pressure from 760 mm. causes approximately an increase or diminution of 1° C. in the boiling-point.

EXPERIMENT 9.—Determine the boiling-point of aniline, using an air condenser; and of chloroform, using a Liebig condenser.

FIG. 20.



BOILING-POINT APPARATUS.

43. Second Method.—The method described below may be employed when only a small quantity of liquid is available. It gives results which are usually within one degree of the true boiling-point.

About 1 c.c. of the liquid is placed in a thin-walled test-tube, which may be about 8 cm. in length and 1 cm. in diameter. The test-tube is fastened to the thermometer by means of fine wire, as is shown in Fig. 20. A fine capillary tube of thin glass, a little more than 8 cm. in length, is then prepared by heating the walls about half an inch from one end in the tip of the flame for a second, so as just to fuse them together; and the tube is placed in the test-tube as is shown in the figure.

The apparatus is now dipped into a beaker containing sulphuric acid, the mouth of the test-tube projecting above the surface of the liquid. When the acid is heated, small bubbles of air will slowly escape from the lower end of the capillary tube. As the temperature gradually rises, the evolution of vapour-bubbles will eventually become rapid and continuous, indicating that the liquid has attained its boiling-point. The temperature is then read upon the thermometer. The determination should be confirmed by repeating the process with a fresh capillary tube.

EXPERIMENT 10.—Determine the boiling-point of a sample of benzene by the above method.

44. Third Method.—This method is also convenient for determining the boiling-point when the quantity of liquid available is small. It depends on the fact that the pressure of the vapour of a liquid at its boiling-point is equal to the pressure of the atmosphere.

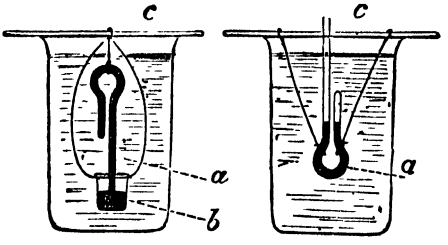
A piece of *thin-walled* glass tubing, sealed at one end, is bent into the shape of the letter U (Fig. 22), the open limb being considerably longer than the closed one. A few drops of the liquid are poured into the tube, which is then inverted so that the liquid occupies the closed end.

The open end is now immersed in a vessel (*b*, Fig 21) containing mercury, a porcelain crucible or a small glass beaker being used for this purpose. The vessel is bound to the tube, and is suspended by wire from a glass rod (*c*) The whole is then plunged into a suitable bath, and is heated to a temperature higher than the boiling-point of the liquid enclosed in the tube (Fig 21) The vapour arising from the boiling liquid will expel the air from the tube, and will itself fill the tube

The tube and vessel are then removed from the bath and are allowed to cool. The mercury will rise and fill the whole of the tube, with the exception only of a small space at the bend of the tube, which is occupied by the liquid formed by the condensation of the vapour, care must be taken that no air-bubbles are present. The tube will then have the appearance shown in Fig 21.

The tube is now carefully inverted in position, so as to cause the liquid to ascend and occupy the closed end. Mercury is removed by pushing a glass rod

Fig 21. Fig 22



Boiling-point Apparatus

down the open tube until the column of mercury is shorter in the open than in the closed limb of the tube, and the tube is immersed in a bath of liquid, the boiling-point of which is higher than that of the liquid in the tube, care being taken that the longer limb extends above the liquid in the bath (Fig 22) A thermometer is then immersed in the bath with its bulb close to the closed limb of the tube, and heat is gradually applied

As soon as the mercury columns assume the same level in both limbs, the temperature is taken The heating is then continued for a short time, and the source of heat is removed The mercury will now be higher in the open than in the closed limb of the tube. As soon as the mercury in the open limb falls to the same level as that in the closed limb, the temperature is again noted These observations are repeated several times The mean of the temperatures thus observed gives the boiling-point of the liquid.

It is necessary to agitate the contents of the bath during the heating and cooling processes, so that the temperature may be uniform throughout the mass of the liquid. This may be effected by an appropriate stirrer (Fig. 16, *b*, p. 20), or by passing a stream of air to the bottom of the vessel, and allowing the bubbles to rise through the whole height of the liquid.

Experiment 11.—Determine the boiling-point of a sample of ether by the above method, using water in the bath.

PART I.—SECTION III.

MECHANICAL PREPARATION OF SOLIDS. DRYING AND DESICCATION. SOLUTION, EVAPORATION. PRECIPITATION, FILTRATION. TREATMENT OF PRECIPITATES. PREPARATION OF PURE SUBSTANCES AND OF DOUBLE SALTS. GENERAL RULES FOR WORKING. ENTRY OF RESULTS.

Mechanical Preparation of Solids.

54. Before commencing the Analysis of a Substance, two conditions must usually be attended to with regard to the substance itself.

(1) The specimen chosen for analysis must be a fair and average sample of the body which is undergoing examination.

(2) The substance, if a solid, must almost invariably be in a finely divided state.

55. Sampling.—The first condition presents no difficulty in the case of a body of homogeneous composition. But in preparing a sample of a heterogeneous mass for analysis, such, for example, as an iron ore, portions should be selected from different parts of the mass. These are then coarsely powdered and mixed, and a small quantity of this mixture is used for the analysis.

Frequently a large quantity of moisture is present. In this case the sample should be selected from the interior, as the outer portions would probably be more or less dried by exposure to the air, and would give too low a percentage of water.

Again, in the examination of certain minerals, the mineral of which the composition is to be ascertained is often embedded in a matrix of earthy matter, or is adherent to other minerals. Care must be taken in this case that a true sample, consisting of the desired mineral only, is detached.

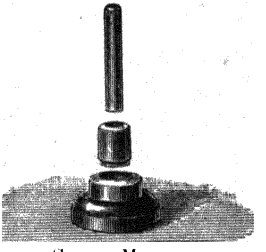
In many of the estimations described in Parts II. and III. pure substances must be used. Although most of these may be purchased in a form suitable for analysis, it is advisable in certain cases to prepare the substance by purifying the ordinary chemicals. Directions are given in paragraphs **106-110** for effecting this purification.

56. Powdering.—The second condition, that the solid substance which is intended for analysis must be in the state of very fine powder, is also usually indispensable, since a substance is more readily acted upon by solvents and by fluxes when it is in fine powder than when it is in mass.

The operation of powdering a substance is usually conducted in a mortar. It is essential that the mortar should be composed of harder material than the body to be powdered, or the powder will be contaminated with particles of the material of which the mortar is composed. For salts and other comparatively soft bodies, a porcelain or a Wedgwood mortar may be used; but for many minerals and other hard bodies, a mortar of steel or of agate is necessary.

When a mineral is being reduced to powder, the large pieces may be first broken by wrapping them in paper and striking them with a hammer upon a steel anvil. The smaller pieces thus produced are then reduced to coarse powder, either in a steel mortar of the usual shape, or in a steel percussion mortar (Fig. 23), which consists of a hollow cylinder fitted into a depression in the base. The substance is placed in the cavity thus formed. The solid cylindrical pestle is then pushed down upon the substance, and is struck repeatedly with a hammer until the substance is powdered.

FIG. 23.



STEEL MORTAR.

Chemical grinding-mills are also supplied which serve for converting hard minerals into coarse powder.

The coarsely powdered substance is next introduced, in small portions at a time, into an agate mortar; and the substance is further powdered by trituration, *not by blows*, until it forms an impalpable powder. If the powder is sufficiently fine, no grittiness will be felt when it is rubbed between the finger and thumb.

To make certain that the substance is sufficiently finely powdered, it is advisable to sift it as follows: A piece of fine muslin, which has been well washed and dried, is stretched over the mouth of a beaker and held in position by a rubber ring. The powdered substance is then poured upon the muslin, and the beaker is gently tapped. The finer particles will fall through into the beaker. The coarser pieces which remain on the muslin may then be returned to the mortar and again triturated until they pass completely through the muslin sieve.

Brass sieves of various mesh are also supplied by the maker for sifting powders. Before using these, they must be perfectly cleansed and dried.

Trituration with water was formerly used in the pulverisation of so-called

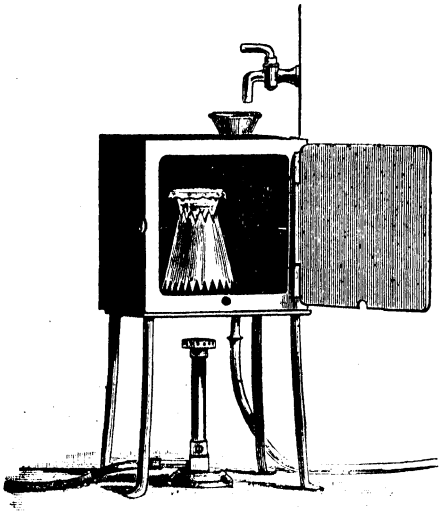
insoluble bodies. Since, however, all solids dissolve to some extent in water, this method has been generally discarded, because it affects the composition of the substance.

Drying, or Desiccation.

57. Most Substances contain Water in varying and unknown quantity. It is frequently necessary to remove this water before the substance is analysed. Some of the methods of effecting this are described below, others are described hereafter.

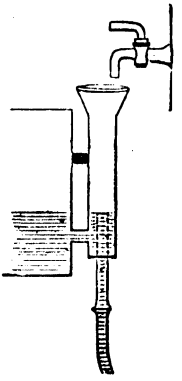
Water may be present either as adherent water, commonly termed mois-

Fig. 24.



Water-oven.

Fig. 25.



Water-supply (Section).

ture, or as combined water, which is frequently water of crystallisation. The operation of drying is usually conducted for the purpose of removing adherent moisture without reducing the amount of combined water or of any other constituent.

The removal of adherent water, or moisture, may be effected in several ways. Five methods are described below. In selecting one of these, attention must be paid to the temperature at which the anhydrous substance begins to decompose, so as to prevent the loss of other constituents besides adherent moisture. Any near approach to a temperature which would cause such a change must be avoided.

58. Drying at Ordinary Temperature and in Vacuo.—If a solid substance is to be superficially dried at the ordinary temperature of the air, as is usually necessary in removing the adherent mother-liquor from crystals, a convenient method of procedure is as follows.

The moist solid is placed in a thin layer upon a porous tile or plate to drain After most of the moisture has been drained off by several hours' standing, the substance is next pressed, in thin layers, between folded sheets of filter-paper. The paper is renewed until the last sheets no longer become moist. The adherent moisture is then known to have been removed. The drying may be completed by exposure in the desiccator mentioned below.

If the substance is a liquid, or if it decomposes when heated, it may be dried by placing it in a desiccator (62) and exposing it to the drying action of sulphuric acid or of some other absorbent of moisture. The production of a vacuum in the desiccator greatly hastens the evaporation and removal of the water (63).

59. Drying at Steam-heat.—Substances are more rapidly freed from water by heating them to a temperature of 100° C., a thin layer of the powdered or liquid substance being spread on a watch-glass, and exposed to a gentle current of air in a steam-oven (Fig. 24). *See also* par. **1022.**

The oven is made of copper, and, with the exception of the door, it is doubly cased throughout. The door may be glazed to give a view of the interior. The casing of the oven is filled to about one-third its height with water. Heat is then applied by means of a Bunsen or other atmospheric burner. When the water boils, the upper part of the hollow casing becomes filled with steam and the temperature of the interior of the oven approaches 100° C.; the steam is either allowed to blow off into the air, or is condensed by a long tube or condenser and returned as water to the steam-oven.

A gentle current of air passes through the oven when it is heated, entering through an inlet near the bottom of the door and escaping from an outlet in the top.

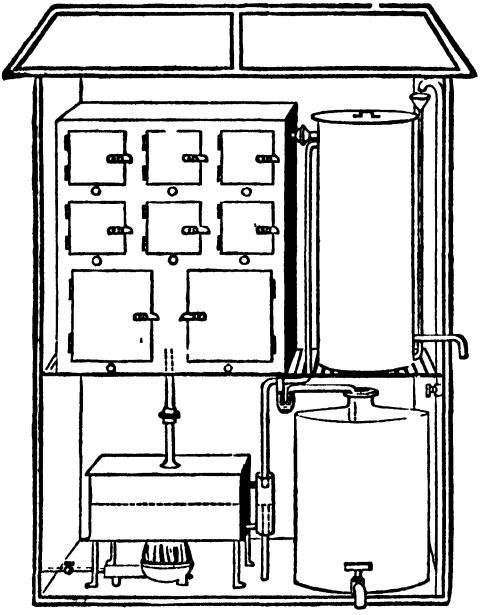
It has been found possible to attain a higher temperature than that usually recorded in a steam-oven, by dispensing with the usual inlet for air through the door. A narrow copper tube is substituted for this one end of the tube is seen immediately beneath the door, and the other end opens into the oven flush with its bottom. The pipe itself is thus constantly surrounded with boiling water, and the air passing through it into the oven enters at a temperature of nearly 100°. There is a small outlet for air provided at the upper part of the back of the oven.

The arrangement for ensuring a uniform level of water in the steam-oven will be understood from the sectional drawing (Fig 25). A constant supply of cold water flows into the vessel which is attached to the side of the steam-

oven, and the excess flows away by the central tube to a sink. The water in the bath is maintained level with the top of this overflow tube by a small connecting tube below.

60. The Heating of Steam-ovens may be advantageously combined with the Distillation of Water. The apparatus suitable for this purpose stands conveniently in a recess in the laboratory wall, which is furnished with a glazed

FIG 26.



STEAM-OVENS AND STILL.

projecting hood, and with a good draught from the top. This arrangement is represented in Fig 26, which is drawn to the scale of one-tenth. A copper boiler on a stand, and a stoneware collecting-jar, are seen resting on the floor of the recess, while the set of double-cased copper ovens and the still-tub are supported on a strong iron grating above.

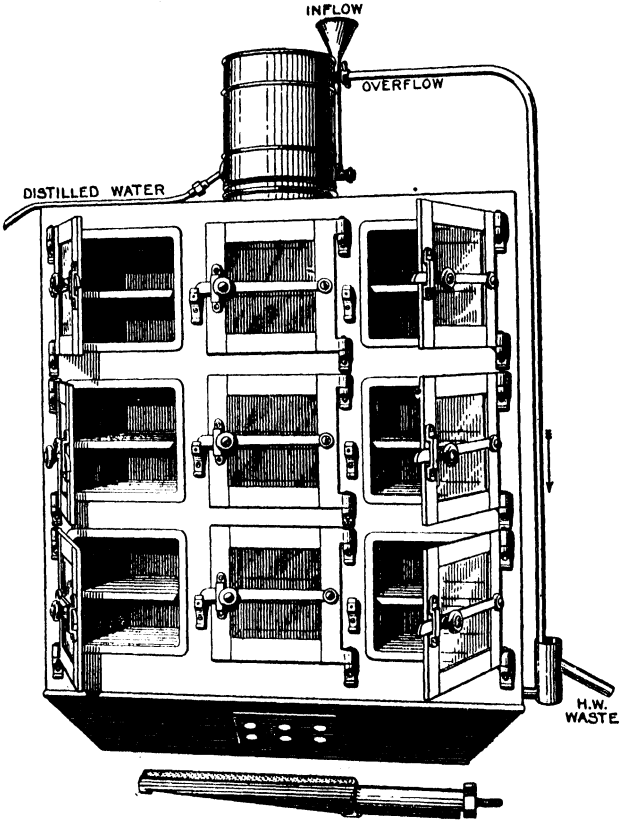
The steam generated by heating the boiler with a powerful Fletcher burner passes from the boiler through a pipe which terminates within the outer casing of the ovens, and several inches above the bottom. The steam then makes its way between and around the various ovens, undergoing partial condensation while heating them. The hot condensed water thus produced flows through a pipe, the opening of which is flush with the bottom of the oven-casing This pipe has a U-bend to prevent the escape of steam. The water is collected in a stoneware jar, from which hot distilled water may be drawn when the apparatus is at work.

Any steam which is not condensed in heating the ovens passes from the upper

part of the oven-casing into a block-tin worm enclosed in the tall still-tub. It is thus condensed, and flows as distilled water from the end of the worm-pipe into a second stoneware store-jar provided with a tap below. The level of the water inside this jar is indicated by a glass syphon-gauge.

It is essential that the coils of the tin pipe shall be so supported as to have throughout a permanent uniform downward slope, else the condensed water will

FIG. 27.



STEAM-OVENS AND STILL.

not drain away from the worm, and a back pressure of steam will be produced in the apparatus.

The still-tub is supplied with a stream of cold water from a pipe, in which is a control tap. This pipe is shown at the extreme right of the figure. From the top of the opposite side of the still-tub the heated condensing water flows into a little feeding-vessel attached to the side of the boiler, such as is shown in section in Fig. 25 (p. 28). A portion of this hot water serves to keep up the water-level in the boiler to the dotted level in the figure; and the rest flows away through a

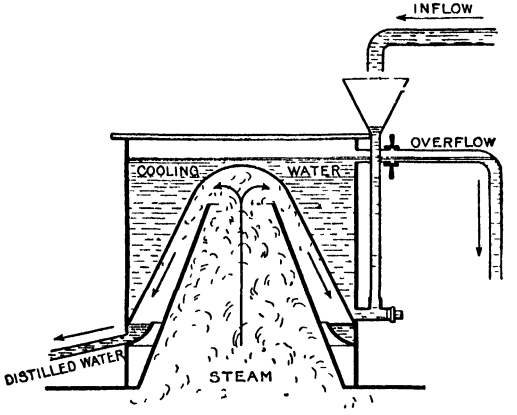
central pipe, seen in the feeding-vessel, into a hot-water supply vessel and hence into the waste

All the connections are made by means of screw-union joints. The apparatus can therefore be quickly and easily disconnected and dismounted for the purpose of removing the incrustation in the boiler and on the condensing worm, and for repairs The incrustation, if strongly adherent, may be dissolved off by commercial hydrochloric acid diluted with four times its volume of water

This apparatus may be allowed to run uninterruptedly without any attention after the gas-burner has been lighted and the supply of condensing water has been regulated by the tap

It is easy to arrange a series of parallel longitudinal heating burners under the

FIG 28.



THE BROWN CONDENSER

boiler, any number of which may be used: the amount of steam generated may thus be varied according to requirements

A removable plate screwed down on the top of the boiler enables the incrustation to be occasionally taken out of the boiler, or dissolved by acid diluted as mentioned above.

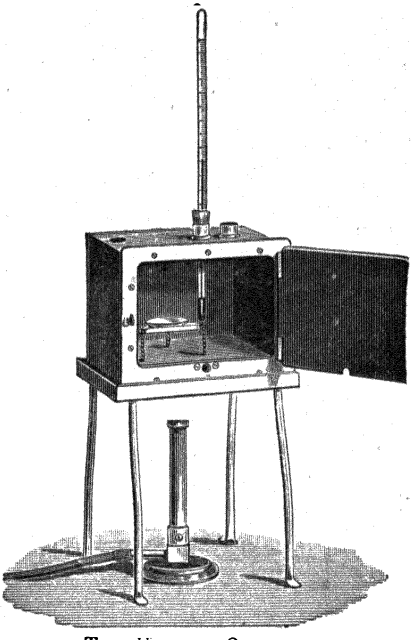
A Modified Form of this Apparatus (Fig. 27) has been recently introduced, in which the boiler forms the bottom of the steam-oven casing and is heated by a powerful longitudinal burner. The steam, after passing between and around the various ovens, is condensed in a special condenser which is seen above the steam-ovens and is described below. The condensed water flows into the store-jar down the pipe shown to the left of the figure. The overflow condensing water is taken away by the tube shown on the right of the figure.

The condenser is made of copper, thickly tinned inside. It is very efficient and is readily cleansed. Its general construction is seen in the sectional drawing (Fig. 28). The steam enters through a wide opening below and

impinges upon the lower surface of the dome, which is kept cool by contact with the constantly renewed cold water on its upper surface. The distilled water formed by condensed steam is collected in an annular internal channel, from the bottom of which it flows through a tube to the storage-jars.

61. Drying above Steam-heat.—When a temperature higher than 100° C. is requisite for the desiccation of a substance, an air-oven (Fig. 29) is usually

FIG. 29.



THE HOT-AIR OVEN.

employed. The construction of the air-oven is almost identical with that of the water-oven. Air, heated to the necessary temperature, however, takes the place of boiling water and steam within the jacket.

Since the walls of the oven are usually much hotter than the air inside, the substance to be dried must not be in contact with the oven. A pipe-clay triangle, with the wire ends turned down at right-angles to the plane of the triangle, makes a convenient stand for the substance and keeps it from touching the oven; or a square porcelain plate, slightly less in size than the bottom of the oven, may be supported about half an inch above the floor.

A thermometer passes through a cork in the top of the oven, and serves

to register the temperature of the interior. Any requisite temperature can be obtained by suitably regulating the stop-cock attached to the gas-supply.

It will be found that, when once the flame has been properly regulated, the temperature will remain fairly constant for several hours if a gas-governor has been introduced into the gas service-pipe. Gas-regulators are also sold by the instrument-makers for insertion into the oven, and these secure the maintenance of a constant temperature.

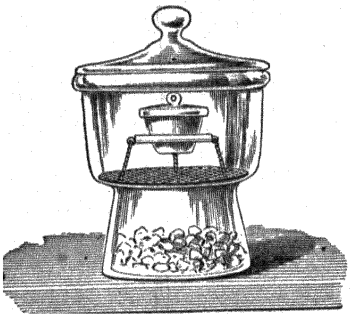
Electrically heated ovens, with a large range of temperature, are now available. They may be connected to the ordinary electric-lighting supply.

Another very efficient form of oven is described in par. **1022**.

The quantitative estimation of water, free and combined, is described under the typical analyses (**188-191**).

62. The Desiccator.—Substances which are too unstable to be dried by heat must be more slowly dried by exposure at ordinary temperature to a dry atmosphere, or to drying agents in vacuo. For this purpose the desiccators shown in Figs. 30, 31, 32 may be used.

FIG. 30.



THE DESICCATOR.

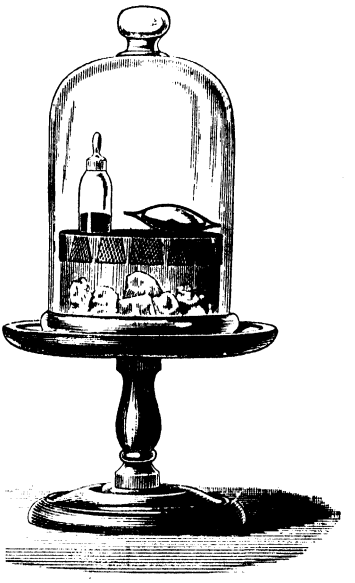
Desiccators are also used for substances which are hygroscopic and absorb moisture from the air after they have been dried by heat. They are thus prevented from remaining in contact with the moist atmosphere while they are cooling, or are waiting to be weighed. The deposition of moisture upon dried apparatus, which is standing aside before it is weighed, may also be prevented by enclosure in the desiccator.

The desiccator is an air-tight vessel, the air in which is kept dry by exposure to a desiccating agent. Either sulphuric acid or calcium chloride may be used as a drying agent.

A small and portable form of desiccator (Fig. 30) is usually employed, because it is easily carried from the working-bench to the balance. It consists of a broad glass jar which is contracted in the middle. The lower portion contains the desiccating agent; the upper portion incloses the body to be weighed. A circular piece of perforated zinc forms a bottom to the upper chamber, and on this a pipe-clay triangle or other support is laid. The body to be cooled and weighed is placed on this support. A flat lid is ground to fit accurately on the upper ground rim of the desiccator; and this rim is lightly greased with lard, so that the lid may fit air-tight.

A larger form of desiccator, which may be conveniently kept in the balance-room, is shown in Fig. 31.

Fig. 31.

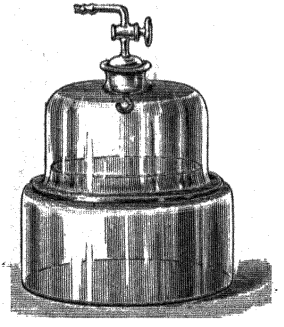


The Desiccator.

63. Drying in Vacuo.—Many substances can only be *completely* dried by exposing them in vacuo in the presence of a drying agent to absorb the water-vapour evolved. This method of drying in vacuo is also suitable for substances which decompose when they are heated. Substances which have been thoroughly dried may be kept for any length of time in vacuo without undergoing increase of weight, as they would do under ordinary conditions.

A convenient form of desiccator for drying in vacuo is shown in Fig. 32. The upper portion is removable and fits closely on the lower portion by means of a ground flange. The joint is rendered air-tight by carefully greasing the ground surfaces. The lower vessel is filled to the depth of about an inch with strong sulphuric acid. The acid may be prevented from splashing by allowing pieces of broken pumice to float in it.

Fig. 32.



Vacuum Desiccator.

The upper portion of the desiccator contains a tubulated stopper which carries a hook below for suspension. The upper portion of the stopper is extended into a tube for connection with a Fleuss air-pump, an efficient water-aspirator, or with some other arrangement for obtaining a good vacuum.

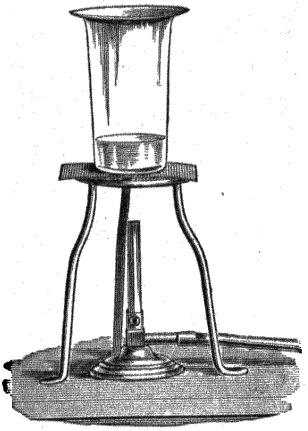
Solution of Solids.

64. The Process of Solution must usually precede the analysis of a solid substance. Several methods of performing this operation are described in this Section.

In most cases it is essential that the solid substance to be dissolved should be in a fine state of division. It is powdered, if necessary, according to the directions already given in paragraph 56.

65. A Substance which is Soluble in Water may be dissolved by mixing it with distilled water in a beaker, which is then placed on wire-gauze over a Bunsen flame (Fig. 33). If the contents of the beaker bump when they are heated, the water and powder should be stirred with a glass rod. In order to prevent loss of solution by spirting during effervescence or ebullition, the beaker should be covered with a clock-glass.

FIG. 33.



SOLUTION OF SOLID.

66. If the Liquid is Boiled, or if Effervescence occurs, as is frequently the case during solution in acids, one of the following methods may be substituted for that described above. See also 74a.

(a) The substance is placed in a conical flask. The solvent is added through a small glass funnel (Fig. 34), which is left in the mouth of the flask and serves to partially close it during the process of solution.

FIG. 34.

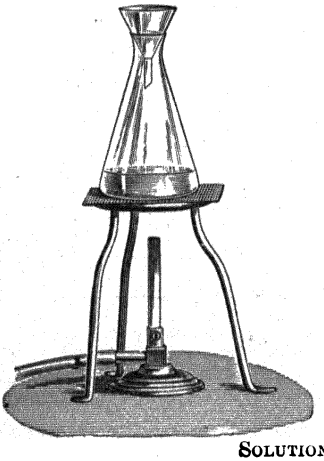
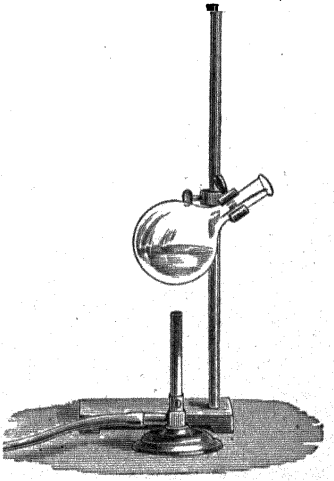


FIG. 35.



SOLUTION OF SOLID.

The loss of the liquid by spirting is thus prevented, and the escape of gas is not impeded.

(b) Or the substance may be placed in a round flask, which is tilted at an angle of about 45° (Fig. 35). In this case the drops, thrown up by effervescence or by ebullition, will be retained by striking the inside of the flask, while gas will freely escape.

67. Insoluble Substances.—A process which serves for the decomposition and solution of many substances which are insoluble in water and in acids is described in paragraph **134**.

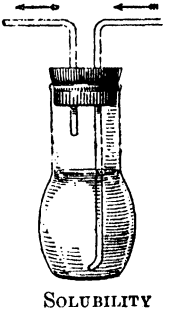
68. Material of Vessels used for Solution.—Care must be exercised in selecting vessels which will not be acted upon by the solvent during the processes of solution and evaporation. Glass, silica, porcelain, and in certain cases platinum vessels may be used for acid liquids. Porcelain, silver, and nickel vessels may be used for alkaline liquids: glass vessels are less suitable, since glass is appreciably acted on by alkaline liquids, although it should be remembered that Jena glass is much less affected than ordinary glass by solvents, and is usually also better able to stand sudden changes of temperature.

Solubility of Solids.

69. The Solubility of a Substance may usually be readily determined by means of the following simple apparatus:

The mouth of a thin-walled glass beaker-flask, about 250 c.c. in capacity, is closed with an india-rubber cork in which two holes have been bored. In one of the holes is fitted a short piece of glass tube bent at right-angles, the tube passing just through the cork (Fig. 36). Through the other hole passes a piece of glass tube, also bent at right angles, and long enough to nearly reach the bottom of the vessel. The lower end of this tube is slightly contracted and is bent obliquely.

Fig. 36.



Solubility Apparatus.

The flask is now about two-thirds filled with distilled water, and it is then immersed, up to the level of the neck, in a large vessel containing water. This water must be maintained, by means of a suitable regulator, at the temperature which has been selected for determining the solubility of the substance. The coarsely powdered solid is then introduced into the flask in quantity more than would be sufficient to form a saturated solution.

The rubber stopper is now inserted, and the end of the shorter tube is connected by rubber tubing with the high-pressure water-aspirator (80) The stream of air-bubbles which is drawn by the aspirator through the liquid causes the solid and the water in the flask to constantly circulate, and to produce a saturated solution of the solid in about fifteen minutes.

Some of the clear solution may then be weighed in a stoppered bottle (Fig. 5, p. 9), and the amount of solid matter dissolved in it may be estimated either by evaporation or by precipitation, according to the nature of the substance.

The insertion of a plug of cotton-wool into the upper end of the longer tube will serve to filter off the dust of the air, and to prevent it from being introduced into the liquid and the supersaturation of the solution, which may arise from the evaporation caused by the passage of the air through the solution, may be prevented by saturating the air with moisture by allowing it to bubble through water on its way to the flask.

If high-pressure water cannot be used, suction may be obtained by blowing steam from a boiling flask of water through an aspirator (80), or a special form of apparatus for producing aspiration may be used, such as that shown at (*h*), Fig 68 (p. 104)

If the solid to be dissolved would undergo chemical change by exposure to oxygen, a stream of coal-gas or other inert gas may be substituted for the air current. If the coal-gas is drawn from the ordinary service-pipes, it should be freed from oxygen by being passed through at least three 23 cm. U tubes filled with pumice soaked in alkaline pyrogallate solution (863).

Example.—The method of calculating the solubility of a substance from the results of an actual experiment is given below:

	Gram.
Weight of solution + bottle . .	31 8910
Weight of bottle	16 2655
Weight of solution . .	15 6255
Weight of solid + dish . .	22 5100
Weight of evaporating-dish .	21 6110
	0 8990

Accordingly 0 8990 gram of the solid has been dissolved by
15 6255 − 0 8990 = 14·7265 grams of water.

Therefore the weight of the solid which would be dissolved by 100 parts by weight of water $= \frac{0\ 899 \times 100}{14\ 7265} = 6\ 104.$

EXPERIMENT 12.—Weigh out roughly 30 grams of $KClO_3$, and pour this into the apparatus (Fig 36) Pour in water until the flask is about two-thirds filled, and pass the current of air through the liquid for half an hour, the flask being immersed in a vessel of water kept at the requisite temperature. Filter off the liquid through a dry filter-paper, rejecting the first portion of the

filtrate, which will have been partially deprived of its salt by the action of the filter-paper.

Then collect about 20 c.c. of the solution in a weighed bottle (Fig. 5, p. 9), insert the stopper, and weigh the bottle and solution.

Now pour the solution from the bottle into a weighed porcelain dish, and rinse the bottle into the dish several times with small quantities of distilled water. Evaporate this liquid to dryness over the water-bath (**71, 72**). Then place the dish in the steam-oven (**60**) for about twenty minutes, allow it to cool in the desiccator, and weigh it.

The necessary data are now obtained for calculating the weight of the solid which is present in 100 grams of water, which has been saturated with the solid at the temperature of the experiment. The process of calculation is illustrated by the example given on p. 38.

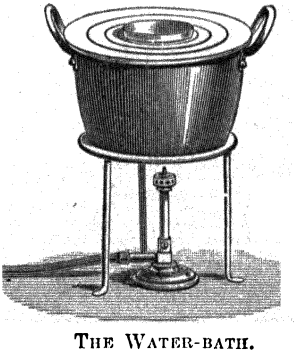
EXPERIMENT 13.—A saturated solution of crystallised copper sulphate, $CuSO_4.5H_2O$, is made as is directed in Exp. 12. But since copper sulphate loses a part of its water of crystallisation when it is dried at steam-heat, the true weight of the salt in solution cannot be obtained by evaporating the weighed solution, and then drying the residue and weighing it as in the case of $KClO_3$. After accurately weighing about 5 c.c. of the $CuSO_4$ solution, the Cu should therefore be completely precipitated and weighed, as is described in the estimation of Cu (**126**). From the weight of CuO thus obtained, the weight of $CuSO_4.5H_2O$ which was present in 5 c.c. of this solution can be calculated, and the percentage solubility of the salt can be found.

Dictionaries giving the solubility of substances at different temperatures should be referred to in order to control the results (**1021**).

EVAPORATION OF SOLUTIONS.

70. The Process of Evaporation serves either to concentrate a solution or to totally expel the liquid. Evaporation is usually effected by applying heat to the liquid contained in a basin made of porcelain, platinum, nickel, or silver. Occasionally a beaker or crucible is used.

FIG. 37.



THE WATER-BATH.

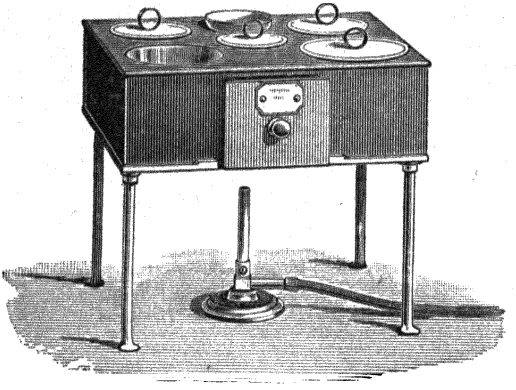
71. Evaporation by Steam.—The evaporation of a liquid is frequently conducted over boiling water upon a water-bath, steam being in this case the heating agent.

A simple form of water-bath is shown in Fig. 37. It consists of a copper vessel rather more than half-filled with water, and heated by a Bunsen burner. The upper portion can be fitted with

flat sheet-copper rings of gradually diminishing diameters, and the top of the bath can thus be made to support vessels of various sizes.

A more complex form of water-bath is shown in Fig. 38. In the upper

FIG. 38.

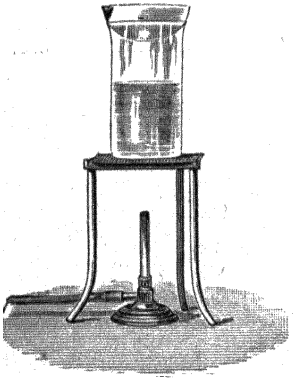


THE WATER-BATH.

surface of this bath there are holes of various sizes, designed to fit vessels of different dimensions. These holes, when not in use, are covered by lids as is shown in the figure. Both forms of water-bath should be fitted with a constant water-supply, such as that represented in Fig. 25 (p. 28).

When the vessel, in which the evaporation is conducted on a copper water-bath, is to be afterwards weighed, it should rest on a glass ring, since contact with the copper edge is apt to stain it. The upper part of a beaker makes a suitable support of this kind. A beaker, the lower part of which has been cracked or broken, may readily be converted into such a ring-support, by leading a crack round it about an inch below the upper edge, by means of a hot wire.

FIG. 39.



WATER-BATH.

72. A Simple Water-bath may be improvised from a beaker partially filled with water and heated over a Bunsen burner (Fig. 39). A few small pieces of paper thrown into the water will prevent it from bumping during the boiling. The dish will rarely fit the top of the beaker so as to be steam-tight: if this should be the case, some strips of paper may be inserted.

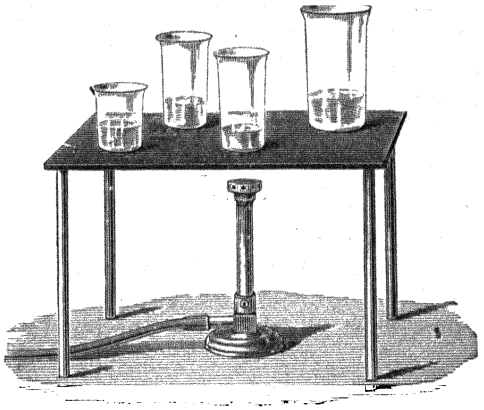
73. Evaporation at Temperatures above Steam-heat.—When a temperature higher than 100° C. is required during the evaporation, one of the following methods may be used:

(a) *The Sand-bath.*—The vessel containing the liquid may be placed on a sand-bath which is heated by a burner. The sand-bath is a shallow sheet-iron saucer or tray, which is covered with a layer of silver sand. A uniform heat can be applied to the bottom of the vessel, by placing it on the heated sand.

(b) *The Naked Flame.*—The vessel may be heated directly over a naked flame, using preferably a rose burner for large vessels. The hot air arising from an Argand burner of the Wallace form also answers well (Figs. 57, 58, p. 57).

In order to avoid the overheating of the sides of a dish above the liquid by the flame, the dish may be allowed to rest in a circular hole made in a metal or asbestos-cardboard sheet; the sheet serves as a screen to the upper part of the dish. If the

FIG. 40.



EVAPORATION ON HOT PLATE.

dish is kept supplied with liquid, this method may be substituted for the water-bath.

(c) *Wire-gauze, Asbestos, or Iron-plate as support.*—The vessel may be supported on wire-gauze, on a sheet of asbestos mill-board, or on an iron-plate. This last support is shown in Fig. 40. It is a convenient source of heat for evaporating a liquid in a beaker, since the rate of evaporation can be reduced by removing the beaker to a greater distance from the part of the plate which is directly over the flame.

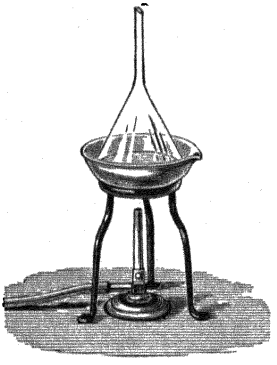
(d) *The Air-bath.*—Beakers may be conveniently heated in a copper air-bath. The bath is similar in shape to the water-bath represented in Fig. 38 (p. 40), but is deeper and contains no water. It is heated by a ring burner placed beneath. The beakers are supported by their curved-over edges in the holes in the top of the bath, the holes being reduced, if necessary, by means of flat copper rings. The beakers are thus immersed in the hot air inside the bath, and are exposed to a uniform temperature, which can be ascertained and

regulated by means of a thermometer, the bulb of which is situated half-way down the inside of the bath. The air-bath may be employed not only for evaporating solutions in beakers to dryness, but also for drying at a particular temperature the residue which is left on evaporation.

74. The Following Precautions should be observed during Evaporation:

(a) If effervescence occurs during evaporation, a tilted flask (Fig. 35, p. 36) may be used to avoid loss by spirting. Another plan is to use an evaporating-dish, and to cover it with a large inverted funnel, as is shown in Fig. 41.

FIG. 41.



PROTECTED EVAPORATION.

(b) Vigorous ebullition must not be allowed to take place in an open vessel, as this would lead to a loss of substance by spirting. The means of preventing loss from this cause are the same as those described under (a).

(c) If the evaporation of a solution is conducted over a naked flame or over a sand-bath, the vessel should, if possible, be transferred to a water-bath towards the end of the process. This is advisable, because when a liquid is rendered thick and pasty by the separation of solid matter, it is apt to spirt considerably even when it is heated below its boiling-point.

(d) Frequently the liquid creeps up the sides of the vessel during evaporation. This is particularly the case with solutions containing ammonium salts. The evaporation in these cases should be carefully watched, and the incrustation which forms near the edge of the vessel should be detached and pushed down by means of a glass rod. If the inner edge of the vessel is lightly greased, the ascent of the liquid will be prevented. If the liquid is heated from above (Fig. 60, p. 58), the ascent of the solution may also be prevented: an example is afforded in the estimation of Na as Na_2SO_4 (170).

PRECIPITATION FROM SOLUTION.

75. Precipitation is effected by converting a substance which is in solution into an insoluble form. The process commonly involves a change in the composition of the substance. A substance is usually precipitated in order

to obtain it in a form in which it may be collected and weighed, but the process is also applied to effect the separation of bodies from one another.

Precipitation is usually performed in a glass beaker; but if strongly alkaline liquids are used, which would attack glass, a vessel of porcelain or platinum is preferable.

Precipitation is usually most rapidly and completely effected in hot liquids. If the solution is boiling, it should be contained in a beaker covered with a clock-glass, or in a flask inclined at a suitable angle, so as to prevent loss by spirting (65, 66). After the addition of the precipitant the liquid is well stirred, and is usually allowed to stand for some time to ensure complete precipitation. The formation of the precipitate in a granular condition tends to facilitate filtration.

Some precipitates form rapidly, and being flocculent may be filtered off at once. $Fe(OH)_3$ and $Al(OH)_3$ are of this description.

Agitation frequently assists precipitation. For instance, the complete precipitation of Mg as $MgNH_4PO_4.6H_2O$ will require several hours under ordinary conditions, whereas it may be effected in a few minutes by the violent agitation of the liquids.

In most cases of precipitation, the addition of a *large* excess of the precipitant should be avoided, but the presence of a slight excess is requisite in order to ensure the completion of the process.

The presence of excess of the precipitant should be always proved. This is usually effected by adding a few drops of the precipitant solution to the clear liquid from which the precipitate has subsided. The clear filtrate should be subsequently tested in the same way as a safeguard. In neither case must any further precipitation occur.

It is advantageous that reagent solutions should be of normal or some multiple or sub-multiple of normal strength, and that each solution should be labelled with the volume necessary for the exact precipitation of a certain weight of the substance to be precipitated. This enables the analyst to avoid adding an undue excess of the reagent, and ensures complete precipitation.

When a liquid is to be transferred from one vessel to another, that part of the outside edge of the vessel over which the liquid will be poured should be slightly greased. The liquid should then be poured down a wet glass rod pressed against the edge of the upper vessel (Fig. 42, p. 45), and the lower end of the rod should touch the liquid surface, or the inside of the vessel into which the liquid is being poured. These precautions prevent the liquid from running down the outside of the upper vessel, and from splashing as it falls into the lower vessel.

EXPERIMENT 14.—Partially fill a weighing-bottle (Fig. 5, p. 9) with pure recrystallised potash alum, $AlK(SO_4)_2.12H_2O$, in a powdered condition. Carefully

weigh the bottle Then shake out about 1 gram of the salt into a 500 c c. beaker, and carefully weigh the bottle again The difference between the two weighings will give the weight of the salt which has been transferred to the beaker.

Dissolve this salt in about 100 c c of distilled water, which contains a little dilute HCl; add some AmCl solution to cause the precipitate to form subsequently in a granular condition, and heat the contents of the covered beaker to boiling. Then heat about 50 c c. of $BaCl_2$ solution to boiling, and add the greater part of this to the contents of the beaker. A granular white precipitate of $BaSO_4$ will form, and will quickly subside.

More $BaCl_2$ solution should be dropped into the clear liquid, to see if the precipitation is complete As soon as this is the case, the covered beaker and its contents may be put by for Experiment 16 (77)

EXPERIMENT 15.—Weigh accurately about 1 gram of $AlK(SO_4)_2\,12H_2O$ into a 500 c c beaker. Dissolve the salt in water, heat the solution to boiling, and add AmHO solution in *slight* excess. A white gelatinous precipitate of $Al(OH)_3$ will form. Boil the liquid until the smell of ammonia has almost disappeared, then put by the covered beaker with its contents.

FILTRATION AND WASHING OF PRECIPITATES.

76. A precipitate is separated from the liquid in which it has been formed, by passing the liquid through a suitable filter-paper. The papers which are commonly used are 9 or 11 cm. in diameter.

Note.—The filter-paper will usually be burnt at a later stage, and the weight of its ash will then be deducted in order to obtain the true weight of the ignited precipitate The paper should therefore contain the least possible weight of mineral matter or ash The best quantitative filter-paper is usually called "ash-less"; it has been treated with hydrochloric and hydrofluoric acids and then thoroughly washed, in order to remove mineral matter. an 11 cm filter of this description will leave less than 1 milligram of ash when it is burnt.

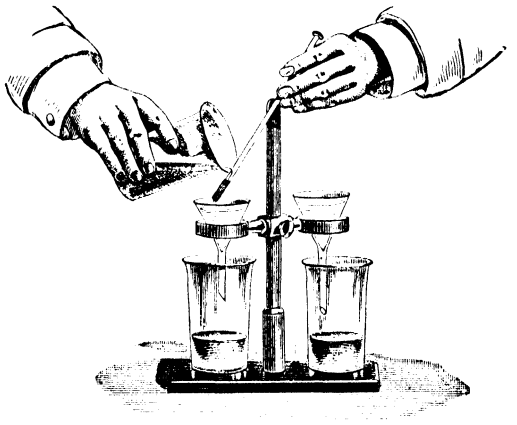
In certain cases, however, the filtration is effected through a dried weighed, or *tared* filter, and the weight of the filter is subsequently deducted from the weight of the dried filter and precipitate (86).

The operations of filtration and decantation are usually combined in the following manner: The precipitate is allowed to settle; most of the clear liquid is then decanted off through the filter-paper without disturbing the precipitate (Fig. 42). After the liquid has been decanted through the filter, a fresh quantity of distilled water, or other washing liquid, is poured upon the precipitate, and the contents of the beaker are stirred or boiled. The precipitate is then allowed to subside, and the clear washing liquid is decanted off through the same filter. These operations are repeated several times with fresh portions of distilled water. Finally the precipitate is transferred to the filter-paper by means of the fine stream from the wash-bottle; the removal of the precipitate being assisted, if necessary, by the use of a glass rod, tipped with about an inch of tightly fitting smooth india-rubber tubing.

The washing of the precipitate and of the filter is then completed by the stream from the wash-bottle.

If part of the precipitate adheres firmly to the interior of the vessel, it

FIG. 42.

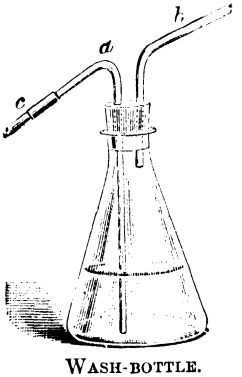


FILTRATION.

may generally be removed by rubbing it with the rubber end of the glass rod. Occasionally it must be dissolved and reprecipitated in the vessel.

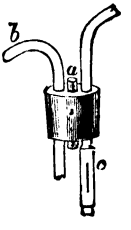
The rubber-tipped end of the glass rod should not be introduced into the liquid until the main precipitate has been removed to the filter, since the precipitate is likely to find its way between the glass and the rubber, and to be retained, unless the end of the rubber has been closed so as to form a cap.

FIG. 43.



WASH-BOTTLE.

FIG. 44.



VALVE FOR WASH-BOTTLE.

A Convenient Wash-bottle is shown in Fig. 43. It consists of a 500 c.c. conical flask fitted with an india-rubber cork and tubes in the ordinary

way The jet, however, is movable, since it is attached by india-rubber tubing. This enables the stream of liquid to be projected in any direction.

When Boiling Water, or a Liquid which gives off Vapour or Gas, is used in the wash-bottle, a special stopper, shown in Fig 44, should be used, to prevent the gas or vapour from entering the mouth

The stopper is perforated with three holes Through the centre hole is pushed a short glass tube (*a*) which terminates just above and just below the stopper.

The other holes carry the jet (*b*) and blow-tube (*c*), as in the ordinary bottle. The lower end of the blow-tube, however, is fitted with a valve by slipping over it a piece of rubber tube, which has a slit cut in it as is shown at (*c*), and is closed by a piece of glass rod.

While the wash-bottle is being used the tube (*a*) is closed by the finger, and air is blown in through the valve (*c*) The valve (*c*) prevents the air from returning through the blow-tube, and no vapour or gas can therefore make its way into the mouth As soon as the washing is finished, the finger is removed from (*a*) and the stream of liquid is thus at once stopped

77. The Following Precautions should be observed during filtration and while the precipitate is being washed on the filter-paper:

The filter should be as small as is consistent with its holding the precipitate and a sufficient quantity of washing liquid. It must fit closely to the funnel, and the overlapping parts of the paper must be pressed together by the finger so that the precipitate cannot get between them.

The end of the stem of the funnel should be cut or ground down to an angle of 45°, and the tip should touch the inside of the vessel into which the filtrate passes. This arrangement not only prevents splashing, but hastens filtration.

The liquid should never fill the filter; but the upper edge of the filter must be carefully washed with the stream from the bottle.

The total amount of washing water used should be as small as possible, since no precipitate is absolutely insoluble, and because the washing should be accomplished in the smallest space of time possible. Amorphous and gelatinous precipitates require more prolonged washing than those which are crystalline and granular.

The washing liquid should be allowed to drain away completely from the filter before a fresh portion is added.

The precipitate should not rise more than half-way up the filter-paper.

If the washing liquid is distilled water, it should be used hot when permissible, as hot water passes through the filter more rapidly than cold water does.

In all cases the final washing water from the filter should be tested to prove that all soluble matter has been removed. This may be ascertained by

applying a delicate test for the substance which is being removed by the washing process.

EXPERIMENT 16.—The precipitate of $BaSO_4$ (75, Exp. 14) may be washed by pouring off the supernatant liquid through the filter, taking care that no precipitate is poured off with the liquid. The precipitate is then stirred up and boiled three times in succession with fresh portions of hot water, the precipitate being allowed to subside after each addition of water, and the supernatant liquid being poured off through the filter-paper.

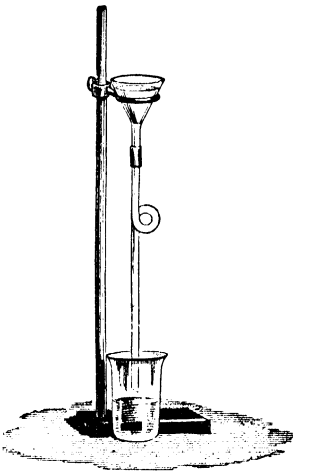
Finally the precipitate is transferred to the filter in the manner already described. The washing is then continued on the filter, until the addition of $AgNO_3$ solution to the last few drops of the washing water no longer gives any turbidity. This precipitate is reserved for the further treatment which is described in Experiment 18 (85).

ACCELERATED FILTRATION.

It is often desirable to hasten the processes of filtration and of washing. This is especially the case when a flocculent precipitate is being dealt with.

78. Acceleration by Lengthened Funnel-tube.—One of the simplest means of increasing the rate of filtration is to attach to the funnel an ordinary glass tube, bent as is shown in Fig. 45. As soon as the filtrate has filled the tube, the weight of the column of liquid tends to draw the liquid through the filter, and the rate of filtration is accordingly increased.

FIG. 45.



ACCELERATED FILTRATION.

Another simple method is to attach to the funnel a *straight* piece of thick glass tube about two feet in length and only one millimetre in bore. The liquid passes down the tube in a nearly unbroken column, the weight of which tends to draw the liquid through the paper.

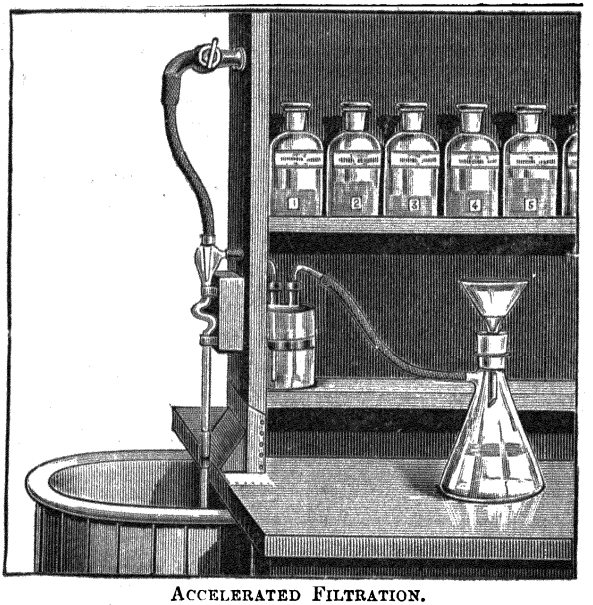
In order that these methods may be effective, it is necessary that no air shall pass through the filter, and that the neck of the funnel and the attached tube shall remain filled with water throughout the process of filtration. In order to insure this, the filter-paper must be fitted into the funnel with great care, and must be proved to be air-tight by pouring distilled water through it. If air is drawn through between the glass and the paper, gentle pressure of the finger on the moist paper will usually prevent this leakage by bringing the paper permanently into contact with the funnel.

79. Acceleration by Filter-pump.—The most rapid filtration, however, is secured by reducing the atmospheric pressure beneath the funnel. The full

atmospheric pressure, being still exerted on the surface of the liquid in the filter, forces the liquid through the filter.

The pressure thus brought to bear on the filter may be greater than ordinary paper in the wet condition can support. It becomes necessary, therefore, either to use specially prepared toughened filter-paper, or to support the ordinary paper in a suitable way (81), so as to enable it to withstand the pressure. Another means of obtaining a sufficiently resistant medium is to

FIG. 46.



ACCELERATED FILTRATION.

produce a filter from fine asbestos fibre in the manner described in paragraph 82.

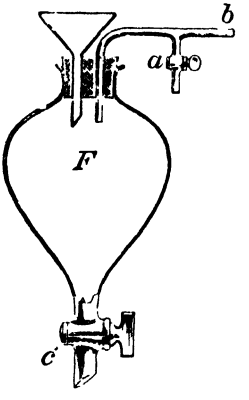
If filter-paper is used, it is fitted as follows: A funnel is selected, the sides of which inclose an angle of 60°. The muslin, platinum or porcelain cone, if required (81, b, c, d), is placed in the funnel; and then a dry filter-paper, folded in the ordinary manner, is inserted. The filter-paper is pressed with the finger until the supporting muslin or platinum and the paper fit the sides of the funnel closely: and while it is thus held in position, the filter is wetted by pouring in a little distilled water. The overlapping edges of the filter-paper are pressed down by the finger, and any air-bubbles between the funnel and the paper are also carefully removed by pressure.

The funnel is then fitted by means of a perforated rubber stopper into the neck of a clean, strong, conical filtering-flask, of about 750 c.c. capacity.

The flask is placed in connection with an exhausting-syringe, or better, with a suitable water-aspirator (80), by means of the side-tube in its neck (Fig. 46)

For convenience in withdrawing the filtrate or washings during the filtration, it will often be found convenient to substitute a vessel, provided with a tube and stop-cock below, for the filter flask The butter-flask (Fig 97, par 688) may be used for this purpose. Or an ordinary separating-funnel (*F*, Fig 47) may be employed The vessel is fitted, as is shown in Fig 47, with a branched tube, one branch (*b*) being connected with the filter-pump and the other (*a*) being provided with a stop-cock for the admission of air into the vessel. The filtrate can be allowed to flow out from this flask at any time during the process by opening the stop-cocks (*a*) and (*c*).

Fig. 47.



Receiver for Filtrate.

Before the filtration is started, it is well to fill the filter with distilled water and to start the exhaustion of air from the flask, in order to ascertain that everything is in working order. If any air is seen to be sucked down between the filter and the funnel, this may be stopped by gently pressing the moistened edges of the paper against the funnel.

The exhaustion should be started gradually, since the particles of some precipitates may be easily drawn through the paper at first.

During the filtration and washing, liquid should be constantly poured into the filter so that it is never quite empty, otherwise fissures are apt to form in the mass of the precipitate. If this should occur, efficient washing becomes impossible, since the water ceases to pass through the whole of the precipitate.

Fig. 48.



The operation of washing gelatinous precipitates is very much shortened by the above procedure; moreover, if air is drawn through the precipitate for a few minutes after the washing-water has run through, the time required for drying the precipitate in the steam-oven is considerably lessened.

80 The Geissler Water-aspirator.—A convenient form of water-aspirator or filter pump is that invented by Geissler (Fig. 48). It is shown in Fig. 46 attached to a high-pressure water-supply by means of stout india-rubber tubing: this tubing should have sufficiently strong walls to enable it to withstand the pressure of the water. The rubber tubing should be firmly bound with copper bell-wire to the water-tap and to the aspirator.

Geissler Aspirator

This aspirator has three tubes fused into the chamber in the upper part. The upper vertical tube conveys the water, which passes through the contracted end of this tube into the opening immediately below it. During its free passage, after

leaving the jet, the water draws air from the chamber and carries it away through the lower vertical outlet tube Air is thus drawn through the side horizontal tube, and any vessel which is placed in connection with this tube will consequently be gradually exhausted of its air.

The side tube of the filter-pump is connected with a tube which passes to the bottom of a small two-necked bottle (Fig 46) The other tube of this bottle passes just through the cork in the second neck, and is connected by rubber tubing with the side-tube of the filtering-flask.

The two-necked bottle serves to prevent any tap-water from the aspirator from finding its way back into the filtering-flask. When the water-supply is suddenly checked, the water from the aspirator is drawn back through the side-tube by the partial vacuum; but instead of entering the filtering-flask, it is received by the two-necked bottle The water is thus prevented from mixing with the filtrate in the flask. As soon as the pump is again started, the water in the bottle is rapidly sucked out

A current of steam from a vessel of boiling water may be blown down the top tube of the aspirator, instead of using high-pressure water for producing suction.

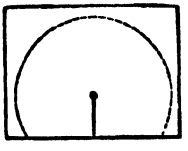
81. Special Filter-paper, and Supports for the Filter, when the filter-pump is employed, are described below.

(a) *Thin Toughened Filter-papers* can now be obtained, which will satisfactorily withstand the atmospheric pressure when it is brought to bear on them.

(b) *Toughened Paper, or Muslin Support* —If ordinary untoughened filter-paper is used, it may be most simply supported at the conical point by means of a small toughened paper cone or filter dropped into the funnel, or a small circular piece of muslin may be folded like a filter and placed in the funnel; the filter-paper is then folded and pushed into position over this support.

(c) *Platinum Cone Support* —The apex of the untoughened filter may also be supported by a platinum cone To prepare this, a piece of platinum foil, 4 cm long by 3 cm. broad, is pierced a little below its middle point by a pin (Fig 49). A cut is made from the middle of the longer edge to this hole. The corners are then removed by cutting with scissors round the segment of an inscribed circle, whose centre is the pin-hole, as is shown by the dotted line The foil is annealed by being heated to redness, it is then folded into a cone with the pin-hole as an apex, and is adjusted to fit into the funnel.

Fig 49.



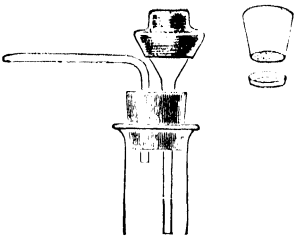
Platinum Support

(d) *A Perforated Porcelain Cone Support* may be used with either a paper filter or with an asbestos filter prepared on the Gooch plan as is explained in paragraph 83.

82. The Gooch Method of Filtration through an asbestos filter is very convenient and expeditious. The filter is made immediately before use either in a suitable crucible or in a porcelain cone. If the crucible is used, it presents the advantage that the precipitate can be filtered, washed, dried, and ignited in the crucible itself

The platinum or porcelain crucible (Fig. 50) has a number of small perforations in its bottom. A platinum cap may be fitted upon the bottom of the crucible during the processes of drying or igniting the precipitate. The porcelain crucible must be used for those precipitates which attack platinum at a high temperature.

Fig. 50.



The Gooch Crucible.

The filtration is effected through an inner lining of asbestos-felt which is introduced into the bottom of the crucible.

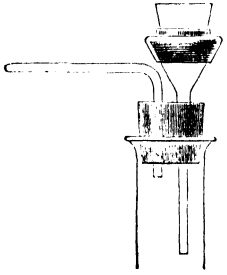
The crucible is prepared for use in the following way:

A short piece of broad rubber tubing is stretched over the mouth of a funnel which has been fitted into a filtering-flask in the ordinary manner (Figs. 46, 47). This is shown in Fig. 50. The crucible is inserted in the rubber ring formed by the free end of the tube (Fig. 51).

Some silky, fine-fibred asbestos is then mixed up with water containing some hydrochloric acid by rubbing it with a pestle in a mortar, and the water containing the suspended asbestos is stored for use in a bottle.

Some of the freshly shaken liquid is poured into the crucible, and the filter-pump is started slowly. The asbestos will at once form a firm, compact felt, which covers the perforated bottom of the crucible. The felt is washed with water, and is made as dry as possible by drawing air through it by means of the pump. The crucible is then removed from the rubber, its bottom is covered with the cap, and its weight is carefully taken after it has been dried (84), and ignited (90-98), and cooled in the desiccator.

Fig. 51.



Crucible Filter.

It is well to subject the crucible containing the asbestos to a further washing, drying, and weighing. The weight should remain unchanged by this treatment. If the weight is reduced, this proves that some of the asbestos has been washed through; it then becomes necessary to repeat these operations until the weight remains constant.

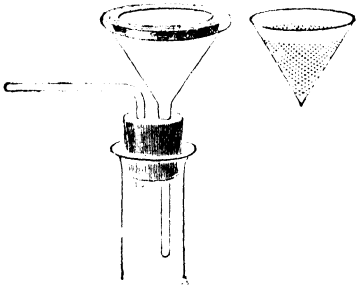
A precipitate is filtered and washed in this crucible in the same way as in a filter and funnel, and it may afterwards be dried and ignited without being removed from the crucible.

A porcelain perforated crucible containing the dried precipitate may be placed within a larger porcelain crucible; a gentle heat is then applied at first, and the ignition is finished at a high temperature if necessary (98).

83. A Perforated Porcelain Cone may be used for the rapid filtration of a gelatinous precipitate which is to be subsequently dissolved from the filter and is not to be dried and weighed.

It is fitted into the funnel by means of a rubber band in a similar manner to the crucible (Fig. 52). The pressure of the air, when the pump is in action, forces the overlapping part of the rubber band down, and thus forms an air-tight joint.

FIG. 52.



GOOCH FILTER-CONE.

The cone is then filled with asbestos suspended in water, and when the pump is started the asbestos forms a firm film, which covers the perforations of the cone.

The cones are made of various sizes. They may be used either with an asbestos film or with an ordinary paper filter.

EXPERIMENT 17.—Transfer the liquid and precipitate of $Al(HO)_3$ (75, Exp. 15) to a filter-paper fitted into a cone support (81) in a funnel which is connected with the filter-pump. Wash with successive quantities of hot water, until the washing-water as it leaves the funnel no longer turns turmeric-paper brown. Afterwards continue the washing, until the last few drops of the washing-water give no precipitate when they are boiled with $BaCl_2$-solution and allowed to stand for a few minutes. Reserve the precipitate in the filter for further treatment.

DRYING PRECIPITATES.

84. The filtered and washed precipitate must now be dried and weighed.

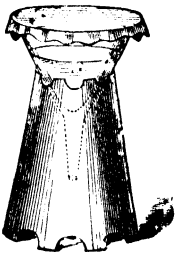
The precipitate may generally be dried in a filter of unknown weight (85). The dry filter is then burnt, and the ignited precipitate is weighed together with the ash of the filter (101–105). The weight of the filter-ash is usually so small as to be negligible : but if it affects the result, its amount must be determined (89) and subtracted from the total.

It is, however, sometimes necessary to directly weigh the dried filter and precipitate. The filter-paper alone must for this purpose be dried at 100°–110° C. and weighed : the filter containing the precipitate is then dried at the same temperature and weighed, and the weight of the precipitate is found by difference (86).

A special method of procedure must be adopted (87) when the precipitate requires to be heated above 110° C. in the process of drying, since the filter would be charred if it were heated above that temperature.

85. The Filter and Precipitate are Dried at 100° C., for subsequent Incineration of the Filter, as follows: The funnel containing the filter and precipitate is covered loosely with a filter-paper, so as to exclude dust, and is then placed in the steam-oven (59). The funnel is usually supported on a shelf which is perforated with holes to receive the stems of the funnels: but a truncated tin cone (Fig. 53), or any other suitable arrangement which allows the heated air to circulate freely around the funnel, and to heat and dry the filter and precipitate, may be adopted.

FIG. 53.



FILTER-DRYER.

EXPERIMENT 18.—The washed precipitates of $BaSO_4$ and of $Al(HO)_3$, from Experiments 16 and 17 (pp. 47, 52), are dried in the above manner.

86. The Filter and Precipitate are Dried at a Temperature not exceeding 110° C., and are then Weighed without further Treatment by one of the following methods (a, b). Of these the first is the usual method of procedure, but the second is sometimes adopted because it can be more rapidly carried out.

(a) If the precipitate requires to be dried at 100° C., the steam-oven may be used (85). If a temperature higher than 100° C. is requisite the air-oven (61) is substituted, but in this case the temperature must not exceed 110° C. else the paper will be charred.

When a number of filters have to be dried at the same time a special air-bath of the general shape shown in Fig. 38 (p. 40) will be found convenient. It is closed above by a flanged lid provided with air outlets and carrying a thermometer: there are air inlets below, and midway in the interior is supported a metal frame carrying cross-wires at right-angles to one another, and in the squares thus formed the funnels are supported.

In all cases the weight of the dried filter, which is to be used in the filtration, must first be ascertained. If the liquid which will pass through the filter-paper is likely to extract any constituent from it, the paper should first be treated with this liquid; but paper already prepared in this way can usually be bought.

In order to dry the filter, it is folded and placed in a small beaker, or in one of the filter-tubes (Fig. 6, p. 9), or upon one of the watch-glasses with clip (Fig. 7). The vessel containing the filter-paper may then be placed on the floor of the steam-oven. If the air-oven is used, the vessel should be placed on a tripod, made of a pipe-clay triangle or other non-conducting material, and must not rest directly on the metal floor of the oven. If this is not attended to, the temperature of the filter may become much higher than that registered by the thermometer inside the air-oven, since the heat

will be conducted directly from the hot floor of the oven to the glass and filter. The filter would then become charred.

After the filter-paper has been in the oven for about an hour, it is taken out and the beaker is at once covered with a watch-glass, or the paper is quickly inclosed in the tube by pushing over it the second tube, or it is clamped between the watch-glasses. It is then allowed to cool in the desiccator, and is weighed when it is cold. The difference between the weight of the empty glasses and that of the glasses + filter gives the weight or *tare* of the filter.

The precipitate is next transferred to the filter in the funnel and is washed and dried as has been already described (76–84). The filter and precipitate are finally allowed to cool in the glasses, and are weighed while thus inclosed.

In order to make sure that the filter and its contents are perfectly dry, the cover-glass is removed and the drying process in the oven is repeated for twenty minutes. The filter is then covered, transferred to the desiccator, allowed to cool, and weighed again. These operations are repeated until two consecutive weighings do not differ by more than one milligram. From two to three hours usually suffice for drying a filter and precipitate in this way.

The weight of the precipitate is then obtained, by subtracting the weight of the glasses + filter from the weight of the glasses + precipitate + filter. It would appear from this that it is not necessary to know the weight of the filter itself, it is, however, advantageous to know this, in case the glasses should be broken before the final weighing has been taken.

(b) **Another Method** consists in drying two similar filter-papers in the way already described, placing them on separate scale-pans, and then adjusting them to precisely the same weight by trimming the heavier one with scissors One of these filters is then placed beneath the other in the funnel during the processes of filtration, washing and drying. The lower filter is now removed and is placed, during the weighing, upon the pan with the weights, and serves as a counterpoise to the filter which contains the precipitate. The weight of the precipitate is thus obtained directly by the one weighing.

87. When the Precipitate requires to be Dried at a Temperature above 110° C., and to be Weighed without further Treatment, the weight of the filter dried at steam-heat is first determined; and the weight of the filter and precipitate, after being dried at 100° C., is next ascertained (84).

Then a portion of the precipitate is removed from the filter to the watch-glasses (Fig. 7, p. 9) and is weighed. This portion is heated to the required temperature for at least thirty minutes, then cooled in the desiccator and weighed; and these processes are repeated until the precipitate ceases to lose in weight. From this result the weight which the whole

precipitate would possess, when dried at the higher temperature, can be calculated.

Ignition of Precipitates.

88. After the precipitate has been dried (**85**) it is usually ignited and then weighed.

If filter-paper has been used, it is burnt, and the weight of the ash, if appreciable, is subtracted from the total weight of the ignited precipitate and filter-ash. The ignition of the precipitate may in some cases be combined in one operation with the incineration of the filter (**99, 100**); but the two processes must be separately conducted if the composition of the precipitates is affected by the burning paper (**101–105**).

The Gooch asbestos filter will not in any case require this separate treatment. The crucible containing the dried asbestos filter and precipitate can be ignited as is described in paragraphs **99, 100,** disregarding the directions for dealing with the filter-paper.

89. The Weight of the Filter-ash is usually less than a milligram, and is negligible, but it is well to determine the average weight of the ash of a filter-paper of each size which is in use. This may be found as follows:

Six of the cut filter-papers are selected from different parts of the packet, or six circular filter-papers are cut of precisely the same size from different sheets of the paper. These are carefully folded and burnt, one by one, to a perfectly white ash in a weighed platinum crucible. The crucible containing the ash is then weighed. The total weight of the ash thus obtained, when divided by six, will give the average weight of the ash from one filter-paper.

90. The Vessels used for the Ignition of precipitates are crucibles or capsules made of platinum, silver, nickel, porcelain, or fused silica.

A Platinum Vessel should be used whenever it is permissible from considerations of suitability and cost. Platinum is attacked by fused caustic alkali, and silver or nickel vessels should be employed for fusions with caustic alkali but these vessels are not suitable when they have to be weighed after the fusion, as they undergo change in weight. Caution must also be used not to heat silver vessels too strongly, as they are relatively easily fusible.

A thin platinum vessel can be more rapidly and uniformly heated than one made of porcelain, and it is not fragile; it resists the action of a coal-gas flame better than nickel does, and it is practically infusible. A crucible 3 cm. in height and 3 cm. in diameter will be found convenient for most purposes (Figs. 59, 60, p. 58).

A small open platinum dish or capsule (Figs. 57, 58, p. 57) will often be

found more convenient for the ignition of substances than a platinum crucible. The dish may be about 5 cm in diameter, and have an extreme depth of about 2 cm

The clean empty crucible or capsule should always be heated to redness, and then cooled in the desiccator and weighed, before it is used.

Porcelain Vessels are much less costly than platinum vessels, and may be used for the same purposes as platinum they are rapidly attacked by fused caustic alkali and by fused lead oxide, and cannot be rapidly heated and cooled without risk of fracture.

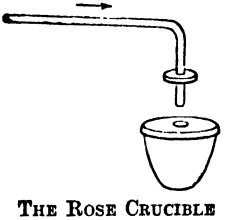
Fused Silica vessels can be broken by a blow but not by rapid change of temperature. They may be used for acid substances, but not for fused or dissolved alkalis or even for strongly basic solids such as PbO and CaO. They are practically infusible, and the loss of weight which they undergo by use and cleansing is less than with platinum, while the weight for equal capacity is about the same.

91. A Platinum or Nickel Crucible or Capsule may readily be Cleaned by rubbing the metal with the moistened finger, which has been dipped into whiting, crushed pumice, or sea-sand If sand is used, it should be examined through a lens before it is used for this purpose · if the grains are seen to be rounded and pebble-like, the sand is suitable, but if they are angular the sand should be rejected, since it would scratch the metal

If the stains cannot be thus removed from the surface mechanically, a little $KHSO_4$ may be fused in the vessel The sulphate, when cold, is removed by boiling it with water, and the dull surface of the platinum is finally polished by rubbing it with whiting, pumice-powder, or sea-sand.

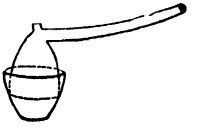
92. Prevention of Reduction or Oxidation during Ignition —When a precipitate which can suffer reduction or deoxidation is being heated, care must

FIG. 54.



THE ROSE CRUCIBLE

FIG. 55.



IGNITION IN GAS.

be taken that the flame does not come into contact with the interior of the crucible, else reduction of the substance may take place This is best avoided by applying a small flame to the bottom of the crucible, and slanting the crucible (Fig 60, p 58).

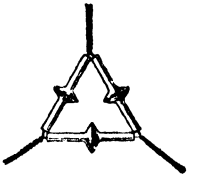
When, on the other hand, oxidation during the ignition of the precipitate must be avoided, air is excluded by passing a current of dried coal-gas or hydrogen constantly through the crucible Rose's perforated lid and flanged porcelain

tube (Fig. 54) may be used for this purpose. A slow stream of gas is conveyed into the crucible by the tube, and escapes from beneath the lid.

An inverted clay tobacco-pipe, of suitable size, may replace Rose's lid and tube: the stem of the pipe serves as the gas-tube, and the inverted bowl takes the place of the lid, as is seen in Fig. 55.

93. The Crucible is usually Supported upon a pipe-clay triangle (Figs. 56, 58, 59, 60), or upon a triangle made of stout platinum wires twisted together (Fig. 57). Triangles are now made with fused silica coverings to the wire in place of pipe-clay.

FIG. 56.



PIPE-CLAY TRIANGLE.

The pipe-clay triangle should have a projecting edge in the middle of each side (Fig. 56). This enables the flame to pass between the crucible and the triangle, and secures a more uniform heating of the crucible; it also strengthens those parts of the triangle which are most subject to wear and breakage.

The triangle is usually supported over the flame by a tripod-stand (Fig. 59), or by the ring of a retort-stand (Fig. 60, p. 58). Occasionally the burner itself serves to support the triangle (Figs. 57, 58).

94. The Temperature and Duration of the Ignition will vary with the nature of the precipitate.

In all cases the heat should be applied gradually. This is especially necessary when the substance is imperfectly powdered, when it is not perfectly dry, or when it is in the form of a very light powder.

95. A Convenient Method of Igniting Precipitates at a comparatively Low Temperature is shown in Figs. 57, 58. The crucible is placed

FIG. 57.

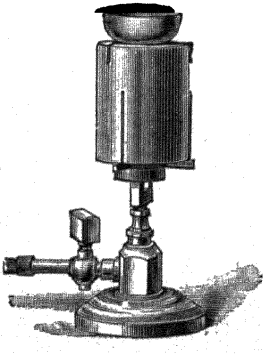
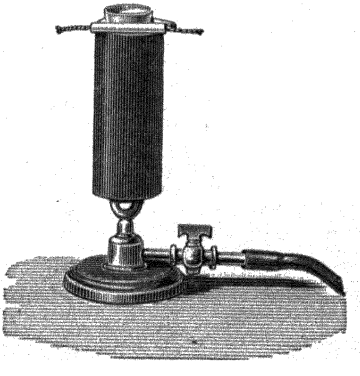


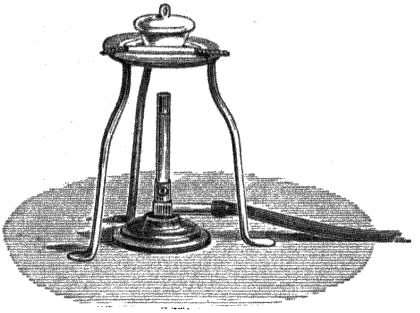
FIG. 58.



IGNITION OVER THE WALLACE-ARGAND BURNER.

upon a triangle which rests upon the chimney of a Wallace-Argand burner, the gauze top of which has been removed. When the gas, issuing from the ring at the bottom of the burner, is kindled and is checked sufficiently by the tap, a current of heated air plays against the sides of the crucible; the crucible thus becomes uniformly heated without being soiled by contact with the flame. Any temperature up to a red-heat may be imparted to the crucible or capsule in this way.

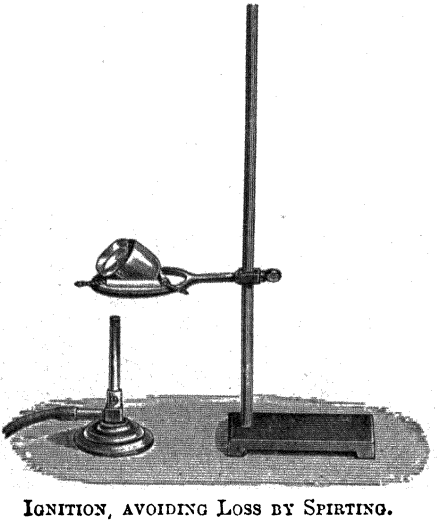
FIG. 59.



IGNITION IN PORCELAIN CRUCIBLE.

96. The Ordinary Method of Ignition by means of a Bunsen Burner is shown in Figs. 59, 60. The crucible rests upon a pipe-clay triangle on the ring of a tripod-stand or of a retort-stand. A retort-stand (Fig. 60) is generally to be preferred as a support, since it enables the height of the crucible

FIG. 60.



IGNITION, AVOIDING LOSS BY SPIRTING.

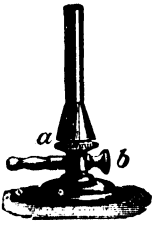
above the flame to be suitably adjusted, so as to expose the crucible to the desired temperature.

97. When Loss of Liquid by Spirting might occur, the Substance is Heated from Above.—The crucible containing the substance is inclined as is shown in Fig. 60. A small flame is placed under the upper edge of the crucible, and the substance is heated partly by heat radiated from the lid, and partly by the conduction of heat down the side of the crucible. The ignition of the substance is finished by placing the flame immediately below the bottom of the crucible.

98. Ignition at Higher Temperatures is secured by using the foot blowpipe in which air is blown from foot-bellows into a gas-flame. But for most purposes the Fletcher Safety Bunsen or the Méker burner will amply suffice. These burners are specially designed to yield a "solid" flame of high temperature, which is more than sufficient to melt copper.

Another form of high-temperature burner is the Teclu burner (Fig. 61), in which the air-supply enters the conical portion of the burner and is regulated by rotating the disc (*a*), while the screw (*b*) regulates the supply of gas. When a high temperature is required, the full supply of gas is turned on, and the disc is then rotated until a roaring flame is produced.

Fig. 61.



Teclu Burner.

Ignition of the Precipitate and Incineration of the Filter in One Process.

99. This method is employed when the combustion of the filter-paper can exert no reducing action upon the precipitate. It is carried out as is described below.

The filter and precipitate are first thoroughly dried in the steam-oven. The filter-paper, still containing the precipitate, is then folded together; and the free edge of the paper is turned down, so as to inclose the precipitate in as small a space as possible. The filter is now placed in the crucible, which is nearly covered with the lid, a small space only being left for the escape of the gases which are formed by the combustion of the filter-paper.

The heat must be applied with moderation at first. But as soon as the flame due to the burning of the combustible gases is no longer seen, the lid may be removed, and the heat may be increased until the required temperature is attained. After the filter-paper has been converted into ash, and

the black carbon from the paper has been completely burnt, the source of heat is removed. As soon as the crucible has cooled below redness, it is removed by means of a pair of *clean* crucible-tongs to the desiccator. The crucible lid is then ignited, if necessary, until it is clean, and is placed upon the crucible. The crucible is weighed with its contents as soon as it is cold. It will usually require about twenty minutes for cooling.

If the Filter-paper is Difficult to Incinerate, and black particles of carbon persistently remain, the combustion may be hastened by bringing the portions of unburnt filter-paper against the hottest portion of the crucible This may be effected by a stout platinum wire, which has been fused into a piece of glass tubing to serve as a handle A small blowpipe flame may be used to produce a higher temperature, and thus aid in effecting the complete incineration of the paper Another plan for hastening the combustion of the carbon is to introduce a gentle stream of oxygen into the crucible Or the cold ash may be moistened with a drop of saturated ammonium nitrate solution, and then be carefully dried and again ignited.

100. Ignition of the Undried Precipitate—Some precipitates, such as those of aluminium and chromium hydroxides, may be ignited without having been previously dried in the steam-oven, after they have been washed and drained by means of the filter pump In this case the lid must cover the crucible until all the moisture and gases have been expelled by means of a small flame placed at some distance below the crucible, and the heating must then be gradually increased The method of heating described in paragraph 97 also answers well for this purpose.

EXPERIMENT 19.—Carefully wrap up the precipitate of $Al(HO)_3$, which has been already dried (85), and place it in a platinum or porcelain crucible, which has been recently ignited and weighed Nearly cover the crucible with the lid. Ignite the crucible, placed in an upright position (Fig 59, p 58), very slowly at first Then gradually increase the temperature until the crucible becomes red-hot. Maintain this temperature for ten minutes, and finally heat the crucible to bright redness for five minutes (98)

Remove the flame, then transfer the crucible to the desiccator by means of the crucible-tongs, and weigh it as soon as it is cold Heat the crucible once more, cool it in the desiccator, and weigh it again Repeat this process, if necessary, until the weight does not become reduced by more than a milligram by the last ignition.

From the original weight of the salt used (75, Exp 15), and the weight of the precipitate (Al_2O_3) obtained after ignition, the percentage of aluminium in potassium alum may now be calculated.

An Example of the method of entering the results of the weighings and of making the calculations is shown below:

Estimation of Al in $AlK(SO_4)_2.12H_2O$:

First weight of bottle + alum	19 8635
Second weight of ditto	18 3980
Weight of alum used . .	1 4655

Weight of precipitate (Al_2O_3) + crucible + filter-ash .	16·7403
Weight of crucible alone	16·5809
	0·1594
Weight of filter-ash	0·0022
Weight of Al_2O_3	0·1572

The weight of aluminium in this Al_2O_3 is found by the following proportion:

As the molecular weight Al_2O_3: the molecular weight Al_2: : weight of Al_2O_3 found: weight of Al.

Or, as 102·16 : 54·16 : : 0·1572 : : 0·08334

And the percentage of aluminium in the salt is found by the proportion:

As the weight of substance taken : the weight of Al found : : 100 : the percentage weight of Al.

Or, as 1·4655 : 0·08334 : : 100 : 5·69

The two proportion statements may be combined into one compound proportion statement as follows:

102·16 : 54·16 : : 0·1572 : weight of Al

1·4655 : weight of Al : 100 : : percentage of Al

Hence the percentage of $Al = \frac{54{\cdot}16 \times 0{\cdot}1572 \times 100}{102{\cdot}16 \times 1{\cdot}4655} = 5{\cdot}69$

Now the percentage of Al in potash alum is found by the proportion:

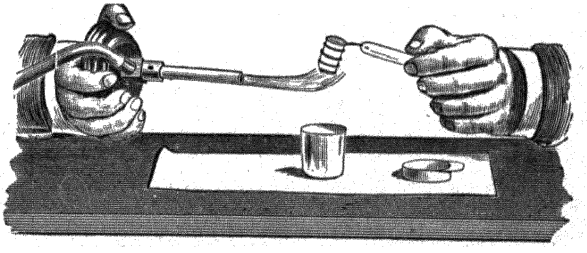
Molecular weight of alum.		Atomic weight of Al.		
474·41	:	27·08	: :	100 : 5·59

Hence the percentage error = 5·69 − 5·59 = + 0·10.

Ignition of the Precipitate, and Separate Incineration of the Filter.

This process is employed when the combustion of the filter-paper might exert a reducing action upon the precipitate, and in other cases in which it is desirable to keep the precipitate apart from the ash. Three methods of carrying out this process are described in paragraphs **101**, **104**, **105**.

Fig. 62.



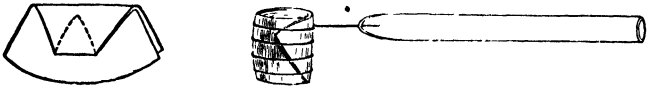
Incineration of the Filter.

101. First Method.—The Filter is Burnt in a Platinum-wire Coil, and the Ash and the Precipitate are Ignited together in the Crucible. The dry precipitate and filter are taken from the funnel, and the precipitate is carefully shaken out of the filter into the crucible or capsule.

The crucible should meanwhile be placed on a piece of glazed paper (Fig. 62), which serves to catch any particles of precipitate which may fall outside the crucible. For dark precipitates white paper may be used, but for light-coloured precipitates dark paper is preferable. Any particles of the precipitate which remain adhering to the filter-paper should be detached as far as possible, by gently rubbing the sides of the filter-paper together, and transferred to the crucible.

The filter-paper is now folded up as is shown in Fig. 63, and is finally rolled up as is shown in Fig. 64. It is then bound by a piece of platinum wire,

Fig. 63. Fig 64



Preparing Filter for Incineration.

which is coiled round it in a spiral form. Some fairly stout platinum wire about six inches in length, one end of which has been fused into a piece of glass tubing to serve as a handle, will be found suitable.

The filter-paper is then kindled by a Bunsen flame, and is kept glowing by occasionally introducing it into the flame, until the carbon is burnt away. A slight tap of the wire on the edge of the crucible will cause the ash to fall into the crucible. If the wire has been coiled into a *conical* spiral, the folded filter may be dropped into it, and the ash may be readily turned out after the ignition by simply inverting the spiral.

Any particles of the precipitate or of the filter-ash which may have fallen upon the sheet of paper are then carefully transferred to the crucible by means of a *small* camel's-hair brush, and the crucible and its contents are ignited, allowed to cool in the desiccator, and weighed.

102. If the Precipitate contains a Metal, which may be Reduced by the Filter during its Incineration and may then alloy with the platinum wire, great care must be taken to fold the filter so as to inclose the adherent precipitate in the *middle* of the paper coil. Or the wire may be dispensed with, and one of the methods of incineration which are described in paragraphs **104**, **105** may be employed.

103. If the Substance can be Altered in Composition by Contact with the Burning Filter, it is usually necessary to treat the filter-ash with a suitable liquid, in order to restore that part of the substance, which has been ignited on the paper, to its original composition. In this case the ash is allowed to fall upon a

separate part of the bottom of the crucible or capsule: the ash can then be treated apart from the main part of the precipitate. Alternative methods are described in paragraphs 104 and 105.

104. Second Method.—The Filter-paper is Incinerated on the Crucible lid, and the Precipitate is Ignited in the Crucible, and both are ultimately weighed together.

The precipitate is shaken out into the crucible, and the last traces of the substance are detached from the paper as completely as possible.

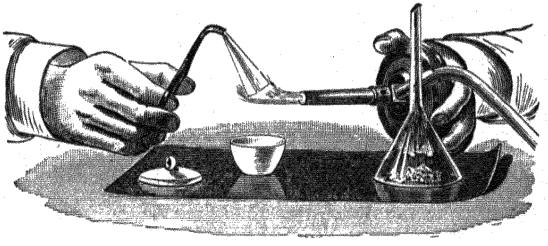
The filter-paper is then cut up into strips by a clean pair of scissors, and these strips are incinerated one by one upon the inverted lid of the crucible, which is supported on a pipe-clay triangle. The crucible and its lid are then ignited together.

The filter-paper may be incinerated in a separate crucible instead of on the lid.

105. Third Method.—The Filter is Burnt in the Crucible, and the Precipitate is then Added and Ignited. This method gives satisfactory results with careful manipulation, but it will be seen that a greater risk of loss of precipitate is incurred than by the preceding methods. The procedure is as follows:

The precipitate is carefully transferred to a watch-glass or to a piece of glazed paper, and is covered with an inverted funnel (Fig. 65).

FIG. 65.



INCINERATION OF THE FILTER.

The filter-paper is then folded up and is incinerated by heating it in the crucible. Or the filter may be held over the crucible by clean crucible-tongs in the Bunsen flame, until most of the carbon is burnt off; the residue is allowed to drop into the crucible, and the incineration is finished in the crucible over the Bunsen flame.

The precipitate is then placed in the crucible, a *small* camel's-hair brush or smooth spatula being used to sweep off the last particles from the glazed

surface. Finally, the crucible and its contents are ignited at the required temperature.

EXPERIMENT 20.—The precipitate of $BaSO_4$, which has been obtained from alum, and has been washed and dried (Exp. 18, 85), is ignited according to the first method (101)

The precipitate is detached as completely as possible from the filter-paper, and is shaken into a platinum crucible standing upon black glazed paper

The filter-paper, which still retains some of the precipitate, is carefully folded and bound round by a platinum wire It is then held over the crucible, and is kindled by a Bunsen flame applied to it in the manner shown in Fig. 62. When the paper has been burnt to a white ash, this ash is shaken into the crucible by gently tapping the wire against the edge of the crucible

Since the burning of the filter paper may have reduced the adherent $BaSO_4$ to BaS, it is necessary to ensure the reconversion of this BaS into $BaSO_4$ in the following way: The ash is moistened with one or two drops of dilute HCl and with one drop of dilute H_2SO_4 The lid is then placed on the crucible, and the crucible is heated *very* gently over the Bunsen flame As soon as all the liquid has been evaporated, the crucible is gradually raised to a dull red-heat, and is kept at that temperature for about fifteen minutes The crucible is then allowed to cool in the desiccator and is weighed It is again heated for ten minutes at the same temperature, and is weighed again as soon as it is cold These operations are repeated as long as the contents of the crucible alter in weight

From the weight finally obtained, the weight of the $BaSO_4$ can be found: and from this the percentage weight of SO_4 in the alum can be calculated.

An Example which serves to illustrate the methods of entry and of calculation is given below:

Estimation of SO_4 in $AlK(SO_4)_2\,12H_2O$:

First weight of bottle + salt	15 8723
Second weight of ditto	14 7954
Weight of salt used . . .	1 0769
Weight of crucible + $BaSO_4$ + ash . . .	17 6415
Weight of crucible alone	16 5806
	1 0609
Weight of filter-ash . .	0 0022
Weight of $BaSO_4$	1 0587

The weight of SO_4 in the $BaSO_4$ is then found by the following proportion:

$BaSO_4$	SO_4	$BaSO_4$ found
233 06 .	96 06 : :	1 0587 : 0 4363 gram SO_4.

And the percentage weight of SO_4 in the potassium alum is then calculated from the weight of the alum used, by the following statement:

1 0769 : 0 4363 : : 100 : 40 52 SO_4 per cent (found).

Now the percentage weight of SO_4 actually present in alum is calculated from the above formula for alum by the following statement:

Alum	$2SO_4$
474 41 :	192 12 : : 100 : 40 50 SO_4 per cent (by theory).

Hence the percentage error = 40 52 − 40 50 = + 0 02.

Preparation of Pure Substances.

The use of pure substances for practice in the analytical processes of quantitative analysis is generally indispensable. Some general methods of purifying substances are described in the following paragraphs. Pure chemicals can now, however, usually be obtained by purchase.

106. The Process of Crystallisation is applied to the preparation of pure substances and of double salts

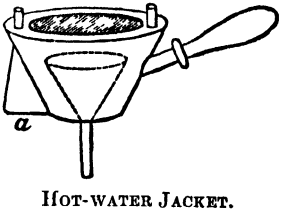
The purity of a soluble and crystallisable chemical compound can usually be ensured by dissolving it in a suitable medium and repeatedly crystallising it, since by this treatment the impurities which were present in the original substance are left behind in the mother-liquor. Many commercial salts may be purified by crystallising them once or twice from their solution in water (**107**).

Double salts can usually be made by dissolving their component salts in suitable proportions in as little hot water as possible, and crystallising the mixed solutions. It should be noted, however, that in the preparation of a double salt, it is frequently necessary to mix the component salts in proportions different from those in which they are present in the double salt (**108**).

107. In the Crystallisation of Salts or of Simple Bodies, the following is the usual mode of procedure.

A beaker, or flask, or a porcelain dish is used for the solution of the solid A hot and nearly saturated solution of the solid in water, or in some other suitable liquid, is made by stirring the coarsely crushed solid with the hot liquid until the solid no longer dissolves. The hot clear solution is then decanted from the excess of solid into a crystallising dish.

Fig. 66.



Hot-water Jacket.

Many salts form insoluble basic salts when they are dissolved in water, and these cause the solution to become cloudy. This may be avoided by previously mixing with the water a few drops of the acid corresponding to the acid-radicle which is present in the salt.

If any suspended matter is present, the solution must be passed through a filter in a funnel which is surrounded by a hot-water jacket.

The apparatus which is used for this purpose is shown in Fig 66. It consists of a double-walled copper vessel in the shape of a truncated cone. In communication with the interspace of this is a hollow projection (*a*). The apparatus is

half-filled with water, and the water is heated to boiling by placing a Bunsen flame beneath the projection (*a*). In this way hot water is caused to circulate throughout the copper jacket, and the funnel is kept hot during the filtration

The clear hot solution is now received in a thin glass vessel which is surrounded with cold water, and the solution is constantly stirred while it is cooling, so as to promote the formation of small crystals. As soon as the crystals have ceased to form, the supernatant liquid is poured off, and the crystals are placed upon a porous plate to drain. After the crystals have drained for several hours, they are broken up, and are finally dried by pressing them between folds of filter-paper. They are then preserved in a well-stoppered bottle.

Larger crystals may be obtained by allowing the solution to cool slowly, but they are liable to contain inclosed mother-liquor and to be less pure than small crystals.

EXPERIMENT 21.—Weigh out roughly 120 grams of potassium alum, $AlK(SO_4)_2\,12H_2O$, and dissolve it in 100 c.c. of boiling distilled water. Filter the solution, if necessary; cause it to crystallise by cooling, then dry the crystals as is described above, and place them in a clean, dry, stoppered bottle.

EXPERIMENT 22.—Weigh out roughly 100 grams of copper sulphate crystals, $CuSO_4\,5H_2O$; dissolve the salt in 100 c.c. of boiling distilled water, crystallise, dry the crystals, and place them in a bottle for subsequent use.

Some of the following substances may also be crystallised for practice. They will be of use in estimations, which are described hereafter:

KCl; $AmCl$; $MgSO_4\,7H_2O$, $BaCl_2\,2H_2O$; $ZnSO_4\,7H_2O$, $Pb(C_2H_3O_2)_2\,3H_2O$; $K_2Cr_2O_7$; and $H_2C_2O_4\,2H_2O$.

108. In the Formation and Crystallisation of Double Salts, the mode of procedure varies with the properties of the substances to be used.

(a) The usual method of preparing a double salt consists in weighing the simple salts in the proportions in which they are contained in the double salt. A hot strong solution is then made of each salt separately; these two solutions are mixed together, and the liquid thus obtained is crystallised (**107**).

(b) This method, however, cannot always be employed, since a solution of the component salts, prepared as is directed above, will occasionally furnish not only crystals of the double salt, but also of one of the component salts. This difficulty is obviated in the following preparation by using an excess of $MgSO_4.7H_2O$:

EXPERIMENT 23.—**Preparation of $MgSO_4\,K_2SO_4\,6H_2O$.** Weigh out 87 grams of pure K_2SO_4 and 160 grams of pure $MgSO_4\,7H_2O$. It will be noticed that the weight of the $MgSO_4\,7H_2O$ is in excess of the molecular proportion for the reason already stated. Dissolve these portions separately in boiling distilled water; mix the solutions, crystallise, and dry the crystals of the double salt.

(c) In the preparation of double salts, it must also be remembered that certain salts, when they are treated with hot water, are converted partially into insoluble basic salts. Hence boiling water must not be employed in dissolving them. The following preparation will serve as an example :

EXPERIMENT 24.—**Preparation of $Fe(NH_4)_2(SO_4)_2\,6H_2O$.** Weigh out 62 grams of pure Am_2SO_4, and 140 grams of pure recrystallised $FeSO_4\,7H_2O$. It will be noticed that these weights are in molecular proportion. Dissolve each of these salts separately in the smallest possible quantity of distilled water, at a temperature not exceeding 40° C ; then mix the two solutions, add a few drops of dilute sulphuric acid to clear the solution, cool, crystallise, and dry the crystals (107).

(d) Some double salts are most readily and completely separated from solution by pouring the solution into a liquid in which the salt is insoluble. Thus the solution of ferrous ammonium sulphate (Exp. 24) may be poured into alcohol, when the double salt at once separates in a granular condition. The yield of the salt which is furnished by this method is also larger than that obtained by crystallisation.

The following Double Salts may be Prepared, using the molecular proportions of the component salts denoted by the formulæ of the double salts. The weighed salts are dissolved in the least possible quantity of boiling water, and are treated as has been described above

$AlK(SO_4)_2.12H_2O$; $Cu(NH_4)_2(SO_4)_2\,6H_2O$; $CuCl_2\,2AmCl.2H_2O$.

OTHER WAYS OF PREPARING PURE SUBSTANCES.

109. By Precipitation (75) and subsequent Washing (76) and Drying (84) many chemicals may be prepared in a pure state.

EXPERIMENT 25.—**Preparation of Pure $CaCO_3$.** Dissolve 100 grams of pure calcium chloride in 250 c c of distilled water. Heat the solution to boiling, filter if necessary, and then add a strong solution of pure Am_2CO_3 as long as any precipitate is caused. Allow the precipitate to subside, and wash it by decantation. Then transfer the precipitate to a filter and wash it with hot water until the washing-water no longer gives any turbidity with $AgNO_3$, showing that all the dissolved chloride has been washed away.

Since this precipitate is voluminous, it is advisable to use the filter-pump (79) in order to hasten the process of filtration. A still better plan is to place a 7 cm. perforated porcelain disc in a large-sized funnel, cover this with a filter-paper 7·5 cm. in diameter, and then use the filter-pump. By continuing the suction the precipitate may also be almost freed from water by the passage of air.

Finally, dry the precipitate in the steam-oven, detach it from the filter-paper, and place it in a bottle for further use.

Pure $BaCO_3$ and $SrCO_3$ may be prepared in a similar way.

EXPERIMENT 26 —**Preparation of Pure NaCl** Dissolve 100 grams of NaCl in 400 c c of distilled water Precipitate the NaCl by passing into this solution a current of HCl gas, which has been washed by bubbling through a little water in a bottle (*Note*) The delivery-tube should have an inverted funnel attached to it, by means of a piece of india-rubber tubing, the mouth of the funnel dipping just beneath the surface of the sodium chloride solution This precaution is necessary in order to prevent the salt solution from ascending the delivery-tube

The passage of the gas into the solution will cause the NaCl to be precipitated in small crystals As soon as the precipitation ceases, the NaCl is thrown upon a funnel containing a perforated disc, as described above in Experiment 25, and is washed twice by decantation with pure strong HCl The salt is then placed upon a porous tile or plate to drain, and is finally freed from HCl and from water by heating it in a porcelain dish over a small Bunsen flame

This pure dry NaCl is preserved for use in a stoppered bottle

Note —The NaCl may be precipitated from its saturated solution by the addition of strong hydrochloric acid solution instead of by passing the gas

EXPERIMENT 27 — **Preparation of Pure Anhydrous Tartar Emetic** [$K(SbO)C_4H_4O_6$]. Dissolve 100 grams of tartar emetic in the smallest possible quantity of water Add to this solution about twice its volume of methylated spirit Wash the salt thus precipitated with methylated spirit, and dry it at once in the steam-oven.

110. Sublimation is occasionally used for the purpose of separating volatile from non-volatile substances, and thus effecting their purification. If a volatile substance is to be purified, sublimation may be effected by placing the substance in a porcelain crucible, and inverting over it a similar vessel. The lower crucible is then gently heated; the substance will volatilise and the vapour will condense in the upper crucible. This crucible must be replaced if it becomes hot.

Another method consists in heating the substance in a porcelain dish, and condensing the vapour by means of an inverted funnel placed as a cover to the dish.

Unless the substance which is to be sublimed is known to be perfectly dry, it is best to allow the first portion of its vapour to escape and carry off the moisture with it.

EXPERIMENT 28 —**Purification of Iodine** Partly fill a porcelain crucible with a finely powdered and intimate mixture of three parts of iodine with one part of potassium iodide. Cover this with a second crucible, and heat the mixture gently Remove the sublimed crystals from the upper crucible, and store them in a clean dry bottle.

The mixture of potassium iodide with the iodine, followed by sublimation, serves to remove chlorine and bromine from the iodine · $Cl + KI = KCl + I$.

EXPERIMENT 29 —**Resublimation of Arsenious Oxide.** Introduce into a small porcelain dish a thin layer of As_4O_6. Invert over this a clean glass funnel, and heat the dish gently Detach the sublimate from the funnel, and keep it in a bottle for future use.

General Rules for Working.

III. Many rules and precautions have already been given among the preceding general directions for carrying out analytical processes. In the following statement these directions are summarised, and others are added which will be of great assistance to the student.

1. Before commencing work, see that the requisite reagent bottles are filled, and filter those liquid reagents which are not clear. Keep the bench surface scrupulously clean and dry during work.

2. All the apparatus which is required for use should be perfectly clean.

Glass and porcelain vessels may usually be cleansed by washing them with the brush. Or the surface may be rubbed with moistened sea-sand or pumice-powder, or water containing sea-sand or powdered pumice may be shaken in the vessel.

Grease is generally removed by the application of a hot solution of caustic alkali. Strong acid serves to remove many other substances.

Metal crucibles and dishes are cleansed and polished by rubbing them with moist whiting, sea-sand or crushed pumice.

The stains on a platinum crucible may usually be removed by fusing a little $KHSO_4$ inside the vessel, or by dipping the crucible into the fused salt if the stains are on the outside.

3. Before commencing the quantitative analysis of a substance of unknown composition, a careful qualitative analysis should invariably be made.

4. Before starting any analytical process, which is unknown by previous experience, read carefully through *the whole* of the description which is given and master the details of the description.

5. Never place a substance directly on the scale-pan of the balance, but put it on a watch-glass or other suitable support.

6. No body which gives off corrosive gas or vapour should be weighed on a delicate balance, unless it is contained in an accurately stoppered vessel.

7. When a weighing is finished, note down the weight at once in the Note-book and check it. Take care that the weight is entered correctly, as one wrong weighing will spoil an analysis. Do not use slips of paper for this purpose, as they may be lost.

8. Never leave weights on the scale-pan after a weighing has been finished and recorded and always close the balance-case as soon as a weighing is completed

9. After a body has been heated, it should be allowed to cool in the desiccator before it is weighed, and it should be weighed as soon as it is cold. A

substance should not be allowed to remain very long in the desiccator before weighing it.

Crucibles should be heated shortly before they are used, then allowed to cool in the desiccator and weighed. These processes should be repeated each time a crucible is used.

10. Platinum vessels and other metallic vessels, which have been heated to redness, should be allowed to cool below redness before they are touched with brass crucible-tongs.

11. All splashing while filtering and pouring off liquids must be avoided. With this object a liquid may be poured from one vessel to another by pressing a wetted glass rod against the edge of the upper vessel, and thus conducting the liquid to the inside surface of the lower one or to the surface of the liquid it may contain. The outer edge of the upper vessel should be greased where the liquid is poured, in order to prevent the liquid from running down the outside of the vessel.

12. Vessels of porcelain, nickel, or platinum should be used in preference to glass vessels for holding alkaline liquids. Nickel and silver basins and crucibles should not be used with acid liquids. Platinum should not be used in the presence of aqua regia, of nitric acid and a chloride, of hydrochloric acid and a nitrate, or of fused caustic alkalis.

13. Platinum vessels should not be used for heating reducible compounds of As, Sb, Zn, Pb, Sn nor should they be used for alkalis, or for alkaline nitrates or cyanides, or for reducible or fusible phosphates. Free carbon and silicon are also very injurious to platinum at high temperatures, and a platinum vessel is rendered brittle by being heated for any length of time in a gas-flame which deposits carbon.

14. Capsules and crucibles of fused silica may be used for heating non-alkaline substances.

15. Vessels which require to be heated to high temperatures should be supported on platinum, pipe-clay or fire-clay supports. Porcelain and other dishes, when they are heated on a water-bath and are to be subsequently weighed, should be supported on glass rings. Fused silica supports are applicable in all these cases.

16. A flame which is used for heating crucibles should be free from luminosity and strong colour. If the flame is luminous it will deposit soot on the vessels with which it is in contact. If it is coloured, it will probably deposit zinc or copper, or their oxides, upon the vessel upon which it plays.

17. If an operation is unfinished when work ceases, the vessels containing the substances should be labelled before they are put away. *Never trust to memory in these matters.*

Entry of Results and Calculation.

112. Entry in the Note-book.—A Note-book of not less than quarto size will be found convenient for the entry of the results obtained during quantitative analysis. The description and general results of the analytical process may be entered on the right-hand page, the left-hand page being reserved for the necessary calculations.

Each stage of the analysis should be carefully and accurately entered in the Note-book as soon as it is completed.

The rough entry in the laboratory may conveniently be made in pencil. Pencil writing is not obliterated by the chemical action of acids or of alkalis, as is the case with writing made by various kinds of ink.

When quantitative analysis is carried out under a teacher's direction, the student may advantageously copy out in ink, in a second Note-book, all the examples worked by him; and no estimation should be considered as completed until its entry has been carefully examined, checked, and initialled by the teacher.

A difference of 0·2 per cent. from the theoretical quantity, or from the result of a duplicate analysis, is usually the maximum error which is allowed in the case of simple quantitative estimations.

113. Example of Entry and Calculation in the Note-book.—The following will serve as an example of the method of full descriptive entry recommended for the student's Note-book:

Estimation of the Percentage amount of Water in $CuSO_4.5H_2O$.—1 8645 grams of the coarsely powdered recrystallised salt were carefully weighed in the watch-glasses and clip. The air-oven was next regulated so as to maintain a uniform temperature of 210° C. The clip and the upper watch-glass were removed and the lower watch-glass containing the salt was placed upon a pipe-clay triangle in the air-oven.

The salt was heated in the oven for two hours. The glass containing the copper sulphate was then taken out, the upper glass and clip were quickly replaced, and the glasses were allowed to cool in the desiccator, and were weighed. The uncovered salt was again placed in the air-oven and was heated for half an hour; it was then allowed to cool and was weighed again. These processes were repeated until no further loss of weight occurred.

Weight of glasses and salt		24 7840
Weight of glass alone		22·9195
Weight of salt taken		1 8645
Weight of glasses and salt		24 7840
„ after 2 hours' drying	24 1125	24 1115
„ after another half-hour	24 1115	
Weight of water driven off		0 6725

Hence 1 8645 grams of the salt contain 0 6725 gram of water:

$$\text{Therefore the percentage weight of water} = \frac{0\ 6725 \times 100}{1\ 8645} = 36{\cdot}06.$$

The calculated percentage of water . .	= 36 13
The percentage found . .	= 36 06
Hence the error	= − 0 07

114. Calculation of the Results of Analysis.—Several examples have been given of the method of calculating the percentage weight of a substance present from the weight actually obtained. These calculations may be shortened by the use of factors and logarithms.

115. The Use of Factors.—The process of calculation may be shortened by multiplying the result, obtained by the analysis, by a factor. A table of such factors will be found in paragraph **981**. The following example, applied to the calculation on page 61, will illustrate the use of a factor:

In this estimation, 0 1572 gram of Al_2O_3 was found. The factor to be used to convert Al_2O_3 into Al_2 = $\frac{Al_2}{Al_2O_3} = \frac{54\ 2}{102\ 2} = 0{\cdot}53015$. Hence the weight of Al found = 0 1572 × 0 53015 = 0 08334.

The Use of Logarithms.—The logarithms used should consist of at least five figures. Logarithms corresponding to the factors mentioned above will be found in paragraph **981**, and a table of logarithms is given in paragraphs **1001** and **1002**.

116. Decimal Measures (**996**) are used in this book, but since capacities are often elsewhere stated in ounces of water, and lengths in inches, the roughly equivalent values are given below.

4 oz = 120 c c	10 oz = 300 c c.
6 oz = 200 c c	18 oz = 500 c c
8 oz = 250 c c.	and so on.

¼ inch	= 0 6 cm	3 inches	= 7 5 cm.
⅜ ,,	= 1 ,,	3½ ,,	= 9 ,,
½ ,,	= 1 3 ,,	4 ,,	= 10 ,,
1 ,,	= 2 5 ,,	4½ ,,	= 11 5 ,,
1½ ,,	= 4 ,,	6 ,,	= 15 ,,
2 ,,	= 5 ,,	and so on	

PART II.

SIMPLE GRAVIMETRIC ESTIMATIONS.

SECTION IV.

125. Introductory Remarks.—In the following descriptions of the processes for estimating various substances, the most important and typical processes are printed in ordinary type. Those which are of less importance are printed in smaller type, and are placed, as far as is possible, after the typical estimation which they most nearly resemble. The estimations of metals and acid-radicles are generally arranged as exercises of increasing difficulty, rather than in the order of their analytical groups.

In most of the exercises the substances upon which the processes of estimation are carried out are of known and definite composition. The accuracy of the student's result can therefore be checked in each case by calculating the percentage of the constituent from the formula of the substance. When the body is of unknown composition, two estimations should be made. It is usual to consider the percentage result which is obtained sufficiently accurate if it does not differ by more than 0·2 from the duplicate result or from the calculated theoretical result. The ordinary methods of stating results and of calculation will be found in the examples on pages 64 and 71.

It will be noticed that the substances which are usually given for practice are soluble in water. If a substance in which an estimation has to be made is insoluble in water, the student should ascertain, by experiments made upon a small portion of the finely powdered body, what is the most suitable means of obtaining it in the dissolved state. The acids may be tried as solvents in the following order: hydrochloric acid, nitric acid, and then a mixture of these two acids.

If treatment with these solvents does not effect solution, the substance may generally be decomposed by treating it with about six times its weight of a fused mixture of sodium and potassium carbonates. The fused mass, after cooling, is then fully extracted with water, and the well-washed insoluble residue is dissolved by treatment with acid.

The process of treatment of an insoluble substance will probably be familiar to the student from his qualitative work. The special precautions which should be observed when this process is used in quantitative analysis will be understood by reference to paragraphs **134**, **136** and **211**.

Estimation of Copper in its Soluble Compounds.

126. The Copper is precipitated as Hydroxide by solution of Potassium or Sodium Hydroxide; the precipitate is ignited, and is weighed as CuO (See *Note*, page 75).

Weigh out accurately about 0·5 gram of crystallised copper sulphate, $CuSO_4\,5H_2O$ (Exp. 22, **107**), into a 500 c.c. beaker (**116**), or, better, into a porcelain or platinum dish (**111**, 12). Dissolve the salt in about 100 c.c. of distilled water, and add a few drops of dilute HCl if the liquid is not clear.

Cover the beaker or dish with a clock-glass to prevent loss by spirting, and heat the solution to boiling. As soon as the solution boils remove the flame, take off the clock-glass, and add boiling potassium hydroxide solution gradually until it is present in excess. Then boil the liquid again, and allow the precipitate to subside.

In order to ascertain whether KHO is present in excess, stir well, then allow the precipitate to subside, and observe whether the supernatant liquid has become colourless, also test the clear liquid with turmeric-paper. If the liquid is colourless, and gives a brown stain on the paper, the presence of excess of the alkali is indicated. The addition of a large excess of the alkali should be avoided

The clear liquid is now decanted through a paper or asbestos (**82**) filter, the filtration being hastened by the filter-pump (**79**). The precipitate is twice washed by decantation by boiling it with water (**76**); it is then transferred to the filter by means of a glass rod and a wash-bottle with a fine jet. The precipitate which adheres to the beaker is removed by rubbing it with a short piece of tightly fitting rubber tube pushed upon the end of the glass rod. The washing is continued until a few drops of washing-water from the funnel no longer give a white precipitate when they are warmed with $BaCl_2$ solution and allowed to stand for five minutes.

As soon as the precipitate has been completely washed, the precipitate and filter are dried in the funnel or in the Gooch crucible in the steam-oven (**59**).

The precipitate is then detached from the paper filter as completely as possible (**101–105**), and is placed in a crucible, preferably of platinum. The filter is folded up with the soiled surface in the middle, and is bound round with a spiral of platinum wire. It is then burnt in the Bunsen flame until

all the carbon is consumed. The crucible is now tapped upon the bench so as to cause the precipitate to collect on one side, and the filter-ash is dropped by itself upon the other side of the bottom of the crucible.

The filter-ash is then moistened with two drops of strong HNO_3, and is gently heated until the excess of the acid has been driven off. The crucible and its contents are heated to redness for fifteen minutes, and are weighed after they have cooled in the desiccator.

The ignition is repeated for another five minutes, and the cold crucible is again weighed these operations being repeated until the weight is constant.

The dried precipitate is directly ignited, as is directed above, if the Gooch crucible has been used.

The weight of CuO thus obtained from the known weight of the salt enables the percentage of copper in the crystallised salt to be calculated.

Note —Copper cannot be completely precipitated by alkaline hydrate from solutions which contain a large quantity of alkaline nitrate or of ammonium salts

The presence of certain non-volatile organic substances also prevents the precipitation from being complete · these substances should therefore be removed before the copper is precipitated by potassium hydroxide This may be effected by adding sodium carbonate and potassium nitrate to the solution, then evaporating it to dryness, and fusing the residue The copper is dissolved out of the residue by heating it with dilute hydrochloric acid, and the filtered solution is treated as is directed below.

Copper may, however, be completely precipitated from its solutions in the form of sulphide, even in the presence of organic substances or of an alkaline nitrate (474)

Other methods for estimating copper will be found in paragraphs **405-408**, and **474**.

Estimation of Nickel in its Soluble Compounds.

127. The Nickel is precipitated as Nickelic Hydroxide; this is converted into Oxide, NiO, by ignition, and is weighed as such (*Note* 1, page 76).

Weigh out accurately about 0·5 gram of pure nickel ammonium sulphate, $Ni(NH_4)_2(SO_4)_2.6H_2O$ (**108**), into a 500 c.c. beaker (**116**), or, better, into a porcelain or platinum dish (**111**, 12). Dissolve the salt in about 100 c.c. of water, heat the liquid nearly to boiling, and add a slight excess of solution of pure potassium hydrate which has been permanently coloured by the addition of excess of bromine-water.

Now heat the liquid for some time nearly to boiling, allow the precipitate to settle, and wash it with hot water three or four times by decantation.

Finally transfer the precipitate to a filter, and continue to wash it until the washings cease to give a precipitate with barium chloride solution.

Then dry the precipitate in the steam-oven, and ignite it in a platinum crucible apart from the filter (**104, 105**), heating the crucible at first in the Bunsen flame, and finishing by heating it more strongly (**98**). The flame must not be allowed to enter the crucible during the heating process, since the hot gases of the flame might reduce the oxide of nickel to metallic nickel, and thus cause the resulting weight to be too low.

Note 1.—If non-volatile organic substances are present in the solution, these must be removed before precipitating the nickel (**126**, *Note*)

An Electrolytic Method for determining Ni is given in paragraph **219**.

ESTIMATION OF COBALT IN SOLUTION.

128. The Cobalt is precipitated as an indefinite mixture of Hydroxides: which is dried, ignited in a current of Hydrogen, and weighed as Metallic Cobalt.

Weigh out accurately about 0·5 gram of crystallised cobalt sulphate, $CoSO_4.7H_2O$. The salt must be freshly prepared as it is efflorescent. Dissolve the salt in about 100 c.c. of water in a porcelain or platinum dish, and heat the solution nearly to boiling.

Add to the boiling liquid a slight excess of pure potassium hydrate solution which has been permanently coloured by the addition of Br-water in excess: black cobaltic hydroxide will be precipitated. Wash the precipitate with boiling water three times by decantation; then transfer it to a filter, and wash it on the filter until the washing-water is free from alkali. Dry the precipitate in the steam-oven, and ignite it together with the filter (**99**) in a porcelain crucible.

The residue will consist of an indefinite mixture of CoO and Co_3O_4 together with traces of alkali and silica. Wash this with hot water until the washing-water is free from alkali, then dry and ignite it again. Now place either an inverted clay tobacco-pipe, or a Rose's lid and tube, upon the crucible (Figs. 54, 55, page 56), and continue the ignition while a gentle current of pure dry hydrogen is passed through the pipe or tube (*Note*)

The contents of the crucible are heated to dull redness in the stream of hydrogen for about fifteen minutes, and the metal is then allowed to cool in the stream of gas.

The ignition in hydrogen must be repeated until the weight becomes constant.

From the weight of metallic cobalt finally obtained, the percentage of cobalt in the compound may be calculated.

Note.—The hydrogen is generated by the action of pure dilute sulphuric acid upon granulated zinc (**1012**), or is supplied from a cylinder of the compressed gas (**1013**). It must be completely dried by being passed through strong sulphuric acid.

Estimation of Iron in its Soluble Compounds.

129. The Iron is precipitated as Ferric Hydroxide; this is ignited, and weighed as Ferric Oxide, Fe_2O_3. (*Note* 1)

Weigh accurately about 0·5 gram of ferrous ammonium sulphate, $Fe(NH_4)_2(SO_4)_2\,6H_2O$ (**108** c), into a 500 c.c. beaker (**116**), or, better, into a porcelain or platinum dish (**111**, 12). Dissolve this in about 100 c.c. of distilled water, containing a little dilute sulphuric acid.

Convert the ferrous into ferric salt by heating the solution and then adding gradually sufficient strong nitric acid or bromine-water (*Note* 2). This change is known to be nearly complete when the addition of the last drop of strong nitric acid produces no brown colour in the solution, or when the colour of the bromine is retained by the liquid for about ten minutes. The change to ferric salt should be proved to be complete, by adding a small drop of the dilute solution to a drop of freshly prepared potassium ferricyanide solution on white porcelain, when no blue colour must appear.

To the hot solution of the ferric salt add a little AmCl solution and then AmOH solution in excess, and boil. Wash the precipitate twice by decantation; then transfer it to the filter, using the filter-pump to hasten the filtration. Continue the washing with the wash-bottle until the washing-water gives no precipitate with $BaCl_2$ solution.

Dry the precipitate in the steam-oven, and then transfer it to a crucible. Incinerate the filter apart (**101–105**) and add it to the precipitate. Finally, ignite the precipitate at a bright red heat over the Bunsen flame until its weight is constant.

From the weight of the Fe_2O_3 thus obtained, the percentage of iron may be calculated.

Note 1.—If non-volatile organic substances are present, these must be removed before precipitating the iron (**126**, *Note*).

If the iron is present either as the ferrous or ferric salt of a volatile acid, including sulphate, it can be readily converted into Fe_2O_3 by evaporation with sulphuric acid, and subsequent ignition to bright redness over the Bunsen-flame as long as it continues to lose weight.

Note 2.—Solutions of ferric salts will not require the above preliminary treatment with nitric acid, or bromine-water, but may be precipitated at once with AmOH solution.

Volumetric Methods for Estimating Iron will be found in paragraphs 308–314, 322 and 323.

Estimation of Aluminium in its Solutions.

130. The Aluminium is precipitated by Ammonium Hydrate solution, as Aluminium Hydroxide; this is converted into Oxide, Al_2O_3, by ignition, and is weighed as such (*Notes* 1, 2).

Weigh out accurately about 0·6 gram of pure recrystallised potassium alum, $AlK(SO_4)_2.12H_2O$ (Exp. 21, 107), into a 500 c.c. beaker (116), or, better, into a porcelain or platinum dish (111, 12). Dissolve the salt in about 100 c.c. of water, add ammonium chloride solution in moderate quantity (*Note* 3), and then ammonium hydrate solution in slight excess. Cover the dish with a clock-glass, and heat the liquid to boiling. Continue the boiling until the liquid smells only faintly of ammonia.

Wash the precipitate by decantation, and transfer it to a filter, using the filter-pump to facilitate filtration. Continue the washing of the precipitate upon the filter until the washing-water is free from sulphate; dry the filter and precipitate in the steam-oven, unless they have been already considerably dried by use of the filter-pump, and ignite the precipitate together with the filter in a crucible (Exp. 19, page 60). Heat the crucible gently at first, and finally expose it to a white heat over the blowpipe-flame. Repeat the ignition until the weight becomes constant.

From the weight of Al_2O_3 thus obtained, the percentage of aluminium may be calculated.

Note 1.—If the student has already estimated aluminium (Exp. 19, page 60) the process need not be repeated here

Note 2 —If non-volatile organic substances are present, these must be removed before the Al is precipitated (126, *Note*)

If aluminium is present only in the form of chloride, nitrate or sulphate, it may be directly converted into Al_2O_3 by evaporation with sulphuric acid and subsequent ignition over the blowpipe until the residue ceases to lose weight.

Note 3 —Aluminium hydroxide may exist in solution in the colloidal state It is precipitated from this solution in the gelatinous form by the addition of ammonium chloride.

Estimation of Chromium in Solutions of Chromic Salts.

131. The Chromium is precipitated by Ammonium Hydrate as Hydroxide; this is converted into Oxide, Cr_2O_3, by ignition, and is weighed as such (*Note*).

Weigh out accurately about 0·6 gram of pure recrystallised chrome-alum, $CrK(SO_4)_2\,12H_2O$, into a porcelain or platinum dish. Dissolve the substance in about 100 c.c. of water, add a little Am'Cl solution and then a slight excess of ammonium hydrate solution. Then heat the contents of the dish to a temperature

just below the boiling-point, and continue the heating until the supernatant liquid becomes perfectly colourless.

Then filter, wash, dry, and ignite the precipitate in the same manner as was described in the estimation of aluminium (130)

From the weight of the Cr_2O_3 thus obtained, the percentage of chromium is calculated.

Note —If non-volatile organic substances are present, they must be removed before precipitating the chromium (126, *Note*).

Estimation of Chromium in a Soluble Chromate.

132. The Chromate is reduced to a Chromic Salt by Sulphurous Acid, or by some other suitable Reducing Agent: the Chromium is then precipitated as Hydroxide and is estimated as Cr_2O_3 (131).

Weigh out accurately about 0·5 gram of pure potassium dichromate, $K_2Cr_2O_7$, and dissolve it in about 100 c.c. of water Add a strong aqueous solution of sulphur dioxide, or pass sulphur dioxide gas through the liquid, until the red colour of the solution changes to pure bluish green

Estimate the chromium in this solution in the same manner as has been described above (131)

A Volumetric Process for estimating Chromate will be found in paragraph 354.

Estimation of SO_4 in a Soluble Sulphate.

133. The SO_4 is precipitated as $BaSO_4$, and is weighed in this Form (*Notes* 1, 2, page 80).

Weigh out about 0·5 gram of pure recrystallised $CuSO_4.5H_2O$ (Exp. 22, 107) into a 500 c.c. beaker. Dissolve this in about 100 c.c. of distilled water containing a little dilute HCl, and heat the solution to boiling (*Note* 3, page 80).

To the boiling $CuSO_4$ solution add excess of boiling $BaCl_2$ solution drop by drop, and keep the liquid just boiling for about fifteen minutes. Then allow the white precipitate to subside. Pour off the supernatant liquid through a filter, taking care not to disturb the precipitate. Wash the precipitate twice by decantation. Finally, transfer it to the filter, and continue the washing until the last few drops of the washing-water give no turbidity with $AgNO_3$ solution.

Dry the filter with the precipitate, and ignite the precipitate apart from the filter (101–105), preferably in a platinum crucible (*Note* 4, page 80).

Before igniting the precipitate detach it as completely as possible from the

filter. Then ignite the precipitate and the filter-ash together for about fifteen minutes at a dull red heat, allow the crucible to cool, and weigh it. These operations must be repeated until the weight is constant.

Any $BaSO_4$ which is left adhering to the filter-paper will be reduced to BaS during the incineration of the filter. If BaS is thus produced in any appreciable quantity it will cause the weight of the precipitate to be too low. The BaS in the filter-ash should therefore be converted into $BaSO_4$ by the following procedure.

The filter-ash, which has been dropped into a separate part of the crucible, is moistened with two drops of dilute HCl, and a drop of dilute H_2SO_4 is added The contents of the crucible are then very gently heated until the liquid has been evaporated, great care being taken to avoid loss by spirting. The crucible and its contents are finally strongly ignited, and are weighed after they have been allowed to cool.

From the weight of $BaSO_4$ thus obtained, the percentage of SO_4 may be calculated.

Note 1 —This estimation need not be repeated here, if it has been already carried out (Exp 20, 105)

Note 2 —The presence of nitric or chloric acid causes the $BaSO_4$ to be mingled with a precipitant of barium nitrate or chlorate Since these salts cannot be removed from the $BaSO_4$ by washing, the nitric or chloric acid must be removed by evaporation with HCl before the sulphate is precipitated by $BaCl_2$

Certain metallic salts also show a tendency to be precipitated with the $BaSO_4$. Ferric and copper salts may give trouble in this way and are best removed by suitable precipitants before the addition of the $BaCl_2$ solution. Potassium salts and other substances are removed from the $BaSO_4$ precipitate by the method described in *Note* 4 below

Note 3 —It is well to add about 20 c c. of strong ammonium chloride solution; the precipitate of $BaSO_4$ will then be granular, and will therefore subside rapidly and be readily filtered.

Note 4 —When very accurate results are required, the precipitate should be purified in the following way from co-precipitated substances Moisten the precipitate in the crucible with a few drops of water, then add a little very dilute hydrochloric acid, warm gently and decant off the liquid through a small filter. Repeat this operation several times, dry the crucible, incinerate the filter, adding the filter-ash to the precipitate, ignite and weigh again.

Estimation of SO_4 in an Insoluble Sulphate.

134. If the Sulphate is Insoluble in Water and in Acids it must be decomposed by fusion with alkaline carbonates The following example will illustrate this process:

Weigh out accurately about 0 5 gram of pure finely powdered $BaSO_4$ into a platinum crucible, and add to it about 6 grams of finely powdered fusion mixture

($Na_2CO_3 + K_2CO_3$). Mix the substances in the crucible by stirring them with a thin glass rod rounded at its end. Then heat the covered crucible over a small Bunsen flame, the size of which is gradually increased until the alkaline carbonates begin to fuse. Now change the position of the crucible lid until a slight opening is formed, through which the progress of the fusion can be watched, and so adjust the flame that the alkaline carbonates remain in a fused condition for at least ten minutes. Complete the process by heating the crucible over the blowpipe flame.

Now cool the crucible rapidly by placing it upon a mass of iron. Then lay it upon its side in a porcelain dish or beaker, and allow it to stand in cold distilled water until the solid mass can be readily detached from its interior by a glass rod. This process may be hastened by heating the water.

Remove the crucible from the water by a clean pair of tongs, and carefully rinse it out into the solution with the wash-bottle Crush any solid particles which remain, filter the liquid, and wash the undissolved $BaCO_3$ upon the filter with boiling water, until the washing-water gives no alkaline reaction. Mix the filtrate with the washings, and acidify the liquid with dilute HCl, guarding against loss by effervescence (66)

Then precipitate the sulphate as $BaSO_4$ from the acidified solution, as is directed in paragraph 133.

ESTIMATION OF BARIUM IN ITS SOLUBLE AND INSOLUBLE COMPOUNDS.

135. The Barium is precipitated from solution as Barium Sulphate, and is weighed as such (133, *Note* 1).

Weigh out accurately about 0·5 gram of pure recrystallised barium chloride ($BaCl_2 2H_2O$) into a 500 c c beaker (116), and dissolve it in 100 c c of water, to which some dilute hydrochloric acid has been added.

Heat the solution to boiling, and add a slight excess of boiling dilute sulphuric acid Wash the precipitate by decantation; filter, wash and dry the precipitate, and ignite it as was described under the estimation of sulphate (133).

From the weight of the $BaSO_4$ thus obtained, calculate the percentage of barium.

136. Barium Compounds, which are Insoluble in Acid, are first subjected to fusion with alkaline carbonates (134). The barium carbonate residue, which is left upon the filter, after the fused mass has been treated with water, is well washed and transferred to a beaker This may be effected by pushing a hole through the filter with a thin glass rod, and then rinsing both rod and filter with the stream from the wash-bottle.

Hot dilute HCl is then poured through the filter into the beaker, in order to dissolve the $BaCO_3$ still adhering to the filter as well as that in the beaker. The filter is then washed well, the washings being allowed to flow into the beaker The solution is finally precipitated and the weight of the $BaSO_4$ is determined as is directed above (135)

The weight of Ba is then calculated from the weight of $BaSO_4$.

ESTIMATION OF STRONTIUM IN ITS SOLUBLE AND INSOLUBLE COMPOUNDS.

137 The Strontium is precipitated from solution as Strontium Sulphate, and is estimated as such.

Weigh out accurately about 0·5 gram of pure precipitated strontium carbonate, $SrCO_3$ (109, Exp. 25), into a covered 500 c.c. beaker (116). Dissolve the carbonate in a little dilute HCl, and add about 50 c.c. of distilled water. Add dilute sulphuric acid in excess to this solution. Then add a quantity of methylated spirit, about equal in volume to the liquid in the beaker, in order to render the precipitation complete. Allow the liquid to stand until the precipitate has subsided; then filter and wash the precipitate with methylated spirit until the washings give no precipitate with $BaCl_2$ solution. Dry the precipitate in the steam-oven, and ignite the precipitate as was described under the ignition of $BaSO_4$ (133).

From the weight of $SrSO_4$ thus obtained, the percentage of strontium may be calculated.

138. Strontium Compounds, which are Insoluble in Acids, are fused with alkaline carbonates (134). The residue, which is insoluble in water, is dissolved in HCl (136), and the Sr is precipitated as is directed above (137).

ESTIMATION OF SULPHUR IN SULPHIDES.

139. The Sulphide is converted by a Suitable Oxidising Agent into Sulphate, and the Sulphate is precipitated and estimated as Barium Sulphate, $BaSO_4$. From the weight of $BaSO_4$ obtained, the weight of sulphur, which was originally present as sulphide, is calculated.

The choice of the oxidising agent to be employed will depend upon the nature of the sulphide which is to be oxidised. Three methods are described below.

The first method (140) is specially applicable to soluble sulphides.

The other two methods (141, 142) are used for insoluble sulphides.

140. Oxidation by Bromine.—The solution of sulphide may be oxidised by adding bromine-water free from sulphuric acid (*Note*), and then gently warming the liquid.

The solution is at first coloured by the bromine, but the colour disappears as the oxidation proceeds. In order that the oxidation may be known to be complete the bromine-water must be added until the warm liquid retains its colour for about ten minutes. The liquid is then boiled until the bromine has been expelled, and the sulphate produced by the oxidation is precipitated by $BaCl_2$ solution, as is directed in paragraph 133.

Note.—Bromine is freed from sulphuric acid by careful redistillation, and is then shaken with water until the water is saturated. This bromine-water must

be proved to be free from sulphuric acid by giving no precipitate on the addition of $BaCl_2$ solution.

141. Oxidation by Sodium Peroxide.—Weigh accurately about 0·5 gram of very finely powdered zinc-blende, free from lead, into a platinum crucible (*Note*). Mix it intimately in the crucible with about 4 grams of the sodium peroxide in very fine powder, and heat the covered crucible by supporting it about two inches above a small Bunsen flame.

The mass will glow throughout, and will then settle down in the fused condition. Allow the mass to remain fused for three minutes; and extract it, when it is cool, with water (**134**), taking due precaution against loss of liquid which might arise from the effervescence caused by the evolution of oxygen. Neutralise the greater part of the NaOH, if the liquid is strongly alkaline, with HCl; filter the liquid if necessary, acidify the clear solution with hydrochloric acid, and precipitate the sulphate by barium chloride solution (**133**).

Note.—Since sodium peroxide attacks platinum somewhat seriously, it is well to use a silver or nickel crucible. Some samples of the peroxide contain metallic sodium, which alloys with platinum and spoils the crucible. A small quantity of the peroxide should therefore be heated in the flame on platinum foil before it is heated in the crucible. If the foil is affected, the peroxide must not be heated in a platinum crucible.

It should be remembered that the peroxide must not be brought into contact with combustible substances or with water, since it produces a violent reaction with these substances.

142. Oxidation by Nitric Acid.—Weigh out accurately about 0·5 gram of very finely powdered zinc-blende, free from lead, into a 300 c.c. flask. Introduce into the neck of the flask a small funnel to prevent loss by spirting during solution (Fig. 34, p. 36), and pour upon the powder some strong nitric acid. When the powerful action of the acid has somewhat abated, heat the flask in the water-bath until the sulphur, which may separate at first, has dissolved.

The solution of the sulphur is more rapidly effected by allowing the acid to cool, then adding about one cubic centimetre of bromine, free from sulphuric acid, and warming.

Then carefully transfer the liquid to a porcelain dish, add a little sodium chloride to convert the free sulphuric acid into non-volatile sodium sulphate, and evaporate the liquid to a small volume over the water-bath.

Remove the nitric acid by repeatedly evaporating the solution to dryness with strong hydrochloric acid, and as soon as the nitric acid has been expelled, dilute the liquid with much water, precipitate the sulphur, present as sulphate, with $BaCl_2$ solution, and weigh the $BaSo_4$ thus formed (**133**).

Since the composition of zinc-blende is variable, and the mineral seldom consists

of pure ZnS, the theoretical percentage of sulphur required by the formula ZnS is rarely found. The accuracy of the analysis must therefore be checked by making a duplicate determination of the sulphur.

A Volumetric Method for estimating H_2S will be found in paragraphs 339–341; another method, depending on the evolution of H_2S is described under Iron and Steel analysis (534).

Estimation of SO_3 in a Sulphite.

143. The Sulphite is converted into Sulphate by the addition of Bromine-water, and is estimated as Barium Sulphate, $BaSO_4$.

Weigh out accurately about 0·5 gram of crystallised sodium sulphite, $Na_2SO_3.7H_2O$, into a 500 c.c. beaker. Dissolve it in about 100 c.c. of water, containing a little dilute HCl. Then add bromine-water free from sulphuric acid (140, *Note*), until the liquid remains distinctly yellow in colour. Now nearly cover the beaker with a clock-glass and boil the liquid until the bromine is expelled.

To the colourless liquid add $BaCl_2$ solution in excess, and determine the weight of the $BaSO_4$ precipitate in the manner already described in paragraph 133.

From the weight of $BaSO_4$ thus obtained, the percentage of SO_3 present in the sulphite may be calculated.

A Volumetric Process for estimating sulphite is given in paragraphs 342–344.

Estimation of S_2O_3 in a Thiosulphate.

144. The Thiosulphate is converted into Sulphate by Bromine-water, and is estimated as Barium Sulphate, $BaSO_4$.

For practice in this process about 0·5 gram of recrystallised sodium thiosulphate, $Na_2S_2O_3.5H_2O$, is accurately weighed and is dissolved in water. Bromine-water, free from sulphuric acid (140, *Note*), is then added until the solution remains yellow in colour, and the liquid is heated until the sulphur, which separates, is redissolved. The excess of bromine is then removed by boiling the liquid, and the sulphate is estimated as is described in paragraph 133.

From the weight of $BaSO_4$ obtained, the percentage of S_2O_3 is calculated.

A Volumetric Process for estimating thiosulphate is given in paragraph 345.

Estimation of Calcium in its Soluble Compounds.

The Calcium is precipitated from the solution of the calcium salt as Calcium Oxalate, which is converted either into Carbonate or into Oxide, and is weighed as such.

145. Weigh out accurately into a 500 c.c. beaker about 0·5 gram of precipitated calcium carbonate (109, Exp. 25), or of Iceland-spar. Pour in some

water, and add dilute hydrochloric acid gradually in quantity sufficient to dissolve the carbonate, guarding against loss of liquid by effervescence (65) Dilute this solution with water until its volume is about 100 c.c.

Heat the liquid nearly to boiling. Then add a slight excess of ammonium hydrate solution, and finally add a boiling solution of ammonium oxalate in moderate excess. Allow the liquid to stand until the precipitate has subsided

Note.—The precipitate of CaC_2O_4 usually settles very slowly, and passes at first through the filter To obviate these inconveniences the method of precipitation may be altered as follows

Make the liquid alkaline, and heat it to boiling. Then take away the flame and add gradually about 1 gram of pure finely powdered ammonium oxalate, while stirring continuously, and again heat the liquid to boiling. When the flame is taken away, the precipitate will subside in a few minutes.

As soon as the precipitate has completely subsided, pour off the liquid through a filter, taking care not to disturb the precipitate. Wash the precipitate in the beaker two or three times with hot water by decantation. Finally, transfer the precipitate to the filter by means of a glass rod tipped with rubber tubing, and a wash-bottle with a fine jet. Wash the precipitate on the filter, until the last few drops of the washing-water no longer render silver nitrate solution turbid. Then dry the filter and precipitate in the steam-oven.

146. The Precipitate of Calcium Oxalate is now converted into Carbonate. With this object it is transferred, as completely as possible, to a platinum crucible. The filter-paper is burnt in a platinum-wire spiral (**101**), and the ash is allowed to drop into the crucible. The crucible is then covered with the lid and is heated very gently ; it is finally heated for about twenty minutes to a temperature sufficient to cause the bottom of the crucible to appear faintly red when it is shaded from direct light. The crucible is weighed, after it has been allowed to cool in the desiccator.

Note —The burner represented in Figs 57, 58 (p 57) will be found specially suitable for the above purpose, since by its means a moderate and uniform temperature is easily obtained. The platinum capsule shown in these figures may also advantageously replace the crucible.

After the crucible has been weighed, its contents should be moistened with strong ammonium carbonate solution. It is then dried in the steam-oven, heated again to faint redness for a few minutes, allowed to cool, and once more weighed. These operations must be repeated until the weight no longer increases by the treatment. The object of the above procedure is to ensure the conversion into carbonate of any calcium oxide, which may have been formed by heating the precipitate too strongly.

From the weight of $CaCO_3$ thus found, the filter-ash is subtracted, and the percentage of calcium may then be calculated.

147 **Conversion of the Calcium Carbonate into Oxide** —If the weight of the calcium carbonate, obtained by igniting the oxalate, does not exceed one gram, the result of the above estimation may be controlled by weighing the calcium also as oxide. Indeed, if the original precipitate is small in amount, the oxalate may with advantage be converted directly into oxide, and be weighed as oxide instead of as carbonate

In order to convert the calcium carbonate into oxide, the crucible and its contents are heated to bright redness (98) for fifteen minutes; they are then allowed to cool, and are weighed The crucible is once more heated for five minutes in the same way, and is weighed again after it has cooled. These operations must be repeated as long as they cause the crucible and its contents to lose in weight. The weight of substance finally left in the crucible is that of the calcium oxide and the filter-ash.

From the weight of CaO thus found, the percentage of calcium may be calculated

A Volumetric Method for estimating Calcium is given in paragraphs 326-328.

Estimation of C_2O_4 in a Soluble Oxalate.

148. **The Oxalate is precipitated as Calcium Oxalate, either in neutral solution or in a solution rendered acid by acetic acid The Calcium Oxalate is then ignited and is weighed either as Carbonate or as Oxide.**

Weigh out accurately about 0·5 gram of pure crystallised ammonium oxalate, $(NH_4)_2C_2O_4\ H_2O$, and dissolve it in about 100 c c of water. Heat the solution to boiling, and precipitate the oxalate by adding a solution of calcium acetate in slight excess Filter off the precipitated calcium oxalate and convert it into carbonate or oxide by ignition, as has been described in the estimation of calcium (146, 147).

From the weight of $CaCO_3$ or of CaO thus obtained, the percentage of C_2O_4 is calculated.

A Volumetric Method for estimating oxalate is given in paragraph 325.

Estimation of Chlorine in a Soluble Chloride.

149. **The Chlorine is precipitated as Silver Chloride, AgCl, and is weighed as such** (*Note* 1).

Weigh out accurately about 0·3 gram of pure sodium chloride (109, Exp. 26), and dissolve this in about 100 c.c. of *cold* water in a 500 c.c. beaker.

Add to the *cold solution* a little dilute nitric acid, and then *excess* of silver nitrate solution. Shield the precipitate from daylight as much as possible during the whole of the estimation, since AgCl darkens in the light and suffers slight decomposition and loss of weight during this change. Heat the liquid in the beaker for some time, taking care not to let it boil; this will cause the small particles of AgCl to unite together into flocks.

Wash the precipitate in the beaker by decantation three times with hot water containing a little nitric acid; then transfer it to a filter (*Note* 2), and continue the washing with water acidified with HNO_3, and finally with hot water only. The washing may be considered to be finished, when the addition of a drop of hydrochloric acid to the last few drops of the washing-water produces only a very faint turbidity (*Note* 3)

Dry the precipitate in the steam-oven. Then ignite it apart from the filter-paper in a *porcelain* crucible, following one of the three methods (**150–152**) which are described below.

From the weight of silver chloride obtained, the percentage of chlorine is calculated.

Note 1 —If a heavy metal is present in the solution, a basic chloride may be formed Any heavy metal should therefore be removed by precipitation with AmOH, KOH or Na_2CO_3 solution before the estimation is commenced.

Note 2 —If a Gooch crucible (**82**) is used the washing is much more rapidly effected. The crucible and contents are dried first at 100° C. and finally at 130° C. until the weight is constant.

Note 3 —The filtrates and washings from the above estimation contain silver, and should be preserved in the silver-residue bottle together with the precipitate (**153**).

150. First Method.—The precipitate is detached from the filter-paper as completely as possible, and is placed in a porcelain crucible. The filter is folded and rolled up, carefully keeping the small portion of adherent precipitate in the *centre* of the roll and out of contact with the wire (**101, 102**). The paper is then supported by a coil of platinum wire, and is incinerated in the usual manner.

During the incineration of the filter, metallic silver is always formed. This will alloy with the platinum if it comes into contact with the red-hot wire, causing a loss in the weight of the AgCl found. This explains the necessity of keeping the precipitate from contact with the wire during incineration (*Note*).

The filter-ash is added to the precipitate in the crucible, and the metallic silver in the ash is converted into chloride by moistening the ash with two drops of strong nitric acid, and then adding two drops of hydrochloric acid. The excess of acid is finally removed by evaporating cautiously to dryness.

The crucible is then gently heated over a small Bunsen flame, until the silver chloride begins to fuse at its edges. It is allowed to cool in the desiccator, and is weighed. The ignition should be repeated until the weight of the silver chloride becomes constant.

Note.—The possibility of loss of Ag from this source is reduced in proportion to the care with which the AgCl is removed from the paper. The loss is entirely avoided by employing either of the methods described in paragraphs **104, 151.**

151. **Second Method.**—The method described in paragraph 105 is well suited for the ignition of this precipitate, since silver chloride can be readily transferred without loss from the filter to the crucible.

The dry precipitate is turned out upon a piece of glazed paper, and is covered with a funnel. The filter is then folded, and its upper edges, which are free from silver chloride, are held in the flame by means of the crucible tongs, and the ash thus produced is allowed to drop into the crucible. Or the filter may be cut into strips, which are separately burnt in the crucible. The removal of any unburnt carbon from the ash is completed by heating the crucible. The ash is now treated with nitric acid and then with hydrochloric acid as is directed above (150), and is dried by evaporation. The precipitate is finally transferred to the crucible and is ignited with the ash.

152. **A Third Method** of igniting the precipitate and burning the filter is described under the estimation of bromide, which follows in paragraph 154.

153. **Removal of AgCl from the Crucible.**—After the determination has been finished, the silver chloride may be detached from the crucible as follows: Place on the silver chloride a few pieces of granulated zinc, and pour in sufficient dilute sulphuric acid to cover the zinc and the chloride completely. The silver chloride will be gradually reduced to metallic silver, which is easily detached from the crucible and poured off with the liquid into the silver residue bottle.

Two Volumetric Methods for estimating chloride are given in paragraphs 373, 376.

Estimation of Bromine in a Soluble Bromide.

154. **The Bromine is precipitated as Silver Bromide, AgBr, and is weighed as such.**

Weigh out accurately about 0·3 gram of pure sodium bromide, NaBr, and proceed to estimate the bromine which it contains by a method similar to that described for estimating chlorine in a chloride (149).

According to this method, solution of hydrobromic acid is required for the conversion of silver in the filter-ash into silver bromide. Hydrobromic acid solution is rarely kept in the laboratory, and the necessity for using it may be avoided by adopting the following special process of weighing the filter-ash.

Transfer the precipitate from the filter to a porcelain crucible as completely as possible, and ignite it in the same manner as has been already described for the silver chloride precipitate (150). Allow the crucible to cool, and weigh it.

Incinerate the filter in a coil of platinum wire, allow the ash to fall into the weighed porcelain crucible containing the precipitate, and then weigh the crucible again. The increase of weight of the crucible after the ash has been added, less the weight of the filter-ash, will give the weight of metallic silver which has been formed from the AgBr which remained adhering to the filter-paper.

Almost the whole of the precipitate is thus weighed as AgBr. The weight of the AgBr which remained in the filter-paper is calculated from the weight of silver

found in the filter-ash. This weight is added to the weight of AgBr already obtained, and thus the total weight of the original silver bromide is found.

From this weight the percentage of bromine is calculated.

A Volumetric Process is described in paragraph 373.

Estimation of Iodine in a Soluble Iodide.

155 The Iodine is precipitated as Silver Iodide, AgI, and is weighed as such.

Weigh out accurately about half a gram of pure potassium iodide, KI. Proceed to estimate the iodine which it contains, in a similar way to that already described for the determination of chlorine in a chloride (149).

The silver iodide, which remains adhering to the filter, is not reduced to metallic silver during the incineration of the filter, as is the case with the chloride and the bromide: the special treatment of the filter-ash is therefore unnecessary.

Silver iodide, however, undergoes appreciable loss by volatilisation when it is heated to a high temperature Care must therefore be taken to detach the precipitate as completely as possible from the filter, so as not to expose any appreciable quantity of silver iodide to the high temperature produced by the incineration of the filter. The silver iodide in the crucible must also, for the same reason, be heated only to a dull red heat.

From the weight of AgI obtained, the percentage of iodine is calculated.

A Volumetric Process which serves for estimating iodide is given in paragraph 373.

Estimation of ClO_3 in a Soluble Chlorate.

156. The Chlorate is converted by a suitable Reducing Agent into Chloride and is estimated as Silver Chloride (149).

Weigh out accurately about 0 3 gram of pure recrystallised potassium chlorate, $KClO_3$, into a 500 c c. beaker. Dissolve the salt in about 100 c c of water, and add 50 c c of a 10 per cent solution of ferrous sulphate crystals Heat the liquid with constant stirring until it begins to boil, and maintain the boiling for fifteen minutes. Then allow the liquid to cool and add nitric acid until the precipitated basic ferric salt is dissolved.

Precipitate the chloride, which has been produced by the deoxidation of the chlorate, with silver nitrate, and collect and weigh the AgCl as has been described in paragraph 149.

From the weight of AgCl thus obtained, the percentage of ClO_3 is calculated.

A Volumetric Method for estimating chlorate is given in paragraph 355.

Estimation of Cyanogen in a Soluble Cyanide.

157. The Cyanogen is precipitated as Silver Cyanide, AgCN, and is weighed as such; or the AgCN is ignited, and the Ag is weighed.

Weigh out accurately about 0·5 gram of potassium cyanide, KCN, and dissolve it in about 100 c.c. of water in a 500 c.c. beaker. Add excess of silver nitrate solution, and then acidify the liquid with dilute nitric acid. Allow the precipitate to settle in the cold, and treat it in one of the following ways (a, b).

(a) Wash the precipitate in a Gooch crucible (82) or on a tared filter (86), and dry it at 100° C. in the air-oven until the weight is constant. From the weight of AgCN thus obtained, the percentage of cyanogen may be calculated.

(b) Wash the precipitate on an untared filter; dry it in the steam-oven, ignite the filter in a porcelain crucible, and then add the precipitate (105). Heat the crucible again over the Bunsen flame and weigh it, and repeat the ignition until the weight becomes constant. From the weight of metallic silver which remains after the complete expulsion of the cyanogen, the percentage of cyanogen present in the original cyanide can be calculated.

Note.—Commercial potassium cyanide is not pure, and varies in composition; hence it will not yield the theoretical percentage weight of cyanogen corresponding to the formula KCN. In order to check the accuracy of the result obtained, it is necessary either to use chemically pure potassium cyanide or to make a duplicate determination of cyanogen in the commercial salt.

A Volumetric Method for estimating cyanide is given in paragraph 374.

Estimation of Silver in its Soluble Compounds.

158. The Silver is precipitated as Chloride, and is weighed as such.

Weigh out accurately about 0·3 gram of pure recrystallised silver nitrate, $AgNO_3$, and dissolve it in about 100 c.c. of cold distilled water; then add a small quantity of dilute nitric acid.

To this solution add dilute hydrochloric acid, with constant stirring, and in slight excess. The addition of another drop of HCl must not cause any further precipitate in the clear liquid from which the precipitate has subsided.

Boil the liquid containing the precipitate for a short time; then decant the liquid, and wash the precipitate three times by decantation with boiling water containing a little HNO_3. Transfer the precipitate to the filter, and complete the washing with water acidified with HNO_3, and finally with hot water only.

As soon as the washing-water is shown to be free from chloride, by remaining clear when it is tested with $AgNO_3$ solution, dry the filter containing the precipitate in the steam-oven. Then ignite the precipitate in a porcelain

crucible, apart from the filter, in the manner described under the estimation of chloride (150–152).

From the weight of silver chloride thus obtained, the percentage of silver can be calculated.

Volumetric Methods for estimating silver are given in paragraphs 371, 372, 375.

Estimation of Lead in its Soluble Compounds.

159. The Lead may either be precipitated as Carbonate, which is converted by ignition into Oxide, and is weighed as such (160); or the Lead may be precipitated as Sulphate, and be weighed as such (161).

160. Estimation of Lead by precipitation as Carbonate, and conversion into Oxide, PbO.—Weigh out accurately about 0·5 gram of crystallised lead acetate, $Pb(C_2H_3O_2)_2.3H_2O$, and dissolve it in about 100 c.c. of distilled water containing a little acetic acid. Add ammonium carbonate solution, containing a small quantity of AmOH, in *slight* excess, and warm. Addition of the ammoniacal salt in large excess must be avoided, since this would redissolve some of the precipitate which is formed.

Wash the precipitate until it is free from alkali, and dry it in the steam-oven. Detach the dry precipitate from the filter-paper as perfectly as possible, and ignite it in a *porcelain* crucible. Since lead very readily alloys with platinum, the methods described in paragraphs **104**, **105** will be found most suitable for the incineration of the filter.

After the filter has been burnt, moisten the ash with nitric acid, and remove the excess of acid by cautious evaporation. Now heat the precipitate together with the filter-ash to redness in order to expel the carbon dioxide completely from the precipitate, taking care not to fuse the residue of lead oxide.

As soon as the weight becomes constant after repeated ignition, the percentage of lead can be calculated from the weight of PbO found.

161. Estimation of Lead by precipitation as Lead Sulphate, and weighing the Sulphate.—Weigh out the lead acetate and dissolve it in water as is described above (160). Then add dilute sulphuric acid in slight excess, and mix with the liquid twice its volume of methylated spirit. This addition of alcohol is necessary in order to render the precipitation complete. Allow the precipitate to settle, and filter off and wash it on the filter with methylated spirit until the sulphuric acid is removed.

Dry the precipitate in the steam-oven, and ignite it apart from the filter (104, 105). Then reconvert any lead sulphate, which has been reduced during the incineration of the filter, into sulphate, by treating the filter-ash with a few drops of nitric acid and one drop of dilute sulphuric acid. Evaporate the excess of the acids, and finally ignite the dried residue. Then heat the crucible repeatedly to dull redness until the weight of the sulphate becomes constant.

From the weight of $PbSO_4$ thus obtained, the percentage of lead is calculated.

A Volumetric Method for estimating lead is given in paragraph 329.

Estimation of Bismuth in its Soluble Compounds.

162. The Bismuth is precipitated as Carbonate, and is subsequently converted into Oxide by ignition, and is weighed as such.

Add water to the solution of bismuth nitrate (*Note* 1), acidified with nitric acid (*Note* 2), until the volume of the liquid is about 100 c.c. Then add solution of ammonium carbonate in very slight excess, and heat for a short time It is necessary to guard against the presence of a large excess of ammonium carbonate in the liquid, since the bismuth carbonate precipitate is distinctly soluble in this reagent. Filter, wash and dry the precipitate, and ignite it apart from the filter, as is described under the estimation of lead as PbO (160).

From the weight of Bi_2O_3 thus obtained, the weight of bismuth may be calculated.

Note 1.—It should be noted that neither chloride nor sulphate of bismuth must be present in a solution in which bismuth is to be estimated by this method, since these salts are first converted by ammonium carbonate into basic chloride or sulphate, which is not decomposed by the further addition of ammonium carbonate. A solution containing chloride, sulphate, or other salt of bismuth may be precipitated as sulphide; the sulphide is then dissolved by heating it with somewhat dilute nitric acid; this solution is filtered, if necessary, and is then precipitated by ammonium carbonate as is directed above.

Note 2.—In order to obtain a known weight of bismuth nitrate in solution for carrying out the process described below, pure bismuth oxide, Bi_2O_3, is ignited to redness until its weight is constant: about half a gram of the oxide is exactly weighed, and is dissolved in a little dilute nitric acid.

Estimation of Zinc in its Soluble Compounds.

163. The Zinc is precipitated as Carbonate, and is subsequently converted into Oxide by ignition, and is weighed as such.

Weigh out accurately about 0·5 gram of pure recrystallised zinc sulphate, $ZnSO_4.7HO_2$ (**107**, Exp. 22). Dissolve this in a 500 c.c. beaker in about 150 c.c. of water. Heat the solution nearly to boiling, and add sodium carbonate solution in very slight excess. Boil for a short time; then allow the precipitate to settle, and wash it three times by decantation with boiling water; finally filter off the precipitate, and finish the washing on the filter. The washing should be continued until the washing-water shows no alkalinity to test-paper, and gives no precipitate with $BaCl_2$ solution.

Dry the precipitate in the steam-oven, and ignite it apart from the filter (**101**), using a porcelain crucible.

In order to prevent the zinc oxide from being reduced during the incineration of the filter, which would result in the loss of zinc by volatilisation, the following precautions are necessary. The filter-paper must be freed from the precipitate as far as possible, and must then be wetted with strong ammonium nitrate solution and dried. It must then be carefully incinerated at the tip of the flame in a coil of platinum wire, and the ash added to the precipitate in the crucible.

The crucible and its contents are heated to redness over the Bunsen flame until the weight becomes constant, care being taken to guard against the flame entering the interior of the crucible during the ignition. The flame might reduce the zinc oxide, and cause loss of zinc by volatilisation.

From the weight of ZnO thus obtained, the percentage of zinc may be calculated.

Volumetric Methods for estimating zinc are given in paragraphs **378**, **379**.

Estimation of Manganese in its Soluble Compounds.

164. The Manganese is precipitated as Carbonate; this is converted by ignition into Mn_3O_4, and is weighed as such.

Note.—A known weight of manganese in solution is most easily obtained by reducing a weighed quantity of pure potassium permanganate in solution by sulphurous acid.

Weigh out accurately about 0·5 gram of pure recrystallised potassium permanganate, $KMnO_4$, into a large porcelain dish. Pour sulphurous acid solution upon the crystals, or pass sulphur dioxide gas into their aqueous

solution, until the colour of the permanganate disappears. Continue the addition of sulphurous acid, until any oxide of manganese, which forms, is redissolved. Then add sodium carbonate solution in excess.

Wash the precipitate first by decantation and then on the filter, until the washing-water gives no alkaline reaction to test-paper. Then dry the filter and precipitate in the steam-oven.

Mix together the filtrate and washing-water, which always contain a little manganese, and evaporate the liquid to dryness in a platinum or porcelain dish. Then treat the residue in the dish with hot water, filter, wash the insoluble hydrated oxide of manganese with hot water on a separate filter, and dry it in the steam-oven.

Ignite both of the precipitates apart from the filters (101) in the same crucible, and proceed in the following manner to free the manganese oxide from the alkali which it still retains.

Turn out the precipitate and ash into a small porcelain or agate mortar, add hot water, and rub the precipitate with the pestle to ensure thorough mixture of the solid with the water. Filter through a fresh filter, and wash the manganese oxide on the filter with hot water until no sodium coloration is given to the Bunsen flame, when the last drop of the washing-water is evaporated and ignited in a loop of clean platinum wire.

Then dry the precipitate and ignite it apart from the filter (101) at a bright red heat (98), taking care that the flame does not enter the crucible. Repeat the ignition until the weight is constant (*Note*).

From the weight of the Mn_3O_4 thus obtained, the percentage of manganese is calculated.

Note.—The composition of this precipitate will vary with the temperature and the degree of exposure to air during its ignition It may, however, be converted definitely into Mn_3O_4 by dissolving it in sulphuric acid, carefully evaporating the solution of $MnSO_4$ to dryness and then heating the residue to redness over the Bunsen burner

Volumetric Methods for estimating manganese dioxide are given in paragraphs 351-353, and a method for estimating permanganate will be found in paragraphs 318-320.

Estimation of Magnesium in its Soluble Salts.

165. The Magnesium is precipitated as Magnesium Ammonium Phosphate ($MgNH_4PO_4.6H_2O$); this is converted by ignition into Magnesium Pyrophosphate, $Mg_2P_2O_7$, and is weighed as such.

Weigh out accurately about 0·5 gram of pure recrystallised magnesium sulphate, $MgSO_4.7H_2O$ (107), into a 500 c.c. beaker. Dissolve this in about

50 c.c. of cold water, add a little AmCl solution, and then AmOH solution in moderate excess.

The presence of AmHO in excess is necessary, since the phosphate precipitate is slightly soluble in pure water, but is practically insoluble in water containing ammonia. If a precipitate forms when the AmHO solution is added, this precipitate must be redissolved by adding more AmCl solution.

To the clear alkaline liquid add an excess of sodium phosphate solution (*Note* 1), and stir the liquid vigorously. Take care that the stirring-rod does not touch the inside of the beaker, as this would lead to deposition of the precipitate on the glass.

Allow the liquid to stand at rest for twelve hours, and then filter it. This delay is recommended in order to ensure the complete precipitation of the double phosphate. But if the solutions are mixed in a stoppered vessel instead of in a beaker, and the mixture is at once vigorously shaken for five minutes, the precipitation is rendered complete without this lengthened standing, and the precipitate may be filtered off in about half an hour.

The precipitate is washed on the filter with AmHO solution. This is made by diluting one measure of AmHO solution, of 0·880 specific gravity, with three measures of water. The washing must be continued until a few drops of the washing-water, after being acidified with nitric acid, give no opalescence with silver nitrate solution.

The precipitate is now dried in the steam-oven, and is either ignited apart from the filter (**101**), as is directed under (a); or the filter and the precipitate are ignited together (b).

(a) The precipitate is detached as completely as possible from the filter and is transferred to a platinum crucible. The filter is incinerated in a coil of platinum wire, by heating it at first very gently and finally exposing it to a red heat. The filter-ash (*Note* 2) is then dropped into the crucible.

The crucible is now covered with the lid, and is heated for about ten minutes gently by a small flame; it is then heated to redness, and finally to bright redness (**98**). It is now allowed to cool in the desiccator, and is weighed. The ignited precipitate should be perfectly white, and the ignition should be repeated until it ceases to lose in weight.

(b) The precipitate may be wrapped up in the dry filter, and ignited at a red heat in a platinum capsule (**95**). The use of the blowpipe is unnecessary. The process will usually require about twenty minutes.

From the weight of $Mg_2P_2O_7$ thus obtained, the weight of Mg may be calculated.

Note 1.—Some authorities state that the addition of AmOH before the phosphate causes the formation of $Mg_3P_2O_8$ which remains unaltered when it is heated. The following procedure will obviate this: To the boiling solution, which must be

neutral or slightly acid and free from ammonium salts, add sodium ammonium phosphate or microcosmic salt solution, drop by drop, until precipitation is complete. The greater part of the magnesium will now have been precipitated as $MgHPO_4$. Allow the solution to cool and add with constant stirring one-third its volume of ammonia solution of 0·88 specific gravity. The amorphous precipitate will be at once changed into crystalline $MgNH_4PO_4\,6H_2O$, and the magnesium still in solution will be thrown down in the same form.

Note 2.—The ash should contain no particles of carbon. These may remain if the precipitate has been heated too strongly at first, since the precipitate is thus partially fused, and incloses charred particles of the filter which are then burnt only with extreme difficulty.

Estimation of PO_4 in a Phosphate.

166. The PO_4 is precipitated as Magnesium Ammonium Phosphate, $MgNH_4PO_4.6H_2O$; this is converted by ignition into Magnesium Pyrophosphate, $Mg_2P_2O_7$, and is weighed as such.

Weigh out accurately about 0·5 gram of pure recrystallised sodium phosphate, $Na_2HPO_4\,12H_2O$, into a 500 c.c. beaker, and dissolve it in about 100 c.c. of water. Add sufficient ammonium hydrate solution to make the liquid smell slightly of ammonia, then add a slight excess of "magnesia mixture" (**167**). Stir the liquid vigorously with a glass rod without touching the interior of the vessel, and allow the vessel to stand for at least twelve hours to ensure complete precipitation; or shake the liquid vigorously in a stoppered glass cylinder for five minutes, when precipitation will be complete (*Note*). Then treat the precipitate in the manner described under the estimation of magnesium (**165**).

From the weight of $Mg_2P_2O_7$ thus obtained, the percentage of PO_4 may be calculated.

Note.—The precipitation may also be effected as is described in *Note* 1 (**165**), the "magnesia mixture" being added before the ammonia solution.

167. Preparation of "Magnesia Mixture"—Dissolve one part of crystallised magnesium sulphate, or, better, the equivalent weight of magnesium chloride, in eight parts of distilled water. Dissolve in this solution two parts of ammonium chloride, and then add four parts of ammonium hydrate solution of 0·88 specific gravity. Allow this mixture to stand for several days, and then decant the liquid from any solid matter which has settled down. The clear liquid is used for the precipitation of phosphate.

168. Phosphates which are Insoluble in Water should be dissolved in dilute nitric acid. The solution, which must contain very little phosphate, is mixed with a large excess of solution of ammonium molybdate in nitric acid (**520**), and the temperature of the liquid is maintained at about 40° C. for some hours. The precipitate thus obtained is filtered off, and the filtrate is treated as above

with additional molybdate solution. The whole of the precipitate producible by the molybdate is then filtered off and washed with water containing a little nitric acid. It is then dissolved in ammonium hydrate solution, and this solution is precipitated by magnesia mixture as is described above (166).

A Volumetric Method for estimating phosphate is given in paragraph 380.

Estimation of AsO_4 in a Soluble Arsenate.

169. The AsO_4 is precipitated as $Mg(NH_4)AsO_4.6H_2O$; this is converted by ignition into $Mg_2As_2O_7$, and is weighed as such.

Weigh out accurately about 0·5 gram of pure recrystallised sodium arsenate, $Na_2HAsO_4.12H_2O$, into a 500 c.c. beaker. Dissolve the solid in about 100 c.c. of cold water, then add some ammonium hydrate solution and excess of magnesia mixture (167). Stir well and allow the liquid to stand for twenty-four hours, or shake it vigorously for five minutes in a stoppered glass cylinder. Then filter, and wash the precipitate thoroughly with ammonium hydrate solution as was described in the estimation of Mg (165). Finally, dry it in the steam-oven.

Separate the dry precipitate as completely as possible from the filter, and place it on a sheet of glazed paper (105). Then saturate the filter with strong ammonium nitrate solution; dry it, and incinerate it in a porcelain crucible, heating gently at first and gradually raising the temperature to a red heat.

As soon as the filter has been completely incinerated, transfer the precipitate also to the crucible (*Note*). Cover the crucible with a perforated lid carrying a gas-tube, as is shown in figure 54 or 55 (page 56), and heat the precipitate in a slow current of oxygen, which may be supplied from a cylinder of the compressed gas (1013). Gradually raise the temperature to bright redness, and then allow the crucible to cool, and weigh it. Repeat the above process of heating in oxygen until the weight of the crucible and its contents becomes constant.

The above special method of ignition is necessary in order to prevent the occurrence of reduction and the consequent loss of As by volatilisation; it further serves to secure a residue of fixed composition.

From the weight of $Mg_2As_2O_7$ thus obtained, the percentage of AsO_4 may be calculated.

Note.—Instead of heating the precipitate in a current of oxygen, a small crystal of ammonium nitrate may be dropped into the crucible, which is then heated gradually to redness, care being taken that the flame does not enter the crucible.

Estimation of Sodium in Sodium Chloride.

170. The Sodium Chloride is converted into Sodium Sulphate, Na_2SO_4, by treatment with H_2SO_4 followed by evaporation and ignition, and is weighed as such.

This process is applicable to any sodium compound which, after it has been treated with strong H_2SO_4 and the residue left after evaporation has then been ignited, leaves pure Na_2SO_4 as a residue.

Weigh out accurately about 0·5 gram of purified NaCl (**109**, Exp. 26) into a platinum crucible. Moisten this with as small a quantity of water as possible, and add concentrated sulphuric acid drop by drop, quickly replacing the cover of the crucible after each addition of acid. As soon as the whole of the salt has been acted upon, heat the crucible and its contents cautiously over a small Bunsen flame.

The crucible should be supported in an inclined position, and be almost covered by the lid, a small opening only being left to permit the fumes of the sulphuric acid to escape; and the heat should be applied near the top of the crucible, in order to prevent the liquid from creeping up the sides of the vessel (Fig. 60, page 58).

White fumes must escape during the process of heating, since their evolution proves that H_2SO_4 has been added in excess. The crucible should be heated to redness for at least fifteen minutes after the fumes have ceased to appear. It is then allowed to cool in the desiccator, and is weighed. The above processes should be repeated until two consecutive weighings are identical, after the crucible has been reheated for five minutes.

The saline mass becomes pasty during the process of heating. This is due to the change of the sodium bisulphate, which is first formed, into the less fusible normal sulphate.

The change from bisulphate into normal sulphate may be accelerated by the introduction of a little powdered ammonium carbonate into the crucible, while it is faintly red hot. The lid is then replaced, and the crucible is strongly heated for a few minutes. This treatment should be repeated until the weight of the crucible and its contents becomes constant.

From the weight of Na_2SO_4 thus obtained, the percentage of Na can be calculated.

Estimation of Potassium in Potassium Chloride.

Two methods of estimation are described. The potassium is either weighed as platini-chloride (**171**) or as sulphate (**172**).

171. The Potassium Chloride is precipitated as the Double Chloride of Platinum and Potassium, K_2PtCl_6, and is weighed as such.

This method is only applicable to those potassium compounds which can be completely converted into potassium chloride by evaporation with hydrochloric

acid, since it is only as chloride that the potassium can be completely precipitated by $PtCl_4$ solution.

Weigh out accurately into a 10 cm porcelain dish about 0·25 gram of pure recrystallised potassium chloride (107). Dissolve this in a small quantity of water, and add a few drops of hydrochloric acid. Then add platinum chloride solution in such quantity that it contains a weight of $PtCl_4$ at least three times as great as that of the KCl used; and evaporate the liquid on the water-bath, until a semi-solid crystalline mass is obtained.

It is absolutely necessary that the platinum chloride should be present in excess. This is proved to be the case if the liquid is of an orange colour after it has been concentrated to a small bulk on the water bath.

Proceed to treat the residue which is left by evaporation, according to one of the methods (a) or (b) described below, of which (b) is somewhat the quicker.

(a) **First Method.**—Pour alcohol upon the residue, using either absolute alcohol or rectified methylated spirit. Gently shake the liquid round in the dish, so as to mix the contents uniformly together. Allow the precipitate to settle completely, and pour off the liquid through a tared filter or through two counterpoised filters (86, a, b). Repeat these operations twice, and finally transfer the undissolved double salt to the filter by means of a small wash-bottle containing alcohol.

Wash the precipitate upon the filter with alcohol until the washings are no longer coloured; then dry the filter with its contents in the funnel at 100° C., and transfer it while hot to a weighed tube (Fig. 6, page 9), or to a small weighed beaker covered with a watch-glass; then weigh the whole.

The weight of the precipitate must now be ascertained after it has been dried at 160° C. (87). As this temperature would char the filter, the following special procedure is necessary. If the quantity of the precipitate suffices, the greater part of it may be transferred to a weighing-bottle and weighed, and then heated in the air-oven to 160° C until its weight becomes constant. The weight which the whole precipitate would have at 160° C. may be calculated from this result.

If the precipitate is small in amount, as much as possible is removed to a clean watch-glass: the remainder is dissolved off the filter by a few c.c. of hot water into a crucible and evaporated to dryness; the precipitate from the watch-glass is then added, and the whole is dried at 160° C. and weighed.

(b) **Second Method.**—Wash the precipitated double salt with alcohol in the dish by decantation until the alcohol is no longer coloured. Then decant off the alcohol through an untared filter-paper, taking care that as little as possible of the precipitate is poured off with the alcohol. Now rinse the

double salt by means of the alcohol wash-bottle into a platinum crucible, dry it at 160° C., and weigh it.

Incinerate the filter (101), which will contain a little of the double salt, drop the ash into the crucible, and again weigh the crucible. The weight of the filter-ash is now deducted from the increase noted in the weight of the crucible, and the approximate weight of platinum which has been left in the filter-ash is thus found. The weight of double salt which would contain this platinum is calculated, and this weight is added to that of the double salt already found in the crucible (*Note* 1).

From the weight of the double salt, K_2PtCl_6, thus found, the percentage of K can be calculated (*Note* 2).

Note 1.—If the quantity of precipitate which was left on the filter is appreciable, the weight of KCl which remains unchanged in the filter-ash will introduce an error: this weight cannot be allowed for, since much of the KCl will have been lost by volatilisation. If great accuracy is necessary, the filter is ignited in a separate crucible; the KCl is then washed out from the ash by hot water, and the dried residue is weighed. The true weight of the platinum in the ash is thus ascertained, and the weight of double chloride which contained it is calculated, and is added to that already found.

Note 2.—If the modern atomic weight for platinum, 195·2, has been adopted, the weight of K found is too low. This is due to the fact that the formula K_2PtCl_6 does not represent precisely the composition of the dried precipitate, the molecular weight of which is slightly higher than that indicated by this formula. If, however, the old atomic 197·2 is adopted, the results obtained by calculation will be correct, and the weight of the double chloride when multiplied by the factor 0·30561 will give the true weight of KCl which it contains.

172. **Estimation of Potassium as Sulphate.**—The process is precisely similar to that described in paragraph 170 for sodium compounds. It is only suitable for those potassium compounds which leave pure potassium sulphate, K_2SO_4, when the residue, left after evaporation with sulphuric acid, has been ignited.

Estimation of Ammonium in its Compounds.

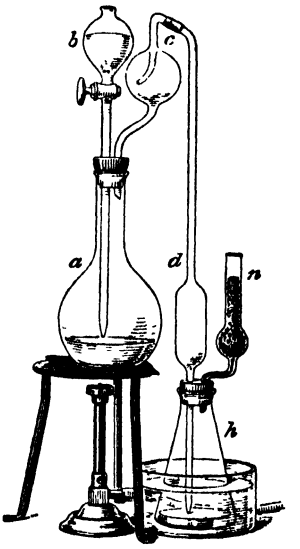
The ammonia gas is driven off by heating the substance with caustic alkali solution, and is estimated either gravimetrically (173) or volumetrically (295, 296).

173. The Ammonia is expelled by heating the ammonium compound with Sodium Hydrate Solution, and is absorbed in dilute HCl; the Ammonium Chloride thus produced is precipitated as the Double Chloride $(NH_4)_2PtCl_6$ by Platinic Chloride, and is weighed as such.

The General Description of the Process will be understood by reference to Fig. 67. The weighed ammonium compound is introduced into the decomposition-flask (*a*), and the caustic alkali solution is allowed to drop upon it

from the dropping-tube (*b*). When this flask is heated, ammonia is evolved, and is absorbed by the dilute acid in the cooled absorption-flask (*h*). The absorption-tube (*n*) contains glass moistened with dilute acid: this acid retains traces of ammonia which may not be arrested by the acid in the flask (*h*). The enlargement in the tube (*d*) receives any acid which may be sucked back from the absorption-flask (*h*), and prevents it from entering the decomposition-flask (*a*).

FIG. 67.



Another form of apparatus suitable for this process and for that described in paragraph 295 will be found figured in paragraph 808. The ammonium compound is mixed with sodium hydrate solution in the large flask, and the ammonia is expelled in steam by heating the large flask by a flame so as to keep the liquid boiling briskly, or steam is blown through the liquid from a separate vessel as is shown in the figure The steam is condensed by a condenser (1016), and carries the ammonia into the acid in the receiving-flask.

Description of the Apparatus (Fig. 67).—A 500 c c. round flask (*a*) is fitted with a rubber cork, through which passes a dropping-tube (*b*) of about 50 c.c. capacity. The lower end of this tube is drawn out to a fine point.

ESTIMATION OF AMMONIA.

Instead of a funnel, a 50 c c. pipette may be used, the lower end of which is drawn out; the upper end of the pipette is fitted with a piece of rubber tubing which can be closed by a screw-clamp, so as to prevent the liquid which it contains from descending into the flask (Fig. 68, *b*, p. 104). The screw-clamp takes the place of the stop-cock.

This flask is connected by means of a bent tube, carrying a bulb (*c*), and a rubber joint with a 50 c.c. pipette (*d*). The connecting-tube and the top of the pipette must be of the same diameter, and their ends must be brought into close contact within the joint. This pipette passes through a rubber cork which is fitted in the neck of a 300 c c. conical flask (*h*). The lower end of the pipette is drawn out to a fine point. Through the same cork a small absorption-tube (*n*), filled with broken glass, also passes.

The conical flask is filled to the depth of about half an inch with hydrochloric acid, made by diluting the strong acid with six times its volume of water. The acid, preferably mixed with a drop of methyl-orange (268), is poured into the flask through the absorption-tube (*n*) containing the broken glass, and the glass is thus wetted with the liquid. The point of the pipette is adjusted so as to dip just below the surface of the acid.

The whole apparatus should be screened, or placed in a fume-closet, in order to shelter it from draughts while it is being used, since the cooling action of an air-current renders the process very irregular.

Description of the Process of Estimation.—About 1 gram of pure crystallised ferrous ammonium sulphate, $Fe(NH_4)_2(SO_4)_2\,6H_2O$, is accurately weighed, all crystals which show a yellowish tinge being rejected. The salt is introduced into the round flask (*a*), and is then dissolved in about 50 c.c. of water.

The bulb of the dropping-tube (*b*) is now filled with sodium hydrate solution, prepared by dissolving one part of NaHO in four parts of water. The rubber cork, bearing the funnel and bulb-tube, is fitted into the flask, and is bound down with copper wire to the neck of the flask. The connection (*c*) with the other flask (*h*) is then made by means of the rubber joint.

The contents of the round flask are now heated to incipient ebullition, and the NaHO solution is allowed to drop slowly into the flask by slightly opening the stop-cock of the dropping-tube (*b*).

As the ammonia gas is driven off, it is absorbed by the acid in the conical flask (*h*), which is kept cool by being placed in a dish of water.

The bulb-tube (*c*) arrests any alkaline liquid projected by spirting from the boiling flask. The bulb of the pipette (*d*) prevents the acid from being sucked back into the heated flask (*a*) by the absorption of the ammonia, since, as soon as the bulb becomes partially filled with the acid, the tip of the pipette is no longer submerged; accordingly air passes up in bubbles through the pipette and restores the equilibrium. The point of the pipette must always be just immersed in the acid, and must therefore be occasionally raised as the volume of liquid in the flask increases by the condensation of steam.

As soon as all the NaHO solution has flowed from the tube (*b*) into the flask, the stop-cock is closed; the flame is then raised, and the contents of the flask are kept boiling briskly for about twenty minutes. Some acid must now remain un-neutralised; this is known to be the case if the methyl-orange in the absorption-flask does not become yellow (268).

The two flasks are now disconnected, and the absorption-flask (*h*), together with its pipette and absorption-tube, is rinsed out with water into a porcelain dish. Excess of platinum chloride solution is added to the contents of the dish: the liquid is evaporated on the water-bath; and the $(NH_4)_2PtCl_6$ is estimated in the same way as the corresponding potassium salt (**171**) except that the precipitate is finally dried at 130°.

Note.—For the reasons already stated (*Note* 2, **171**) the atomic weight 197·2 should be adopted for platinum in calculating the result of the estimation or the weight of double chloride obtained may be multiplied by the factor 0·20141 to

obtain the weight of NH_4Cl, by 0 08107 to obtain the weight of NH_4, or by 0·0766 to obtain the weight of NH_3.

The Determination may be Controlled by igniting the precipitate to redness, and weighing the metallic platinum which remains.

For this purpose the crucible, containing the double salt with the filter above it, is covered and heated very gently for a time. The lid is then removed and the heat is gradually increased, care being taken to burn away the carbon of the filter-paper completely. The contents of the crucible are finally heated to bright redness and the residue of metallic platinum is weighed. This residue does not require to be washed, as is the case with the estimation of potassium platino-chloride, since AmCl is volatile and cannot remain after ignition.

The weight of platinum obtained must be multiplied by 0 54527 to obtain the corresponding weight of NH_4Cl, by 0 18416 to obtain NH_4, and by 0·17388 to obtain NH_3. Calculations involving the use of the atomic weight of Pt, 194 8, do not give correct results (**171**, *Note* 2).

Estimation of Carbon Dioxide in a Carbonate.

174. Three methods of estimation are described below.

The first method is the most trustworthy and accurate. By this method (**175**) the carbon dioxide is liberated, and is then absorbed and weighed directly.

The second method (**182–185**) depends upon finding the loss of weight which the carbonate undergoes by the removal of its carbon dioxide. It is liable to yield somewhat high results (**183**, *Note*).

The third method (**186**) measures the volume of CO_2 which is evolved by the carbonate when it is decomposed by an acid.

175. By Direct Weighing. The Carbon Dioxide gas is liberated by treating the Carbonate with an Acid; it is then absorbed by means of Soda-lime, and is weighed.

The General Description of the Process will be understood by referring to Fig. 68.

The carefully weighed carbonate is introduced into the flask (*a*), and is decomposed by acid from the pipette (*b*). The carbon dioxide which is evolved passes through strong sulphuric acid in the glass-bulb apparatus (*d*), and then through the tube (*e*) in which it is freed by copper sulphate from any hydrogen chloride which has been expelled by heat from the acid in the flask (*a*). The carbon dioxide is finally absorbed by the soda-lime contained in the weighed tube (*f*).

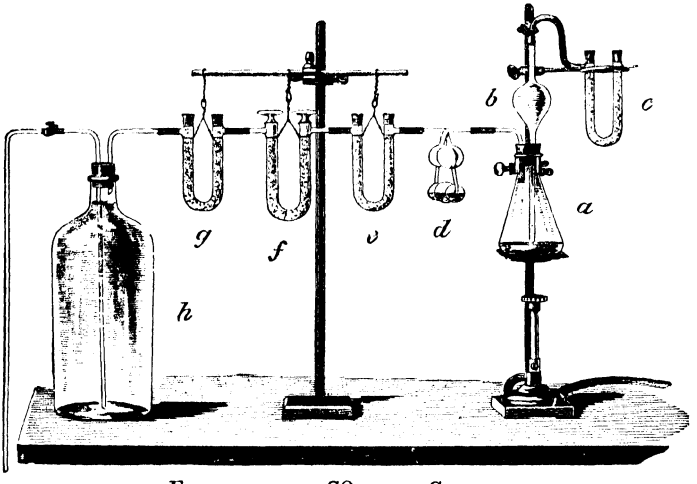
The tube (*g*) contains calcium chloride, and is intended to prevent water-

vapour from passing back from the aspirator to the tube (*f*). The aspirator-bottle (*h*) serves to draw air through the whole apparatus at the end of the process, so as to carry over all the carbon dioxide into the absorption-tube (*f*); this air is freed from carbon dioxide by passing through the soda-lime tube (*c*) on its way to the pipette (*b*) and the flask (*a*).

The tube (*f*) is weighed at the end of the process, and the increase in its weight gives the weight of carbon dioxide which has been evolved from the known weight of carbonate.

Detailed Description of the Apparatus.—The apparatus employed for this estimation consists of a 250 c.c. conical flask (*a*) which is fitted with a

FIG. 68.



ESTIMATION OF CO_2 IN A CARBONATE.

rubber cork bored with two holes. Through one of the holes passes a dropping-tube (*b*, Fig. 67, p. 101), or a 50 c.c. pipette (Fig. 68, *b*), the lower end of which is drawn out to a fine point. The bulb of the pipette is filled with the dilute acid which is later on to effect the decomposition of the carbonate, and its lower end is situated about 2 cm. from the bottom of the flask.

On the upper end of this acid-vessel is a piece of rubber tube 20 cm. long, on which, if the pipette is used, a screw-clamp serves to control communication with the soda-lime U-tube (*c*). One end of this U-tube is connected with the rubber tubing, the other end being open to the air. This tube is intended to free the air, which is finally drawn through the apparatus, from carbon dioxide.

A piece of bent glass tube is pushed through the second hole of the rubber

cork in the flask (*a*) to the distance of about 2 cm., the lower end of the tube being cut off obliquely, as is shown in Fig. 67 (page 101). Attached to this tube are bulbs and U-tubes, connected with each other by rubber joints: these serve respectively for drying, purifying, and absorbing the carbon dioxide gas, as is explained below.

The bulb-tube (*d*) contains strong sulphuric acid: it serves for drying the gas, and also acts as a gauge to indicate the rate at which the gas is passing over from the flask (*a*). Liebig's or Geissler's potash-bulbs serve well for this purpose. The sulphuric acid should half fill the three lower bulbs.

The U-tube (*e*) has the limb nearest the bulb-tube (*d*) filled with granular calcium chloride (179 *Note*). The other limb of this U-tube is filled with dehydrated copper-sulphate-pumice (179) in order to absorb any HCl which may be given off during the heating of the liquid in the flask (*a*).

The stoppered U-tube (*f*), which is the absorption-tube for the CO_2 evolved from the carbonate (178), has the limb nearest to the copper-sulphate tube (*e*), the bend, and half the other limb filled with soda-lime; the remainder of the tube is filled with solid calcium chloride. The soda-lime in this tube becomes heated when it absorbs CO_2; any moisture which is thus expelled is absorbed by the calcium chloride, and loss of weight by escape of moisture from the tube is thus prevented.

The remaining tube (*g*) is filled with granular calcium chloride, and is shown in the figure to be in connection with a water-aspirator (*h*). The aspirator (176) is connected with the calcium-chloride tube only when the evolution of CO_2 has ceased. It serves to draw air through the flask and tubes at the end of the process, and thus to carry the CO_2 over into the absorption-tube (*f*).

176. **The Syphon Aspirator** is made from a Winchester quart-bottle (Fig. 68, *h*) in the following way: A sound cork bored with two holes is fitted into the neck of the bottle. Into one of these holes a piece of glass tube bent at right-angles is fitted, the tube passing just through the cork. Through the other hole in the cork passes a tube, which is bent at right-angles and reaches to the bottom of the bottle. When the bottle is to be used as an aspirator, a rubber tube, extending below the level of the bench on which the bottle stands, is attached to the longer glass tube, which is thus enabled to act as a syphon. A screw-clamp on the rubber joint serves to regulate the outflow of the water.

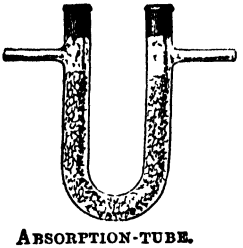
The bottle is now filled with water, and suction is applied to the lower end of the rubber tube until it is filled with water. A continuous stream of water will flow out through the syphon-tube after the suction is stopped. Air will enter the bottle through the shorter tube to supply the place of the water. A continuous current of air can accordingly be slowly drawn through the series of tubes and the flask by attaching them by rubber tube to the shorter tube in the bottle after the rate of aspiration has been regulated by the screw-clamp.

177. **Preparation of the Absorption-tubes.**—Figure 69 represents a convenient form of U-tube for containing the solid absorbents. The tube is washed perfectly clean and then rinsed with distilled water. It is then dried in the steam-

oven, or more quickly by driving a current of air through the tube by means of a foot-bellows while it is being heated gently over a Bunsen flame.

When the absorbent is in the tube, it must always be protected from the external atmosphere. This is effected by closing the vertical limbs with corks, pushing over the side-tubes short pieces of rubber tubing closed with little plugs of glass rod. The side-tubes are only unstopped when the U-tube is being connected for use in the process of absorption, and while it is being weighed.

Fig. 69.



Absorption-tube.

The granulated solid, which is to be introduced into the U-tube, must be freed from fine powder, which would stop the passage of the gas But since the solid particles absorb gas or vapour by their exterior only, they should be small and uniform in size so as to expose the largest possible absorbent surface.

A suitable granular powder may be produced in the following manner: The solid is coarsely powdered in a porcelain mortar, and this powder is then shaken upon a perfectly dry and clean fine brass-wire sieve of twenty strands to the inch. The powder which passes through is rejected. The remainder is freed from large lumps by causing it to pass through a coarser sieve of eight strands to the inch. The particles which pass through this sieve are used for filling the absorption-tubes. The larger pieces, which do not pass through the coarser sieve, are broken up again in the mortar, and are subjected once more to the above processes of sifting.

The U-tube is filled with the granular solid almost up to the level at which the side-tubes enter. Loose plugs of cotton-wool or glass-wool are then inserted to prevent the solid particles from entering the side-tubes Two sound corks of suitable size are softened by pressure, and are fitted into the open ends of the U-tube. Each cork is then cut off level with the top of the tube, and a little melted paraffin-wax is brushed over the cork to make it perfectly gas-tight. The stoppered U-tube (178), which is commonly used only when weighing is necessary, may also be used as an ordinary absorption-tube, and *vice versâ*.

178. **The Stoppered U-tube** —The stoppered tube differs from he one just described by having a hollow stopper, open below, ground into the upper part of each limb. These stoppers are wiped perfectly clean with filter-paper and are then greased with a little lard or vaseline to make them fit air-tight in their seats, At the side of the hollow stopper, and on a level with the entrance of the side-tube, is a perforation ; so that by simply turning the stopper round in its seat, communication between the U-tube and the side-tube may be opened or closed at pleasure.

It will be seen that by this arrangement the contact of the absorbent with the atmosphere may be prevented by simply turning the stopper, and caps for the side-tubes are unnecessary. This closed stoppered tube can accordingly be weighed in a more leisurely fashion than the open tube, since it cannot increase in weight during the process. Solid particles are prevented from entering the side-tubes by loosely filling the hollow stoppers with plugs of cotton-wool or glass-wool.

179. **The Copper-sulphate-pumice**, which the tube (*c*) contains in addition to the calcium chloride (*Note*), may be made in the following way : Pumice-stone is granulated by powdering and sifting it in the manner already described (177). It is

then heated with a moderately strong solution of copper-sulphate, and the liquid is poured off. The pumice, which is now saturated with the solution, is heated in the air-oven to a temperature of 200° C. until the blue colour of the copper salt disappears, and is used for partially filling the tube (*e*) as has been already described.

Note.—Calcium chloride almost invariably contains a little caustic lime, which would absorb some carbon dioxide gas before it could reach the proper absorption-tube (*f*), and would lead to a low result being obtained in the estimation. Before using the calcium chloride for tube (*c*) it is therefore always desirable to pass a current of dry carbon dioxide gas through it in a U-tube, then to allow the tube to remain filled with the gas for about thirty minutes, and finally to replace the CO_2 by passing a current of dry air through the tube.

180. Testing the Apparatus.—As soon as the tubes have been connected with one another and with the decomposition-flask by means of rubber tubing, the apparatus should be tested in the following manner in order to ascertain whether it is gas-tight. To the last U-tube (*g*) is attached a piece of glass tube, which dips into a beaker of water. Gentle suction is applied at (*c*) so as to cause the water to ascend about 15 cm. in the glass tube, and the screw-clamp on (*b*) is then closed. If the level of the water in the tube does not fall after an interval of about ten minutes, the apparatus is air-tight.

If the level of the water in the tube descends, the apparatus must admit air. The faulty rubber connection must then be found out, and the rubber must be bound upon the glass tube with fine copper wire. If this is insufficient, the rubber joint must be replaced by a new one.

181. Description of the Process of Estimation.—As soon as the apparatus has been proved to be air-tight, the estimation may be proceeded with as follows:

The absorption-tube (*f*) is first wiped clean and dry, and carefully weighed; it is then connected in its place in the series of U-tubes. About 1 gram of precipitated calcium carbonate (**109**, Exp. 25), or of Iceland spar, is accurately weighed into the flask (*a*). The funnel-tube or the pipette (*b*) is then filled by suction with hydrochloric acid, which has been made by diluting the strong acid with three times its volume of water, and the acid is kept in the pipette by closing the clamp at the top. The cork carrying the pipette is then inserted into the neck of the flask and is bound down by means of thin copper wire. The aspirator (*h*) and the tube (*c*) are not attached until a later stage of the process.

The clamp above the pipette, or the stop-cock of the dropping-tube, is now slightly opened, and the acid is allowed to drop slowly upon the calcium carbonate in the flask. Carbon dioxide gas will be evolved, and will drive out the air of the flask. The bubbles should pass through the acid-bulbs at such a speed that they can be easily counted.

As soon as all the acid has flowed from the pipette into the flask the clamp or stop-cock is closed, and the point of the pipette is carefully pushed down beneath the surface of the liquid in the flask.

When no further effervescence occurs, the U-tube (*c*) and the aspirator are attached, the clamp above the pipette or stop-cock is opened, and slow aspiration is started. At the same time a small Bunsen flame is placed under the flask, so as to maintain the liquid at incipient ebullition and expel the dissolved CO_2. The current of air, which is drawn through the apparatus by the aspirator, displaces the CO_2 from the flask, the bulbs, and the first U-tube, and carries it into the absorption-tube (*f*). The speed of the air-current is so regulated by means of the clamp attached to the aspirator that the bubbles can be counted as they pass through the bulb-tube (*d*).

The soda-lime in the tube (*f*) becomes heated by its chemical combination with CO_2 during the early stages of the process. It cools again as the absorption of CO_2 ceases. Hence most of the CO_2 gas is known to have been absorbed when the absorption-tube (*f*) becomes cold.

In order to ensure the passage of the whole of the carbon dioxide into the absorption-tube (*f*), a volume of air, equal to about six times the capacity of the flask (*a*), should be drawn through the apparatus.

The U-tube (*f*) is then disconnected. The stoppers are at once turned so as to close the side-tubes; or, if the ordinary U-tube has been used, the rubber stoppers are slipped upon the side-tubes. The tube is weighed in about half an hour, after it has assumed the temperature of the air. The increase of weight which it has undergone is the weight of CO_2 originally present in the calcium carbonate taken.

From these weights the percentage of CO_2 in the $CaCO_3$ can be calculated.

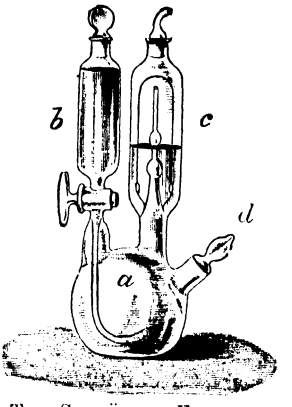
182. Estimation of Carbon Dioxide by Difference. The Carbon Dioxide gas is driven off by treating the Carbonate with an Acid, and the loss of weight, thus caused, gives the amount of Carbon Dioxide in the Carbonate.

This method is sometimes applied to the decomposition of a carbonate by dilute HCl or HNO_3, but it is better suited for carbonates which are completely decomposed by H_2SO_4. When one of the more volatile acids is used the results obtained are usually too high, since part of the acid is driven off when the liquid is heated at the end of the process. This loss may be prevented, when dilute HCl is used, by causing the CO_2 to pass over copper-sulphate-pumice (**179**) before it leaves the apparatus; any HCl is absorbed and retained by the copper sulphate.

Two forms of apparatus are described below for use in this process in paragraphs **183** and **184**.

183. **The Schrötter Apparatus**, shown in Fig. 70, is made of thin blown glass; its total weight should not exceed 50 grams. A modified form of this apparatus (Fig. 71) should be used when the carbonate is decomposed by dilute hydrochloric acid. Each figure represents the apparatus at one-third its actual size.

Fig. 70.



The Schrötter Flask.

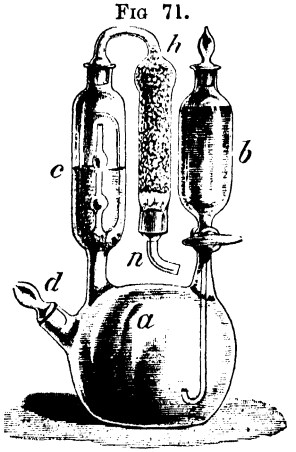
Description of the Apparatus.—It consists essentially of a flask (*a*), in which the decomposition of the carbonate is effected. Communicating with this flask there are two reservoirs (*b*) and (*c*); also a stoppered opening (*d*), which serves for introducing the carbonate.

The reservoir (*b*) is filled with the dilute acid. This acid is afterwards introduced gradually into (*a*) by removing the stopper and then turning the stop-cock; it serves to decompose the carbonate.

The reservoir (*c*) is half filled with strong sulphuric acid, which dries the CO_2 gas as it leaves the apparatus. The gas passes up through the vertical inner tube, then down again and out through the two holes at the base of the second tube. It then bubbles up through the strong sulphuric acid before making its escape through the upper exit-tube into the air.

The Process of Estimation.—The proportion of CO_2 in pure sodium carbonate may be estimated by this method. The salt may be prepared by heating the pure bicarbonate in a platinum crucible to a dull red heat, until it no longer loses weight by repeating the ignition. About 1 gram of this pure sodium carbonate is weighed with accuracy, and is introduced into the apparatus through the opening (*d*). The receptacle (*b*) is then nearly filled with sulphuric acid, which has been diluted with five times its volume of water and cooled, and the receptacle (*c*) is half filled with strong sulphuric acid. The apparatus is then accurately weighed.

Fig 71.



Modified Schrötter Flask.

The dilute acid in (*b*) is now allowed to flow slowly into (*a*) by removing the stopper and gradually turning the stop-cock. As the acid attacks the carbonate, bubbles of gas will be seen passing through the strong acid in (*c*). The speed at which these bubbles pass must be so regulated, by adjusting the flow of the dilute acid, that they can be easily counted. If they pass more rapidly than this, the gas will not be perfectly dried.

As soon as all the dilute acid has flowed into the flask, and bubbles of gas no longer escape, the apparatus is placed upon wire-gauze on a tripod-stand over a small Bunsen flame. At the same time the aspirator (176) is attached by a piece of rubber tubing to the exit-tube of (*c*), and a gentle current of air is drawn through the flask. The liquid in the flask is heated just short of boiling, until a volume of air, equal

to about three times the capacity of the flask and tubes, has been drawn through them. The flask is then allowed to cool, and is finally weighed The loss of weight which it has suffered gives the weight of carbon dioxide in the sodium carbonate used.

Note —This method is not suitable for very accurate analyses. The results are usually too high, since water may be lost from the apparatus during the heating and aspiration.

184. *Decomposition by Dilute Hydrochloric Acid.*—Keane's modification (Fig. 71) of the Schrotter apparatus should be used when the carbonate is acted upon by dilute hydrochloric acid instead of by sulphuric acid The apparatus generally corresponds to that shown in Fig 70, but the upper part of the drying-chamber (*c*) is connected by a ground joint with a tube (*h*), which is filled with copper-sulphate-pumice (179), the pumice being kept in its place by plugs of glass-wool above and below. The small exit-tube (*n*) is ground into this absorption-tube below, and is greased or wired so as to make it keep its seat.

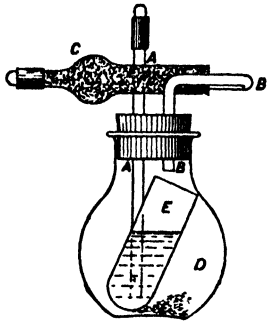
The absorption-tube may be turned round in the ground socket of the drying-chamber. The exit-tube can thus be brought into a convenient position for being connected with the aspirator, while the flask is being heated. When the tube is in the position shown in the figure, the whole apparatus is compact and will be stable on the scale-pan.

The addition of this absorption-tube causes the apparatus to yield results with hydrochloric acid which are as satisfactory as those usually obtained with sulphuric acid.

185. **A Simple Form of Apparatus,** which may be fitted from materials which are available in any laboratory, is shown in Fig. 72.

It consists of a light 120 c c. flask with a short wide neck A short doubly perforated rubber stopper is fitted into the neck, and carries a tube, *AA*, which passes nearly to the bottom of the flask, and a small calcium chloride drying-tube, *C*. The external ends of these tubes are fitted with short pieces of rubber tubing, which are closed with small rounded glass rods

Fig. 72.



CO_2 Estimation Flask.

The dilute acid required for decomposing the carbonate is contained in a short tube, *E*, the length of which must be so adjusted that it stands obliquely in the flask without touching the stopper and without slipping into a horizontal position.

The procedure with this apparatus differs from that with the preceding apparatus (183) in several details.

As soon as all is ready for the decomposition, and the whole apparatus has been weighed without the caps, the cap is restored to the tube *AA*, and the acid is caused to flow slowly upon the carbonate by tilting the flask, so as to cause a gradual evolution of the CO_2. When all the acid has been poured from the tube and the effervescence has ceased, the flask is warmed, and finally the cap of the tube *AA* is removed, and a slow stream of air is drawn by the aspirator (176) through the drying-tube and flask to displace the CO_2. The caps are then restored; and the apparatus is weighed again, without the caps, as soon as it cold.

If dilute Hydrochloric Acid is used for the decomposition of the carbonate, the bulb of the absorption-tube (*C*) must be filled with dried copper-sulphate-pumice (179) in order to prevent loss of HCl from the apparatus, the cylindrical part of this absorption-tube containing granular calcium chloride.

186. Estimation of Carbon Dioxide by measuring the Volume of Gas evolved by the action of an Acid upon the Carbonate.—The description of this method will be found in paragraph 900.

A Volumetric Method for estimating CO_2 in air is given in paragraphs 912–914.

A Method for the Estimation of C_2O_4 in an Oxalate.

187. The Oxalate is mixed with Manganese Dioxide, and the mixture is heated with Sulphuric Acid. The weight of the CO_2 evolved is either found by absorption by Soda-lime or by the loss of weight of the Apparatus. The weight of the CO_2 evolved is equal to that of the C_2O_4 in the oxalate.

The following equation represents the reaction:

$$H_2C_2O_4 + MnO_2 + H_2SO_4 = 2CO_2 + 2H_2O + MnSO_4.$$

It must be remembered that free oxalic requires to be neutralised by AmHO before it can be estimated by this process.

The different forms of apparatus which are used in the estimation of CO_2 (Figs 68, 70, 72) may be used for this determination.

Weigh out accurately about 0·6 gram of finely powdered pure ammonium oxalate, $(NH_4)_2C_2O_4\,H_2O$, and intimately mix it with about three times its weight of finely powdered manganese dioxide, which must be free from carbonate. (See *Note* below.)

Introduce this mixture into the decomposition-flask. Add to it dilute sulphuric acid, and conduct the operation exactly as has been described above (175–185), starting the decomposition by heating the flask. The weight of the CO_2 evolved gives the amount of C_2O_4 in the oxalate taken, and from this the percentage of oxalate may be calculated.

Note.—The manganese dioxide which is used in this estimation must be carefully tested for traces of carbonate. If any carbonate is found, the oxide should be finely powdered and heated for about fifteen minutes with a little very dilute sulphuric acid. The oxide is then washed free from acid, and dried.

A Volumetric Method for the estimation of an oxalate is given in paragraph 325, and another **Gravimetric Method** is given in paragraph 148.

Estimation of Water, present in the Free or Combined State.

188. Three methods are described below for estimating the water adhering to, or chemically combined with, a substance.

The first and second methods (189, 190) are applicable to substances which lose all their water, but undergo no further change in composition, when they are heated. The water may be estimated in such cases by the loss of weight which the substance suffers when it is heated to a suitable temperature

The third method (191) is generally applicable to all substances. But it is necessarily resorted to for substances which, when they are heated, not only part with their water, but also undergo further chemical change which is attended with alteration in weight.

Instances of such substances are furnished by ferrous hydrate and ferrous carbonate, which increase in weight by oxidation when they are heated in the air; the latter undergoes change of weight also by loss of CO_2, an effect usually produced by heating a carbonate. The water, which is evolved when such substances are heated, must be absorbed by a weighed desiccating agent, and must be estimated by the increase of weight which the absorbent undergoes by taking up the water.

189. The Substance is dried by Heating it in a Steam-oven or other suitable apparatus (59, 61, 1022), and the loss of weight is estimated.

This Method is applicable to substances which lose their Moisture, without undergoing further chemical change, when they are heated moderately.

Weigh out accurately about 1·5 grams of crystallised oxalic acid, $H_2C_2O_4.2H_2O$, between the weighed pair of watch-glasses with clip (Fig. 7, page 9). Then remove the upper glass and clip, and heat the lower glass containing the substance for about two hours in the steam-oven Replace the upper glass and the clip, and weigh the glasses with their contents, after they have cooled in the desiccator.

Repeat the above processes of heating, cooling, and weighing, until two successive weighings give the same result. The water, which can be expelled at 100°, is then known to be completely removed, and its percentage amount may be calculated from the loss of weight which is suffered by the substance taken (113).

190. The Substance is dried by Igniting it, and the loss of weight is estimated.

This Method is applicable to substances which lose all their Water, without suffering further chemical change, when they are heated to a high temperature.

This method is generally to be preferred to any other, if the nature of the substance to be dried permits of its adoption, since it can be carried out with greater ease and rapidity.

Weigh out accurately about 1·5 grams of finely powdered pure recrystallised barium chloride, $BaCl_2.2H_2O$, into a platinum crucible of known weight. Heat the covered crucible gradually over a small Bunsen flame, slowly raising the temperature until the bottom of the crucible is at a dull red heat. Remove the lid and keep the crucible at this temperature for at least fifteen minutes; then allow it to cool in the desiccator, and weigh it.

Repeat the above processes, heating for five minutes only, until two consecutive weighings give identical results. The water, which can be removed by ignition, is then known to have been expelled; and its percentage amount may be calculated from the loss of weight which has been caused by heating the weighed substance (113).

191. The Substance is Heated to a suitable temperature, and the Water-vapour is conveyed by a stream of gas into an Absorbent Substance and weighed.

This Method is applicable to substances which lose their water when they are heated, but which also undergo further change of weight during the process owing to some other chemical change.

General Description of the Process.—The process will be understood by reference to Fig. 73. The weighed substance is heated in a bulb-tube (*a*), which is connected at each end with a U-tube charged with a desiccating agent, preferably calcium chloride. The U-tube (*c*) is connected with a small washing-bottle containing strong sulphuric acid.

The air enters through the tube (*b*), passes over the substance in the bulb-tube, and leaves the apparatus after passing through the U-tube (*c*) and the wash-bottle. The air may be drawn through the apparatus by attaching an aspirator (176) to the wash bottle connected with the tube (*c*), or air may be driven through the apparatus from a gas-holder which is connected with the tube (*b*).

Detailed Description of the Apparatus.—A hard glass tube, of about 1 cm. bore and 15 cm. in length, has a bulb about 4 cm. in diameter blown in its middle (Fig. 73, *a*). The sharp edges of the ends of this tube are rounded by being held for a short time in the blowpipe-flame.

Two sound corks are softened by pressure and are fitted air-tight into the ends of the bulb-tube, and are then perforated to receive the side-tubes of two U-tubes.

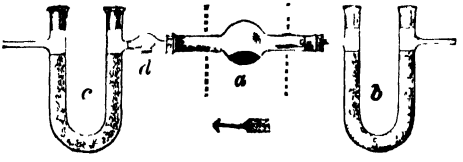
The U-tubes are filled nearly to the level of their side-tubes with granular calcium chloride; cotton-wool or glass-wool plugs are then pushed into each limb, and the open ends are finally closed with sound corks, which are

cut off level with the glass, and are then brushed over with melted paraffin wax. A full description of the fitting of the U-tubes and of the preparation of the calcium chloride will be found in paragraphs **177**, **178**, and attention must be paid to the *Note* (**179**) in filling tube (*c*), if CO_2 is evolved when the substance is heated.

When a high temperature is to be applied to the bulb by a flame, discs of metal or of asbestos millboard should be slipped upon the bulb-tube in the positions shown by the dotted lines of the figure, in order to shield the corks and prevent them from being scorched.

After the separate parts have been fitted together, the whole apparatus must be tested to ascertain if it is air-tight. For this purpose a short piece of

FIG 73.



ESTIMATION OF WATER.

rubber tube, carrying a screw-clamp, is pushed upon the free side-tube of tube (*b*), and by careful suction the sulphuric acid is raised several inches in the tube of the wash-bottle attached to (*c*). The rubber tube is then closed by tightening the screw-clamp. If the level of the acid does not fall in about ten minutes, the apparatus may be considered to be air-tight.

The Process is carried out as follows · The U-tube (*c*) is detached and is accurately weighed. The perfectly clean and dry bulb-tube (*a*) is then weighed.

About 2 grams of the finely powdered substance, $BaCl_2.2H_2O$, are placed near the end of a little trough of stiff glazed paper, which will easily slip into the bulb-tube. This paper is pushed into the tube until the powder is within the bulb, and by rotating the bulb-tube or the trough on a horizontal axis the whole of the powder is deposited in the bulb. The paper trough is then removed, and the bulb is weighed. Its gain in weight represents the weight of salt taken.

The apparatus is then fitted together again, and may be once more tested to see that it is air-tight.

An aspirator (**176**) is then attached by rubber tubing to the wash-bottle connected with the tube (*c*), the flow of water from the aspirator having been adjusted so as to draw a slow stream of air through the apparatus.

The air must pass through the acid in the wash-bottle at such a rate that the separate bubbles can be easily counted.

By this arrangement the air is dried by the calcium chloride in the tube (*b*) before it passes into the bulb-tube. It then passes through the bulb-tube, and carries the water-vapour, which is expelled from the substance by heat, into the bulb (*d*) and the calcium chloride of the weighed U-tube (*c*). The wash-bottle prevents the weighed U-tube from gaining weight by absorbing moisture, which might diffuse backwards from the aspirator. This bottle also serves as a gauge to measure the rate at which the air-current passes.

When the water is to be expelled from the substance at a known temperature, it is necessary to have the bulb-tube (*a*) either surrounded with an air-bath made of asbestos cardboard, or bent in such a way that the bulb can be immersed in a hot liquid The air-bath or liquid is heated to the requisite temperature, which is shown by a thermometer dipping into it Tubes specially shaped for immersion in the liquid may be made or purchased.

In the present example the bulb-tube may be gradually heated by a small Bunsen flame, as soon as the air-current through the apparatus has been adjusted. The flame should be surrounded by a suitable screen (*e.g.*, Fig. 53, p. 53), in order to prevent the absorption-tubes from being heated, and the corks and U-tubes may be further shielded by means of asbestos discs, as has been already described.

The temperature of the bulb is slowly raised until it reaches dull redness, and the salt is heated in the air-current until no small drops of water remain on the cool part of the bulb-tube (*a*). The weighed U-tube (*c*) is then detached and reweighed, and from its gain in weight the amount of water in the weighed salt is ascertained; the water is then poured out of bulb (*d*).

From this result the percentage weight of water in crystallised barium chloride may be calculated.

Estimation of Cadmium in its Soluble Compounds.

192. The Cadmium is precipitated as Sulphide, CdS, and is weighed as such.

Weigh out accurately about 0·5 gram of pure recrystallised cadmium sulphate, $3CdSO_4.8H_2O$. Dissolve it in about 250 c c. of water, and add a few drops of dilute HCl. Pass hydrogen sulphide (**1012**) into this solution, until the liquid smells strongly of the gas.

Filter off the CdS upon a weighed filter (**86**), and make certain that all the cadmium has been precipitated, by diluting a portion of the filtrate and passing H_2S through it again. If no further precipitation occurs, wash the

precipitate first with dilute hydrogen sulphide solution mixed with a little HCl, and finally with pure water. Dry the filter containing the precipitate in the steam-oven, and weigh it after referring to paragraph 193. See also paragraph 194.

From the weight of CdS obtained, the percentage of cadmium may then be calculated.

193. **This Precipitate frequently contains Free Sulphur.**—In accurate determinations the dried precipitate should therefore be repeatedly washed with recently distilled carbon disulphide, as long as any residue is left when the last drops of the washings are evaporated upon a watch glass The precipitate is then again dried and weighed Any loss which it has undergone by being washed will be due to the removal of free sulphur.

194. **Conversion of the CdS into $CdSO_4$.**—If the precipitate of CdS has been formed in an acid solution it may contain some basic salt, and this may lead to serious error if the amount of acid is large Under these circumstances it is preferable to convert the precipitated sulphide into $CdSO_4$ and to weigh this salt For this purpose dissolve the precipitate in hydrochloric acid diluted with its own volume of water, and evaporate the solution on the water-bath until it can be transferred to a porcelain crucible Add a slight excess of sulphuric acid, and heat cautiously over a small flame until no more fumes of sulphuric acid are evolved. Then allow the residue to cool and weigh it

An Electrolytic Method for estimating Cd is given in paragraph 221.

Estimation of Antimony in its Solutions.

The Antimony is precipitated as Sulphide, Sb_2S_3, and is weighed either as such (195), or, if it is small in amount, as the oxide, Sb_2O_4 (198).

195. **Precipitation as Sulphide, Sb_2S_3, and Estimation as such.**—About 0·5 gram of anhydrous tartar emetic, $K(SbO)C_4H_4O_6$ (109, Exp. 27), is accurately weighed. This is dissolved in about 200 c c. of distilled water, and a moderate quantity of tartaric acid solution, together with a few drops of dilute hydrochloric acid, are added. If an insufficient quantity of tartaric acid is added, the antimony will be precipitated on the addition of the HCl or on dilution.

The clear liquid is transferred to a 500 c c. flask, which is fitted with a doubly perforated rubber cork. Through one of the holes in the cork a glass tube bent at right-angles passes, and reaches nearly to the bottom of the flask. Through the other hole a second tube is passed, one end of which terminates just below the cork, the other end being slightly contracted so as to hinder the diffusion of air into the flask.

A gentle stream of hydrogen sulphide gas (**1012**) is passed through the longer tube into the liquid until it is saturated with the gas. The flask is then set aside for some hours in a warm place to ensure complete precipitation.

Carbon dioxide gas is next passed through the liquid until the excess of H_2S is removed. During the passage of the CO_2 the liquid is gradually heated to boiling to assist the removal of the H_2S, and to render the precipitate more dense and therefore more easy to wash.

The liquid and precipitate are poured upon a tared filter which has been dried at 100° (**86**), or are filtered by means of a Gooch crucible (**82**). The filtration is hastened by means of the filter-pump, and the precipitate is washed rapidly with hot water to which a little hydrogen sulphide solution has been added. During the washing, the precipitate is protected against oxidation by the air by covering the funnel with a round glass plate.

In order to ascertain whether the precipitation of the antimony as sulphide is complete, H_2S is passed into the filtrate and washings, and the liquid is then warmed and allowed to stand. If any further precipitate forms, it is added to the main portion already on the filter.

When the precipitation and washing are complete, the precipitate is dried in the steam-oven until its weight becomes constant. This weight is noted down.

The precipitate will still contain water and possibly free sulphur, and will therefore require further treatment before it is finally weighed. A small quantity of the precipitate is heated with strong hydrochloric acid. If it dissolves to a clear liquid, no free sulphur is present and the directions given in paragraph **196** may be followed. If the acid solution is turbid, free sulphur is present and the precipitate must be treated as is directed in paragraph **197**.

196. *In order to Remove the Water*, the greater part of the dried precipitate is weighed in a tared porcelain boat. The boat is then introduced into a piece of combustion-tube about 25 cm. in length, and a current of dry carbon dioxide gas (**1012**) is passed over it. The boat is meanwhile gently heated with a Bunsen flame until the sulphide becomes black. The boat is then allowed to cool in the current of gas, and is finally weighed.

From the weight of the anhydrous Sb_2S_3 found in this part of the precipitate, the amount of the sulphide in the entire original precipitate is then calculated, and from this result the percentage of antimony present can be ascertained.

197. *In order to Remove the Sulphur as well as the Water*, the larger part of the precipitate is weighed and is treated as is described above (196), but the boat is heated to a higher temperature, and the heating is continued until no more sulphur is volatilised and the weight is constant. Since long-continued heating will volatilise a little antimony sulphide, the treatment may be considered complete when successive weighings give a difference of one milligram only.

From the residue of pure anhydrous Sb_2S_3, the weight present in the whole original precipitate may be calculated, and from this the percentage of antimony in the original substance is found.

198. **Precipitation as Sulphide, Sb_2S_3, followed by conversion into Oxide, Sb_2O_4, and Estimation as such.**—The antimony compound is precipitated in the form of sulphide, according to the directions which have been already given (195). The sulphide is filtered off by a filter-paper which has been previously dried in the steam-oven and weighed (86). After the precipitate has been thoroughly washed, it is dried on the tared filter and weighed. The weight of the whole precipitate is thus obtained.

The precipitate is then transferred as completely as possible to a large weighed porcelain crucible, and the weight thus transferred is ascertained by again weighing the crucible. The precipitate is then moistened with several drops of strong nitric acid of 1·42 specific gravity; the crucible is covered with a watch-glass, and a quantity of fuming nitric acid of 1·5 specific gravity, sufficient to cover the precipitate, is quickly added from a pipette. For this purpose the cover is merely slipped aside to admit the point of the pipette, since violent oxidation and frothing at once sets in.

The covered crucible is heated on the water-bath, as long as any further chemical action occurs. The cover is then removed, and the acid is evaporated by heating the crucible on the water-bath. The cover is then replaced, and the crucible is finally heated over the Bunsen flame until its weight is constant.

Care must be taken that the flame does not enter the crucible, else volatile Sb_2O_3 will be formed and loss will occur. This may be avoided by placing the crucible in a circular opening cut in a disc of asbestos millboard. The disc is then inclined and the bottom of the crucible is exposed gradually to a bright red heat (98).

From the weight of Sb_2O_4 thus found, the weight of Sb_2O_4 corresponding to the whole of the sulphide precipitate is calculated, and from this the percentage of antimony is obtained.

If the antimony sulphide contains much free sulphur, this must be removed from the dried precipitate by means of carbon disulphide (193) before the treat-

ment with nitric acid is carried out, else the action of the acid will be so violent as to give rise to loss of substance.

It sometimes happens that the amount of antimony sulphide on the filter is too small to be transferred to the crucible. If this is the case, the dried filter and precipitate are treated together in the crucible with about ten times their weight of the strong acid The procedure is the same as that already described.

A Volumetric Method for estimating antimony is given in paragraph 336.

Estimation of Arsenic in Solutions containing this Element in the Arsenious Condition.

Two methods of estimation are described below.

According to the first method (**199**), the arsenic is precipitated as As_2S_3 and is weighed as such.

According to the second method (**200**), the arsenic is precipitated as $Mg(NH_4)AsO_4\ 6H_2O$, this is converted into $Mg_2As_2O_7$ by ignition, and the arsenic is weighed in this form.

199. The Arsenic is precipitated as Arsenious Sulphide, As_2S_3, and is weighed as such.

Weigh out accurately about 0·5 gram of pure resublimed arsenious oxide (**110**, Exp. 29). Place the substance in a 500 c c flask, and add about 50 c c. of dilute hydrochloric acid. Heat the flask on a water-bath until all the solid is dissolved, care being taken that the temperature of the solution does not reach 100° C., else some of the arsenic will be volatilised as chloride.

If any As_2O_5 is present, a few drops of sulphurous acid solution are added in order to convert the As_2O_5 into As_2O_3, and the flask is heated on the water-bath until all smell of So_2 has disappeared.

The liquid is then considerably diluted, and the arsenic is precipitated as As_2S_3 by passing hydrogen sulphide gas through the solution in the same manner as was described for antimony (**195**).

Carbon dioxide gas is then passed through the solution (**195**), until the smell of H_2S has almost disappeared. This tedious operation may be omitted, if great care is taken that the precipitate is kept covered and is exposed as little as possible to the air during filtration.

The liquid is poured through a tared double filter which has been dried at 100° C., or through a Gooch crucible filter (**82**), and the precipitate is washed with hot water containing a little H_2S until it is free from hydrochloric acid.

The filtrate and washings are tested by saturating the liquid with H_2S gas

and allowing it to stand, in order to make sure that all the As has been precipitated.

The precipitate is then dried at 100° C. in the steam-oven until the weight becomes constant.

Since the precipitate may still contain a little free sulphur, it should be treated with carbon disulphide (193). After this treatment the precipitate is again dried at 100°, and is finally weighed.

From the weight of As_2S_3 thus obtained, the percentage of arsenic is calculated.

200. The Arsenic in the Arsenious compound is converted into Arsenic acid; this is precipitated as Magnesium Ammonium Arsenate, $Mg(NH_4)AsO_4.6H_2O$ (169), which is then converted by ignition into Magnesium Pyrarsenate, $Mg_2As_2O_7$, and is weighed as such.

Add strong HCl to the arsenious solution, heat gently, and drop in from time to time a crystal of potassium chlorate until the liquid smells strongly of chlorine. Allow the liquid to stand in a warm place until the smell of chlorine has nearly disappeared. The arsenic will now be present as arsenic acid.

Make the solution faintly alkaline by the addition of ammonium hydrate, then precipitate by the addition of magnesia-mixture, ignite the precipitate in oxygen, and finally weigh the arsenic as magnesium pyrarsenate (169).

From the weight of $Mg_2As_2O_7$ thus obtained the percentage of As which was originally present may be calculated.

Volumetric Methods for estimating arsenic are given in paragraphs 337 and 398.

Estimation of Tin in a Stannous or Stannic Compound, and of Metallic Tin.

201. The Tin is precipitated from solution as Sulphide; this is converted by ignition in the air into the Dioxide, SnO_2, and is weighed as such.

Weigh out accurately about 0·5 gram of pure crystallised stannous chloride, $SnCl_2\,2H_2O$, which has been kept in a well-stoppered bottle. Place the salt in a 500 c.c. beaker, dissolve it in a small quantity of dilute hydrochloric acid, and make up the solution with distilled water to about 200 c.c.

Through this solution pass H_2S gas to saturation. Cover the beaker

loosely with a filter-paper, and allow it to stand in a warm place until the smell of hydrogen sulphide has almost disappeared. Transfer the precipitate to a double filter, wash it until it is free from dissolved salts, and then dry and ignite it.

Since tin alloys with platinum, a porcelain crucible should be used, and one of the methods described in paragraphs 101–105 should be chosen for the ignition of the precipitate and the incineration of the filter.

Incinerate the filter-paper apart from the precipitate. Moisten the filter-ash with two drops of strong nitric acid, heat gently until the excess of acid has been expelled, and then raise the temperature to a red heat. Allow the crucible to cool; then add the precipitate, cover the crucible with the lid, and heat it gently for some time. Then remove the lid, and heat gently until the smell of escaping sulphur dioxide is no longer perceptible, and finish by heating to bright redness (98).

In order to ensure the complete removal of the sulphur, allow the crucible to cool, add a little powdered ammonium carbonate, and heat again strongly. Repeat these operations until the weight remains constant.

From the weight of SnO_2 thus obtained, the percentage of tin in the original substance is calculated.

Volumetric Methods for estimating stannous chloride are given in paragraphs 338 and 504.

202. Metallic Tin is converted directly into Dioxide, SnO_2, by heating the Metal with Nitric Acid and igniting the product.

The tin is oxidised by heating it with moderately strong nitric acid. Hydrochloric acid must not be present, else some tin chloride will be formed and volatilised. As soon as all action has ceased, the solution is evaporated nearly to dryness on the water-bath. The residue is then diluted with water, and the white SnO_2 is filtered off, washed and dried.

If a filter-paper is used, it is burnt separately and the ash is treated with strong nitric acid as is directed above (201). The SnO_2 is then added to the filter-ash in the crucible, and the whole is finally ignited over the blowpipe until the weight is constant.

Estimation of Mercury in its Compounds.

203. Three methods of estimation are given.

By the first (204) the mercury may be separated from any solid substance which is rich in mercury, and weighed as metal. A modification of this method is described in paragraph 401, in which the mercury is separated

from its ordinary sulphide ore by being heated with iron filings; the mercury is then allowed to amalgamate a sheet of silver and is weighed with the silver.

The second method (205) proceeds by precipitating the mercury as sulphide, and weighing the sulphide. It serves for estimating mercury in the solution of a mercury compound, and for the separation of mercury from metals which are not precipitated from solution by hydrogen sulphide. It gives excellent results.

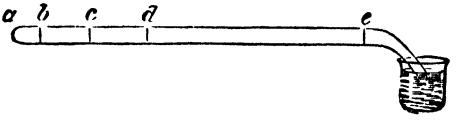
In the third method (206) the mercury is precipitated from solution of mercurous salt as Hg_2Cl_2, and is weighed as such. This method is specially suitable when nitric acid is present.

204. The Mercury Compound is decomposed by heating it with Calcium Oxide, the escaping Mercury vapour is condensed, and the metallic Mercury is weighed.

Note.—This process is not applicable to mercuric iodide, which must be decomposed by heating it with metallic copper instead of with lime. If the mercury is present as sulphide, a little metallic iron may be mixed with the lime and will greatly assist the reduction.

The process of estimation is conducted in the apparatus which is represented in Fig. 74.

FIG 74.



ESTIMATION OF MERCURY.

A piece of combustion-tube, about 1 cm. in internal diameter and about 46 cm. in length, is closed by drawing it off at one end (*a*) in the blowpipe-flame.

Powdered magnesite is introduced into the clean, dry tube in quantity sufficient to form a layer 2 inches in length (*a*-*b*).

About 1 gram of pure mercuric chloride is then accurately weighed, and is mixed intimately with powdered quicklime in a porcelain mortar. This mixture is introduced into the tube (*b*-*c*), and the mortar is rinsed out with a little more quicklime, which is also transferred to the tube (*c*-*d*). The tube is then filled in with powdered quicklime to within 5 cm. of its open end, the powder being kept in its place by pushing in a loose plug of asbestos (*e*).

The open end of the tube is now drawn out in the blowpipe-flame, the narrow tube is bent obliquely, and its end is cut off as is shown in the figure. A passage along the whole length of the tube is formed by holding the tube horizontally, and tapping it gently upon the bench. The tube is then laid

in a combustion-furnace (783) upon an iron trough covered with asbestos, and the end of the bent tube is made to dip just beneath the surface of water contained in a small weighed beaker.

The front portion of the tube (*e-d*) is now gradually heated to redness. The heat is then slowly extended to that part of the tube which contains the mercury compound, and this is heated until the whole of the tube from (*e*) to (*b*) is at a bright red heat. In this way the mercury is set free in the form of vapour, which is condensed to the liquid form as it passes into the water in the beaker.

The magnesite in (*a-b*) is finally heated to redness so as to produce a stream of carbon dioxide gas, which sweeps out the last traces of mercury vapour from the tube into the water.

While the tube is still red-hot, the narrow delivery-tube is cut off at the bend by means of a cold file, and the mercury, which has condensed in this portion of the tube, is washed out and added to the main portion in the beaker.

The globules of metal are now united into one mass by gently agitating the contents of the beaker. The water is then poured off as far as possible, and the rest is removed by absorbing it with filter-paper.

The mercury is finally rendered perfectly dry by exposure over strong sulphuric acid in a desiccator (62, 63) until its weight is constant.

The percentage of mercury present in the original substance may be calculated from the weight of mercury found.

205. The Mercury is precipitated as Sulphide, HgS, and is weighed as such.

Weigh out accurately about 0·5 gram of pure mercuric chloride into a 250 c.c. beaker. Dissolve it in about 100 c.c. of water, add a few drops of dilute hydrochloric acid, and pass hydrogen sulphide into the liquid until it is saturated. The colour of the mercury sulphide precipitate will become perfectly black as soon as the liquid is saturated with the gas.

Allow the liquid to stand for a short time, until the precipitate has subsided, then filter through a tared filter (86) or a Gooch crucible (82). Wash the precipitate quickly with cold water, and weigh it after it has been dried at 100° C.

The precipitate may contain free sulphur. It should therefore be washed with recently distilled carbon disulphide (193) until the last drops of the washings leave no residue when they are evaporated. The precipitate is then dried at 110° C. and is weighed.

From the weight of HgS obtained, the percentage of Hg in the original substance may be calculated.

206. The Mercury is precipitated as Hg_2Cl_2, and weighed as such.

If the mercury is present in solution entirely as mercurous salt, it may be at once precipitated by the addition of dilute sodium chloride solution.

But if a mercuric salt is present, this must be reduced to the mercurous condition as is directed below, before precipitating the mercury.

This process of estimation is suitable even if nitric acid is present.

For practice in the estimation, weigh out accurately about 0·5 gram of mercuric chloride, dissolve it in 200 c.c. of water, and add a little dilute hydrochloric acid and an excess of phosphorous acid (*Note*). Allow the liquid to stand for twelve hours, then filter through a tared filter or a Gooch crucible, and dry the precipitate at 100° and weigh it.

Note.—The solution of phosphorous acid may be prepared by allowing phosphorus to deliquesce in moist air; or it may be obtained by adding phosphorous trichloride to water, evaporating the solution to dryness to expel the hydrochloric acid and dissolving the residue in water.

Estimation of NO_3 in a Nitrate.

207. The estimation may be made by one of three methods. The first of these is described here: the other two processes, which are described later on, involve the application of volumetric methods to liquids and gases.

The first method (**208**) consists in heating the solid nitrate with excess of silica, and ascertaining the loss of weight which results from the removal of the elements of N_2O_5. This method is less accurate than the second and third methods.

The second method (**893**) consists in measuring the volume of NO, which is evolved when the solution of nitrate is shaken with mercury and strong H_2SO_4.

In the third method the nitrate is acted upon by nascent hydrogen, and the NH_3 thus produced is estimated (**623**).

208. The Solid Nitrate is heated with excess of Silica; the loss of weight gives the amount of the elements of N_2O_5 which the nitrate has lost.

From certain nitrates such as $Pb(NO_3)_2$, the elements of nitric anhydride may be expelled by simple ignition, an oxide of the metal remaining. In the case of most nitrates, however, such as those of the alkali-metals and of the alkaline-earth metals, it is necessary to heat the nitrate with silica, else the residue which is left after ignition is not of fixed composition.

Fuse a few grams of pure potassium nitrate in a porcelain crucible at as low a temperature as possible, and pour out the fused salt into a warm porcelain dish. Powder the solid mass while it is still warm, and place the powder in a stoppered weighing-bottle.

For practice in the process, introduce into a weighed platinum crucible about 2 grams of finely powdered quartz or silica. Ignite this, allow it to cool, and weigh it. Add about 0·5 gram of the above powdered potassium nitrate, and weigh the crucible again in order to ascertain the exact weight of the nitrate added. Then mix the powders intimately and without loss by means of a glass rod rounded at the end.

Expose the crucible, covered with the lid, to a dull red heat for thirty minutes; then allow it to cool, and weigh it. Heat it again for ten minutes, and once more weigh it. Repeat these operations until the weight becomes constant.

The loss of weight by ignition will be due to the total expulsion from the nitrate of the elements of N_2O_5. From this loss the percentage of NO_3 in the nitrate may be calculated.

Estimation of Silica in a Silicate.

209 The Silica is separated and converted into the Insoluble Form, by adding excess of acid to the Silicate and evaporating to dryness: the Silica is then rendered completely anhydrous by heat, and is weighed as SiO_2.

The method of procedure will depend upon whether the silicate can be decomposed by acid or not (**210, 211**).

210. If the Silicate is Soluble in Water, or can be Decomposed by strong Hydrochloric or Nitric acid, it is treated as is described below.

For practice in the estimation, weigh out accurately about 0·5 gram of finely powdered "soluble glass," or sodium silicate, into a platinum or porcelain dish. Moisten the powder with water. Place the dish, covered with a clock-glass, upon the water-bath; then gradually add strong HCl, through a small opening left by drawing aside the clock-glass, and constantly stir the contents of the dish.

As soon as the powder is completely decomposed, which is known to be the case when no gritty particles can be felt with the glass rod, remove the cover and evaporate the liquid to dryness. Continually stir the residue, breaking up the lumps by means of the glass rod. When the powder appears

to be perfectly dry, and no moisture is deposited on a cold clock-glass placed upon the dish for a few seconds, the dish is heated in the air-oven to 150° C. for about half an hour. The silica will now be present in the anhydrous and insoluble condition.

As soon as the dish is cold, moisten the powder with strong hydrochloric acid, and warm the dish upon the water-bath. Then add hot water, stir well, allow the solid to subside, and decant the liquid through a filter. Repeat these processes of treatment of the residue three times. Then transfer the silica to the filter, wash it thoroughly with hot water, and dry it in the steam-oven.

Note 1.—Even if the above precautions have been observed, a trace of silica will pass into solution when the residue is treated with HCl. This probably arises from the difficulty of insuring that the silica is wholly anhydrous, and from the fact that silica is appreciably dissolved by prolonged treatment with acid In very exact analyses the acid solution, after being separated from the silica residue, should be evaporated and the residue of silica should be added to that already obtained.

Now transfer the powder to the crucible as completely as possible, incinerate the filter in a platinum-wire coil, and add the ash to the precipitate (**101**). Gently heat the covered crucible, taking care that none of the light, fine silica-powder is lost by being carried off with the escaping moisture.

Gradually increase the temperature until the crucible reaches a bright red heat, and keep it at this temperature for fifteen minutes. Then weigh the crucible, and repeat the above ignition until the crucible ceases to lose in weight by being heated.

Note 2.—The silica which has been separated by the above treatment is almost invariably impure, and should be treated in the following way after it has been weighed:

The ignited silica is heated in a platinum vessel on the water-bath with pure solution of hydrofluoric acid and a few drops of strong H_2SO_4: the whole is then evaporated to dryness, and the residue is ignited and weighed This process is repeated until no further loss of weight occurs. The total loss of weight by the treatment with hydrofluoric acid represents the weight of the silica.

Since the acids may themselves contain non-volatile constituents it is well to evaporate measured portions of them alone: any residue which is left is weighed and a proportionate amount is deducted from the weight of residue found above

From the weight of silica thus found, the percentage of silica may then be calculated.

211. If the Silicate is Insoluble in Acids and is not Completely Decomposed by Acid (460), it is finely powdered and mixed with six times its weight of fusion mixture ($Na_2CO_3 + K_2CO_3$); it is then kept in a fused condition in a covered platinum crucible for about fifteen minutes (**134**). The solid is now detached from the crucible by boiling it with about

ten times its weight of water for half an hour in a covered evaporating-dish. A little strong HCl is added, and when nothing but gelatinous silica remains in the liquid, the contents of the dish are evaporated to dryness and the residue is treated as is described in paragraph **210**.

Estimation of Fluorine in a Fluoride.

212. The Fluoride is precipitated as Calcium Fluoride, CaF_2, and is weighed as such.

Three methods of procedure are described: the first (213) serves for a neutral fluoride, the second (214) for a fluoride with acid reaction, and the third (215) for an insoluble fluoride.

213. Neutral Fluorides.—To the solution of the fluoride, contained in a platinum or porcelain dish, add an excess of calcium chloride solution and heat the mixture to boiling. Allow the precipitate of calcium fluoride (CaF_2) to subside, and wash it twice by decantation. Then transfer the precipitate to the filter, wash it free from dissolved salts by means of hot water, and dry it in the steam-oven

The precipitate and filter are ignited together (99) at a red heat, and are weighed. From the weight of calcium fluoride (CaF_2) thus obtained, the percentage of fluorine can be calculated.

214 Fluorides with Acid Reaction.—The solution of the fluoride, contained in a platinum or porcelain dish, is mixed with sodium carbonate solution in excess. The mixture is heated to boiling, and is filtered if necessary. Calcium chloride solution is then added in excess. When the precipitate, which consists of a mixture of calcium fluoride and calcium carbonate, has subsided, it is washed first by decantation and finally on the filter. The precipitate is then dried, and is ignited in a platinum crucible.

The ignited precipitate is now transferred to an evaporating-dish, and is treated first with water and then with acetic acid in excess. The mixture is evaporated to dryness on the water-bath, and is ignited until it no longer smells of acetic acid. The residue, which consists of a mixture of calcium fluoride and calcium acetate, is washed with hot water until it is free from calcium acetate. It is then filtered, dried, ignited and weighed, as is described in paragraph **213**.

215. Insoluble Fluorides.—The finely powdered fluoride is heated in a platinum crucible with about four times its weight of fusion mixture ($Na_2CO_3 + K_2CO_3$), the alkaline carbonates being kept in a fused state until the fluoride is entirely decomposed (134). The cool mass is then dissolved by heating the crucible with water. The solution is filtered, if necessary, and is precipitated by the addition of calcium chloride solution in excess. The calcium fluoride in the precipitate is then estimated as is described in paragraph **214**.

Indirect Estimation of B_2O_3 in Crystallised Borax.

216. The Borate is Evaporated to dryness with Hydrochloric Acid; the Boric Acid-radicle is thus expelled and is replaced by the chemically equivalent amount of Chlorine, which is estimated in the residue.

Weigh accurately about 1 gram of pure recrystallised borax ($Na_2B_4O_7\ 10H_2O$) into a porcelain dish. Add an excess of hydrochloric acid, and evaporate the solution to dryness on the water-bath. As soon as the liquid has been driven off, add a little more hydrochloric acid, and once more evaporate to dryness Then heat the residue upon a sand-bath until no more acid fumes are given off.

Now estimate the chlorine in the solution of the residue (149, 373), and from the result thus obtained calculate the amount of B_2O_3, assuming that 35 45 of Cl is equivalent to 70 02 of B_2O_3.

Indirect Estimation of B_2O_3 in Boric Acid.

217. The solution of Boric Acid is mixed with a weighed quantity of pure anhydrous Sodium Carbonate in excess; the liquid is evaporated to dryness, and the Carbon Dioxide in the residual Carbonate is determined

Weigh out accurately about 1 gram of pure crystallised boric acid, H_3BO_3, into a 300 c c flask, and dissolve it in about 50 c c. of water. Add about 3 grams of pure anhydrous sodium carbonate, and evaporate the solution to dryness in a small weighed porcelain dish Heat the contents of the dish just to fusion, and maintain this temperature until effervescence ceases, then allow the dish to cool and weigh it.

The residue in the dish contains a known amount of sodium oxide and an unknown amount of CO_2 and B_2O_3. Determine the CO_2 (175), and find the weight of the B_2O_3 by difference The percentage of B_2O_3 may then be calculated.

A method for determining small quantities of boric acid and borate is given under Milk Analysis (675).

ELECTROLYTIC ESTIMATIONS OF METALS.

Methods have been devised for estimating many metals by electrolytic processes. Some of the more satisfactory processes of estimation are described below; they include methods for copper, nickel, cobalt and cadmium.

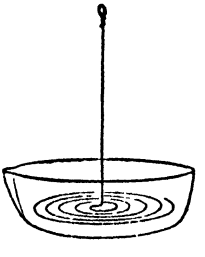
Electrolytic Determination of Copper.

218. Copper may be precipitated accurately and conveniently in the metallic state by means of the electric current. The deposition is best effected from a nitric acid solution in which the amount of the free acid present must not exceed 10 per cent. Sulphate may be present in the solution, but not chloride.

For practice in the estimation, weigh out accurately about 1 gram of pure recrystallised $CuSO_4.5H_2O$. Dissolve the salt in about 100 c.c. of water, and add 10 c.c. of nitric acid of 1·2 specific gravity.

Electrolysis of the Solution.—Now transfer the clear liquid to a weighed platinum dish of about 200 c.c. capacity, which is placed upon the bright metal ring of a retort stand. Twist a stout platinum wire into a flat spiral, leaving about 15 cm. in the centre projecting at right angles to the plane of the spiral (Fig. 75). Attach the spiral to a glass rod, which is clamped upon the retort stand then immerse it in the solution, taking care that there is no metallic contact between the platinum wire and the dish. The spiral should be about 0 3 cm. from the bottom of the dish.

Fig. 75.



Electrolytic Estimation of Copper.

Instead of the spiral, a disc of thick platinum foil, riveted to a long stout platinum wire, may be used.

Now connect the dish with the negative terminal of a storage battery, or of two or three Daniell's cells. This is readily done, since the dish is in metallic connection with the retort stand; it is therefore simply necessary to attach the battery wire to the ring or to the stand, taking care that the surfaces in contact are bright and metallic. The platinum wire from the spiral or disc is then connected with the positive terminal of the battery.

A current of 0 2 to 0·5 ampere and an electromotive force of from 2 to 2·5 volts will be suitable.

During the deposition of the metal, the dish must be covered by a perforated clock-glass, or by an inverted funnel. This prevents the loss of any liquid by the spirting which is caused by the evolution of gas from the surface of the spiral.

The under surface of the cover should be rinsed into the dish during the latter part of the process.

In about twelve hours or less the copper will be completely precipitated, and will adhere to the inside of the platinum dish. The process requires no supervision after it has been started, and may therefore be allowed to proceed during the night.

Weighing the Copper.—As soon as a few drops of the liquid from the dish give no coloration with H_2S solution, the dish is quickly rinsed out first with water, then with alcohol, and finally with a little ether. It is then dried in the steam-oven for a short time and weighed. From the increase of weight of the dish, the percentage of copper is calculated.

Note—The copper may afterwards be removed from the dish by dissolving it in nitric acid.

Electrolytic Estimation of Nickel and Cobalt.

219. Nickel should be precipitated from an ammoniacal solution by means of the electric current: the sulphate or chloride may be used but not the nitrate. The solution should contain ammonium sulphate and free ammonia and for every 0·2 to 0·3 gram of nickel present, about twenty times its weight of ammonium sulphate and 30 to 40 c.c. of strong ammonia solution should be added. The solution is then made up to about 150 c.c., and is electrolysed by a current of 1 to 1·5 amperes and an electromotive force of about 3 volts.

For practice in the estimation, weigh out accurately about one gram of nickel ammonium sulphate, $Ni(NH_4)_2(SO_4)_2.6H_2O$, and dissolve the salt in water: add 3 grams of Am_2SO_4 and 20 c.c. of strong ammonium hydrate solution. Make up the solution to about 100 c.c. and transfer it to a platinum dish. Then connect the solution and the dish respectively with the terminals of a storage battery, and allow the current mentioned above to pass through the solution for several hours.

A dark brown deposit first forms: this disappears, and afterwards an adherent metallic deposit of nickel is formed. If the deposit is not bright and adherent the rate of deposition must be reduced by diminishing the strength of the current.

As soon as a drop of the liquid no longer gives a brown coloration with ammonium sulphide solution, the nickel is known to be completely deposited from the solution and the operation is complete.

When this is the case, the dish is disconnected, and the nickel deposit is washed first with warm water, then with alcohol, and finally with ether: it is then dried in the steam-oven for a short time and weighed.

220. Electrolytic Determination of Cobalt.—The electrolytic deposition of cobalt is carried out under exactly the same conditions as that of nickel (219), and the estimation yields an accurate result.

For practice in the estimation, one gram of pure, freshly recrystallised cobalt sulphate, $CoSO_4 7H_2O$, may be used.

Electrolytic Determination of Cadmium.

221. The solution containing the cadmium as sulphate is made just alkaline by addition of pure sodium hydroxide solution. Pure potassium cyanide solution is then gradually added with constant stirring, until the cadmium hydroxide, which was previously precipitated by the sodium hydroxide, has been just redissolved.

The volume of the liquid is then made up to 100 c.c. with water, and is electrolysed in a platinum dish at first for six hours with a current of 0·5 ampere and an electromotive force of 5 volts, then finally for another hour with an increased current of 1 ampere (*Note*).

The solution is now tested for cadmium by taking off a little by a pipette, heating it with dilute HCl until HCN is expelled, and passing H_2S. If no yellow coloration or precipitate is produced, the deposition of the metal is complete: but if cadmium is found in the test portion, the liquid must be electrolysed for an hour longer and tested again.

When all the cadmium is deposited, wash the metal with water, and then with alcohol and with ether, dry it for a short time in the steam-oven and weigh.

Note.—If the stronger current were used from the start the cadmium would be deposited in the spongy state at first, and not as a silvery white film. But the process may be shortened by increasing the current later on, without altering the character of the deposit.

PART III.

VOLUMETRIC ANALYSIS.

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240. Introductory Remarks.—In the processes of volumetric analysis, volume is determined instead of weight. Volumetric methods are usually applicable only to fluids. The mobility of a fluid enables it to adapt itself to a measuring-vessel, whilst the rigidity of a solid renders this adaptation impossible. Hence the weight of a solid is usually more easily determined than its volume.

Since both liquids and gases may be dealt with volumetrically, volumetric analysis is divided into two branches, the one treating of liquids and the other of gases. The expression "volumetric analysis" is, however, generally applied to liquids only; the term "gas analysis" being usually applied to the estimation of gases.

Advantages of Volumetric Methods.—The ordinary chemical reactions, upon which analysis depends, occur only when one at least of the reacting substances is in the liquid condition. Since liquids have, therefore, to be dealt with during the analysis, a great saving of time may usually be effected, by carrying on the processes in such a way that measurement of volume may, as far as possible, take the place of weighing.

This economy of time is effected by dissolving a known weight of a substance in a known volume of water. If a known fraction of this solution is then measured off, it will contain a corresponding fraction of the weight of the dissolved solid; accordingly the weight of solid present in this portion of the liquid is known without any further weighing. An additional advantage gained by this method of procedure is, that minute quantities of substance can be dealt with which could not possibly be weighed. Hence it will be seen that volumetric methods will in certain cases surpass gravimetric methods in accuracy and in delicacy.

Illustration of a Volumetric Determination.—The estimation of chlorine, present as chloride in neutral solution, will serve as an illustration of volumetric methods. The chloride is precipitated as silver chloride by the addition of silver nitrate solution, thus: $NaCl + AgNO_3 = AgCl + NaNO_3$.

The completion of this change is made evident by causing it to take place in the presence of potassium chromate solution. As soon as the silver nitrate is added in excess, it produces a permanent dark red precipitate of silver chromate, so that the appearance of a slight red coloration throughout the liquid indicates the completion of the reaction.

In a special estimation of chlorine present as chloride, the solution of silver nitrate which was added contained one-tenth of the molecular weight of silver nitrate, or 16·994 grams per litre. Hence, according to the above equation, each cubic centimetre of the silver nitrate solution would precipitate 0·003545 gram of chlorine from the chloride. Of this silver nitrate solution 22·5 c.c. were required to exactly precipitate 2 grams of the substance dissolved in water. Therefore the weight of chlorine in the substance = $22{\cdot}5 \times 0{\cdot}003545 = 0{\cdot}07976$ gram, and the percentage weight of chlorine in the substance $= \frac{0{\cdot}07976 \times 100}{2} = 3{\cdot}99$.

Standard Solutions.—It will be seen from the preceding example that the solutions employed in volumetric analysis are required to be of known strength. Such solutions are commonly termed "*Standard Solutions.*"

Indicators.—It will also be noticed that some visible indication of the termination of the reaction is necessary.

In certain cases this is furnished by a marked change in colour, as when potassium permanganate solution is added to warm acidified solution of oxalic acid: the colour of the permanganate is destroyed in this reaction, and a permanent pink tint in the liquid therefore indicates the presence of permanganate in excess, and proves that the reaction is completed.

In the majority of estimations, however, it is necessary to employ a third substance, which, by producing a change of colour, serves as an "*Indicator*" of the completion of the reaction. An illustration of this is furnished by the use of potassium chromate in the example already given.

Reciprocity of the Process.—The above process may evidently also be utilised for the estimation of silver. For silver, when present in solution, may be estimated by adding its solution to standard sodium chloride solution in the presence of potassium chromate. This reciprocity is generally true of a volumetric process.

In the following Description those processes of volumetric analysis are generally grouped together in which the same liquid reagent or "Standard Solution" is employed. The most important and typical processes in each group are printed in ordinary type. Processes which are similar in principle

to these, or are of less importance, are printed in smaller type. For additional methods of estimation, the student may consult *Sutton's Volumetric Analysis*, *Fresenius' Quantitative Analysis*, and *Treadwell's Quantitative Analysis*.

As a rule, each estimation which is made for practice in the method must be performed in duplicate, so as to check the accuracy of the result, since the substances which are used are not generally of known and definite composition.

PART III.—SECTION V.

MEASUREMENT OF LIQUIDS. CALIBRATION AND USE OF GRADUATED VESSELS. INDICATORS. STANDARD SOLUTIONS.

The Measurement of a Liquid

241. The Measurement of a Liquid may be undertaken for two different purposes.

(1) It may be required to ascertain the volume of the liquid. This is effected by pouring the liquid into a suitably graduated measuring-vessel. The liquid is said to be "measured," after its volume has been noted.

(2) It may be required to obtain a known volume of the liquid. The liquid is then delivered from a suitably graduated measuring-vessel in precisely the requisite quantity. This is termed "delivering" the requisite volume of liquid.

242. The Graduated Glass Vessels which are used for measuring liquids are therefore adapted either to "measure" or to "deliver" definite volumes of liquid.

Vessels of both classes are frequently marked with the temperature at which the liquid is to be measured in them. This temperature is usually 15·5° C., which is equivalent to 60° F. Careful attention to this uniformity of temperature is absolutely necessary when strict accuracy is required, since the volume of a liquid undergoes appreciable alteration by variations of temperature.

243. Absolute Volume.—It should be noted that measuring-vessels are sometimes graduated according to the absolute unit. The cubic centimetre unit which is adopted for the measuring-vessels hereafter described is slightly larger than the absolute cubic centimetre, since the absolute c.c. is the volume of 1 gram of water at 4° C., and the c.c. in the measuring-vessel represents the volume of 1 gram of water at 15·5° C. But since the measuring-vessels are only used for ascertaining the *relative* and not the *absolute* volumes of liquids, no error is introduced if the vessels correspond one with another in the value of their graduations. In order to calibrate in absolute volume at ordinary

temperatures, the weight of water, whose volume at the given temperature is equal to the absolute c.c., must be calculated, and this weight must be substituted for one gram. A correction to absolute volume can be applied from the known expansion of water at different temperatures, which is given in a special Table (982). Thus, if a flask contains 250 grams of water at 15·5°, its capacity in absolute c.c.s will be 250 × 1·00097 = 250 2425 c.c.

Since the absolute c.c. is used in the measuring-vessels employed for gas analysis, the vessels used for gas analysis do not agree in their measurements with those used for liquids. The above correction can, however, be applied, if necessary, to render the volumes comparable.

The temperature of 15·5° has been selected as the average temperature of the laboratory in this country, but Mohr recommended for his volumetric system the temperature of 17·5° C. as more nearly representing a mean value. Any other temperature, which is convenient under special conditions, may be selected; but it must then be employed during the calibration and use of the whole series of measuring-vessels.

244. Relation of Weight to Volume.—It should be remembered also that when ordinary measuring-vessels are used for pure water at 15·5°, the number of c.c. which they indicate will represent the weight of the water in grams. In the case of a liquid of relative density different from water, the number of c.c. read off must be multiplied by the relative density of the liquid, in order to obtain the weight of the liquid in grams.

245. Measuring and Delivering.—A horizontal line, etched upon the measuring-vessel, indicates its capacity to that particular level. In a vessel which is intended both to measure and to deliver liquids, the capacity must be indicated by two marks. One of these serves to *measure* the volume of a liquid, and the other to *deliver* the same volume. The latter will in every case correspond to a larger volume, since a portion of the liquid remains adhering to the inside of the vessel.

246. Reading the Volume.—The vertical section of the surface of a liquid in a tube is a curve or meniscus (Fig. 80, p. 142). It is usual to read the lowest point of the surface-meniscus in measuring the volume of a liquid.

Great care must be taken that the measuring-vessel is placed in a truly vertical position while the volume of the liquid is being read.

247. Calibration of Measuring-vessels.—Each measuring-vessel should be "calibrated," or its accuracy tested, by weighing or measuring a definite amount of water in it at 15·5°. This calibration must be made in a room as nearly as possible at the temperature of 15 5° C., and the process must be

carried on rapidly and without interruption, in order to guard against alteration of volume and loss of water by evaporation.

If it is desired to calibrate the measuring-vessel in absolute c.c.s, the weight of the requisite volume of water at 15·5° to be introduced into the flask must be calculated. Thus, for a 250 c.c. flask, the weight of water at 15·5° to be introduced would be 250 × 0·999081 = 249·77 grams. The above factor is the density of water at 15·5°, as is shown in the special Table (982).

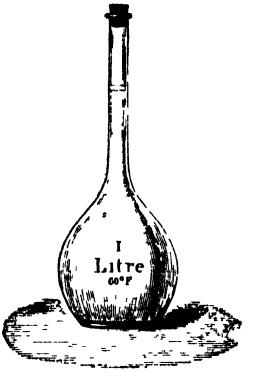
Measuring-vessels are of various forms. Some of these are described below.

THE MEASURING-FLASK.

Note —The measuring-flask is used for obtaining a known volume of liquid. A graduated measuring-cylinder (259) may often replace the measuring-flask.

248. Measuring-flasks graduated for 1 litre (1000 c.c.), for ½ litre (500 c.c.), for ¼ litre (250 c.c.), for 200 c.c., and for 100 c.c., will be found convenient for general use. The level at which the upper surface of the liquid stands must be in the neck of the flask (Fig. 76), and the neck should be narrow to ensure accurate readings.

FIG 76.



THE LITRE FLASK.

Two marks are usually etched upon the neck of the flask, one for measuring and the other for delivering the volume which is marked on the flask (245). When the flask is filled to the lower mark it contains the stated volume ; and when it is filled to the upper mark, the stated volume can be poured out or delivered from the flask.

249. Calibration of the Measuring-flask.— Before a measuring-flask is used, it is well to ascertain whether it holds or delivers exactly the volume which is marked upon it. The following methods, by which the weight of water contained in or delivered by the flask is ascertained, serve to calibrate the flasks for measuring and delivering respectively. The results obtained from the different vessels bear a correct relation to one another.

It must be remembered, however, that the volume of air which is displaced by a large quantity of water, is considerably greater than that which is displaced by the weights which counterpoise it. Hence it becomes necessary to apply a correction to the weight of the water, as is explained in paragraph 13, if great accuracy is required.

250. Calibration of a Flask for Measuring.—The flask is first thoroughly cleansed and dried (**255**, *Note*). It is then placed upon the left-hand pan of a fairly large balance, sensitive to one decigram, and is counterpoised by shot or by weights placed in the other scale-pan.

A weight in grams, equal in value to the number of c.c which the flask should measure, is then placed with the counterpoise on the pan. Thus a quarter-litre flask would require 250 grams to be placed on the scale-pan.

The flask is now removed and placed upon a level surface, and distilled water at 15·5° is poured into it, until the graduation-mark on the neck is exactly touched by the lowest point of the meniscus of the water-surface. The neck of the flask is then carefully dried by means of filter-paper, and the flask is replaced upon the empty pan of the balance. If the balance is now in exact equilibrium, the graduation of the flask is correct, and no further trouble need be taken (**247**).

If the balance is not in equilibrium, one of two courses may be adopted. Either the flask may be regraduated correctly (**251**), or the requisite correction may be applied each time the flask is used (**252**). The latter course is the less convenient in practice.

251. A Correct Graduation is obtained by increasing or diminishing the quantity of water in the flask, until equilibrium is obtained. The flask is then again placed upon a level surface, and a scratch is made on the neck, with a diamond or with the point of a hard file, on a level with the lowest point of the meniscus. This will give the true graduation for measuring.

252. The Correction to be Applied to the Flask is ascertained as follows: The flask, filled exactly to the mark (**250**), is placed upon the left-hand pan of the balance, with the counterpoising weights in the other pan, as has been already described. Equilibrium is then secured by adding the requisite weights to one of the pans. The value of these weights in grams is taken as representing the same number of c.c. This volume must be added to the volume marked on the flask, if the additional weights have been placed upon the counterpoise pan: and the volume must be subtracted from that of the flask, if the additional weights have been placed on the same pan as the flask. The corrected capacity of the flask thus obtained should be marked upon it by means of a diamond or a pointed file.

253. Calibration of a Flask for Delivering.—The flask is filled with distilled water to the graduation on its neck. The water is then poured out, and the flask is allowed to drain in an inverted position for a known time, say fifteen seconds. The flask, with its interior still wet, is now placed upon one pan of the balance, and its neck is closed by the stopper or by a rubber cork to prevent loss of weight by evaporation. The flask is then exactly counterpoised by weights or by shot, and weights are added whose volume in grams is equal to the number of c.c. which the flask is marked to deliver.

The flask is then placed on a level surface, and is accurately filled to the delivering-mark. It is then replaced upon the pan together with the stopper. If the balance is now in equilibrium, the flask was correctly graduated. If equilibrium is not produced, a correction must be applied (251, 252). This corrected volume will be delivered by the flask, when it is accurately filled to the delivering-mark and is allowed to drain for fifteen seconds after pouring out the liquid.

EXPERIMENT.—Calibrate a quarter-litre flask in the manner described above (250–253), so as to measure and to deliver 250 c c If the measuring-flasks of different capacities have not been already calibrated, they may be treated in the same way before they are used.

THE PIPETTE.

254. The Pipette is a tube which is adapted to deliver smaller fixed quantities of liquid than measuring-flasks do, or to deliver varying small volumes of liquid. A pipette for delivering a fixed volume is shown in Fig. 77, and another for delivering varying quantities in Fig. 78.

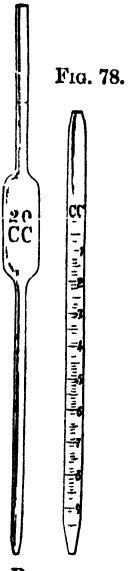
FIG. 77.

The pipette must be narrow at each end. The liquid is introduced by applying suction from the mouth at the upper end, while the lower end is dipped into the requisite liquid. The liquid is thus raised to a higher level than the graduation. The upper end is then rapidly closed by the end of the first finger; and by carefully relaxing the pressure of the finger, the liquid is allowed to flow out below, until the lower curve of the meniscus just reaches the required graduation.

If the pipette has only one graduation, the measured volume may now be delivered into any vessel by removing the finger, and allowing the pipette to empty itself and then to drain for fifteen seconds with its end touching the inside of the vessel.

If the pipette is graduated throughout its length, a certain fractional quantity of its entire contents may be delivered by carefully relaxing the finger-pressure until the requisite quantity only has flowed out.

FIG. 78.



PIPETTES.

255. Calibration of the Pipette.—The process of calibrating, or testing the accuracy of a pipette, may be carried out as follows.

Note —The pipette itself and more especially its interior, must be scrupulously clean for the purpose of calibration, and if this is not known to be the case, it

should be treated as is described below. Any trace of greasy matter will cause drops of water to be left on the inner surface of the pipette after it is emptied, and will give rise to error. Grease may be removed by filling the pipette with moderately strong potassium hydrate solution and allowing it to flow out again in about five minutes. The pipette is then rinsed out several times with water, and is filled with a warm solution of potassium dichromate in concentrated sulphuric acid: after five minutes this is allowed to flow away and the pipette is then repeatedly rinsed out with distilled water.

The clean and dry pipette is first provided with an arrangement for closing its delivering end, so that it may be weighed while it contains water.

This may be simply effected by stretching a strip of thin rubber sheet, about 10 cm. in length and 0·5 cm. in width, over its lower end. An ordinary rubber ring of the proper dimensions, if cut across at one part, answers very well. The middle of the strip is pressed against the tip of the pipette so as to close it, and the strip is retained in position by drawing its free ends up on opposite sides of the pipette. The ends are then fastened down, while the strip is in a state of slight tension, by twisting a piece of copper binding-wire over them and round the pipette-tube. The band thus forms an elastic loop, which can be stretched over the tip of the pipette and will effectually close it.

The rubber loop having been drawn aside, the pipette is filled up to the graduation with distilled water by suction, and its lower end is externally dried. The water is then allowed to flow out, and the pipette is permitted to drain for fifteen seconds in an erect position, with the tip touching the inside of the beaker. The pipette is now held in a horizontal position, and the rubber-loop is stretched over its tip. It is then laid upon the pan of an open balance, and is accurately counterpoised without delay.

The pipette is then held in an upright position, and distilled water at 15·5° is introduced from a long and fine jet of a wash-bottle into the top of the pipette, until the lowest point of the surface meniscus of the water just touches the graduation-mark. The water-level may be adjusted, if necessary, by means of a piece of glass tube drawn out into a long slender capillary; this is pushed down the pipette, and by its means water can be readily either introduced or sucked out, as may be necessary.

As soon as the pipette is exactly filled, it is once more laid upon the scale-pan. A weight in grams, equal in value to the number of c.c. the pipette should deliver, is now added to the counterpoise of the empty pipette (247). If this produces exact equilibrium, the pipette is correctly graduated.

If the balance is not in equilibrium, the quantity of water in the pipette is gradually increased or diminished by means of the drawn-out tube until equilibrium is obtained. A file-mark is now made at the bottom of the water-meniscus, and this will furnish the correct graduation.

An alternative method, if the pipette is found to be incorrect, is to ascer-

tain its true delivering capacity (252), and to consider this as the volume which it delivers.

Another Method which gives satisfactory results consists in filling the pipette up to the mark with distilled water at 15·5° C., allowing the water to flow out into a weighed stoppered flask, and then weighing the flask. From the weight of the water thus obtained, the delivering capacity of the pipette is then calculated.

Occasionally pipettes of large capacity are used. In calibrating these, attention to the correction described in paragraph 13 is necessary, if absolute measurement is required.

EXPERIMENT.—A 25 c.c. pipette may be calibrated as is described above. All the pipettes which are to be used should be similarly calibrated if they are not known to be correct.

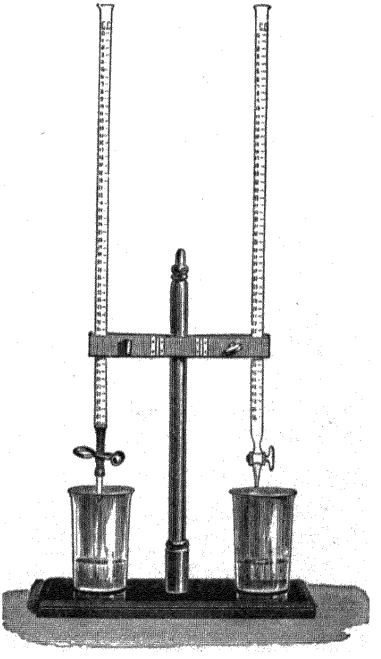
THE BURETTE.

256. The Burette differs mainly from the graduated pipette by being open to atmospheric pressure at the top while it is in use. The outflow of liquid from the lower end is started, regulated and arrested by means of a glass tap or a suitable clamp.

The burette (Fig. 79) is a tube of uniform diameter throughout its graduated part. It will be found convenient to shape the top of the burette into a small conical funnel: this may be effected by softening the glass in the blowpipe-flame, and opening it out by means of a conical piece of charcoal. The lower end is considerably narrowed, and may be closed by means of a glass tap or by a pinch-cock which presses upon a rubber joint.

The burette is graduated into cubic centimetres and fractions thereof, and may contain 20, 50, or 100 c.c. Those in general use have a capacity of 50 c.c., each c.c. being divided into tenths.

FIG. 79.

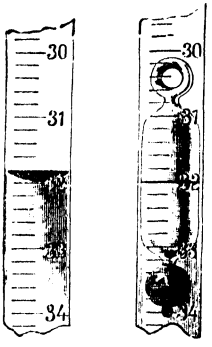


BURETTES.

The burette is usually filled by closing its lower end and pouring in liquid, from the top. The liquid should rise above the highest graduation, and should then be allowed to flow out from below until the lowest point of the meniscus just touches this graduation (Fig. 80).

In filling the burette great care must be taken that no air-bubbles are left in the tap or jet, since when the burette is in use, it is assumed that *liquid only* passes out. The volume of any air-bubble which is swept through would be counted as so much liquid, since the volume of liquid which is assumed to have flowed out of the burette is measured by the fall of the liquid surface.

FIG. 80. FIG. 81.



MENISCUS.

The burette is supported by being clamped in a convenient stand (Fig. 79). It should not be held in the hand after it is filled, else error is introduced by the expansion of the liquid contents, owing to the heat imparted by the hand.

In reading the position of the liquid surface against the graduations, the eye should always be in the same horizontal plane as the liquid surface, in order that errors of parallax may be avoided.

Various forms of float may be used to facilitate the process of reading. The Erdmann float (Fig. 81) is slightly smaller in diameter than the burette, and carries a horizontal mark upon its middle. The float keeps uniformly immersed in the liquid and rises and sinks with it, if the interior of the burette is perfectly clean (*Note*, 255). The graduation on the burette, which corresponds with the mark on the float, is read off as the level of the liquid surface.

If the float is not employed, the meniscus curve of the liquid surface in the burette may be shown with a sharp black outline by holding a card in an inclined position behind the burette and near the surface of the liquid.

If the liquid in the burette is very dark in colour, its upper surface may be read without difficulty.

257. Calibration of the Burette.—The perfectly clean burette (*Note*, 255) is filled with distilled water at 15·5° C., and the tube below is carefully freed from air-bubbles. The calibration is then effected by allowing successive quantities of water, of 5 c.c. each, to flow into a tared stoppered flask or weighing-bottle. The weight in grams of each portion of water should be exactly equal to the volume of the water in c.c. as indicated by the burette, due allowance being made, if necessary, for the expansion of the water (247).

258. If the reading of the burette is found to be inaccurate, a table should

be drawn up showing its true capacity up to each graduation: the error between two successive weighings being distributed equally between the graduations which are included in the 5 c.c. interval.

Thus, in calibrating from 0 to 10 c.c. on a burette, the following weights of water were obtained. From 0 to 5, 4·9549 grams; and from 5 to 10, 4·9781 grams. The first c.c. division on the burette therefore corresponds to $\frac{4·9549}{5}$ = 0·99 c.c.; the second division corresponds to 0·99 × 2 = 1·98 c.c., and so on for the first five divisions. Similarly the sixth division will contain $\frac{4·9781}{5}$ = 0·996 c.c. Therefore the first six divisions of the burette will contain 4·95 + 0·996 = 5·946 c.c.; and seven divisions will contain 5·946 + 0·996 = 6·942 c.c.

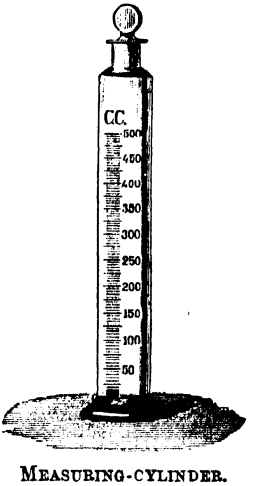
Another method is to draw a curve upon squared paper. The graduations of the burette should be plotted horizontally and the volumes vertically. The true value of any graduation can then be obtained from the curve.

EXPERIMENT.—A 50 c.c. burette may be calibrated in the above manner. All burettes may be similarly tested before being used.

THE MEASURING-CYLINDER.

259. Measuring-cylinders of thick glass often usefully supplement, or replace, the measuring-flasks. Since the upper surface of the liquid in the cylinder, however, is greater than that in the flask, the accuracy of the reading is diminished by using the cylinder.

FIG. 82.



MEASURING-CYLINDER.

The cylinder is usually graduated throughout the greater part of its length, the successive graduations indicating from 1 to 10 c.c. each according to the diameter of the cylinder. The cylinder may be graduated either for measuring or delivering the liquid (245).

Measuring-cylinders are of two kinds. One kind is narrowed at the top, and can be closed by a clean rubber cork or by an accurately ground stopper (Fig. 82). This form is convenient for shaking and mixing the liquid contents without risk of loss. The other kind of cylinder is open at the top, and is furnished with a lip for pouring out.

260. Calibration of the Measuring-cylinder.—A cylinder for measuring liquids is most rapidly calibrated by allowing water to flow into it from a previously calibrated burette. If the graduations are not correct, it will be necessary to construct a table in which the true value of each graduation is shown, as is described above in the case of the burette (258).

If the cylinder is graduated for "deliver ng," the interior must be wetted (253) before applying the above process.

EXPERIMENT.—A quarter-litre cylinder may be calibrated as is directed above, adding 10 c c from the burette each time All other measuring-cylinders may be calibrated in this way before they are used.

AGREEMENT OF MEASURING-VESSELS WITH ONE ANOTHER.

261. It is necessary to ascertain that all the different measuring-vessels agree one with another in the value of their graduations.

For most purposes of volumetric analysis it is not necessary that each vessel should be absolutely accurate, when it is tested by weighing distilled water in it at a standard temperature. It is sufficient that the relative value of the measurements given by the different vessels should correspond. This relative correspondence is absolutely necessary.

Thus two quarter-litres when delivered into the half-litre measuring-flask must fill it to its graduation; and the 50 c.c. pipette, when its contents are emptied five times in succession into the quarter-litre measuring-flask, must exactly fill it to its graduation.

Evidently the application of a strictly accurate system of correction to all the vessels by water-calibration will ensure this relative accuracy. By proceeding as is suggested above, the correctness of the previous calibration can be ascertained.

INDICATORS USED IN THE VOLUMETRIC ESTIMATION OF ACIDS AND OF ALKALIS.

262. Indicators which are required for special purposes will be described hereafter. The following indicators serve to show the approach, and finally the attainment, of the point of neutralisation when an acid and alkali are mixed.

263. General Caution in using Indicators.—It should be remembered that when the completion of a reaction is ascertained by means of an indicator, or by means of any final colour-change, it is necessary that the one

liquid should be added to the other in all cases in the same order, else the results which are obtained will usually not exactly correspond with one another.

Thus if litmus is used as an indicator while an acid is being added to standard caustic alkali solution, the acid should if possible be added to the alkali and not the alkali to the acid, in all processes of estimating acid by the alkali in the presence of litmus.

It is further to be noted that the solutions should be of fair concentration and of approximately equivalent strength. Undue dilution causes some of the indicators to undergo hydrolytic dissociation, and this prolongs the end reaction; but dilution in any case tends to prevent a sharp result being obtained.

The attainment of the point of neutralisation is rarely absolutely correct. Thus methyl-orange (268) is more sensitive towards alkalis than it is towards acids, nevertheless it is usual to take the change from yellow (alkali) to pink (acid) because the eye more readily detects this change of colour than the converse change.

264. Litmus Solution.—This solution is used both for acids and for alkalis. It is most sensitive when it is of a purple colour. The presence of most free acids causes the litmus to assume a bright red tint: the presence of free alkali produces a pure blue tint. The solution may be prepared as follows.

Digest about 10 grams of solid litmus with about 250 c.c. of distilled water for a few hours in a warm place. Decant the clear liquid from the residue, and add dilute nitric acid in sufficient quantity to change the colour of the solution to distinct purple.

A More Sensitive Litmus Solution may be made as follows: Extract all the colouring-matter from the solid litmus, by repeatedly digesting it with hot water. Evaporate this solution to a moderate volume and convert all carbonates present into acetates by adding a slight excess of acetic acid. Again evaporate the solution over a water-bath until it becomes pasty, and then add an excess of methylated spirit. The spirit will precipitate the blue colouring-matter, while a red colouring-matter, together with the alkaline acetates, will remain in solution. The precipitate is transferred to a filter, and is washed with spirit. It is then dissolved in warm water, and the solution is rendered purple by the cautious addition of dilute nitric acid.

Litmus solution should be kept in a corked bottle, the cork being deeply grooved, in order to allow free access of air to the contents of the bottle. Even when this precaution is taken, the colour of the liquid gradually fades. The colour may usually be restored, however, by exposing the solution to the air in an open dish.

Small quantities of this solution may be conveniently transferred to the solutions which are to be titrated, by means of a small pipette made by

drawing out a piece of glass tube at one end. The pipette is fitted into a perforation in the cork, which is in the neck of the store-bottle.

When some litmus solution is to be removed, the narrow end of the pipette is immersed in the liquid, and the upper end is closed by the finger. By this means the requisite quantity of liquid can be taken out. If definite quantities of the solution are to be used, file marks may be made on the tube to denote the volumes. The pipette may be marked for the delivery of 2 c.c., 1 c.c., and 0·5 c.c.

The presence of free carbonic or boric acid in solution changes the blue colour of litmus to reddish purple. Accordingly when an acid solution is added to an alkaline carbonate, the litmus solution acquires a reddish tint, before the point of neutralisation of the carbonate by the acid is arrived at. The error which would arise from this source is prevented by removing the carbonic acid by boiling the liquid. The point of neutrality is known to have been just passed, and the reaction is therefore complete, when the solution has assumed a bright red colour which does not change when the liquid is boiled.

Litmus solution indicates correctly mineral acids and strong organic acids such as oxalic acid. It may also be used for alkalis, alkaline carbonates, alkaline hydroxides and ammonia. Its indications are not interfered with by the presence of ammonium salts.

265. Litmus-paper.—A moderately strong solution of purple neutral litmus solution (264) is prepared, and strips of glazed paper are drawn through it. The strips are hung up to dry in a room free from acid fumes. Ordinary glazed paper produces a more sensitive test-paper than filter-paper does.

266. Cochineal Solution.—The colour of the solution is yellow, and this is turned to reddish violet by alkalis. The reddish violet solution of cochineal is changed to yellow again by mineral acids, but is not easily affected by weak organic acids. The solution should not be used in the presence of compounds of iron or of aluminium, or of acetates.

This indicator is not affected in colour by carbonic acid. It also possesses the advantage over litmus that the change of colour produced by free acid can be more readily seen by artificial light and in the presence of coloured organic matter.

The solution is prepared by digesting about 10 grams of powdered cochineal for several hours at a gentle heat in a litre of weak spirit, made by mixing 200 c.c. of methylated spirit with 800 c.c. of water. The clear liquid is decanted from the sediment, and is then ready for use.

267. Turmeric-paper.—The yellow colour of this paper is changed to reddish brown by alkalis. Since turmeric is gradually bleached by exposure to daylight, the test-paper should be kept in the dark.

The paper is prepared as follows. Powdered turmeric-root is digested two or three times with small quantities of water. This treatment removes some objectionable inert colouring-matter. The active colouring-matter is then extracted by digesting the powder with methylated spirit, which has been diluted with twice its volume of water. Strips of filter-paper are drawn through the clear solution thus obtained, and are hung up to dry in the air with as little exposure to daylight as possible.

Turmeric-paper may be used as an indicator in estimating CO_2 in air by Pettenkofer's method (912).

268. Methyl-orange.—This substance is also known as Tropaeolin D, or Orange III. In alkaline solution its colour is yellow, but this colour changes to red on the addition of a mineral acid. The change of colour is not produced by carbonic acid or other feeble acids. Hence this indicator may be used for the titration of the more powerful mineral acids in the presence of carbonic acid and the feebler organic acids.

The presence of much water causes the red colour of a faintly acid solution of methyl-orange to become yellow This is probably due to hydrolytic dissociation Care must therefore be taken that the concentration of the solution under titration is about the same as that of the standard acids and alkalis used.

The solution is prepared by dissolving 1 gram of methyl-orange in a small quantity of methylated spirit, and making the solution up to a litre with methylated spirit which has been diluted with its own volume of water. The solution does not decompose or undergo change by being kept.

269. Phenol-phthalein.—The solution of this indicator in alcohol is colourless. When a few drops are added to the solution of an alkali, the liquid assumes an intense red colour: this colour is readily destroyed by the addition of an excess of either mineral or organic acid. Phenol-phthalein is suitable for the titration of inorganic and organic acids and of strong bases, but it cannot be used in the presence of carbonic acid, or of ammonium salts; it is therefore not suitable for titrating ammonia by an acid.

The presence of free CO_2 in ordinary distilled water causes a slight error, which should be allowed for, particularly if decinormal acid solution is used.

Concentrated solutions of alkaline hydroxide do not give a red colour with this indicator; such solutions should therefore be previously diluted with water.

The solution is prepared by dissolving 0 2 gram of pure phenol-phthalein in 60 c c. of rectified spirit, adding 40 c c. of water, and then filtering if necessary.

Standard Solutions.

270. Standard Solutions.—The solutions of definite strength which are used in volumetric analysis are termed *Standard Solutions*. A standard solution may be made of any strength, which is suitable for the particular estimation to which it is applied.

271. Normal Solutions.—A standard solution is said to be of *Normal, or Equivalent Strength*, when 1 litre contains the equivalent weight in grams of an element, acid, alkali, or salt.

By the term equivalent is understood the weight in grams of the substance which is chemically equivalent to 1 gram of hydrogen, to 40·06 grams of NaHO, to 36·46 grams of HCl, or to 53·05 grams of Na_2CO_3.

Thus a normal solution of KOH contains 56·16 grams of the solid substance per litre, and a normal solution of HNO_3 contains 63·02 grams of the acid in the litre. But the normal solution of Na_2CO_3 will contain only $\frac{106 \cdot 1}{2} = 53 \cdot 05$ grams of that salt per litre, since two molecules of monobasic hydrochloric acid are required to neutralise one molecule of sodium carbonate. Similarly the normal solution of dibasic sulphuric acid will contain only $\frac{98 \cdot 08}{2} = 49 \cdot 04$ grams per litre.

The capital letter N is used to denote a normal solution. A solution of one-half the normal strength is termed a *Seminormal Solution* $\left(\frac{N}{2}\right)$; if it is of one-tenth the normal strength it is known as *Decinormal* $\left(\frac{N}{10}\right)$; and if it is of one-hundredth the normal strength, it is a *Centinormal Solution* $\left(\frac{N}{100}\right)$.

Note.—The above definition explains the ordinary application of the term Normal and of its derivatives. But these terms are sometimes used with a different implication. Thus the *oxidising power* of potassium permanganate and of potassium dichromate is often the basis on which the above terms are applied. In acid solution $KMnO_4$ is reduced by many substances according to the following equation $2KMnO_4 = K_2O + 2MnO + 5O$ · in which 2 gram-molecules of $KMnO_4$ correspond to 5 gram-atoms of oxygen or to 10 gram-atoms of hydrogen. and in order to place permanganate on a hydrogen basis a normal solution is made to contain $\frac{2KMnO_4}{10} = \frac{316 \cdot 3}{10} = 31 \cdot 63$ grams per litre. Similarly, the molecule $K_2Cr_2O_7$ can impart 3 atoms of oxygen to certain substances in acid solution, and a normal solution therefore contains $\frac{K_2Cr_2O_7}{6} = \frac{294 \cdot 2}{6} = 49 \cdot 03$ grams to the litre, the decinormal solution containing 4·003 grams.

272. Molecular Solution.—A standard solution which contains the molecular weight of the substance in grams in 1 litre, may be distinguished as a *Molecular Solution*, and is distinguished by the capital letter M. Solutions of fractional strength are distinguished by the prefixes semi-, deci-, and centi- respectively, and are shortly denoted by $\frac{M}{2}$, $\frac{M}{10}$, and $\frac{M}{100}$.

Storage and Preservation of Standard Solutions.

273. A Winchester quart-bottle is suitable for the storage of large quantities of solution. The bottle which is to contain the solution should not only be clean but dry. If it has been recently washed and is still wet inside, it must be rinsed out with a portion of the standard solution, since the moisture in the interior of the bottle would alter the strength of the standard solution. As soon as the solution has been introduced, the bottle should be securely stoppered. It is then immediately labelled with the name, strength, and date of the preparation of the solution. The label should also bear the initials of the maker of the solution.

Evaporation of water from the standard solution invariably occurs when the bottle is opened for use, and may even take place slowly while the bottle is closed. Some substances also undergo chemical change in solution in course of time. Hence a standard solution usually alters in strength when it is stored. The amount of this alteration will depend upon the substance dissolved, the age of the solution, and the frequency with which it is used. An opinion may be formed as to the probability of change having occurred in the strength of the solution by noting the date of its preparation.

It must further be remembered that, unless the bottle is completely filled with the solution, internal evaporation and condensation will lead to the formation of drops of pure water on the upper part of the interior of the bottle. Care must, therefore, be taken to shake the bottle before removing the stopper, so as to mingle this water once more with the solution.

Loss by evaporation is checked by drawing a tightly fitting rubber cap or finger-stall down over the stopper and neck of the bottle. This not only keeps the stopper firmly in its seat, but also forms a waterproof covering which serves to keep the lip of the bottle clean.

Another method of preventing evaporation is to close the bottle with a rubber stopper instead of with an ordinary cork. Or a glass stopper, which is somewhat too small for the neck of the bottle, may be used; the stopper has a suitable piece of tightly fitting black rubber tubing drawn over it: the stopper is then virtually a rubber one. A rubber stopper is always to be

preferred for a bottle containing a solution of caustic alkali, since a glass stopper becomes set fast in its seat by the action of the alkali upon the glass.

Standard solutions should be kept in a cool place, as the evaporation of water from the solution will naturally be less when the temperature of the storeroom is low.

Some standard solutions undergo chemical change by the action of light, and should therefore be kept in the dark. A cold, dark closet or cellar is generally the most suitable place of storage for standard solutions; but if they cannot be stored in the dark, the bottles may be externally coated with black paint or with black opaque paper.

PART III.—SECTION VI.

ALKALIMETRY AND ACIDIMETRY.

The student should note that many directions and precautions, which are of general importance in the preparation of standard solutions, are given in paragraphs 283-289. These are not repeated in the subsequent portions of the text.

Normal Sodium Carbonate Solution.

283. This is a semi-molecular solution, and contains 53·05 grams of Na_2CO_3 per litre.

In describing the general method of preparing this liquid, it must be remembered that contraction of volume occurs during the solution of sodium carbonate in water. A similar contraction occurs in the preparation of many other solutions. Hence a standard solution cannot be obtained by pouring water upon the requisite weight of the salt until the necessary volume is attained. The only plan is to make up the solution of the salt to its true volume in the measuring-vessel itself, by adding water at the proper temperature, and constantly mixing it with the solution.

284. Preparation of the Solution.—Na_2CO_3 is most readily obtained in the pure state by igniting pure sodium bicarbonate.

The bicarbonate should first be tested for traces of chloride and sulphate. This is effected by shaking it for some time in a stoppered bottle with a small quantity of distilled water, and then applying the necessary tests to the clear liquid If chloride or sulphate is present, about 100 grams of the bicarbonate are shaken with a small quantity of distilled water, the salt is allowed to settle, and the liquid is decanted. The washing is repeated with fresh portions of distilled water, until the last washing-water gives no reaction for sulphate or for chloride, the bicarbonate is then drained on a porous tile and is dried by pressing it between dry sheets of filter-paper.

100 c.c. of the normal solution will suffice for present purposes. This is prepared as follows:

About 9 grams of the pure bicarbonate are spread in a thin layer inside a weighed platinum or porcelain dish. The dish and its contents are then heated over a Bunsen flame to dull redness for about twenty minutes. Care must be taken not to fuse the salt, else some of the Na_2CO_3 will be decomposed. After the dish has cooled in a desiccator, it is weighed. It is then

heated again for ten minutes, allowed to cool, and weighed. These processes are repeated until the weight remains constant. The weight of pure Na_2CO_3 in the dish is now found by subtracting the weight of the dish. The standard solution may be prepared from this carbonate according to the directions given in (a) or in (b), and is at once stored in an accurately stoppered bottle.

(a) **The Volume of the Normal Solution, which would contain the above weight of Na_2CO_3, is found by Calculation; the carbonate is dissolved and the solution is made up to this volume**.—Thus if the sodium carbonate weighed 5·7 grams, it will furnish $\frac{5\cdot7 \times 100}{5\cdot305} = 107\cdot4$ c.c. of the normal solution, since 5·305 grams of Na_2CO_3 are required for 100 c.c. of normal solution. The procedure is as follows:

The weighed carbonate is transferred from the dish to a small beaker without loss, and the dish is rinsed out into the beaker with successive small quantities of hot distilled water until every trace of the carbonate has been removed.

The carbonate is then dissolved by stirring it with the water in the beaker; the solution is poured down the stirring-rod into the 100 c.c flask, and the beaker is rinsed with three or four successive small quantities of water, which are also poured down the rod into the flask.

The liquid is now made nearly up to the 100 c.c. mark with distilled water at 15·5°, and is constantly mixed by shaking. The neck of the vessel is then closed by a glass stopper or by a clean dry rubber cork, and its contents are thoroughly mixed by shaking. The solution is finally made up precisely to the mark, by placing the vessel on a level surface, and slowly filling in water from a pipette, or burette, or from a wash-bottle with a fine jet. The bottom of the meniscus of the liquid surface must now just touch the graduation.

The volume of water required to make the liquid up to 107·4 c.c., which in the above example amounts to 7·4 c.c., is then added from a burette, and the liquid is once more thoroughly mixed.

The liquid may then be transferred from the flask to a clean, dry, stoppered store-bottle.

(b) **The Weight of the Sodium Carbonate is brought to exactly 5·305 grams; this is dissolved, and is made up with water to 100 c.c.** The adjustment of the weight of the carbonate may be effected by removing small quantities of the carbonate from the dish with the point of a penknife, while the dish is on the scale-pan, the weights having been first adjusted on the other pan so as to be equal to the weight of the dish + 5·305 grams. The salt is then dissolved, and the liquid is brought to the requisite volume as is described above (a). The liquid is then well mixed by shaking it in the flask.

Normal Sulphuric Acid Solution.

285. This solution is a semi-molecular one, and should therefore contain 49 04 grams of pure H_2SO_4 per litre.

The general procedure for the preparation of the solution is as follows: An appropriate quantity of pure strong oil of vitriol is diluted with water in a thin glass vessel. The hot mixture is then cooled, and its strength is ascertained by titrating a portion of it with the standard sodium carbonate solution (**284**). As soon as the strength of this diluted acid is accurately known, the amount of further dilution with water, which is necessary in order to reduce it to the normal condition, may be easily calculated.

286. Preparation of the Solution.—30 c.c. of pure oil of vitriol are allowed to flow into about 200 c.c. of distilled water contained in a thin glass flask. The liquids are well mixed, and the mixture is cooled by shaking it round while a stream of tap-water flows over the flask. The cold liquid is transferred to a litre flask, and its volume is made up to one litre with constant mixing. A portion is then titrated with the standard sodium carbonate solution as is described below.

Preliminary Titration of the Acid Solution.—A clean and well-drained 20 c.c. pipette is rinsed out, by partly filling it with the normal sodium carbonate solution by suction, shaking the liquid round in the pipette, and allowing it to flow away into the sink. The pipette is then once more charged with the normal solution exactly to the 20 c.c. mark, by sucking up more than the requisite volume, quickly applying the first finger to the top of the pipette. The 20 c.c. of liquid is then allowed to flow into a 250 c.c flask or beaker by raising the finger from the end of the pipette, and some water is added.

If the interior of the pipette was not only clean but perfectly dry, the preliminary rinsing with the solution may be neglected, since in that case there is no danger of diluting the standard solution with water adhering to the interior of the pipette.

A burette has now to be charged with the diluted acid. If the interior of the burette and the jet are not perfectly dry, they must be rinsed out with a small quantity of the acid, which is rejected. The burette is then filled with the acid, and air-bubbles are carefully removed from the tap or jet below, by allowing some of the liquid to flow rapidly through into the bottle. The burette is then finally filled precisely to the zero mark.

Sufficient methyl-orange solution (**268**) is now added to the sodium carbonate solution in the flask to give a pale yellow colour to the liquid.

This yellow colour will furnish an indication by changing to pink when the

sodium carbonate has been exactly neutralised by the addition of the dilute acid from the burette.

The flask is placed upon a white plate or tile, and the acid from the burette is dropped gradually into the sodium carbonate solution, and is constantly mixed with the solution by shaking it. The addition of acid is continued until the yellow colour of the whole liquid just begins to change to red.

It is important that the acid should be added in the slightest possible excess, and that the change to permanent red should be produced only on the addition of the last drop of acid.

The volume of the dilute acid solution, which has been required for the neutralisation of the sodium carbonate in the flask, is now read off on the burette, and this result is confirmed by a repetition of the titration in a precisely similar manner, with a fresh quantity of the sodium carbonate solution. The two titrations should not differ by more than 0·1 c.c.

If **Neutral Litmus Solution** (264) is used as the indicator in this titration, it must be remembered that the change of colour to red does not indicate complete neutralisation by the conversion of the alkaline Na_2CO_3 into neutral Na_2SO_4, because the CO_2, which is liberated in the reaction, dissolves in the cold liquid and exerts an acid reaction upon the litmus

In order to expel this dissolved CO_2, the liquid in the flask is boiled for a few minutes, and the blue colour, which is thus restored, is again just converted into red by the cautious addition of acid from the burette

The liquid is now once more boiled, and if the red colour of the litmus remains unchanged the neutralisation is complete. If the colour still changes when the solution is boiled, the above processes must be repeated until the liquid remains red after it has been boiled for a few minutes

A comparison-flask may be prepared in which a similar quantity of water and litmus solution has been made distinctly red by the addition of acid. This will serve to show the red tint which must be obtained in the test-flask.

287. Process of Dilution to Normal Strength.—These titrations will prove that the acid solution is somewhat too strong. It may be made normal by proceeding as is described in the following example:

In a special case, the 20 c.c. of the alkaline solution were exactly neutralised by 18·4 c.c. of the acid solution. It follows that 18·4 c.c. of the acid will require to be diluted to 20 c.c. in order to furnish a standard acid, which is exactly equivalent to the alkaline solution. A litre of normal acid is therefore made by measuring $18{\cdot}4 \times 50 = 920$ c.c. of the acid into a litre flask, and then diluting this to a litre with distilled water. This diluted acid is now thoroughly mixed, and is once more titrated with the alkaline solution, as has been already described (286), in order to ascertain that it is correct.

Titration after Storage.—The acid solution usually becomes more or less altered in strength after it has been stored for some time (273). Its strength

will therefore require to be occasionally ascertained by titrating it with a freshly prepared solution of sodium carbonate.

20 c.c. of the solution may be used for ascertaining its strength by titration, and the titration may be effected from a 50 c.c. burette, which should furnish enough liquid for two titrations.

288. Correction of Standard Solutions by means of Factors.—It is not usual to bring back a solution, which is found to be slightly in error, to its true standard. Instead of this a correction is applied to the solution when it is used. This method of correcting the solution will be rendered intelligible by the following example:

In a special case 19·8 c.c of standard acid solution were required, instead of 20 c.c, to neutralise 20 c.c. of freshly prepared normal sodium carbonate solution. Accordingly the number of c.c. of this acid which have been employed in any titration will require to be multiplied by $\frac{20}{19\cdot8} = 1\cdot01$, in order to find the number of c.c. which would have been required if the acid had been normal. The number 1·01 is termed the "Factor" of the solution.

The factor which is required for the correction of a standard solution should be entered upon the label of the bottle from time to time, with the date of its determination.

Normal Sodium Hydrate Solution.

289. This solution contains 40·06 grams per litre; it is prepared by dissolving about 44 grams of pure sodium hydrate in water.

If the solution is required to be free from sodium carbonate and from other sodium compounds, it may be prepared by the action of metallic sodium upon distilled water.

Sodium hydrate solution is prepared from metallic sodium as follows About 25 grams of clean sodium are cut into small pieces. These pieces are introduced, one by one, into recently boiled and cooled distilled water contained in a platinum or silver dish. The dish is covered with a clock-glass immediately after the addition of each piece of metal, in order to prevent the loss of NaOH by spirting; and the reaction is allowed to complete itself, before each successive addition of the metal.

The strong solution of the hydrate is now diluted to a litre with distilled water, which may have been recently boiled and cooled so as to insure its freedom from carbonic acid. 20 c.c. of the solution are then mixed with a few drops of methyl-orange solution (268), and are titrated by adding normal sulphuric acid (285) from a burette. The sodium hydrate solution is then

brought to the normal strength by diluting it to the requisite extent with distilled water (287).

This solution should be again titrated occasionally by means of the standard acid, since it is subject to change when kept. The bottle, which contains it, should be closed by a rubber stopper (273), since a glass stopper is apt to become set fast by the action of the alkali upon the glass.

Normal Hydrochloric Acid Solution.

290. This solution contains 36·46 grams per litre. About 150 c.c. of pure strong hydrochloric acid, which has a specific gravity of 1·14 and contains 28 per cent of HCl, are diluted to a litre. The exact strength of this solution is ascertained by titration with normal sodium hydrate solution (289) according to the directions given in paragraph 286. The acid solution is then brought to standard strength by dilution with water (287).

Estimation of the Total Acid in Vinegar.

291. This estimation depends upon finding the amount of seminormal sodium hydrate solution, which is required to neutralise the acid present in a known quantity of the vinegar.

25 c.c. of the semi-normal sodium hydrate solution (289) are measured by a pipette into a small flask. The vinegar is then added to the alkaline solution from a burette with constant mixing, until a drop of the liquid, when placed upon litmus-paper (265) by a thin glass rod, just reddens the paper. This indicates the end of the titration.

If the vinegar is colourless or nearly so, a few drops of neutral litmus solution (264) may be added to the liquid in the flask, instead of using litmus-paper, and this renders the process of titration more rapid.

The point of neutrality is still more rapidly ascertained by adding a little phenol-phthalein solution (269) instead of litmus to the sodium hydrate solution in the flask. The vinegar is added from the burette until the red colour disappears. This indicator may be used even with slightly coloured vinegar, and yields more accurate results than litmus does.

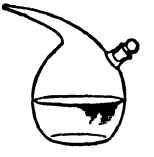
In calculating the percentage weight of pure acetic acid which is present in the vinegar, it should be noted that according to the equation $H.C_2H_3O_2 + NaOH = NaC_2H_3O_2 + H_2O$, 60·03 grams of acetic acid exactly neutralise 40·06 grams of NaOH.

Therefore each c.c. of the seminormal sodium hydrate solution will neutralise $\frac{60{\cdot}03}{2 \times 1000} = 0{\cdot}03$ gram of acetic acid. The amount of vinegar, which is required to neutralise the 25 c.c. of sodium hydrate, will accordingly contain $25 \times 0\ 03 = 0\ 75$ gram of acetic acid. The number of c.c. of vinegar used may be taken as the weight of the vinegar in grams (292), and the percentage weight of acetic acid in the vinegar is then calculated by proportion.

292. **The Weight-burette.**—For ordinary purposes it is sufficiently accurate to assume in the above calculation that each c c of vinegar weighs 1 gram. This assumption is, however, only absolutely true of pure water at 4° C. And since the specific gravity of the vinegar differs slightly from that of water, and its temperature is higher than 4° C, the volume of the vinegar in c c must be brought to 4° C, and this must be multiplied by its specific gravity (33–38), in order to obtain the true weight of the vinegar The correction thus applied necessitates the determination of the specific gravity of the vinegar

This is rendered unnecessary, if the ordinary measuring-burette is replaced by a weight-burette (Fig 83) The weight-burette is a small, thin flask with a narrow delivery-neck, and a broader opening to be closed by the finger The clean and dry burette is half filled with vinegar and weighed

Fig 83



Weight-burette.

The vinegar is then gradually added to the sodium hydrate solution by tilting the burette The burette with the remaining vinegar is again weighed, after the titration has been finished The weight of vinegar, which has been used in the titration, is equal to the difference between these two weighings

The burette must be kept stoppered when it is not in use, in order to guard against loss of weight by evaporation.

Indirect Estimation of Barium or Calcium in Solution by Standard Solutions of Na_2CO_3 and of Acid.

293 The method consists in adding a known volume of decinormal sodium carbonate solution (271, 283) to the neutral solution containing the barium, the sodium carbonate being added in quantity more than sufficient to precipitate the whole of the barium as carbonate. After the solutions have been thoroughly mixed by stirring, the barium carbonate is removed by filtration and washed. The filtrate and washings are mixed and made up to a known volume, and the excess of sodium carbonate is then determined in an aliquot part of this liquid by titration with decinormal hydrochloric acid solution (271, 290).

The difference between the quantity of sodium carbonate thus found by titration, and the original quantity taken, furnishes the weight of Na_2CO_3

which is necessary to exactly precipitate the barium as carbonate; and from this the weight of barium which was originally present in the solution may be calculated as is shown in the following example:

In a special case the barium solution was precipitated by adding to it 30 2 c c. of decinormal sodium carbonate solution The excess of sodium carbonate, contained in the filtrate and washings, required 5 4 c c of decinormal hydrochloric acid for its neutralisation. Hence the volume of sodium carbonate solution, which was required to precipitate the barium, was 30 2 - 5 4 = 24 8 c c. and each c c. of this solution contains 0 005306 gram of Na_2CO_3.

Now from the equation, $BaCl_2 + Na_2CO_3 = BaCO_3 + 2NaCl$, it will be seen that 137 4 parts by weight of Ba are precipitated by 106 1 of Na_2CO_3.

Therefore each c c. of the Na_2CO_3 solution corresponds to

$$\frac{137\ 4 \times 0\ 005306}{106\ 1} = 0\ 00687 \text{ gram of Ba}$$

Hence the weight of Ba which was present in the above solution is $24\ 8 \times 0\ 00685 = 0{\cdot}169$ gram.

294 **A Less Rapid and Less Accurate Method** consists in precipitating the barium as carbonate, from a known quantity of its neutral solution, by the addition of sodium carbonate solution in excess. The filtered and well-washed precipitate is dissolved in a known volume of decinormal hydrochloric acid (65, 66), which must be added in slight excess, the solution is boiled for five minutes, and the excess of acid in the solution is then titrated by adding standard NaOH solution from a burette in the presence of methyl-orange (268)

The results thus obtained furnish the necessary data for finding the weight of HCl, which is required to convert the Ba from carbonate into chloride: $BaCO_3 + 2HCl = BaCl_2 + CO_2 + H_2O$ From this the weight of Ba may be calculated.

Direct Estimation of Ammonium in its Compounds by Evolving, Absorbing and Titrating the Ammonia.

295. The ammonia, expelled by heating the ammonium compound with caustic alkali solution, is absorbed in a known volume of standard acid, and the excess of acid is determined by titration with standard alkali solution.

This method of estimation by means of standard solutions is much more rapidly carried out than that described in paragraph 173.

The ammonia gas is evolved and absorbed in precisely the same way as has been described in paragraph 173. The gas is absorbed, however, in 100 c.c. of normal sulphuric acid (286) in the flask (*h*, Fig. 67, page 101).

As soon as the evolution and absorption of the ammonia is complete, the absorption-apparatus is rinsed out with water as has been already described (173), and the acid and washing-water are made up to 200 c.c. The well-mixed liquid is then transferred to a burette, and is allowed to exactly

neutralise 10 c.c. of normal soda solution (289), using either litmus or methyl-orange as an indicator. Two titrations should not differ by more than 0 1 c.c.

The Following Example will serve to illustrate this process and the method of calculation·

0 935 gram of crystallised ferrous ammonium sulphate was weighed out The ammonia was absorbed by 100 c c of normal sulphuric acid. After the absorption was completed the liquid was made up to 200 c c

. 21 c c of this liquid were found to exactly neutralise 10 c c. of normal NaHO : therefore 200 c c would require $\frac{200 \times 10}{21} = 95\ 24$ c c. of normal NaHO, and the number of c c of H_2SO_4 neutralised by the $NH_3 = 100 - 95\ 24 = 4\ 76$.

And since each c c of acid corresponds to 0 018 gram of NH_4, the weight of NH_4 in the salt $= 4\ 76 \times 0\ 018 = 0\ 08568$.

$$\text{hence the percentage of } NH_4 = \frac{0\ 08568 \times 100}{0\ 935} = 9{\cdot}16$$

Another Method for estimating Ammonia volumetrically is given in paragraph 296.

Indirect Estimation of Ammonium in its Compounds by means of Standard Solutions of Sodium Hydrate and of Acid.

Note.—This method is convenient when free acid is present with the ammonium salt, as in the "sulphate of ammonia" of commerce. The amount of free acid can then be first titrated by standard sodium hydrate solution; a known excess of that solution is then added, and the ammonia is estimated after boiling the liquid as is described below

296. The indirect method described below may be applied to any ammonium salt of definite composition; this excludes the carbonate.

It depends upon decomposing the salt by boiling it with a known volume in excess of standard sodium hydrate solution (289), the boiling being continued until no more NH_3 escapes with the steam. The excess of sodium hydrate present in the liquid is then estimated by titration with a standard acid, using litmus or methyl-orange as an indicator.

In carrying out the process, the ammonia is known to have been completely expelled, when a strip of moistened turmeric-paper is no longer rendered brown by the escaping steam.

In the reaction which occurs, the quantity of sodium hydrate which is neutralised is proportional to the amount of ammonia which is evolved. This is shown by the following equation, which represents the reaction in the case of ammonium chloride:

$$NH_4Cl + NaHO = NH_3 + NaCl + H_2O.$$

From this it is seen that 17 04 grams of NH_3 correspond to 40·06 grams of NaOH neutralised.

The Following Example will serve as an illustration of the process and of the calculation.

1 1302 grams of an ammonium salt were mixed with 50 c c of normal sodium hydrate solution, and the liquid was boiled until turmeric-paper was no longer discoloured when it was held in the escaping steam The liquid was then coloured by the addition of a few drops of litmus solution, and semi-molecular or normal sulphuric acid was added until the litmus just turned bright red The volume of acid required was 30 c c.

Now since the sodium hydrate and the acid solutions are equivalent to one another, the amount of sodium hydrate solution which has been neutralised by the ammonium salt is 50 – 30 = 20 c c And since each c c of the NaOH solution is equivalent to 0 017049 gram of NH_3, the weight of NH_3 present is $20 \times 0\ 017049$ $3 = 0\ 409$ gram Therefore the percentage of NH_3 present is $\frac{0\ 3409 \times 100}{1\ 1302} = 30\ 16.$

And the percentage of NH_4 present is $\frac{18\ 052 \times 30\ 16}{17\ 049} = 31\ 91.$

297. Other Examples for Practice.—Brief details are given below of certain estimations which involve the use of standard acid and alkali Some of them are so simple that they might well precede many which have been already described.

Weigh out accurately about 10 grams of each of the following substances, and dissolve them separately in separate portions of water. Then dilute each solution to 250 c c and make the estimation as is stated below.

(a) Sodium carbonate, sodium bicarbonate, potassium bicarbonate or borax is titrated with normal sulphuric acid, using methyl-orange as an indicator.

(b) Alkaline earth hydroxides or carbonates are mixed with excess of normal hydrochloric acid, and the excess of acid is titrated with normal sodium hydrate solution, using methyl-orange as an indicator

(c) Strong sulphuric, hydrochloric or nitric acid, or an acid salt such as $KHSO_4$ is titrated with normal sodium hydroxide solution, using either methyl orange or litmus as an indicator.

(d) Acetic, oxalic, citric or other organic acid is titrated with normal sodium hydroxide solution, using phenol-phthalein as an indicator

(e) The organic salts of the alkalis and alkaline earth metals are strongly heated and converted into carbonates, and these carbonates are titrated as is directed under (a) and (b).

PART III.—SECTION VII.

PROCESSES OF OXIDATION AND REDUCTION.

Valuation of Bleaching-powder by Oxidation of Alkaline Arsenite.

300. Introductory.—The composition of dry bleaching-powder, when it is in the freshly-prepared state and fully charged with chlorine, may be represented by the formula $2CaOCl_2.Ca(OH)_2$. When this substance is treated with water, it yields a liquid which probably contains $CaCl_2$ and $Ca(OCl)_2$ together with some $Ca(OH)_2$. The value of the bleaching-powder depends on the amount of $Ca(OCl)_2$ which can be produced by dissolving it in water.

In the ordinary applications of bleaching-powder, there is little doubt that the nascent oxygen furnished by the hypochlorite is the active agent. But it is not customary to estimate the value of bleaching-powder from the percentage of the hypochlorite, or of the nascent oxygen which it can furnish. The weight of chlorine, which is chemically equivalent to this oxygen, is ordinarily returned, and this is termed the "available chlorine."

When bleaching-powder of the above composition is acted upon by an acid the whole of its chlorine is set free and becomes "available":

$$2CaOCl_2.Ca(OH)_2 + 3H_2SO_4 = 2Cl_2 + 3CaSO_4 + 4H_2O.$$

Hence the weight of available chlorine in good bleaching-powder corresponds to the whole of the chlorine which it contains. Chlorine compounds, which contain chlorine in a condition unavailable for purposes of chlorination or oxidation, are, however, often present in bleaching-powder. This may arise from careless preparation or storage of the powder. Hence the available chlorine in bleaching-powder is usually less in amount than the total weight of chlorine which it contains.

The above formula represents bleaching-powder which contains about 40 per cent. of chlorine But bleaching-powder does not commonly contain more than 35 per cent. of available chlorine, and the percentage sometimes falls considerably below that amount.

The amount of nascent oxygen which bleaching-powder can yield, or its equivalent of available chlorine, may be estimated in several ways. Three methods are described in paragraphs **301**, **315**, and **350**.

301. Estimation of the Available Chlorine in Bleaching-powder by the Oxidation of an Alkaline Arsenite.—When solution of bleaching-powder is brought into contact with solution of an alkaline arsenite, the relative amounts of arsenious oxide and of the oxidising agent which act upon one another are shown by the following equation:

$$As_2O_3 + Ca(OCl)_2 = As_2O_5 + CaCl_2.$$

Here the semi-molecule of arsenious oxide (As_4O_6) is oxidised by O_2, and this O_2 is chemically equivalent to Cl_4. Hence the amount of oxidation is a measure of the "available chlorine." The following process of estimation depends upon this reaction.

The Standard Solution of Arsenious Oxide.—The most convenient weight of arsenious oxide for this solution is the semi-molecular weight (As_2O_3) divided by 40. This gives a decinormal solution, since As_2O_3 corresponds to Cl_4 in the process of titration.

Accordingly $\frac{198}{40} = 4.95$ grams of pure resublimed arsenious oxide (**110**, Exp. 29) are weighed out accurately into a 500 c.c. flask, and about 25 grams of pure sodium carbonate crystals are added. The flask is then half filled with water, and is heated on the water-bath until the arsenious oxide is dissolved. The solution is cooled under the water-tap, by placing a small inverted beaker over the neck of the flask and then allowing a gentle stream of cold water to run upon the beaker and thence over the surface of the flask.

As soon as the liquid is cooled down to 15·5° C., it is transferred to a litre flask, and the solution is made up to a litre with water at 15·5°. After the contents of the flask have been well shaken, they are transferred to a clean dry bottle, which is at once labelled with the name and strength of the solution and the date of its preparation.

Each c.c. of this solution will contain $\frac{198}{40 \times 1000} = 0.00495$ gram of arsenious oxide, and this corresponds to 0·003545 gram of Cl.

Preparation of the Bleaching-powder Liquid.—Weigh out 10 grams of the bleaching-powder on an open balance. Place the powder in a smooth porcelain mortar, preferably one which is glazed inside, and add a few c.c. of water. Rub the mixture into a paste by means of the pestle, then add more water and continue the rubbing until a thin cream is formed. Allow the solid to subside and decant the supernatant liquid into a litre flask.

Then triturate the residue repeatedly with fresh quantities of water, stirring up the liquid and pouring it off after each addition, until the whole of the solid has been transferred to the flask. Finally, fill up the flask to the mark

with water, and mix its contents well by shaking. The liquid will always be milky, because bleaching-powder is not completely soluble in water. The solution must be at once quickly titrated, since it undergoes rapid change.

Iodide-starch-paper is then prepared as follows. Shake up one part of pure starch with about a hundred parts of distilled water, and heat the mixture to boiling. Then add about one part of pure potassium iodide, and pour off the clear liquid from any sediment which may be present. Moisten strips of unsized paper with this solution, dry them in the air, and keep the paper in a well-stoppered bottle.

The Process of Titration.—Withdraw 25 c.c. of the freshly made and recently mixed bleaching-powder solution by means of a pipette, and allow it to flow into a flask. Rinse out a 50 c.c. burette with a little of the standard arsenite solution, and then fill it above the zero mark with the same solution. Allow the liquid to flow out until the meniscus stands at the zero graduation, making sure that the rubber joint, or the tap, contains no air-bubbles.

Now allow the arsenite solution to flow gradually and with continuous stirring into the 25 c.c. of bleaching-powder liquid. Take out a small drop of the liquid from time to time by means of a glass rod, and bring it into contact with a moistened strip of the iodide-starch-paper placed on a white tile. As soon as no blue coloration is produced upon the paper, the titration is known to be finished. The volume of liquid which has flowed from the burette is then read off

Two titrations should be made, and they should not differ from one another by more than the tenth of a c.c.

From the volume of arsenite solution, which has been required for the titration, the weight of available chlorine present in the 10 grams of bleaching-powder may be calculated, and from this the percentage weight of available chlorine present in the bleaching-powder is deduced.

The Following Example is a record of the results which were obtained in an estimation, together with the calculation of the percentage of available chlorine present in the bleaching-powder:

10 grams of bleaching-powder were treated with water and made up to a litre.

25 c.c. of this liquid required 20·7 c c. of the arsenite solution.

Since 1 c.c. of the arsenite solution corresponds to 0 003545 gram of Cl, the weight of Cl in 25 c.c. of the bleaching-powder liquid is 20·7 × 0 003545 = 0 07338 gram.

Now the 25 c.c. of liquid titrated correspond to 0·25 gram of bleaching-powder; therefore the percentage weight of available chlorine in the bleaching-powder is

$$\frac{0{\cdot}07338 \times 100}{0{\cdot}25} = 29\ 36.$$

Two other Methods for estimating the available chlorine in bleaching-powder are given in paragraphs 315 and 350

USE OF POTASSIUM DICHROMATE SOLUTION.

302. Acidified potassium dichromate solution readily imparts a portion of its oxygen to various substances, and is itself reduced to a salt of chromium which remains mixed with a salt of potassium. Advantage is taken of this property to estimate ferrous salts and other oxidisable substances.

303. Thus an acidified solution of ferrous salt is at once converted into ferric salt by the addition of potassium dichromate solution. The reaction is thus represented:

$$6FeSO_4 + K_2Cr_2O_7 + 8H_2SO_4 = 3Fe_2(SO_4)_3 + Cr_2(SO_4)_3 + 2KHSO_4 + 7H_2O.$$

From this equation it is seen that 294·5 parts of potassium dichromate can convert $6 \times 55{\cdot}9 = 335{\cdot}4$ parts of iron from the ferrous into the ferric state, if acid is present in sufficient amount.

But since potassium dichromate is reddish yellow, and is converted by deoxidation into a green chromium salt, the point at which a slight excess of dichromate has been added to the ferrous salt cannot readily be seen.

The precise point, at which the change of ferrous into ferric salt in the above reaction is complete, is therefore ascertained by using freshly made potassium ferricyanide solution as an indicator. Ferrous salts give, but ferric salts do not give a blue precipitate with this reagent. The dichromate solution is accordingly added to the acidified iron solution, until a drop of the liquid ceases to give a blue coloration when it is brought into contact with a drop of potassium ferricyanide solution on a white tile.

Note —The process of marking the complete oxidation of a ferrous salt solution is very much more simple when standard permanganate solution is used instead of dichromate, since the coloration of the liquid itself becomes the indicator (316 *et seq.*). But the use of permanganate is inadmissible in the presence of readily oxidisable organic matter, and is only possible in the presence of hydrochloric acid under special conditions (399).

PREPARATION OF STANDARD DECINORMAL DICHROMATE SOLUTION.

For the meaning of "decinormal" refer to *Note* (271)

304. Preparation of the Dichromate Solution.—Heat about 10 grams of pure recrystallised potassium dichromate just to fusion in a porcelain dish,

Allow the salt to cool, and then powder it in a clean dry mortar. Weigh out $\frac{294{\cdot}2}{60} = 4{\cdot}903$ grams of the powdered dichromate into a litre flask. Dissolve it in distilled water; then fill up the flask to the mark with water, and mix the liquid by shaking it well. Each c.c. of this solution corresponds approximately to $\frac{55{\cdot}9}{10 \times 1000} = 0{\cdot}00559$ gram of iron.

This solution must only be considered to be of the true strength when it is freshly prepared. It will require to be standardised afresh after it has been kept for some time.

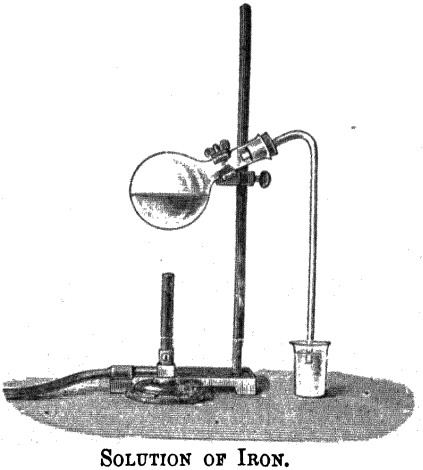
When it is necessary to ascertain the strength of the dichromate solution, a solution of ferrous sulphate of known strength is required. This is prepared either from a weighed quantity of metallic iron, or from a known weight of ferrous ammonium sulphate.

305. Titration of the Dichromate Solution by means of Metallic Iron.—A known weight of pure iron is dissolved in dilute sulphuric acid without contact with air in the following way;

Preparation of the Solution of Iron.—Weigh out accurately about 1 gram of pianoforte wire, which is free from rust and has been cut into pieces about 2·5 cm. in length.

Fit into a 300 c.c. round flask a perforated cork, through which a bent glass

FIG. 84.



SOLUTION OF IRON.

FIG. 85.



AIR-VALVE.

delivery-tube passes (Fig. 84). One end of this tube terminates just below the cork, while the other end dips beneath the surface of a little water contained

in a small beaker. Support the flask in an inclined position by clamping it upon a retort-stand.

Now half fill the flask with dilute sulphuric acid, drop in a small piece of pure crystallised sodium carbonate, and replace the cork and tube. The carbonate will dissolve evolving carbon dioxide, which will replace the air in the flask. When the effervescence has nearly ceased, add the weighed steel wire. Then fit in the cork and tube, and arrange the apparatus as is shown in Fig. 84, page 165, and apply a gentle heat by means of a small flame until the wire is dissolved as ferrous sulphate, and no more hydrogen escapes through the water in the beaker.

The exclusion of air during the process of solution is necessary, in order to prevent the formation of ferric salt:

$$2FeSO_4 + H_2SO_4 + O = Fe_2(SO_4)_3 + H_2O.$$

Another device, which allows the hydrogen gas to escape from the flask and at the same time checks the entrance of air, consists in closing the neck of the flask by a perforated cork through which a short glass tube passes (Fig 85) The lower end of this tube terminates just below the cork, while the upper end is closed by a short piece of rubber tube which is slit in the middle and is closed by a small glass rod The vertical slit is easily opened by the pressure of hydrogen gas from within, but it closes by pressure from without, and therefore prevents the ingress of air.

While the process of solution is proceeding, prepare some cold water free from dissolved oxygen, by boiling distilled water for a few minutes and then cooling it rapidly by immersing the flask in cold water.

As soon as the solution of the iron wire is completed, cool the liquid, transfer it rapidly to a 250 c.c. flask, and rinse out the round flask several times into the measuring-flask with the above air-free water. Finally, make up the solution to the mark with the air-free water.

306. *The Process of Titration.*—Fill a 50 c.c. burette to the zero mark with the potassium dichromate solution. Measure out 25 c.c. of the iron solution into a 300 c.c. flask, dilute it with about twice its volume of air-free water, and add a few drops of strong sulphuric acid. Place a number of drops of very dilute and freshly prepared potassium ferricyanide solution upon a white tile by means of a glass rod. Then allow the solution of dichromate to flow in small successive quantities from the burette into the flask, mixing it well with the iron solution after each addition by stirring or shaking.

From time to time take a drop of the iron solution out of the flask, by dipping into the liquid a thin clean glass rod, and bring the drop into contact with one of the drops of potassium ferricyanide solution on the tile. The first few drops from the flask will cause a strong blue coloration with the ferricyanide, but as the addition of the dichromate proceeds, the colour produced

with the ferricyanide will become more faint. As soon as the coloration becomes very faint the addition of the dichromate solution must be continued very cautiously, until a drop of the liquid containing the iron just ceases to produce a blue coloration with the ferricyanide. The volume of the dichromate solution, which has been allowed to flow from the burette, is then read off.

Two more similar titrations should then be made. In each of these, nearly the whole volume of dichromate solution required should be allowed to flow into the flask at once from the burette, the last half of a c.c. only being gradually added drop by drop. The results of these titrations should not differ by more than the tenth of a c.c.

Calculation of Results.—The weight of iron contained in the solution used in the above titration must be multiplied by 0·996, in order to correct it for impurities present in the steel wire originally employed; and from the weight of pure iron thus found, the exact iron-value of the standard solution of dichromate may be calculated.

The Following Example will serve to illustrate the process of calculation:

1·152 grams of steel wire were dissolved in acid, as is described above, and the solution was made up to 250 c.c.

25 c.c. of this solution required the addition of 21·1 c.c. of the dichromate solution in order to exactly convert the ferrous into ferric salt.

Therefore 211 c.c. of the dichromate solution correspond to 1·152 grams of steel wire.

And 1000 c.c. of dichromate solution will therefore correspond to $\frac{1{\cdot}152 \times 1000}{211}$ = 5·4598 grams of steel, which contain 5·4598 × 0·996 = 5·4379 grams of pure iron.

Each c.c. of the dichromate solution is therefore equivalent to 0·005438 gram of iron.

307. Titration of the Standard Dichromate Solution by means of Ferrous Salt.—The iron solution may be prepared from ferrous ammonium sulphate, $Fe(NH_4)_2(SO_4)_2.6H_2O$, instead of from metallic iron, by dissolving 7 grams of the salt in air-free water, to which a little H_2SO_4 has been added to prevent the formation of basic salt: this solution is made up to 250 c.c. and the liquid is well mixed by shaking the flask.

The above weight of the salt will give a solution containing 4 grams of iron per litre, since the double salt contains one-seventh its weight of iron.

The process of titration is performed in exactly the same way as has been already described (306), a few drops of strong sulphuric acid being added to the iron solution before the dichromate solution is allowed to flow in.

Estimation of Iron in Ferrous and Ferric Compounds by means of Standard Dichromate Solution.

308. The estimation of the total amount of iron present in an iron compound may be effected by means of the standard potassium dichromate solution.

If ferrous compounds only are present, the solution may be titrated at once (**309**) by the process described in paragraph **306**.

If the iron is present in the ferric state only, it is first reduced to the ferrous state (**311**, **312**, **313**), and the ferrous salt is then titrated (**306**).

If the iron is present both as ferrous and ferric compounds, the amount of ferrous iron is first estimated by the dichromate solution in one portion of the solution; and the whole of the iron is then reduced in another portion of the solution, and estimated. The difference between the two quantities of iron found will give the amount of iron which was originally present as ferric iron.

309. Estimation of Iron in Ferrous Compounds.—For practice in the estimation, dissolve 5 grams of ferrous sulphate ($FeSO_4.7H_2O$) in air-free water, add a little sulphuric acid, and make up the solution to 250 c.c. with air-free water. Measure out 25 c.c. of this solution, and titrate it as is described in paragraph **306**. From the weight of iron found the percentage weight of iron in the salt can then be calculated.

310. Estimation of Iron in Ferric Compounds.—Three methods are described below for the reduction of the iron to the ferrous condition before it is titrated by the dichromate solution.

For practice in the estimation, dissolve 10 grams of iron alum, $FeK(SO_4)_2.12H_2O$, in water, add a little dilute H_2SO_4, and make up the solution to 250 c.c. Reduce the ferric salt in the solution to ferrous salt (**311**-**313**), and titrate the iron by the dichromate solution (**306**).

311. Process of Reduction by means of Zinc.—100 c.c. of the iron solution are placed in a flask fitted as is shown in Fig. 84 or 85 (p. 165). The liquid must, if necessary, be first evaporated until it does not more than half fill the flask. Strong hydrochloric acid is then added, and granulated zinc free from iron is dropped into the flask. The zinc will dissolve in the acid with evolution of hydrogen, and a portion of the nascent hydrogen will act upon the ferric chloride, and will reduce it to ferrous chloride. At the same time the colour of the solution will change from yellow to pale green. After a time it will be necessary to heat the liquid gently in order to promote the action. The heating should be continued until all the zinc is dissolved.

Before proceeding to estimate the iron, ascertain that it is present entirely

in the ferrous state, by taking out a drop of the solution with a clean glass rod, and bringing it into contact with a drop of potassium sulphocyanide solution on a white tile or dish. No red colour should appear, or at most only a very faint pink tint. If a distinct red colour is produced, more zinc and hydrochloric acid must be added, and the process must be continued in the reduction apparatus until all the zinc is dissolved. The solution is then again tested with the sulphocyanide, and these operations are repeated until no ferric salt can be detected.

When the whole of the iron is proved to be present in the solution in the ferrous state, the liquid is quickly cooled and is made up at once to 250 c.c. with air-free water. The titration of 50 c.c. of this solution is then immediately proceeded with in the acidified liquid, according to the directions given in paragraph 306, and is completed with as little delay as possible.

312. Process of Reduction by means of Stannous Chloride Solution.—The iron in the acidified iron solution is reduced to the ferrous state by the addition of stannous chloride solution, which must be added in slight excess (*Note*). The excess of the stannous salt is then converted into stannic salt by adding excess of mercuric chloride solution:

$$SnCl_2 + 2HgCl_2 = SnCl_4 + Hg_2Cl_2.$$

25 c.c. of the iron solution are placed in a 120 c.c. flask, 2 c.c. of strong hydrochloric acid are then added, and the liquid is heated to boiling. Clear, freshly made solution of stannous chloride in twenty-five times its weight of water is next added from a pipette. The stannous solution is added drop by drop, until the yellow colour of the iron solution just disappears. About 3 c.c. of a saturated solution of mercuric chloride are then added. This must produce turbidity in the liquid, indicating that the stannous chloride solution has been added in excess. The solution is then cooled to about 60° C., and is titrated with the potassium dichromate solution (306).

Note.—Care must be taken that a large excess of $SnCl_2$ solution is not added, else a very large quantity of $HgCl_2$ solution will be required, and the precipitate of Hg_2Cl_2 will interfere with the titration

This method of reduction is not suitable for iron solutions which are coloured brown with organic matter.

313. Process of Reduction by means of Ammonium Bisulphite Solution.—Prepare some ammonium bisulphite solution by passing SO_2 gas into strong ammonia solution. Continue to pass the gas until the crystals, which may form at first, are redissolved, and the liquid smells strongly of SO_2. The gas may be conveniently supplied from a bottle of the liquid SO_2 (1013).

Pour 100 c.c. of the ferric solution into a small flask covered with a funnel

(Fig. 34, p. 36) and add ammonium hydrate gradually until a slight permanent precipitate is formed. Then add 5 c.c. of the bisulphite solution for each gram of substance taken. Place some pieces of platinum wire in the flask to prevent bumping, shake the liquid vigorously, and heat gently. Gradually increase the heating until the solution boils. If any precipitate forms at first, it will redissolve, and the liquid will gradually lose its yellow colour.

As soon as the liquid is colourless, add some strong H_2SO_4 diluted with four times its volume of water, in the proportion of 30 c.c. to each 5 c.c. of the bisulphite solution which was previously added. Test the solution with KCNS solution to ascertain whether the reduction of the iron is complete, as was directed in paragraph 311. When no ferric salt is present, boil the liquid until all the SO_2 is driven off, make it up to 250 c.c. with air-free water, and titrate the ferrous salt (306) in 50 c.c. of this solution.

Estimation of Iron in an Iron Ore.

314. If the iron exists in the ore partly or wholly in the ferric state, the ore is dissolved in acid, the iron is reduced to the ferrous state by one of the methods described above (311-313), and is then titrated by the potassium dichromate solution.

Process of Solution of the Iron.—Weigh out accurately about 2·5 grams of the powdered iron ore, which has been prepared as is described in paragraphs 55, 56. Heat this in a covered beaker (65) over a small flame for about half an hour with hydrochloric acid diluted with its own volume of water. Dilute this solution slightly with water, allow the undissolved matter to subside, and decant the liquid through a filter. Then treat the residue again with a small quantity of the dilute acid, and decant the liquid through the same filter.

This procedure will usually have extracted all the iron from the ore. But if the further treatment of the residue with a small additional quantity of acid furnishes a filtrate in which iron can be detected when a drop is added to KCNS solution, the ore must be treated again with acid, and this treatment must be repeated until no more iron is found in the last extract.

The residue is now transferred to the filter, and is washed with as small a quantity of water as possible, and the filtrates and washing-water are mixed together and made up to 250 c.c.

The ferric salt present in this solution is then reduced to the ferrous condition by one of the methods described above (311-313), and the ferrous iron is titrated (306).

If both ferrous iron and ferric iron are present, and each of these is to be estimated, the ore must be treated with acid out of contact with the air as is described in paragraph 305. A portion of the acid solution is used for the estimation of the ferrous iron. The ferric iron in the remainder of the solution is then reduced to the ferrous state and the total iron is determined in the ferrous state by the dichromate solution. The difference between the quantities of iron found by the two titrations gives the amount of ferric iron which was originally present in the ore.

The titration may be much more rapidly effected if standard permanganate solution is used in place of dichromate (316 *et seq*).

Valuation of Bleaching-powder by the Oxidation of a Ferrous Compound.

315. When a solution of bleaching-powder is brought into contact with an acidified ferrous solution, the ferrous compound is converted into a ferric compound by the $Ca(OCl)_2$ of the bleaching-powder solution according to the following equation:

$$Ca(OCl)_2 + 4FeSO_4 + 2H_2SO_4 = 2Fe_2(SO_4)_3 + 2H_2O + CaCl_2.$$

Here $2FeSO_4$ is converted into $Fe_2(SO_4)_3$ by O, and this O is chemically equivalent to Cl_2; each atom of Fe which is changed from the ferrous to ferric state, therefore, corresponds to one atom of "available chlorine" (300).

In practice it is found most convenient to add the bleaching-powder solution to an excess of an acidified solution of a ferrous salt, and then to estimate the amount of unchanged ferrous salt by means of dichromate solution (306).

The Standard Solution of Ferrous Salt.—A solution containing 4 grams of iron per litre will be found suitable. The solution is prepared by dissolving iron wire in dilute sulphuric acid, as is described in paragraph 305, or more readily by dissolving the proper quantity of ferrous ammonium sulphate in water as is described in paragraph 307.

Preparation of the Bleaching-powder Liquid.—The solution is prepared from 10 grams of the bleaching-powder and is made up to a litre, according to the directions given in paragraph 301.

The Process of Titration.—Measure out 50 c.c. of the iron solution into a beaker, and, if it is not already acid, acidify it by adding 1 c.c. of strong sulphuric acid. Add to this solution 25 c.c. of the bleaching-powder liquid, mix the liquids well by stirring, and ascertain the weight of ferrous iron remaining in the solution by means of standard potassium dichromate solution (306). The difference between this weight and the weight of Fe in the

50 c.c. originally taken will give the weight of ferrous iron which has been converted into ferric iron by the 25 c.c. bleaching-powder solution.

From this weight the weight of available chlorine present in the 10 grams of bleaching-powder may be calculated, and from this the percentage weight of available chlorine present in the bleaching-powder may be deduced.

The Following Example is a record of the results which were obtained in an estimation, together with the calculation of the percentage of available chlorine present in the bleaching-powder:

10 grams of bleaching-powder were treated with water and the liquid was made up to 1 litre

25 c c of this liquid converted 0·1208 gram of ferrous iron into the ferric state. According to the equation and statement on page 171 this indicates the presence of $\frac{0\ 1208 \times 35\ 45}{56} = 0\ 0765$ gram of Cl in the 25 c.c. of bleaching-powder liquid

Now the 25 c c of the bleaching-liquid correspond to 0 25 gram of bleaching-powder; therefore the percentage weight of available chlorine

$$= \frac{0\ 0765 \times 100}{0\ 25} = 30\ 6.$$

Other Methods for estimating the available chlorine in bleaching-powder are given in paragraphs **301** and **350**.

USE OF POTASSIUM PERMANGANATE SOLUTION.

316. Introductory Remarks.—Potassium permanganate solution readily yields a portion of its oxygen under suitable conditions to certain readily oxidisable substances, and may therefore be used instead of potassium dichromate solution for many volumetric estimations. It presents the advantage over dichromate that its strong colour practically disappears when it is deoxidised: an indicator is therefore unnecessary, since the presence of the slightest excess of permanganate is indicated by its colour.

Potassium permanganate, however, cannot be used for the estimation of ferrous salts or of similar substances in the presence of easily oxidisable organic matter.

The presence of hydrochloric acid also interferes seriously, under ordinary conditions, with the accuracy of the estimation of the iron, owing to the liberation of chlorine from the acid by the oxidising action of permanganate: a special procedure for titrating iron in hydrochloric acid solution is described in paragraph **399**.

A liquid which is to be titrated with permanganate should be acidified with dilute sulphuric acid, if it is not already acid. Nitric acid must not be present in any quantity.

Solution of potassium permanganate becomes gradually weaker by the decomposition of the salt if it is exposed to light, and the solution must therefore be kept in a dark blue Winchester quart-bottle and stored in a cool and dark place. Owing to this liability to change, the permanganate solution should be standardised not only immediately after its preparation, but also at frequent intervals when it is stored.

Some estimations which can be made by means of permanganate solution are described in paragraphs 321–330.

Preparation, Standardisation, and use of Potassium Permanganate Solution.

317. Crush about 5 grams of crystallised potassium permanganate in a glazed mortar in the presence of a small quantity of water, pour off the solution into a litre flask, and repeat the process until all the salt is in solution: then make the volume up to a litre.

The solution is usually standardised by a cold solution of ferrous salt containing some free sulphuric acid (318), but it may also be standardised by a warm solution of oxalic acid (320).

318. **Titration of the Permanganate Solution by means of Ferrous Salt.**—The following reaction takes place when a cold acidified solution of ferrous salt is used in the titration:

$$2KMnO_4 + 10FeSO_4 + 9H_2SO_4 = 5Fe_2(SO_4)_3 + 2MnSO_4 + 2KHSO_4 + 8H_2O.$$

The ferrous sulphate solution should be made immediately before it is required for the titration (305, 307). The further procedure is similar to that already described under the standardisation of potassium dichromate (306); the use of an indicator, however, is unnecessary, since the end of the reaction is easily seen by the appearance of a pink tint in the liquid, as soon as the permanganate is present in excess.

319. Pour some of the permanganate solution into a burette with a glass stop-cock (Fig. 79, page 141), filling the burette to the zero mark. A rubber joint must not be used in the burette, as it would reduce the permanganate. Allow the permanganate solution to flow into the cold ferrous solution, which has been acidified with a few drops of strong sulphuric acid, and has been diluted with freshly boiled and cooled distilled water.

Continue the addition of the permanganate solution until a faint permanent pink colour remains after the liquids have been well mixed. This colour is readily seen when the beaker containing the iron solution is placed upon a

piece of white paper, or upon a white tile, or if the titration is performed in a porcelain dish.

Two titrations should be made, and they must not differ from one another by more than one-tenth of a c.c.

The strength of the solution may be calculated by reference to the above equation (318). It is usually stated in terms of metallic iron, as has been described in the standardisation of potassium dichromate solution (306).

The strength of the solution may also be stated in terms of available oxygen. The oxygen-value of the permanganate solution may be calculated directly from the iron-value, since every 111·7 parts of iron oxidised correspond to 16 parts of oxygen ($2FeO + O = Fe_2O_3$). See *Note*, paragraph 271.

320. **Titration of Potassium Permanganate Solution by means of Oxalic Acid.**—When potassium permanganate solution is added to a warm solution of oxalic acid which has been acidified with sulphuric acid, the following reaction takes place:

$$2KMnO_4 + 5H_2C_2O_4\,2H_2O + 3H_2SO_4 = 10CO_2 + K_2SO_4 + 2MnSO_4 + 18H_2O.$$

It will be seen, on comparing this equation with that given for ferrous salt (318), that 126·02 parts of crystallised oxalic acid are equivalent to 111·7 parts of iron, and require 16 parts of oxygen for their complete oxidation. This relation is shown more simply by the following equation:

$$H_2C_2O_4.2H_2O + O = 2CO_2 + 3H_2O.$$

A Decinormal Solution of pure recrystallised oxalic acid is required for the titration. This is prepared by dissolving 6·301 grams of the pure crystals in water, and making the solution up to a litre.

Fifty c.c. of this solution are measured out into a beaker by means of a pipette, a little sulphuric acid is added, and the liquid is considerably diluted with water. The diluted solution is then heated to 60° C., and the solution of potassium permanganate, containing about 5 grams per litre, is gradually added, until a faint permanent pink tint remains in the liquid after it has been stirred. If the permanganate is added too rapidly, a brown precipitate forms, which is removed with difficulty by adding more sulphuric acid.

The strength of the permanganate solution is readily calculated from the proportions yielded by the above equation.

Estimation of Iron in Ferrous and Ferric Compounds by means of Standard Permanganate.

321. The iron present in a substance in the ferrous or the ferric condition, or partly in both conditions, may be estimated by titration with standard permanganate solution (319), instead of by dichromate, if oxidisable organic matter and hydrochloric acid are not present. The weight of Fe is calculated from the result of the titration, by means of the equation (318).

322. Estimation of Iron in Ferrous compounds.—Care must be taken that the ferrous salt is not exposed to oxidation and conversion into ferric salt during the process of solution. This will be prevented by adopting the method of solution which is described in paragraph 305. The titration is carried out as is directed in paragraph 319.

Substances from which the iron cannot be extracted by treatment with sulphuric acid are fused with $KHSO_4$ in a Rose crucible (92); the cold mass is then dissolved in water and the solution is titrated with the permanganate.

If hydrochloric acid has been used in preparing the solution to be titrated, the special procedure described in paragraph 399 must be adopted.

323. Estimation of the Total Iron in Ferric compounds, and in a mixture of Ferrous and Ferric compounds.

The ferric compound present in the solution is reduced to the ferrous state (311–313), and the iron is then titrated with permanganate (319).

If the solution of the original substance contains ferrous as well as ferric compounds, the iron in the ferrous compounds may be first estimated by titration in a part of the original solution (322). The total amount of iron is then estimated in another part of the original solution by reduction followed by titration: the reduction must be effected by zinc and sulphuric acid instead of hydrochloric acid (311), or by ammonium sulphite (313), since hydrochloric acid and stannous chloride are inadmissible except under the special conditions described in paragraph 399.

The weight of iron in the ferric compounds, which were originally present in the substance, is equal to the difference between the total percentage of iron and the percentage of iron which was originally present in the ferrous state.

Estimation of Oxalate in Solution by means of Standard Permanganate.

325. An oxalate which is soluble in water is readily estimated by means of standard permanganate solution. About 5 grams of the oxalate are

accurately weighed and dissolved in water, and the solution is made up to 250 c.c. A suitable quantity of this solution is acidified with sulphuric acid and is titrated as has been described in paragraph 320.

The weight of C_2O_4 present may be calculated from the equation given in paragraph 320.

Estimation of Calcium in Solution by means of Standard Permanganate.

326. The calcium is precipitated by adding a known volume in excess of standard oxalic acid solution. Either the excess of oxalic acid is then determined by titration with standard potassium permanganate solution (327), or the oxalic radicle present in the calcium oxalate precipitate is estimated (328). The second method should be employed if the quantity of calcium present is considerable and if great accuracy is required, since it obviates the error arising from the volume of the calcium oxalate precipitate.

The Process.—Add to the solution of the calcium compound, contained in a flask, a measured volume of normal oxalic acid solution, in quantity more than sufficient to precipitate all the calcium as oxalate. Add ammonium hydrate solution in excess, then boil the liquid and allow it to cool, and proceed as is directed in paragraph 327 or 328.

327. Titration of the Excess of Oxalic Acid added.—Transfer the liquid containing the precipitate of calcium oxalate to a suitable measuring-flask, make up to the mark with water, and mix the contents of the flask thoroughly. Pour off part of this turbid liquid through a dry filter into a flask of half the capacity, filling the flask to the graduation mark.

Measure out an aliquot part of the filtrate—say one-half. Acidify this with sulphuric acid, heat the liquid to 60° C., and determine the oxalic acid in it by means of potassium permanganate solution (320).

Calculate from this result the weight of oxalic acid which is present in the whole of the filtrate, and subtract this weight from that of the oxalic acid which was originally added for the precipitation of the calcium. The remainder will be the weight of oxalic acid which is chemically equivalent to the calcium which was originally present, and from this the weight of Ca may be calculated on the assumption that 126·02 grams of crystallised oxalic acid correspond to 40 grams of calcium.

328. Titration of the Oxalic Acid which has been Precipitated by the Calcium.—If the calcium oxalate precipitate is large in amount, it is filtered off and is well washed on the filter It is then dissolved in the smallest possible quantity of warm hydrochloric acid, and the solution is diluted with water. This

liquid is mixed with a little sulphuric acid and heated to 60° C ; it is then at once titrated by the potassium permanganate solution. The quantity of oxalic acid thus found is chemically equivalent to the weight of calcium which was originally present, 126·02 parts of oxalic acid ($H_2C_2O_4\,2H_2O$) corresponding to 40 parts of calcium.

Estimation of Lead in Solution by means of Standard Permanganate.

329. Lead may be estimated in a solution, rendered just acid by acetic acid, by methods described in paragraphs **326**, **327**. If the second method of titration (**328**) is employed for this estimation, the lead oxalate precipitate must be dissolved in dilute nitric acid ; sulphuric acid is then added, and the oxalic acid is titrated by permanganate. 126·02 parts of oxalic acid ($H_2C_2O_4\,2H_2O$) correspond to 207·1 parts of lead.

Estimation of Hydrogen Peroxide by means of Potassium Permanganate Solution

330. Commercial hydrogen peroxide is sold of three strengths, and should contain 5, 10 or 20 times its own volume of "available" oxygen. The so-called "ten volume" solution should yield by decomposition ten times its own volume of oxygen, and this corresponds to 3·04 per cent of H_2O_2 and to 1·43 per cent. by weight of "available" oxygen.

In estimating the H_2O_2 by means of potassium permanganate, it is essential that free sulphuric acid should be present, that reducing substances should be absent, and that the solution should be dilute. Under these conditions the reaction which takes place is as follows :

$$2KMnO_4 + 5H_2O_2 + 4H_2SO_4 = 5O_2 + 8H_2O + 2KHSO_4 + 2MnSO_4.$$

Process of Estimation.—Add 5 c.c. of dilute sulphuric acid to about 500 c.c. of water in a porcelain dish, and allow decinormal permanganate solution to flow into the liquid until it retains a faint permanent pink colour ; then add 5 c.c. of the hydrogen peroxide solution, and continue the addition of the permanganate until the faint pink colour again becomes permanent.

If the first drop of permanganate produces a permanent coloration, add a little more sulphuric acid ; if the colour still persists for a few minutes, no hydrogen peroxide is present in the solution.

The proportion of hydrogen peroxide found in the solution can be expressed either as percentage of peroxide by weight, or as percentage of "available" oxygen by volume. As has been mentioned above, a hydrogen peroxide solution containing 3 per cent. by weight of H_2O_2, corresponds to a solution liberating 10 times its volume of available oxygen : and such a solution, 100 volumes of which can evolve 1000 volumes oxygen at 0° and 760 mm., is termed a solution of 10-volume strength, or simply a 10-volume solution.

USE OF STANDARD IODINE SOLUTION.

Iodine dissolved in potassium iodide solution may be used for many different volumetric determinations (*Note*). The chemical reaction on which the estimations are based is usually that of oxidation, as is the case in the estimation of arsenious oxide: $As_4O_6 + 4H_2O + 4I_2 = 2As_2O_5 + 8HI$.

If the iodine solution is used in conjunction with sodium thiosulphate solution, the number of estimations to which it is applicable is increased. In these cases the iodine solution is usually added in excess, and the excess of iodine is then estimated by means of the sodium thiosulphate solution. The following equation represents the reaction which takes place between the iodine and the thiosulphate:

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

As the sodium thiosulphate solution is gradually added to the iodine solution, the brown colour of the iodine solution will change to yellow, and finally the liquid will become colourless; but the exact point at which the yellow colour of the solution disappears is difficult to judge with precision.

If, however, a few drops of starch solution are added to the pale yellow liquid, an intense blue colour will be produced, and this colour will entirely disappear when sufficient thiosulphate solution is added. In this case the completion of the titration is very sharply defined by the precise disappearance of the blue colour.

Occasionally the process of titration is reversed, the iodine solution being added to the liquid containing excess of the thiosulphate. The completion of the reaction will then be shown by the appearance of a faint but permanent blue colour in the liquid containing starch solution.

Note.—The changeable iodine solution may be replaced by the permanent solution of $KH(IO_3)_2$ and KI, iodine being set free in this solution immediately before it is used by adding an excess of HCl:

$$KH(IO_3)_2 + 10KI + 11HCl = 6I_2 + 11KCl + 6H_2O.$$

This iodate solution must be prepared of such strength as to furnish the standard iodine solution (331) when it is mixed with excess of HCl.

PREPARATION AND STANDARDISATION OF THE REQUISITE STANDARD SOLUTIONS.

The following solutions are required for the processes of estimation which involve the use of standard iodine and standard sodium thiosulphate solutions: A decinormal solution of iodine; a decimolecular solution of sodium thiosulphate; and a dilute solution of starch.

331. Preparation of the Decinormal Solution of Iodine, containing $\frac{126\,92}{10}$ = 12·692 grams of pure iodine per litre (*Note*, page 178).

Weigh out accurately (*Note*) into a litre flask from a stoppered bottle 12·692 grams of pure iodine (**110**, Exp. 28), taking care to remove the bottle from the balance-case before taking out the stopper. Then add about 30 grams of pure potassium iodide and about 250 c.c. of water. Shake the contents of the flask until complete solution has taken place, adding more of the iodide, if necessary, to complete the solution of the iodine. Then fill the flask up to the mark with distilled water. The solution is very slightly below its full iodine value, owing to the presence of impurity in the potassium iodide which fixes some iodine.

The solution must be kept in a well-stoppered bottle, and in a cool place.

Note.—Since iodine is volatile, it is difficult to weigh out exactly the quantity which is required for making a litre of the standard solution. Hence about 13 grams may be accurately weighed out by difference. This is dissolved in the manner already described, and is made up to the volume which is necessary to furnish a solution of decinormal strength. Thus, if 12·5 grams were weighed out, the volume of the iodine solution must be $\frac{1000 \times 12\,5}{12\,692}$ = 985 c.c.

332. Preparation of the Decimolecular Solution of Sodium Thiosulphate, containing $\frac{248{\cdot}23}{10}$ = 24·823 grams per litre of $Na_2S_2O_3.5H_2O$.

Weigh out accurately 24·823 grams of the pure recrystallised salt, which has been powdered and then dried by pressure between filter-paper. Dissolve this in water, and dilute the solution to a litre in the measuring-flask or cylinder.

The solution undergoes chemical change by the action of light, hence it should be kept in a dark blue Winchester quart-bottle, in a cool closed cupboard the interior of which is painted dead-black. Even when these precautions against exposure to light are taken, the solution will require frequent titration (335): but its permanency is much extended if 2 grams of potassium bicarbonate are added to each litre of the solution.

333. Preparation of the Starch Solution.—Make about 1 gram of starch, free from acid, into a thin cream with a small quantity of cold water. Pour this into about 100 c.c. of water which is boiling in a porcelain dish, and continue the boiling for a few minutes. Allow the liquid to stand until it is cold, and pour off the clear solution. It is necessary to prepare this starch solution immediately before it is used, since, after the solution has been kept for some time, it does not give an intense colour with iodine.

334. Process of Standardising the Iodine and Thiosulphate Solutions.—If the thiosulphate solution alone is to be standardised, the process which is described in paragraph 335 may be employed. Usually it is only necessary to determine the value of the thiosulphate solution in relation to the standard iodine solution. This is effected in the following manner:

Measure 20 c.c. of the iodine solution into a beaker, and dilute it with water. Then add the thiosulphate solution gradually from a burette, until the colour of the liquid fades to a pale yellow tint. Now add a few drops of the starch solution, and continue the titration until the blue colour thus produced just disappears.

The iodine solution should require the addition of 20 c.c. of thiosulphate solution. If more or less than this volume is required, the factor which is necessary to correct the volume should be noted on the label of the thiosulphate solution, the iodine solution being taken as the standard.

Thus, if 20·2 c.c. of the thiosulphate solution are required for 20 c.c. of the iodine solution, each c.c. of the thiosulphate solution will be equivalent to $\frac{20}{20 \cdot 2} = 0 \cdot 99$ c.c. of the iodine solution. Hence the number of c.c. of thiosulphate solution which have been used in any estimation will require to be multiplied by 0·99, in order to ascertain the corresponding volume of the iodine solution. The number 0·99 is termed the factor of the thiosulphate solution, and is entered as such upon the label of the bottle.

335. The Thiosulphate Solution may be Standardised by adding it to the standard solution of potassium dichromate (304) or of potassium permanganate (317), which has been mixed with excess of KI solution and has then been acidified with H_2SO_4. The following are the reactions upon which the titration depends:

$$K_2Cr_2O_7 + 6KI + 7H_2SO_4 = 3I_2 + 4K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O.$$
$$2KMnO_4 + 10KI + 8H_2SO_4 = 5I_2 + 8H_2O + 2MnSO_4 + 6K_2SO_4.$$

It will be seen that the iodine which is liberated is proportional to the weight of $K_2Cr_2O_7$ or of $KMnO_4$ which is present.

Estimation of Antimony in Tartar-emetic by means of Standard Iodine Solution.

336. When iodine is added to an alkaline solution containing Sb_2O_3, the following reaction takes place:

$$Sb_2O_3 + 2I_2 + 2H_2O = Sb_2O_5 + 4HI.$$

Since free hydriodic acid is formed in this reaction, sufficient alkali must be present to neutralise this acid. A normal alkaline carbonate affects iodine, hence a bicarbonate must be employed for the neutralisation. For

every decigram of Sb_2O_3 present in the liquid, about 25 c.c. of a saturated solution of $NaHCO_3$ in cold water should be added.

Weigh out accurately about 1·5 grams of anhydrous tartar-emetic, $KSbOC_4H_4O_6$ (109, Exp. 27), dissolve it in water, and dilute the solution to 250 c.c. Transfer 25 c.c. of this solution to a beaker, and add an equal volume of a cold saturated solution of $NaHCO_3$ free from Na_2CO_3. Now pour in a few drops of starch solution (333), and add the iodine solution (331) from a burette provided with a glass stop-cock until a faint blue colour just appears. The blue colour will disappear when the liquid is stirred, and more iodine solution must be added until the final permanence of the faint blue tint indicates the completion of the reaction.

The amount of Sb_2O_3 present can be calculated from the above equation, when the amount of iodine which is required for its oxidation is known.

The above method is also applicable to the estimation of antimonious oxide. The oxide is first dissolved in tartaric acid and water. The tartaric acid is then exactly neutralised by means of NaOH solution, the requisite quantity of $NaHCO_3$ is added, and the titration is performed as is described above.

Estimation of Arsenic in Arsen*ious* and Arsen*ic* Oxides, and in their Compounds, by means of Iodine.

337. When iodine solution is added to an alkaline solution of As_2O_3, the following reaction takes place:

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

Before the process of estimation, which is based on this reaction, can be applied to the higher oxide As_2O_5, that oxide must be reduced to As_2O_3 by passing SO_2 gas into the solution to saturation. The excess of SO_2 gas is then driven off by boiling the liquid, and the solution of As_2O_3 is titrated as is described below.

If both oxides of arsenic are present, the As_2O_3 alone is first estimated in part of the solution. A fresh portion of the original solution is then reduced by sulphurous acid as is described above, and the As_2O_3 is again titrated: the total amount of As present in the original solution is thus estimated as As_2O_3. From these two determinations the amounts of As_2O_3 and of As_2O_5 which were originally present may be calculated.

For practice in the estimation, weigh out accurately about 1·5 grams of commercial sodium arsenate, and dissolve it in about 150 c.c. of water. Add a little acetic acid and sodium acetate to the solution, and boil for ten minutes in order to remove any nitrite which may be present: then cool the solution and dilute it to 250 c.c.

The amount of arsenious oxide in 25 c.c. of this solution is determined

by mixing it with saturated $NaHCO_3$ solution in moderate excess, as shown by methyl-orange, then adding starch solution (333), and titrating with standard iodine solution (331), which is added until a faint permanent blue coloration remains.

The arsenic oxide in 100 c.c. of the original solution is then reduced by treatment with excess of SO_2 gas, and the excess is removed by boiling. The solution is then cooled and made up to 200 c.c. The amount of As_2O_3 in 50 c.c. of this solution, which is equivalent to 25 c.c. of the original solution, is found by adding $NaHCO_3$ in moderate excess, as indicated by methyl-orange, and titrating with the iodine solution.

The difference between the two titrations gives the amount of As_2O_3 which was originally present as As_2O_5.

The oxides of arsenic may be estimated by this method. They are first dissolved in HCl. This solution is exactly neutralised by NaOH solution, then mixed with $NaHCO_3$ solution, and is then titrated with the iodine solution.

Estimation of Stannous Chloride by means of Iodine.

338. When iodine solution is brought into contact with stannous chloride solution, one molecule of iodine (I_2) converts one molecule of stannous chloride ($SnCl_2$) into stannic compound.

A process for estimating stannous salt by means of iodine is founded on this reaction.

Dissolve about 1 gram of the tin salt, or 0·5 gram of metallic tin, in hydrochloric acid.

The air should be displaced from the vessel by a current of carbon dioxide gas, so as to prevent oxidation and formation of stannic salt from occurring during the process of solution. The solution of metallic tin may be hastened by the addition of pieces of platinum foil.

To this solution add Rochelle salt solution, and then sodium bicarbonate solution in excess, adding more Rochelle salt solution, if necessary, in order to render the solution clear.

Dilute the solution with water to a volume of 250 c.c., and titrate an aliquot part of the liquid with decinormal iodine solution (331), using starch (333) as the indicator.

253·94 parts by weight of iodine correspond to 189·9 parts of $SnCl_2$ and to 119·1 parts of Sn.

Estimation of Hydrogen Sulphide in Aqueous Solution by means of Standard Iodine Solution.

339. When a sufficiently dilute solution of hydrogen sulphide is brought into contact with free iodine, the following reaction takes place: $H_2S + I_2 = 2HI + S$. Hence in the exact conversion of I into HI by H_2S, 253·94 parts by weight of iodine react upon 34·08 parts of H_2S.

If the solution, in which the H_2S is to be estimated by the above reaction, contains more than 0·04 per cent. by weight of the gas, the change may not occur entirely according to the above equation.

Two methods of procedure are described below:

In the first method (**340**) the hydrogen sulphide is directly titrated by adding the iodine solution under suitable conditions to the hydrogen sulphide solution until the reaction is just completed.

In the second method (**341**) the iodine solution is at once added in excess to the hydrogen sulphide solution. The total volume of iodine solution added must be known. The excess of iodine is then estimated by means of thiosulphate solution (**332**).

The second method is usually more accurate than the first, since it prevents the risk of hydrogen sulphide escaping into the air during the titration. It may be advantageously applied to check the result which has been previously obtained by the first method, the first determination being made in order to ascertain how far it is necessary to dilute the liquid in order to obtain accurate results.

340. Direct Titration with Standard Iodine Solution.—Prepare some solution of H_2S by passing the gas into water; mix a measured quantity of this liquid with a little starch solution (**333**) and titrate it with decinormal iodine solution (**331**). This titration will roughly indicate the volume of iodine solution which is required for the oxidation of the solution of H_2S.

If the weight of hydrogen sulphide in the solution is greater than 0·04 per cent., measure the rest of the solution. Then dilute it with air-free water until it contains less than 0·04 per cent., and titrate a measured volume of this solution with iodine. This titration will indicate very nearly the true amount of iodine solution required. But since loss of the hydrogen sulphide occurs both by escape into the air and by oxidation from the air during the process of the titration, the results will be rather too low. This error may be avoided by proceeding as follows:

Introduce into a flask a volume of the iodine solution somewhat less than that which was required in the last titration, and add to this the volume of diluted hydrogen sulphide solution which was then employed. This amount

will destroy the colour of the iodine solution. Now add a little starch solution, and carefully add more iodine solution gradually from a burette until a permanent blue colour is just obtained.

From the total volume of iodine solution which has been used, the amount of hydrogen sulphide can be calculated by means of the equation (339).

341. Addition of the Hydrogen Sulphide Solution to Excess of Standard Iodine Solution and Titration of the Excess.—Greater accuracy is attained by first diluting the hydrogen sulphide solution, if necessary, with recently prepared air-free water until it contains not more than 0·04 per cent. of the gas (340), and then adding a measured volume rapidly to an excess of the standard iodine solution, the volume of which must be accurately known. The presence of iodine in excess is indicated by a permanent yellow colour remaining in the liquid after it has been stirred.

The amount of free iodine present in the liquid is now estimated by means of standard sodium thiosulphate solution (332) in the presence of starch solution (334), and the weight of iodine required for the oxidation of the hydrogen sulphide may then be found by difference. From this the amount of the sulphide can be calculated.

Estimation of Sulphur Dioxide, in Solution or in Combination, by Iodine and Thiosulphate.

342. Estimation of Sulphurous Acid.—If solution of sulphur dioxide gas is mixed with an excess of the standard iodine solution, the following reaction takes place: $SO_2 + I_2 + 2H_2O = H_2SO_4 + 2HI$. It will be seen from the equation that 253·94 parts by weight of iodine correspond to 64·06 parts of sulphur dioxide.

The sulphurous acid solution may, if very dilute, be measured in a pipette and delivered below the surface of the iodine solution. But it is usually necessary to guard against loss of sulphur dioxide from the solution during the process, and this may be prevented by weighing the solution, previously cooled to 5° C. in a freezing mixture, in a stoppered flask, and then quickly introducing it into a stoppered bottle containing the excess of iodine solution (331).

343. Ascertain by a preliminary trial the proportions in which the solution must be mixed with the iodine solution so as to leave a permanent faint yellow coloration of iodine.

Then introduce a slight excess of the standard iodine solution into a

stoppered bottle: quickly add the cool weighed sulphurous acid solution, insert the stopper, and mix the liquids by shaking. On now titrating the excess of iodine by sodium thiosulphate solution in the presence of starch, the iodine corresponding to the SO_2 is found by difference, and the corresponding weight of SO_2 may be calculated from the equation (342).

344. **Estimation of SO_2 in Sulphite.**—The preceding method may be used in the following way for the estimation of sulphite:

The solid sulphite in fine powder is weighed on a watch-glass and is introduced at once, without previous mixture with water, into a known volume in excess of decinormal iodine solution: the liquid is then well stirred until the reaction is complete, a result which is only slowly obtained with insoluble sulphites such as calcium sulphite. The excess of iodine is now determined by means of standard thiosulphate solution and starch solution (334). A second similar experiment is then made, in which only a slight excess of decinormal iodine solution is used, as has been indicated by the first trial, and the excess is titrated as before.

The weight of SO_2 is then calculated from the relative weights of iodine and of sulphur dioxide shown in the equation in paragraph 342.

Estimation of Thiosulphate by means of Iodine.

345. It has been already stated that a soluble thiosulphate undergoes a definite chemical reaction with iodine. Hence a thiosulphate may be estimated by means of standard iodine solution.

If the sodium salt, $Na_2S_2O_3.5H_2O$, is used, the reaction which takes place is as follows:

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

For practice in the estimation weigh out accurately about 10 grams of sodium thiosulphate, dissolve this in water, and make up the solution to a litre. Titrate 25 c.c. of this solution with standard iodine solution, as is described in paragraph 334.

Estimation of Formaldehyde by means of Standard Iodine and Sodium Thiosulphate Solutions.

346. The solution of formaldehyde, known commercially as "formalin," contains about 40 per cent. of formaldehyde. The formaldehyde may be

estimated in the solution by oxidising it to formic acid by means of iodine in alkaline solution:

$$H.COH + H_2O + I_2 = 2HI + H.COOH.$$

It will be seen that the disappearance of each molecule of free iodine corresponds to one molecule of formaldehyde.

For the estimation 10 c.c. of the formalin are diluted to 400 c.c.; 10 c.c. of this 1 per cent. solution are introduced into a beaker and mixed with 100 c.c. of decinormal iodine solution (331). Sodium hydroxide solution is then at once added, drop by drop, until the colour of the liquid becomes bright yellow. After standing for ten minutes the liquid is acidified with dilute hydrochloric acid, and the iodine thus liberated is titrated with decinormal sodium thiosulphate solution. Each c.c. of decinormal iodine solution which has disappeared in the oxidation of the formaldehyde corresponds to 0·0015 gram of formaldehyde.

USE OF STANDARD SODIUM THIOSULPHATE SOLUTION WITH POTASSIUM IODIDE.

347. Many substances have the power of liberating iodine from a solution of potassium iodide. Thus free chlorine reacts upon potassium iodide solution in the following manner: $Cl + KI = KCl + I$.

Each substance liberates its chemical equivalent of iodine, which is then easily estimated by standard thiosulphate solution (334, 335). Hence the reaction is frequently made use of in volumetric analysis, as an indirect means of estimation.

When some substances are heated with hydrochloric acid, they liberate a definite proportion of chlorine. Thus, when manganese dioxide is heated with hydrochloric acid, the following change occurs: $MnO_2 + 4HCl = Cl_2 + MnCl_2 + 2H_2O$. The chlorine, which is thus evolved, may be conducted into potassium iodide solution, when iodine will be liberated as is described above. The amount of iodine liberated will be equivalent to the chlorine, and is therefore proportionate to the "available oxygen" present in the manganese dioxide.

Estimation of Chlorine in Aqueous Solution by means of KI and Thiosulphate Solution.

348. Mix a measured quantity of dilute chlorine solution with solution of potassium iodide. Take care that an excess of potassium iodide is employed; this is shown by the liquid remaining brown or yellow in colour after it has been well mixed (*Note*).

Then determine the amount of free iodine by titration with standard sodium thiosulphate solution (334).

In calculating the weight of chlorine present, it must be remembered that 35·45 of chlorine liberate 126·92 of iodine.

Note.—The most satisfactory way of insuring the presence of potassium iodide in excess is to mix the chlorine solution with the potassium iodide solution as has been directed above. An aliquot part of this liquid is then removed and titrated with the standard thiosulphate solution. Another equal volume of the liquid is then mixed with additional potassium iodide solution, and is titrated with the thiosulphate. If the two titrations yield identical results, the potassium iodide solution was originally present in excess.

Estimation of Bromine in Aqueous Solution.

349. The bromine solution is diluted, if necessary, and is added to an excess of potassium iodide solution (*Note*, 348). The iodine, which is liberated by the bromine, is then titrated by standard thiosulphate solution (334) In calculating the weight of bromine present in the original solution, it must be remembered the 79·96 of bromine liberate 126 92 of iodine.

Valuation of Bleaching-powder by means of KI and Thiosulphate.

350. Prepare the turbid solution of bleaching-powder in the manner described in paragraph 301. After this liquid has been well mixed by shaking, transfer 25 c.c. of it to a 250 c.c. beaker or flask, add an excess of potassium iodide solution (*Note*, 348), and acidify the liquid with dilute hydrochloric acid. Then determine the amount of iodine, which has been liberated, by means of sodium thiosulphate solution and starch (334).

The amount of "available chlorine" (300) present in the bleaching-powder is chemically equivalent to the iodine liberated, 35·45 of chlorine corresponding to 126·92 of iodine.

Other Methods of Estimating "available chlorine" in bleaching-powder are described in paragraphs 301 and 315.

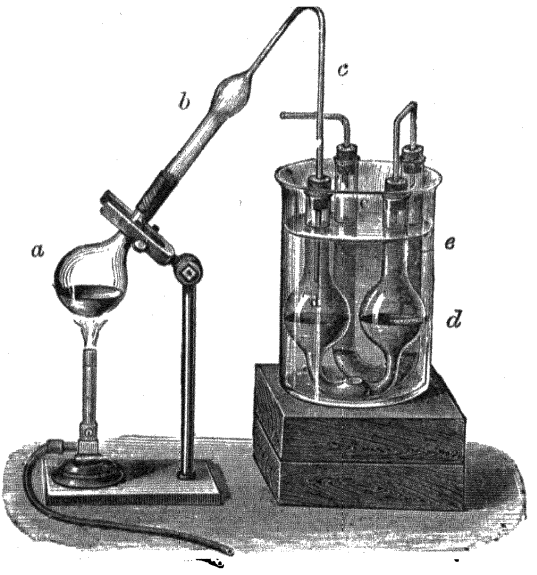
Indirect Estimation of Manganese Dioxide by means of KI and Thiosulphate.

351. The manganese dioxide is heated with excess of hydrochloric acid, and chlorine gas is evolved. This gas is conducted into an excess of potassium

iodide solution, and the iodine which is set free is estimated by means of standard sodium thiosulphate and starch solutions (334). It is evident that 87 parts of MnO_2 will liberate 70·9 parts of chlorine and 253·84 parts of iodine.

352. **The Apparatus**, which is shown in Fig. 86, will be found useful for carrying out the above process of estimation. It is prepared as follows:

FIG. 86.



ABSORPTION OF EVOLVED CL IN KI SOLUTION.

Note.—This apparatus involves the use of corks, which are advantageously dispensed with in some forms of absorption apparatus by making them entirely of glass.

A small flask or bulb-tube (*a*), of about 60 c.c. capacity, is connected with a tube (*b*) by means of a black rubber joint, within which the glass tubes are brought into contact with one another.

Upon the end of *b* is fused a thinner tube (*c*), which is bent as is shown in the figure, and is fitted to the bulbed U-tube (*d*) by means of a rubber cork. This apparatus will be found sufficient for ordinary purposes. But in the figure an additional plain U-tube (*e*) is shown, which may be used as a guard-tube to prevent the escape of any trace of chlorine. These U-tubes are kept cool by immersing them in cold water contained in a beaker.

A plain bent glass tube of the same diameter throughout as the neck of the flask may replace the tubes (*b*) and (*c*). The rubber corks and connections, which are

used in fitting up this apparatus, should have been previously freed from sulphur by boiling them in sodium hydrate solution.

353. **The Estimation** is carried out as follows: Weigh out accurately about half a gram of finely powdered manganese dioxide into the flask (*a*). Half fill the bulbs of the U-tube (*d*) with strong potassium iodide solution. If the second U-tube (*e*) is also used, pour into it sufficient potassium iodide solution to fill the bend. Ascertain that the apparatus is air-tight, and then add about 20 c.c. of strong hydrochloric acid to the manganese oxide in the flask.

It will be found convenient to introduce a small piece of magnesite with the manganese oxide. On the addition of the acid a regular stream of carbon dioxide gas will then flow through the U-tubes with the chlorine, and this will dilute the chlorine and render the absorption less violent.

Now heat the flask gently by means of a small flame: and as soon as the manganese dioxide is completely dissolved, boil the acid until all the chlorine has been expelled.

As soon as all the chlorine has passed into the absorption-tubes, pour out the contents of the first U-tube into a beaker, and rinse out the tube also into the beaker. If the potassium iodide solution in the second U-tube is yellow, the chlorine has not been completely absorbed by the first tube: the contents of the second tube must therefore also be transferred to the beaker. This liquid is well mixed, and is then measured, and the free iodine in two measured portions is at once titrated by means of standard sodium thiosulphate solution and starch (334).

The weight of iodine thus found in the whole liquid is a measure of the chlorine which has been liberated by the manganese dioxide, and two atoms of chlorine correspond to one molecule of MnO_2 as has been already explained.

INDIRECT ESTIMATION OF CHROMATE BY MEANS OF KI AND THIOSULPHATE.

354. When potassium dichromate is heated with strong hydrochloric acid, the following reaction takes place:

$$K_2Cr_2O_7 + 14HCl = 3Cl_2 + 2CrCl_3 + 2KCl + 7H_2O.$$

Accordingly the process which has been already described (351–353) for the estimation of MnO_2 may also be applied to the estimation of chromate. It will be seen that 294·5 of $K_2Cr_2O_7$ yield 212·7 of chlorine, and will therefore correspond to 761·82 parts of iodine liberated. Hence, when the amount of iodine liberated has been estimated by sodium thiosulphate solution, the amount of chromate may be calculated.

Indirect Estimation of Chlorate, Bromate, or Iodate by means of KI and Thiosulphate.

355. Distillation Method.—When a chlorate is heated with excess of strong hydrochloric acid, a mixture of chlorine with oxides of chlorine is evolved. This mixture sets free an amount of iodine from potassium iodide which is equivalent to the total weight of oxygen present in the chlorate.

Hence the above method (351–353) of liberating iodine from potassium iodide, and titrating it with thiosulphate and starch solutions, may be used for the estimation of chlorate.

The acid-radicle of a chlorate (ClO_3) liberates, under the above conditions, six atoms of iodine 122·6 parts by weight of $KClO_3$ will therefore liberate $126·92 \times 6 = 761·52$ parts of iodine.

The corresponding acid-radicle of a bromate (BrO_3) or of an iodate (IO_3) liberates only four atoms = 507·68 parts of iodine, since iodous and bromous chlorides remain in the flask.

These data suffice for calculating the weight of chlorate, bromate, or iodate present, from the result obtained by titrating the iodine which it can liberate.

356. Digestion Method.—A simpler method of estimation depends upon the fact that some substances may be estimated by the amount of iodine which they liberate, when they are simply digested with strong hydrochloric acid and potassium iodide. This process is specially suitable for the estimation of bromate and of iodate, and is carried out as follows:

Select a 120 c.c. bottle, which is fitted with an accurately ground stopper. Test whether the stopper is air-tight by completely immersing the tightly stoppered bottle in hot water: no air-bubbles should escape between the neck and the stopper. If the stopper is not air-tight, grind it into the neck with very fine emery-powder and water until it satisfactorily stands the above test.

Now weigh out from 0·2 to 0·5 gram of the substance into the bottle, add the requisite excess of strong hydrochloric acid and of potassium iodide solution, fasten the stopper down by means of copper binding-wire, and heat the bottle in the water-bath. As soon as the decomposition is complete, withdraw the bottle from the bath and allow it to cool. Then empty the contents into a beaker, dilute the liquid with water, and titrate the free iodine with sodium thiosulphate solution and starch (334).

In this process *six atoms* of iodine are liberated by (ClO_3), (BrO_3), and (IO_3).

Indirect Estimation of Copper in Solution by means of KI and Thiosulphate.

357. The process of estimation depends upon the following reaction: $2CuSO_4 + 4KI = Cu_2I_2 + I_2 + 2K_2SO_4$.

The potassium iodide is added in excess to the copper solution, and the

liquids are thoroughly mixed. The amount of free iodine in the solution is then titrated by standard sodium thiosulphate solution and starch (334). The amount of iodine which is found by titration will be proportional to the amount of copper which was originally present in solution, as is shown by the above equation.

In order that the result may be accurate, the copper solution must contain no free acid except acetic acid. To secure this, sodium carbonate solution is added to the copper solution until a slight permanent precipitate remains: and this precipitate is then removed by the careful addition of acetic acid.

It is also necessary that the copper solution shall be fairly concentrated, else the reaction is not complete. About 0·5 gram of Cu should be present in the solution which is used for each titration. The amount of KI used should be ten times that of the copper present in order to secure satisfactory results.

PART III.—SECTION VIII.

UNCLASSED VOLUMETRIC ESTIMATIONS.

Estimation of Silver by Standard Sodium Chloride Solution.

370. When solution of silver nitrate is mixed with solution of sodium chloride, the silver is precipitated as the white insoluble chloride according to the following equation:

$$AgNO_3 + NaCl = AgCl + NaNO_3.$$

A similar reaction occurs with any soluble silver salt.

Accordingly the amount of silver present in a solution may be volumetrically estimated by exactly precipitating a known volume of NaCl solution of known strength by means of the silver solution.

The most convenient method of judging precisely the end of the reaction consists in adding a few drops of potassium chromate solution to the chloride solution (**371**). Dark red silver chromate will then be formed as soon as the silver salt has been added in slight excess.

The method of procedure will be different when the silver solution contains free acid, since free acid interferes with or prevents the formation of silver chromate (**372**).

371. Estimation of Silver in Neutral Solution.—As has been stated above, a few drops of neutral potassium chromate solution are added to a known volume of standard sodium chloride solution before the silver solution is allowed to flow in. The presence of the slightest excess of silver solution, after the precipitation of chloride is complete, is then indicated by a permanent red colour remaining in the turbid liquid after it has been well mixed.

Process of Estimation.—Prepare a decinormal solution of NaCl, by dissolving $\frac{58{\cdot}5}{10}$ = 5·85 grams of NaCl in water, and diluting the solution to a litre.

Measure 10 c.c. of the above solution into a porcelain dish, dilute it with a little water, and add three drops of neutral potassium chromate solution. Measure accurately the volume of the well-mixed silver solution which is

to be titrated, and then charge a 50 c.c. burette with the liquid. Now add the silver solution from the burette, with constant stirring, until a faint permanent red tint remains in the liquid in the dish.

It is well to assist the eye in detecting this tint by adding to sodium chloride solution and chromate, in a second similar dish, sufficient silver solution to produce a faint but permanent red tint. This dish should stand beside the first during the process of titration. The appearance of the slightest permanent red tint in the first dish is then easily seen by comparing the colours of the contents of the two dishes.

Since each c.c. of the NaCl solution corresponds to 0·010793 gram of silver, the amount of silver present in the liquid which has been added from the burette is easily calculated. From this result the amount of silver in the whole solution may then be found.

372. Estimation of Silver in Acid Solution.—Since silver chromate cannot be precipitated from an acid solution, the precipitation of this compound cannot be used as the indication of the completion of the process of titration, when silver is to be estimated in an acid solution.

The precipitation of the whole of the silver from solution is, however, known to have taken place when no turbidity is formed by the further addition of the chloride solution. This method of judging the end of the reaction is possible, since silver chloride is insoluble in solutions containing a little free nitric acid, and it quickly subsides, leaving a clear supernatant liquid, after the solution has been vigorously shaken.

Decinormal sodium chloride solution is usually employed for this estimation. It is added to the silver solution, which has been acidified with nitric acid, and the liquid is vigorously shaken. Towards the end of the precipitation, the sodium chloride is added drop by drop until no further precipitate appears on the addition of the last drop. In cases where great accuracy is required, centinormal sodium chloride solution may be used towards the end of the process.

Process of Estimation.—Weigh out accurately about 0·3 gram of pure recrystallised silver nitrate into a well-stoppered 200 c.c. bottle. Add about 100 c.c. of water, and a few drops of strong nitric acid. Cover the bottle during the titration with black velvet or cloth to prevent access of light. Then add nearly the total requisite quantity of decinormal sodium chloride solution, about 20 c.c., and shake the bottle vigorously until the silver chloride precipitate is clotted together. Tap the bottle on the bench to cause any floating precipitate to subside.

Now drop in a little more sodium chloride solution. If the clear super-

natant liquid becomes turbid, add more sodium chloride solution cautiously, taking care to shake the bottle well after each addition. Continue this procedure until no further turbidity appears after the addition of the last drop of the chloride solution.

When the point of complete precipitation has been nearly reached, the precipitate will be found to subside slowly: but as soon as a drop of sodium chloride has been added in excess the liquid clears more rapidly. This indication of the presence of excess of chloride solution is often valuable.

Since each c.c. of the decinormal sodium chloride solution corresponds to 0·010793 gram of silver, the percentage of silver in the salt is readily calculated.

Estimation of Chloride, Bromide or Iodide in Solution by Standard Silver Nitrate.

373. The processes for the estimation of silver by standard sodium chloride solution (**371**, **372**) also serve for the estimation of a chloride, bromide or iodide in solution by standard silver nitrate solution.

The amount of chloride in neutral solution may be readily estimated by adding a few drops of potassium chromate solution to serve as an indicator, and then titrating the liquid with decinormal silver nitrate solution.

Decinormal silver nitrate solution is made by dissolving 16·994 grams of $AgNO_3$ in water and diluting to a litre: each c.c. of this solution corresponds to 0·003545 gram of Cl.

If the solution of chloride contains free acid, the acid may be exactly neutralised by means of pure sodium hydrate solution, and the chloride may then be titrated in the usual way (**371**). Or the neutralisation and the indicator may be dispensed with, and the chloride solution may be added from a burette to a measured volume of the standard $AgNO_3$ solution, the procedure being similar to that already described in paragraph **372**.

Estimation of Cyanide by means of Standard Silver Nitrate Solution.

374. The hydrocyanic acid, or soluble cyanide, is rendered alkaline by the addition of potassium hydrate solution in excess, and standard solution of silver nitrate is added. As soon as the silver solution is present in excess, a precipitate of silver cyanide is formed.

During this reaction a soluble double cyanide of silver and potassium is produced at first and therefore no precipitate is formed:

$$2KCN + AgNO_3 = KCN.AgCN + KNO_3.$$

But as soon as the silver solution has been added in quantity more than sufficient for the formation of the double cyanide, a precipitate of silver cyanide is produced:

$$KCN.AgCN + AgNO_3 = 2AgCN + KNO_3.$$

The first appearance of this precipitate, therefore, serves to indicate the end of the first stage of the reaction referred to above.

At the conclusion of the first stage of the reaction, each c.c. of decinormal $AgNO_3$ solution which has been added will correspond to 0·013032 gram of KCN.

The solution in which the cyanide is to be estimated should be largely diluted with water before it is titrated.

A solution of cyanide containing free ammonia—such as the cyanide solution which has been used for gold extraction—may be mixed with a few drops of potassium iodide solution The first drop of silver solution which is added in excess of that required by the first reaction will then produce a precipitate of yellow silver iodide, showing that the reaction is complete.

If the amount of hydrocyanic acid present in solution is to be estimated by this process, the acid should be neutralised by quickly mixing it with excess of potassium hydrate solution in a beaker, so as to prevent loss of the volatile acid. The amount of potassium hydrate solution which is added should correspond as nearly as possible to that necessary for converting the acid into KCN.

In order to prevent the inhalation of poisonous vapour, the solution of hydrocyanic acid should be weighed instead of being measured by sucking it up into a pipette.

Dilute hydrocyanic acid may be measured in a pipette, if a plug of cotton-wool moistened with silver nitrate solution is pushed into the upper end of the pipette, since this liquid absorbs the vapour of the acid and prevents it from being inhaled.

For practice in the estimation use commercial potassium cyanide. Weigh accurately about 1 gram of the solid cyanide, dissolve it in 250 c c. of cold water, and use 25 c.c. of this solution for the titration. No potassium hydrate solution need be added to this solution, since the commercial salt is always alkaline. Add decinormal $AgNO_3$ solution until a very slight permanent precipitate appears. Then calculate the amount of KCN present, on the assumption that each c.c. of the silver solution added indicates the presence of 0·013032 gram of KCN.

Estimation of Silver by Potassium Thiocyanate Solution.

375. When a solution of silver in nitric acid is mixed with a sufficient amount of solution of potassium thiocyanate, the silver is precipitated as white silver thiocyanate: $AgNO_3 + KCNS = AgCNS + KNO_3$; and if a few drops of ferric sulphate have been previously added to the silver solution, the presence of thiocyanate in the slightest excess will be indicated by the formation of a distinct and permanent red coloration of ferric thiocyanate.

These reactions may be utilised for estimating the proportion of silver present in silver alloys which have been dissolved in nitric acid.

The following solutions will be required:

(a) *Decinormal Silver Nitrate Solution*, prepared by dissolving $\frac{169{\cdot}97}{10} = 16{\cdot}997$ grams of $AgNO_3$ in water, and diluting to a litre.

(b) *Approximately Decinormal Potassium or Ammonium Thiocyanate Solution.*—As both the above salts are hygroscopic and are decomposed by heat, about 10 grams of the salt are dissolved in water, and this solution is then diluted to a litre and standardised by titration with the silver solution (a).

(c) *Ferric Sulphate Solution*, prepared by adding strong nitric acid to a strong solution of ferrous sulphate and boiling until oxides of nitrogen are no longer evolved.

The Standardisation of the Thiocyanate Solution is effected by placing 20 c.c. of the silver solution (a) in a beaker, diluting it with water to about 100 c.c. and adding a few c.c. of dilute nitric acid; 1 c.c. of the iron solution (c) is then added to serve as an indicator, and the thiocyanate solution (b) is allowed to flow in from a burette, with constant stirring, until the red coloration of the liquid becomes permanent. From the volume of the solution required, its strength is then calculated.

For Practice in the Estimation the proportion of silver in any silver alloy, such as a silver coin, may be determined. Any other silver alloy may be used if none of the other metals present strongly colour the nitric acid solution.

Weigh out accurately about 0·3 gram of the silver alloy, dissolve this in nitric acid of 1·2 specific gravity, boil until no more nitrous fumes are evolved, and dilute the solution to 100 c.c. with water. Now add 1 c.c. of the ferric solution (c) as an indicator, and allow the standard thiocyanate solution (b) to flow in from a burette until a permanent faint red tint is produced.

Indirect Estimation of Chlorine in a Soluble Chloride by Thiocyanate Solution.

376. The solution of chloride is mixed with excess of decinormal silver nitrate solution, and the excess is estimated by standard thiocyanate solution as has been described in paragraph 375. From the amount of silver precipitated by the chloride, the percentage of chlorine present as chloride is calculated.

Estimation of Copper in Solution by means of Potassium Cyanide Solution.

377. When an ammoniacal solution containing copper is brought into contact with a solution of potassium cyanide, it is decolorised. On this fact, a process for the volumetric determination of copper in solution is based.

Since the reaction is influenced by the quantities of copper, of free ammonia and of ammonium salts which are present, care must be taken that the amounts of these substances shall be approximately the same in every estimation.

A standard solution of the copper salt is first prepared by dissolving 5 grams of pure electrolytic copper in moderately strong nitric acid. The solution is evaporated to dryness on the water-bath to expel the excess of acid; the residue of copper nitrate is then dissolved in water, and the solution is made up to a litre.

A moderately strong solution of potassium cyanide is now poured into a burette. 20 c.c. of the copper solution, which correspond to 0·1 gram of Cu, are measured into a beaker, and 10 c.c. of ammonium hydrate solution of 0·9 specific gravity are added. The potassium cyanide solution is then added to the copper solution, until the full blue colour disappears and only a very pale lavender tint remains. The end of the reaction is marked with greater precision by the appearance of this tint than by the total removal of the colour.

When the copper value of the potassium cyanide solution has been thus determined, the solution should be diluted until 20 c.c. correspond to 20 c.c. of the copper solution. Each c.c. of the potassium cyanide solution is then equivalent to 0 005 gram of copper.

For practice in this method, weigh out accurately about 10 grams of pure crystallised copper sulphate, $CuSO_4.5H_2O$. Dissolve this, and make up the solution to half a litre with water. Take out 20 c c. for the titration. Add

to this 10 c.c. of ammonium hydrate solution of 0·9 specific gravity; and allow the potassium cyanide solution to flow in from the burette until only the very pale lavender tint remains.

From the volume of the standard potassium cyanide solution which is required, the weight of copper present and its percentage proportion in the substance are readily calculated.

Estimation of Zinc in Ammoniacal Solution by Ferrocyanide or by Sodium Sulphide Solution.

378. Estimation by Ferrocyanide Solution.—When sufficient potassium ferrocyanide solution is added to an acid solution of zinc, the zinc is completely precipitated as double ferrocyanide. In using this reaction volumetrically, the completion of the titration may be indicated by the brown colour produced when the slightest excess of the soluble ferrocyanide is brought into contact with solution of uranium acetate.

The following solutions are required for the process:

(a) *Standard Ferrocyanide Solution* is made by dissolving about 45 grams of pure potassium ferrocyanide in water and making the solution up to a litre: each c.c. of this solution will correspond approximately to 0·01 gram of zinc, its exact strength being later on determined by titration with the zinc solution.

(b) *The Standard Zinc Solution* is prepared by dissolving 2·5 grams of pure zinc in a little hydrochloric acid which has been diluted with its own volume of water, carefully avoiding loss by spirting (66): this solution is then made up to 250 c.c. An alternative method consists in dissolving 10·97 grams of pure $ZnSO_4.7H_2O$ crystals in water and making the solution up to 250 c.c. Each c.c. of this solution contains 0·01 gram of zinc.

(c) *Uranium Acetate* in saturated solution.

Standardise the Ferrocyanide Solution (a) by introducing 25 c.c. of the zinc solution (b) into a beaker of about 400 c.c. capacity, adding 10 c.c. of strong hydrochloric acid and 5 grams of solid AmCl, diluting to 250 c.c. and heating to about 38° C. Then add the ferrocyanide solution gradually from a burette, with constant stirring, until a brown coloration just appears when the liquid is mixed with a drop of the uranium acetate solution on a white porcelain plate. As the precipitation of the zinc is not immediate, it is necessary to continue the stirring of the solution for a minute or two and then test again with the indicator, more ferrocyanide solution being added, if necessary until the brown coloration with the uranium solution persists.

From the volume of ferrocyanide solution required, its precise zinc-value may then be calculated.

The Process of Estimation of zinc is carried out precisely as is described under the above titration of the ferrocyanide solution, and the amount of free hydrochloric present as well as the temperature of the liquid should correspond generally to the directions there given, else chlorine might be liberated and cause the liquid to become greenish yellow in colour.

It is evident that the estimation of zinc by this process cannot be made, if metals which form ferrocyanides insoluble in hydrochloric acid are present in solution.

379. **Estimation by Sodium Sulphide Solution.**—When an ammoniacal solution of a zinc compound is mixed with sodium sulphide solution, the zinc is precipitated as sulphide: $ZnSO_4 + Na_2S = ZnS + Na_2SO_4$. The presence of excess of sodium sulphide may be readily detected by the brown precipitate which it forms in an alkaline solution of a lead salt. The lead solution is therefore used as an indicator of the completion of the titration.

The following solutions are required:

Sodium Sulphide Solution.—Hydrogen sulphide is passed into a moderately strong solution of sodium hydrate, until the liquid smells strongly of the gas. Sodium hydrate solution is then added in quantity sufficient to remove the odour of the gas. This solution is suitably diluted, and is used for the titration.

Alkaline Solution of Lead.—Lead acetate solution is heated with a mixture of tartaric acid solution and excess of sodium hydrate. Neutral sodium tartrate solution may be substituted for the mixture of tartaric acid with sodium hydrate. As soon as the lead solution becomes clear, the heating is stopped, and the liquid is ready for use.

Standard Solution of Zinc Sulphate, made as directed in paragraph 378.

The Process of Titration.—Transfer 25 c.c. of the zinc solution to a beaker. Then dissolve some ammonium carbonate in five times its weight of water, and mix this with three times its volume of dilute ammonium hydrate solution, prepared by mixing strong ammonium hydrate solution with three times its volume of water. Add this reagent to the zinc solution until the precipitate, which forms at first, is just redissolved.

Lay a piece of filter-paper upon a white tile and place upon it at intervals separate drops of the alkaline lead solution by means of a glass rod.

Now add the solution of sodium sulphide to the zinc solution with constant stirring. From time to time allow a drop of the liquid to fall from the stirring-

rod upon the filter-paper, so close to a drop of the lead solution that it will expand and join it. In this way the precipitate is filtered off from the drop, and the liquid, in which the ZnS was suspended, alone comes into contact with the lead solution. The lead solution is blackened by contact with the moist ZnS, and the above precaution is therefore necessary.

As soon as a dark line is produced by the contact of the two liquids upon the paper, the precipitation of the Zn is complete. A little experience renders it possible to judge the end of the reaction with great precision.

The sodium sulphide solution, which has been prepared as is directed above, will probably be shown by this titration to be too strong. It must be diluted, if necessary, with air-free water until from 15 to 20 c.c. of the solution are required to precipitate 25 c.c. of the zinc solution.

When zinc is to be estimated in a solution by this method, an aliquot part of the solution is rendered ammoniacal, as has been already described, and it is then titrated with the sodium sulphide solution in the manner just stated.

Estimation of P_2O_5 in Soluble Phosphates by means of Uranium Solution.

380. This process depends upon the fact, that when solution of uranium nitrate or of uranium acetate and solution of a phosphate are mixed together, in the presence of an alkaline acetate and free acetic acid, the whole of the phosphate is thrown down as uranium phosphate.

In carrying out the process volumetrically, the uranium solution is usually added from a burette to the solution of the phosphate, and the presence of an excess of the uranium solution is detected by the formation of a brown precipitate of uranium ferrocyanide, when a drop of the mixed liquids is brought into contact with a drop of freshly prepared potassium ferrocyanide solution.

The following solutions are required:

Standard Solution of Uranium Nitrate.—Weigh out roughly 35 grams of crystallised uranium nitrate $[UO_2(NO_3)_2.6H_2O]$, or 29 grams of uranium acetate $[UO_2(C_2H_3O_2)_2\ 2H_2O]$, add 25 c.c. of glacial acetic acid, dissolve the salt in water, and dilute the solution to a litre.

Standard Sodium Phosphate Solution.—Weigh out accurately 10·085 grams of the pure, recrystallised, non-effloresced salt, $Na_2HPO_4.12H_2O$. Dissolve this in water and dilute the solution to a litre. 50 c.c. of this solution correspond to 0·1 gram of P_2O_5.

A Solution of Sodium Acetate containing Acetic Acid.—This solution is

prepared by dissolving 100 grams of sodium acetate in water, adding 100 c.c. of acetic acid of about 1·04 specific gravity, and diluting the liquid to a litre.

A Solution of Potassium Ferrocyanide, which must be freshly prepared.

381. *The Process of Titration.*—Add to 50 c.c. of the sodium phosphate solution 5 c.c. of the sodium acetate solution, and heat the liquid to 90° C. by placing the beaker upon a hot plate or on a water-bath. Now add the uranium solution from a burette, until a drop of the well-mixed liquids, when it is brought into contact with a drop of potassium ferrocyanide solution, gives a faint reddish brown coloration.

Heat the liquid once more to 90° C., and test a drop again with ferrocyanide. If the brown coloration still appears, the titration has been completed. If, however, no coloration appears, continue to add the uranium solution, until the brown colour is produced with the ferrocyanide after the liquid has stood for some time.

The uranium solution should now be diluted until 50 c.c. of the phosphate solution require 20 c.c. of the uranium solution. Each c.c. of the uranium solution will then correspond to 0·005 gram of P_2O_5.

In the final titration it is best to add nearly the whole of the uranium solution rapidly, and to finish the titration by gradually and cautiously adding the remainder.

The uranium solution must be titrated by a special method, if it is to be used for the estimation of calcium phosphate or magnesium phosphate in acid solution (382).

The above procedure indicates the method of estimation of phosphate in aqueous solution.

382. **Estimation of Calcium and Magnesium Phosphates.**—These phosphates cannot be correctly estimated by uranium solution, which has been standardised by means of sodium phosphate solution. The uranium solution, which is used for the estimation of P_2O_5 in either of these phosphates, must be standardised by a solution which contains 5 grams per litre of tricalcium phosphate instead of by the sodium phosphate solution.

Before this solution is prepared the purity of the tricalcium phosphate must be tested as follows: Weigh out accurately about 0·25 gram of pure commercial calcium phosphate. Dissolve this in a small quantity of nitric acid, add a large excess of ammonium molybdate solution (520), and allow the liquid to stand in a warm place for several hours. The process of precipitation must be proved to be complete by warming some of the clear liquid with more molybdate solution. Dissolve the precipitate thus produced in ammonium hydrate solution, and estimate the P_2O_5 as $Mg_2P_2O_7$ (166). From this

result, the amount of pure $Ca_3(PO_4)_2$ in the commercial phosphate can be calculated.

Now weigh out a quantity of the commercial phosphate, which contains 5 grams of pure $Ca_3(PO_4)_2$. Dissolve this in a slight excess of dilute HCl, and dilute the solution to a litre. Mix 50 c.c. of this solution in a beaker with 5 c.c. of the sodium acetate solution, and add the uranium solution to the cold liquid until the final point is nearly reached; then heat to 90° C. and complete the titration (381).

Note.—If the phosphate solution is heated at the beginning of the titration, calcium or magnesium phosphate may be precipitated, and it is then redissolved in acetic acid only with much difficulty.

From the result of this titration the phosphate-value of the uranium solution, when it is applied to the estimation of calcium or magnesium phosphate, may be determined.

383. **Estimation of Phosphates of Unknown Composition.**—A substance of unknown composition, in which phosphate is to be estimated by standard uranium solution, must first be subjected to qualitative analysis The conditions which are specified in paragraphs 381, 382 with respect to the process of titration must then be observed.

PART IV.

GENERAL QUANTITATIVE ANALYSIS

Introductory.—The student who has worked according to the directions given in the preceding pages will have gained experience in many ordinary processes of simple gravimetric and volumetric analysis, and will be in a position to understand and perform more complicated analyses.

Some analyses are accordingly described in this part of the book, most of which involve quantitative separations. The processes which are made use of are either gravimetric or volumetric, each method being selected on account of its special suitability. Most of the processes which are described are those actually in use for technical, manufacturing, and agricultural purposes; others serve for the examination of articles of food and drink. Most of these analytical processes are also suitable for determinations required for purely scientific purposes; those described under Organic Analysis are more especially of this nature.

Some of the methods afford a complete quantitative chemical examination of the substance under examination: in other cases the process is simply an "assay" or "valuation" of the material, which furnishes as a result only the percentage of some element upon which the value of the ore or material depends.

When several constituents are to be estimated in a substance, time may frequently be economised by weighing out separate portions of the substance for each estimation. It will be understood that this procedure will frequently entail the preliminary separation and rejection of certain constituents, under the scheme of analysis given in the text, before the particular constituent can be estimated.

The process of calculation may also be facilitated by weighing out a suitable quantity of substance for the estimation: thus if the "factor quantity." that is 0·4702 gram of iron, is used for the estimation of Si (536), the weight of Si found when multiplied by 10 gives the percentage of Si present in the iron

A list of books of reference from which fuller information on special subjects may be obtained, and a list of journals which describe new analytical methods, will be found in paragraph **1021.**

PART IV.—SECTION IX.

ANALYSIS, VALUATION AND ASSAY OF ALLOYS, ORES, MINERALS, IRON AND STEEL, COAL, &c.

Estimation of Silver and Copper in a Silver-copper Alloy.

Two methods of estimation are here described, one of which is volumetric and the other gravimetric. It may be stated that English silver coinage contains 92·5 per cent. of silver and 7·5 of copper.

396. **Volumetric Method.**—Weigh accurately a threepenny piece, or about 1 gram of clippings or turnings obtained from a silver-copper alloy. Introduce the alloy into a small flask, and place a small funnel in the neck of the flask (66). Pour a few c c. of strong nitric acid and then a little water through the funnel into the flask. A violent reaction will ensue. As soon as this ceases, heat the flask on the water-bath, adding a little more nitric acid, if necessary, to complete the solution of the metal.

Now heat the solution in an evaporating-dish on the water-bath, until most of the free acid has been expelled. Then add water and make up the solution to 200 c.c. with distilled water.

Estimation of the Silver.—Measure 20 c.c. of this solution into a well-stoppered bottle, add decinormal sodium chloride solution gradually from a burette, and shake the liquid in the bottle vigorously. The standard solution must be added until no further precipitate is produced in the clear liquid in the bottle by the addition of the last drop of the sodium chloride solution (372).

Each c.c. of the sodium chloride solution corresponds to 0·01079 gram of silver, hence the percentage weight of silver in the coin is readily calculated from the result of the titration.

Another method of estimation is described in paragraph 375.

Estimation of the Copper.—Measure 50 c.c. of the solution of the alloy into a beaker, add excess of sodium chloride solution and filter off and wash the silver chloride precipitate. Add to the filtrate and washings 20 c.c. of ammonium hydrate solution of 0·93 specific gravity, and estimate the copper in this liquid by titration with standard potassium cyanide solution (377).

An alternative method for estimating the copper is that effected by means of potassium iodide and sodium thiosulphate solution (357).

397. **Gravimetric Method.**—Weigh accurately half a threepenny-piece, or about 0·5 gram of the clippings or turnings from a silver-copper alloy. Dissolve this in nitric acid, and expel most of the free acid by evaporation.

Estimation of the Silver.—Add to this solution an excess of sodium chloride solution. Boil the liquid, and filter off, wash, and weigh the precipitated silver chloride (149).

Estimation of the Copper.—Heat the filtrate and washings from the silver chloride to boiling, and add a slight excess of potassium hydrate solution. Then filter off and weigh the copper oxide thus precipitated (126).

The thiocyanate method of estimation (408) may be substituted with advantage for the above method.

Indirect Estimation of Arsenic in Ores by Thiocyanate.

398. In the following method the arsenic is converted into alkaline arsenate by fusion with alkaline carbonate and nitrate: the solution of arsenate is then precipitated by an excess of silver nitrate solution, and the silver in the silver arsenate is titrated by thiocyanate solution (375). It is evident that the ore must contain no phosphorus, since this would be estimated as arsenic by this process.

From 0·1 to 1·0 gram of the finely powdered ore is fused with ten times its weight of a mixture in equal proportions of Na_2CO_3 and KNO_3, in a porcelain or copper crucible, taking care that a layer of the alkaline salts covers the mixture. The cold mass is extracted with boiling water, and the insoluble matter is filtered off. The filtrate is then acidified with dilute nitric acid and is boiled to expel carbon dioxide and nitrogen oxides. The solution is now made just alkaline by the addition of ammonia and is boiled again and filtered from any slight precipitate which may have been produced.

This solution is made just acid by adding dilute nitric acid, and silver nitrate solution is added in quantity more than sufficient to precipitate the arsenate: 2 grams of solid sodium acetate are now introduced and the liquid is well stirred.

The silver arsenate is allowed to settle, and is filtered off and washed with cold water. It is then placed, while wet and in the filter-paper, in a beaker, and is dissolved in a small quantity of nitric acid which has been diluted with three times its volume of water. 1 c.c. of the ferric sulphate

solution (375, c) are then added, the liquid is diluted to about 100 c.c., and the silver is titrated by the standard thiocyanate solution (375, b).

Valuation of Iron-ore.

399. The valuation of an iron-ore has been described in paragraphs 314 and 321–323, but the procedure described below is that best suited to give a rapid result when many ores are under examination. It has been already stated (316) that a solution of iron containing hydrochloric acid cannot be correctly estimated under ordinary conditions by standard permanganate. By the procedure described below, however, the titration of iron with permanganate in hydrochloric acid solution furnishes accurate results; and this is important in the quick assay of iron-ore, since the iron is usually much more rapidly extracted from the ore by means of hydrochloric acid than by sulphuric acid, and the solution is more rapidly titrated by permanganate than by dichromate.

The modification of the ordinary procedure consists in determining the value of the permanganate solution by means of iron solution, under precisely similar conditions to those under which the acid iron solution of the ore is subsequently titrated by the permanganate. The liberation of chlorine from the hydrochloric acid by the action of the permanganate is minimised by properly diluting the solution and by adding manganese sulphate: while the masking effect of the bright yellow colour of the ferric chloride upon the pink permanganate coloration at the conclusion of the titration is prevented by the addition of phosphoric acid, which converts the ferric chloride into colourless ferric phosphate.

The solutions required are the following:

(a) *Standard Potassium Permanganate*, prepared by dissolving from 4 to 5 grams of the crystals in water and diluting this solution to a litre (317).

(b) *Phosphoric and Manganous Solution.*—50 grams of crystallised manganous sulphate are dissolved in about 250 c.c. of water, adding a few drops of sulphuric acid if necessary: 250 c.c. of phosphoric acid solution of 1·3 specific gravity are added, together with 150 c.c. of water and 100 c.c. of strong sulphuric acid.

(c) *Stannous Chloride Solution* is made by dissolving 30 grams of pure granulated tin in 125 c.c. of strong hydrochloric acid, and diluting with water to 250 c.c.: this is filtered through asbestos, and the filtrate is mixed with 250 c.c. of strong hydrochloric acid and 500 c.c. of water.

(d) *Mercuric Chloride Solution.*—50 grams are dissolved in a litre of water

To Standardise the Permanganate Solution weigh off exactly 2·5 grams of pure iron wire, containing 99·7 per cent. of iron, and dissolve this in a small quantity of strong HCl in a 250 c.c. flask: then cool the solution and dilute it to the 250 c.c. mark on the flask.

Transfer 50 c.c. of this solution, corresponding to 0·4985 gram of pure iron, to a small flask, add 25 c.c. of strong HCl and heat to boiling. Then add the stannous chloride solution (c) from a burette, with constant shaking, until the iron solution just becomes colourless (312).

Add to the solution in the flask 60 c.c. of the mercuric chloride solution (d). Mix well by shaking the flask, and pour the solution into a large porcelain dish which contains 600 c.c. of water and 60 c.c. of the special solution (b): then rinse the flask into the dish, using plenty of washing-water.

Now add the permanganate solution (a) from the burette, with constant stirring, until the liquid just assumes a faint permanent pink tinge. Then read off the volume of solution used from the burette and calculate the iron value of 1 c.c. of the permanganate solution.

Determination of Iron in Iron Ore.—1 gram of the finely powdered and dried ore is placed in a flask of about 250 c.c. capacity: 30 c.c. of strong hydrochloric acid are added and the mixture is heated until the iron is completely extracted from the ore. This is known to be the case when the ore is completely dissolved, or when the residue is quite white (314).

The unfiltered solution, which may contain white silica, is then treated precisely as is directed above in the use of the iron solution for standardising the permanganate solution.

Valuation of Chrome Iron-ore.

400. The value of this mineral for commercial purposes depends almost entirely upon the proportion of chromium which it contains: the percentage of chromic oxide (Cr_2O_3) which it contains should not fall below 40, if the ore is to be of commercial value.

The chromium may be determined by fusing the ore with sodium peroxide. Treatment with boiling water and filtration from the insoluble oxide of iron will then furnish a solution of Na_2CrO_4, which may be converted into $Na_2Cr_2O_7$ by the addition of H_2SO_4 in excess. The acidified solution may now either be titrated with standard ferrous sulphate solution (307), or excess of KI solution may be added and the free iodine titrated by standard $Na_2S_2O_3$ solution in the presence of starch solution (332–335).

The solutions required for the latter process of titrating the chromium are as follows:

(a) *Decimolecular Sodium Thiosulphate Solution* (332).

(b) *Starch Solution* (333).

(c) *Potassium Iodide Solution*, containing 10 grams of the iodide in 100 c.c. of water.

Standardising the Thiosulphate Solution.—This may be effected by dissolving exactly 5 grams of pure dry $K_2Cr_2O_7$ in water, and diluting the solution to 500 c.c. 10 c.c. of this solution, containing 0·03537 gram of chromium, are transferred to a beaker about 800 c.c. in capacity, and are then diluted to 600 c.c. with water and acidified with 20 c.c. of dilute H_2SO_4, made by diluting the strong acid with three times its volume of water. From 15 to 20 c.c. of the iodide solution (c) are now added, and the mixture is stirred and allowed to stand for ten minutes in order that the reaction may be complete. The liberated iodine is then titrated with the thiosulphate solution (a), using the starch solution (b) as an indicator towards the end of the process, and the value of 1 c.c. of the thiosulphate solution in terms of Cr or Cr_2O_3 is calculated. The titrated solution contains chromic sulphate and is therefore of a greenish blue colour; this renders necessary the dilution directed above in order that the end of the process may be evident by the starch coloration.

Process of Determining Cr in the Ore.—About 0·5 gram of the finely powdered and dried ore is exactly weighed and is mixed in a nickel crucible with from 3 to 4 grams of sodium peroxide. This mixture is gently heated until it fuses, the crucible being held in a pair of iron crucible tongs and shaken until a clear liquid, free from lumps, is obtained; a little more peroxide is added, if necessary, during the process.

The cold crucible is placed in a beaker with about 100 c.c. of distilled water and is heated until the yellow mass has completely disintegrated; the crucible is then removed and the solution is allowed to cool. A little solid sodium peroxide is now added, and the liquid is boiled for about five minutes in order to decompose any manganate or ferrate which may have been formed during the fusion. The cool liquid is then filtered and the residue is well washed with hot water, and the filtrate and washings are diluted to 500 c.c.

Half of this solution is transferred to a beaker and is made just acid by the addition of dilute H_2SO_4, after which an excess of 20 c.c. of dilute H_2SO_4 is added. The liquid is then further diluted, the potassium iodide solution is added, and the titration with the standard thiosulphate is carried out as is described above for the process of standardising the thiosulphate.

VALUATION OF MERCURY-ORE.

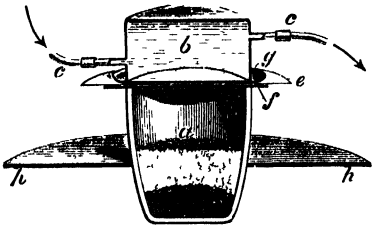
401. In estimating the percentage of mercury present in cinnabar, or native sulphide of mercury, the method described in paragraph **204** may often be replaced by the following procedure. The process is suitable to any mercury-ore which is not rich in mercury and which contains the metal in the condition of sulphide. Rich ores require a preliminary dilution, as is described below, before they are treated by this process, or they may be treated directly as is directed in paragraph **204**.

The following method depends upon decomposing the sulphide by heating it with iron, and condensing the mercury vapour, which is evolved, upon a cooled sheet of silver of known weight: the mercury forms an amalgam with the silver, and its weight is found by reweighing the silver.

The Apparatus shown in Fig. 88 is prepared as follows:

The upper edge of a glazed porcelain crucible (*a*) about 4·5 cm. in height and 4 cm. broad, is ground down flat on a rough surface: and the crucible is supported on a stand by dropping it into a suitable hole in a metal or asbestos sheet (*h*).

FIG. 88.



VALUATION OF CINNABAR.

A 5 cm. disc or square of "fine" silver-sheet (*f*), weighing about 0·3 gram per square cm., is then annealed in the flame, and is rubbed between smooth surfaces until it lies perfectly flat upon the top of the crucible. Upon this is placed a somewhat larger sheet of thin silver-foil (*e*) to keep the sheet (*f*) clean.

A copper cooler (*b*) through which cold water constantly passes by two pipes (*c*) is now laid upon the silver-foil (*e*) and is pressed down by placing a weight upon it. A gutter (*g*) should run round the cooler to collect any condensed moisture, which may be removed from time to time by blotting-paper.

The iron filings, which are to be mixed with the ore, are cleansed by heating them for an hour to redness in a covered crucible and sifting them, when cool, through a sieve of 80 meshes to the inch: another batch of filings for placing above the mixture in the crucible may be sifted through a 30-mesh sieve. These are preserved in separate stoppered bottles.

For the Estimation the ore is finely powdered. If it must be dried, the

drying should be carried out with care, as free mercury is often present and might be partially removed as vapour.

The powdered ore is introduced in weighed amount into the crucible (*a*). About 2 grams may be taken if the percentage of mercury present is less than 1 per cent., 1 gram if the percentage is between 1 and 2, and 0·5 gram or less if the percentage is between 2 and 5.

If the process is applied to an ore containing more than 5 per cent. of mercury, the ore should be diluted by grinding 10 grams until it passes a sieve of not less than 120-mesh, and mixing it intimately with a known weight of sand or calcite which has been ground to pass the same sieve: a known weight of this mixture is introduced into the crucible, a note being made of the weight of ore which it contains.

The ore is now mixed in the crucible with about 10 grams of the finer prepared iron filings, and the mixture is covered with about 5 grams of the coarser prepared filings. The crucible is supported in the aperture of the hole in the plate, which rests upon a tripod or retort-stand. The freshly cleaned and weighed silver-plate is placed centrally upon the crucible and covered with the silver-foil, and the cooler is placed upon this and is pressed down by a suitable weight.

A flame is then applied which just suffices to heat the bottom of the crucible to redness and which does not come into contact with the sides of the crucible. After the heat has been applied for about twenty minutes the flame is removed, and as soon as the whole is cool the silver-plate is removed, dried for one or two minutes in the steam-oven, and weighed when cold (*Note*). If any tarry matter has collected on the plate this must be removed by alcohol before the plate is dried.

The increase in the weight of the silver-plate gives the weight of mercury in the weight of ore taken, and from this the percentage can be calculated.

Note.—Unless some experience has been obtained in the adjustment of the size of the flame and the length of time required for the heating, it is well to repeat the process of heating the residue in the crucible with a fresh silver-plate in order to make sure that the whole of the mercury has been removed from the ore: the second treatment should cause no increase of weight to the silver, and any such increase must be added to the weight of mercury already obtained.

The silver-plate is freed from mercury by being gently heated and may then be used for a fresh estimation.

It is possible to judge whether the plate has lain absolutely flat on the edge of the crucible by noting whether the mercury stain upon it is perfectly circular and does not extend beyond the edge of the crucible. This close fitting of the plate is essential to insure against possible loss of mercury vapour.

Valuation of Zinc-ores.

402. The volumetric processes in paragraphs **378, 379** are convenient for estimating the percentage of zinc in many of its ores.

Blende and other zinc-ores often contain lead, copper, and cadmium. These metals must be removed from the solution of the ore by precipitation with hydrogen sulphide before the zinc is estimated. Iron and manganese also interfere with the accuracy of the titration, and may be removed as is described below. A preliminary qualitative analysis of the zinc-ores should always be made, in order to ascertain whether any of these metals are present.

403. Estimation of the Moisture.—It is advisable in all cases to estimate the amount of moisture in the ore, since this renders it possible eventually to calculate the percentage of zinc in the dry ore.

For this purpose weigh out accurately from 1 to 2 grams of the finely powdered ore. For rich ores 1 gram, and for the poorer ores 2 grams, will be found a suitable quantity for analysis. Heat this portion of the ore in the steam-oven until its weight becomes constant (**189**): the loss of weight which it suffers represents the amount of moisture.

404. Estimation of the Zinc.—Place the dried ore (**403**) in a 250 c.c. beaker, and add a little aqua regia. Heat until solution is complete, and remove the excess of acid by heating the liquid in an evaporating-dish.

If lead is present, add a few drops of strong sulphuric acid, and evaporate until dense white fumes appear. Extract the residue with water, and filter. If any other metals of the hydrogen sulphide group are present, such as copper, they must be precipitated by passing hydrogen sulphide.

If the solution contains iron and manganese, convert the iron into the ferric condition by heating the solution or filtrate with a little strong nitric acid. Add bromine-water in excess to the cold solution, then ammonium hydrate in slight excess, and boil. Filter off the precipitate, which consists mainly of ferric hydrate, and wash it free from zinc; Am_2S must produce no precipitate when it is added to the last few drops of the washings. Add the washings to the filtrate.

If the iron precipitate is large in amount, it must be dissolved in hydrochloric acid, and then reprecipitated and washed as before. This procedure will dissolve out the zinc which is invariably precipitated with the iron.

Add the second filtrate and washings to those previously obtained.

The zinc in this solution may then be estimated by standard ferrocyanide solution, taking the precautions mentioned in paragraph **378**; or it may be estimated directly in the ammoniacal solution by sodium sulphide solution, the strength of which has been recently determined (**379**).

Valuation of Copper-ores.

Four methods for estimating the amount of copper in the solution of a copper-ore are described below. The first is an electrolytic method (405). The second, or Mansfeld method (406), is an application of the cyanide process (377). The third is commonly known as the iodide method (407). The fourth is the thiocyanate method (408).

405. The Electrolytic Method.—In this process the copper is precipitated from the solution of the ore by an electric current and is then weighed in the metallic state.

Preparation of the Solution of the Ore.—Weigh accurately about 2 grams of the finely powdered sample: and, if it contains bituminous matter, oxidise and expel the organic matter by igniting the powder in the air.

Then proceed to dissolve the copper by pouring a little moderately dilute nitric acid upon the ore in an evaporating-dish, and adding about the same quantity of dilute sulphuric acid. Cover the dish with an inverted funnel (Fig. 41, p. 42), and evaporate nearly to dryness on a sand-bath in order to expel the excess of nitric acid. Dissolve the residue in water, adding a few drops of nitric acid if necessary, then filter off the residue and wash it twice with water.

Transfer the filtrate to a platinum dish, add 10 c.c. of nitric acid of 1·2 specific gravity, and dilute the liquid until its volume is 150 c.c. Then proceed to deposit the copper electrolytically and to weigh it, as is described in paragraph **218**.

Note.—It is essential in this process that an amount of free nitric acid not exceeding 10 per cent should be present before electrolysis, since the strength of the acid is diminished during electrolysis by the formation of ammonia. If the solution becomes alkaline from this cause the copper is deposited as a brown, loosely adherent coating, and it is very difficult to wash this without loss.

406. The Mansfeld Method.—The ore is first dissolved in acid, and the whole of the copper is precipitated from this solution by immersing in it a piece of zinc and a strip of platinum-foil. The copper is then dissolved from the platinum strip by nitric acid. The acid solution is rendered alkaline by the addition of ammonium hydrate in excess, and the alkaline solution is titrated with standard potassium cyanide solution (377).

(a) *Solution of the Copper.*—Weigh accurately about 5 grams of the finely powdered ore into a 300 c.c. flask. Add 40 c.c. of hydrochloric acid of 1·16 specific gravity. After a time add 6 c.c. of dilute nitric acid, made by mixing nitric acid of 1·2 specific gravity with an equal measure of water. Gently heat the flask for thirty minutes on a sand-bath, and finally boil the liquid for fifteen minutes. The whole of the copper will now be in solution. Remove the insoluble residue by filtration, receiving the filtrate in a 500 c.c. beaker.

(b) *Precipitation of the Metallic Copper.*—A zinc rod, free from lead, and weigh-

ing about 50 grams, is attached to a piece of platinum-foil. This is placed in the filtrate containing the copper. The precipitation of the copper in the metallic state commences as soon as the warm filtrate comes into contact with the zinc and platinum, and is complete in about half an hour. The spongy copper partly adheres to the platinum, and is partly suspended in the liquid. Detach the copper from the platinum, remove the zinc and platinum, and wash the precipitated copper repeatedly by decantation.

(c) *Titration of the Standard Cyanide Solution.*—Standard potassium cyanide solution must now be prepared as follows: Weigh into a litre flask exactly 5 grams of chemically pure copper, which has been preferably deposited electrolytically. Dissolve this in 266·6 c.c. of nitric acid, consisting of equal measures of water and of nitric acid of 1·2 specific gravity, and dilute this solution to a litre.

Pour 30 c.c. of this copper solution, which is equivalent to 0·15 gram of metallic copper, into a small beaker. Add 10 c.c. of dilute ammonium hydrate solution, made by mixing one volume of ammonium hydrate of 0·93 specific gravity with two volumes of water. Then add the potassium cyanide solution from a burette to this solution, until its blue colour fades to a very pale lavender (377).

The copper-value of the potassium cyanide solution is thus determined, and the strength of the solution must then be so adjusted that each c.c. is equivalent to 0·005 gram of copper.

(d) *Estimation of the Copper.*—Dissolve the copper, which was precipitated from the solution of the ore (b), in 8 c.c. of nitric acid of the strength described above (c). Add 10 c.c. of the dilute ammonium hydrate solution (c), and proceed with the titration as is described above (c).

If the amount of copper in the ore exceeds 6 per cent., dissolve the precipitated copper in 16 c.c. of the dilute nitric acid, make up the solution to 100 c.c. with distilled water, and withdraw 50 c.c. for the titration.

The calculation of the percentage weight of copper in the ore from the result of the titration is very simple. For since 5 grams of the ore are used, and each c.c. of the potassium cyanide solution corresponds to 0·005 gram of copper, each c.c. of the cyanide solution used in the titration represents 0·1 per cent. of copper.

This method is rapid, and is accurate if it is always carried out under the same conditions. Care must, however, be taken that lead is not present in large quantity, and that zinc is entirely absent. The solution should be at the ordinary temperature, since heat seriously affects the result. The strength of the copper solutions to be titrated should not vary greatly, and finally the same amount of ammoniacal salt should be present in each determination.

407. Iodide Method.—Weigh accurately about 2 grams of the finely powdered ore, and prepare the solution of the ore as is directed under the electrolytic method (405). Then either precipitate the copper completely from the diluted solution by passing hydrogen sulphide, filter, and wash the precipitate with water containing hydrogen sulphide: or precipitate the metallic copper as is directed in paragraphs 405, 406.

Dissolve the precipitate by heating it with a small quantity of nitric acid, evaporate nearly to dryness, add some water, and boil the liquid until it ceases to evolve nitrous fumes. Add sodium carbonate until a small permanent

precipitate is formed, then add acetic acid in slight excess. Dilute this liquid to 200 c.c., and estimate the copper by adding potassium iodide solution in excess, and titrating the iodine by standard sodium thiosulphate solution (357).

408. Estimation of Copper as Cuprous Thiocyanate.—The copper ore is treated as is directed in paragraph 405 in order to prepare a solution of the copper. For this estimation, however, the copper solution must not contain free nitric acid. Hence the free acid is neutralised by adding ammonium hydrate in slight excess, and the liquid is then rendered faintly acid in reaction by the addition of dilute hydrochloric acid.

The copper is then precipitated from the solution by adding, with continuous stirring, an excess of a solution of equal weights of ammonium thiocyanate and of ammonium bisulphite, and allowing the liquid to stand for several hours. It is then poured through a tared filter-paper or Gooch filter (82). The white precipitate of cuprous thiocyanate, $Cu_2(CNS)_2$, is washed with cold water until the washings only show a faint red coloration with ferric chloride, and finally with 20 per cent. alcohol. It is then dried in the air-oven at 110° C. until its weight is constant. For another method see paragraph 496.

Note.—Since copper is the only metal which is precipitated as thiocyanate from a solution of chlorides acidified with hydrochloric acid, the above process serves to separate it from all other metals.

Valuation of Soda-ash.

409. Soda-ash consists essentially of anhydrous sodium carbonate, but it always contains sodium hydrate and other substances.

Moisture, sodium carbonate, and sodium hydrate are commonly estimated in soda-ash.

410. Estimation of Moisture.—Weigh 10 grams of the powdered soda-ash into a platinum crucible. Heat the covered crucible for about half an hour over a small Bunsen flame, and weigh it when it is cold. The loss of weight represents the moisture contained in the sample.

411. Estimation of Sodium Carbonate and Sodium Hydrate.—Transfer the dried salt (410) to a beaker and dissolve it in air-free water. Filter off and wash any insoluble matter; then dilute the filtrate and washings to 500 c.c. with air-free water, and make the liquid uniform by shaking it well.

Mix 50 c.c. of this solution with a few drops of phenol-phthalein solution

(269), and then add normal sulphuric acid (285) slowly until the red colour of the liquid is just destroyed.

At this point all the sodium hydrate and one-half of the sodium carbonate will have been neutralised. For since phenol-phthalein is sensitive to free carbonic acid, its red colour will disappear as soon as the whole of the sodium carbonate has been converted into bicarbonate and a trace of carbonic acid has been liberated by the action of the sulphuric acid upon the bicarbonate.

In order to prevent the escape of carbon dioxide, which would lead to an inaccurate result being obtained, the point of the burette should be immersed in the liquid, and the liquid should be kept at as low a temperature as possible. This applies to the addition of the acid throughout the process.

Now add a few drops of methyl-orange solution (268), and continue the addition of the standard acid until the colour of the solution changes from yellow to pink. At this stage the whole of the bicarbonate will have been converted into neutral sulphate.

It is evident that the sodium, which was present as carbonate in the original solution of the soda-ash, is equivalent to twice the quantity of acid which was required for neutralisation after the addition of the methyl-orange. Also that the amount of sodium hydrate in the original solution is equivalent to the total amount of acid used, less that corresponding to the carbonate.

The following example illustrates the procedure and the method of calculation:

Example.—In a particular estimation, 10 024 grams of soda-ash were dissolved in water, and the solution was made up to 500 c c.

This liquid was titrated with normal sulphuric acid solution, each c.c. of which corresponds to 0 05306 gram Na_2CO_3, and to 0 04006 gram NaHO.

With phenol-phthalein as an indicator, 50 c c. of this solution required 9 6 c.c. of normal sulphuric acid

On the addition of methyl-orange, 8 4 c c of additional acid were required.

Therefore the total amount of acid required was 9 6 + 8 4 = 18 0.

Hence the amount of acid equivalent to the sodium carbonate present in 50 c.c of this solution was = 8 4 × 2 = 16 8 c c.

And 500 c.c. would require = 16 8 × 10 = 168 c.c. of acid.

Therefore the amount of Na_2CO_3 in 10 024 grams of the soda-ash = 168 × 0·05306 = 8 9141 grams.

Hence the percentage of $Na_2CO_3 = \frac{8{\cdot}9141 \times 100}{10{\cdot}024} = \underline{88\ 93.}$

The amount of acid equivalent to the sodium hydrate in 50 c.c. of the solution is 18 - 16 8 = 1 2 c c.; hence the acid equivalent to 500 c c = 1 2 × 10 = 12 c.c.

Therefore the amount of NaHO in 10 024 grams of the soda-ash is 12 × 0 04006 = 0 48072.

Hence the percentage of NaHO = $\frac{0\ 48072 \times 100}{10{\cdot}024} = \underline{4{\cdot}79.}$

Note.—In technical analyses it is usual to state the weights of Na_2O which are present as carbonate and as hydrate respectively.

Valuation of Manganese-ores.

412. The value of a manganese-ore for the preparation of chlorine, and for many other purposes, depends upon the amount of "available oxygen" which it contains. The available oxygen is that part of the oxygen which is available for effecting oxidation during the process of solution of the oxide in an acid. It will be seen from the following equation that half the oxygen in MnO_2 is thus "available":

$$MnO_2 + H_2SO_4 = MnSO_4 + H_2O + O.$$

Three methods for estimating the commercial value of manganese-ore are described below. The methods described in paragraphs **414**, **415** determine the amount of oxygen which is actually available in practice. The methods described in paragraph **416**, however, indicate the amount of manganese peroxide present with greater accuracy.

Many samples of manganese-ore contain ferrous oxide. This reduces the actual amount of available oxygen in the manganese oxide, since the ferrous oxide is converted into ferric oxide, and thus appropriates some of the oxygen, during the applications of the manganese oxide.

When the estimation is to be made, about 10 grams of the oxide are finely powdered as rapidly as possible, and the powder is placed in a stoppered weighing-bottle.

413. Estimation of Moisture.—Most manganese-ores contain combined water, in addition to hygroscopic moisture. The latter is usually estimated as follows:

Weigh out from 2 to 4 grams of the ore accurately in the watch-glasses and clamp, and heat it in the air-oven (**420**) to 120° C. until the weight becomes constant. This temperature drives off the hygroscopic moisture only.

414. Indirect Estimation of the Available Oxygen by Potassium Iodide and Thiosulphate.

About 0·5 gram of the finely powdered dried ore (**413**) is accurately weighed into the small flask (*a*) (Fig. 86, p. 188) and is warmed with about 25 c.c. of strong hydrochloric acid, the chlorine which is given off being absorbed in potassium iodide solution contained in the U-tube. The chlorine liberates

its chemically equivalent quantity of iodine, and this is then titrated with standard sodium thiosulphate solution (353).

The available oxygen is usually calculated in terms of manganese dioxide according to the equation,

$$MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2.$$

415. Estimation of the Available Oxygen by the Oxidation of a Ferrous Salt.—Weigh accurately from 1 to 2 grams of pianoforte-wire, and dissolve it in dilute sulphuric acid as is described in paragraph 305. Then weigh accurately about 1·5 gram of the dry finely powdered manganese-ore (413), and add it to the iron solution. Heat the solution until the ore is dissolved, carefully avoiding the access of air.

As soon as the solution of the ore is complete, estimate the amount of unaltered ferrous salt by means of standard potassium permanganate (319) or by standard potassium dichromate solution (306).

The available oxygen is usually calculated from this result in terms of manganese dioxide, from the equation,

$$2FeSO_4 + MnO_2 + 2H_2SO_4 = Fe_2(SO_4)_3 + MnSO_4 + 2H_2O.$$

416. Estimation of the Available Oxygen by the Oxidation of Oxalic Acid.—Reference to paragraph 187 will indicate another method of valuing manganese-ore, which may be applied either gravimetrically or volumetrically.

The weight of oxalic acid which can be oxidised by the manganese oxide is obtained by this method. 90 parts of $H_2C_2O_4$ correspond to 87·05 parts of manganese dioxide, and from this relation the weight of MnO_2 may be calculated

$$H_2C_2O_4 + MnO_2 + H_2SO_4 = 2CO_2 + 2H_2O + MnSO_4.$$

Gravimetric Estimation.—Weigh out accurately about 3 grams of the finely powdered manganese-ore (*Note*, 187). Introduce this, together with 2½ times its weight of neutral potassium oxalate, into the decomposition-flask (175, 183, 185), allow strong sulphuric acid to flow in, and estimate the CO_2 which is evolved as is directed in the paragraphs referred to.

Volumetric Estimation.—Pour upon 2 grams of the ore, contained in a flask, 100 c.c of normal oxalic acid solution and 5 or 6 c c of strong sulphuric acid. Heat the mixture until all black grains have disappeared. Then filter the liquid, make the filtrate up to 250 c c and determine the amount of undecomposed oxalic acid in this solution by titrating it with standard permanganate solution (320); the weight of oxalic acid which has been oxidised by the MnO_2 is then found by difference.

Estimation of the Amount of Hydrochloric Acid required to decompose a Manganese-ore.

417. It is sometimes necessary to determine for technical purposes the amount of hydrochloric acid which is necessary to decompose a manganese-ore.

The amount of manganese peroxide found in a manganese-ore does not give a true indication of the amount of hydrochloric acid necessary for its decomposition, since in many manganese-ores earthy carbonates and iron compounds are present. Hence the amount of free acid which disappears during the solution of the manganese-ore is usually in considerable excess of the amount actually decomposed by the MnO_2.

418. For the estimation of the amount of acid actually required for the solution of the ore, use hydrochloric acid of about 1·12 specific gravity. First ascertain the strength of the acid by means of normal sodium hydrate solution (289). Then pour 1 gram of the finely powdered ore into a small flask, add 10 c.c. of hydrochloric acid of the above gravity, connect the flask with an inverted condenser (1016), and heat the acid until all action ceases.

Now add standard sodium hydrate solution from a burette to the cool residual acid liquid, until the reddish brown precipitate of ferric hydrate, which first appears, does not redissolve when the liquid is well shaken. This will measure the excess of acid which remains after the decomposition of the manganese-ore has been effected.

The amount of acid required for the decomposition of the ore is that which is found to have disappeared during the process of heating.

The amount of chlorine which has been evolved during the action of the acid may then be found (414), and the quantity of chlorine which remains combined as chloride in the solution can be calculated by difference.

Analysis of Limestone, Magnesian Limestone and Lime.

419. Limestone consists essentially of varying proportions of calcium and magnesium carbonates. If the proportion of magnesium carbonate is large, the limestone is called magnesian limestone or dolomite. Limestone also usually contains moisture, silicious matter, iron, and aluminium; and occasionally manganese, alkali-metals, and carbonaceous matter. Since the constituents of limestone may vary, an exhaustive qualitative examination should precede the quantitative analysis.

A quantitative analysis of lime may also be made by following the scheme

arranged below: moisture removable in the air-oven will usually be absent, and little or no carbon dioxide will be found if the lime has been thoroughly and recently burnt.

For practice in the following method of quantitative analysis, select a homogeneous piece of dolomite. Reduce about 10 grams of the substance to fine powder, and place the powder at once in a stoppered weighing-bottle.

420. Estimation of Moisture.—Dolomite rarely contains much moisture. In order to ascertain whether any moisture is present, and at the same time to estimate its amount, weigh out accurately from 1·5 to 2 grams of the powder in the watch-glasses and clip (**16**), remove the clip and upper glass, and heat the lower glass and powder in the air-oven (**61**) for an hour at a temperature of about 200° C.

Then remove the substance from the air-oven, immediately covering it with the other glass; replace the clip, allow the glasses to cool in the desiccator, and weigh the glasses when they are cold. If any loss of weight has occurred, heat again in the same way in the air-oven for half an hour and weigh once more. Repeat these processes until the weight remains constant in two successive trials. The loss of weight thus found gives the amount of moisture present.

421. Estimation of Carbon Dioxide.—Transfer the dried dolomite (**420**) to the flask (*a*) shown on page 104. Decompose the carbonate with hydrochloric acid, and estimate the carbon dioxide gas which is evolved exactly as is described in paragraph **175**.

The soda-lime absorption-tube (*f*, p. 104) must be of sufficient capacity to absorb the gas completely As a precaution, a second somewhat smaller soda-lime tube may be attached to this larger tube and any increase of weight which occurs in this second tube is added to the gain of weight of the larger tube (*f*). This second tube, or "guard-tube," serves to insure complete absorption of the gas. It also indicates when the soda-lime in the larger tube (*f*) is nearly saturated by repeated use and requires to be replaced, since when this is the case the smaller absorption-tube undergoes marked increase in weight during the process of estimation.

Caution.—Care must be taken to preserve without loss the solution which remains in the decomposition-flask (*a*), as well as all the filtrates and washing-waters which are obtained in the following processes, since these liquids are employed in the estimation of constituents of the limestone.

422. Estimation of Silicious Matter.—The insoluble residue which is left in the flask (**421**) consists mainly of sand and clay. A small quantity of silica will probably also have passed into the acid solution. The whole of the silica which was originally present in the limestone may be estimated as follows:

The contents of the decomposition-flask are carefully rinsed out into a porcelain dish 10 cm in diameter, a little strong nitric acid is added, and the liquid is evaporated to dryness on the water-bath. The dish is then heated in the air-bath to 150° C. for an hour in order to convert the silica into the anhydrous insoluble condition.

The dish is now allowed to cool, and its contents are heated with a small quantity of strong hydrochloric acid, which will dissolve everything except the silica and the clay. A little water is added, the liquid is filtered, and the residue is washed in the filter until it is free from acid.

The residue is then ignited. If it is small in amount, it is ignited together with the filter (99). If, however, the amount of residue is considerable, the filter is more conveniently incinerated apart (101).

The residue thus estimated consists of silica and clay. Refer to paragraph 210 and *Note* 1.

423. Estimation of Ferric Oxide and Alumina.—Add to the filtrate and washings from the estimation of silica (422) a considerable quantity of ammonium chloride solution, and then add ammonium hydrate in very slight excess. Heat the solution nearly to boiling, and filter.

Wash the precipitate of aluminium and iron hydroxides twice with hot water: then dissolve it in hot dilute hydrochloric acid, and reprecipitate the iron and aluminium hydroxides by adding ammonium hydrate in slight excess.

This second precipitation separates the calcium, which is precipitated with the iron and aluminium hydroxides as carbonate by the trace of ammonium carbonate in the ammonium hydrate.

Filter, and wash the precipitate until it is free from dissolved chlorides. Carefully reserve and mix together the above filtrates and all the washings.

If the precipitate is small in amount, and it is not intended to estimate the iron and the aluminium separately by paragraph 424, a, the precipitate may now be dried in the steam-oven, and the filter and precipitate may be ignited together (99) at a bright red-heat in a platinum crucible. The ignited residue of Fe_2O_3 and Al_2O_3 is then weighed.

This residue is reserved, if necessary, for the estimation of the Fe and the Al which it contains, according to the directions given in paragraph 424, b.

424. Separate Estimation of Iron and of Aluminium, or of Aluminium by Difference.—If the amounts of iron oxide and of aluminium oxide present are to be determined, proceed either to separate the oxides of these metals and to estimate them separately (a), or to determine the aluminium by difference (b).

(a) *Separate Estimation of Aluminium and of Iron.*—Dissolve the washed

precipitate of aluminium and iron hydroxides (423) upon the filter in hot dilute hydrochloric acid, and allow the solution to flow into a porcelain or nickel dish containing about 50 c c. of strong potassium hydrate solution, which must be free from alumina. Wash out the acid, which remains adhering to the filter-paper, with a small quantity of water, and allow these washings also to flow into the dish. Boil the contents of the dish for a few minutes. The iron will thus be precipitated as ferric hydroxide, while the aluminium hydroxide will remain in solution.

The iron precipitate is filtered off and washed. It is then dissolved in hydrochloric acid and reprecipitated by ammonium hydrate, in order to free it from alkali. The precipitate is then filtered off and washed, then ignited at a red heat (99), and weighed as Fe_2O_3 (129).

The original alkaline filtrate, which contains the aluminium hydroxide, is mixed with a slight excess of strong hydrochloric acid, and then with ammonium hydrate in very slight excess. The precipitate is filtered off, washed, dried, and ignited, and is weighed as Al_2O_3 (130).

(b) *Estimation of Iron and of Aluminium by Difference.*—The ignited and weighed precipitate of Fe_2O_3 and Al_2O_3 (423) is dissolved by prolonged heating with strong HCl. The iron in the solution is reduced by means of stannous chloride (312), or by ammonium bisulphite (313), and is titrated by means of dichromate solution (306): or more rapidly by the method described in paragraph 399.

The weight of Fe thus found is calculated as Fe_2O_3, and this weight is subtracted from the original weight of the precipitate containing the Fe_2O_3 and Al_2O_3. The difference represents the weight of the Al_2O_3.

425. **Estimation of Manganese.**—If only a trace of manganese is present in the limestone its estimation may be neglected, since it will be precipitated with the iron and will cause no appreciable error in the weight of Fe_2O_3 obtained. If, however, there is any quantity of manganese present, the iron and aluminium must be first precipitated as basic acetates (435): the manganese is then precipitated from the filtrate as hydrated peroxide and is estimated as is directed in paragraph 438.

426. **Estimation of Calcium.**—Mix together the ammoniacal filtrates and washings from the iron and aluminium precipitate (423), heat the liquid to boiling, and add a moderate excess of solid ammonium oxalate (145, *Note*). Filter, and wash the precipitated calcium oxalate two or three times. Dissolve the precipitate in hot dilute hydrochloric acid: filter if necessary, and re-precipitate the calcium oxalate by adding a slight excess of ammonium hydrate solution, together with a few drops of ammonium oxalate solution. Filter; wash, dry, and ignite the precipitate, and weigh it as carbonate or as oxide (146, 147).

The excess of ammonium oxalate retains most of the magnesium in solution, but if much Mg is present the above reprecipitation is necessary to remove magnesium from the precipitate of calcium oxalate.

427. Estimation of Magnesium.—Pour the filtrates and washings from the calcium oxalate precipitate (426) into a porcelain dish 15 cm in diameter. Evaporate this liquid to dryness, lightly greasing the inside edge of the dish to prevent the solution from creeping over. As soon as all the liquid has been driven off, place the dish on a sand-bath or on a piece of wire-gauze, and heat it as long as fumes of ammonium salts are driven off. This removal of ammonium salt is necessary, since they prevent the complete precipitation of magnesium.

Treat the residue in the cool dish with a little strong hydrochloric acid; then warm, add water, and filter if necessary. To the clear solution, contained in a beaker, add ammonium hydrate in moderate excess, then add excess of sodium hydrogen phosphate solution and allow the liquid to stand for a few hours Filter, and wash the precipitate with dilute ammonium hydrate solution; then ignite it, and weigh the Mg as $Mg_2P_2O_7$.

The precipitation may be very much hastened by shaking the liquid well in a stoppered bottle (165 and *Note* 1).

428. Estimation of the Alkali-metals.—Sodium and potassium may be estimated, if necessary, as follows:

Five grams of the dolomite are dissolved in hydrochloric acid, sulphate is completely precipitated by adding $BaCl_2$ solution, and the solution is made alkaline by the addition of excess of "milk of lime," so as to precipitate all the metals except those of the alkalis.

The milk of lime is prepared by stirring up freshly slaked lime, which must be free from alkalis, to a creamy consistency with water.

The milky liquid is heated and then filtered. The excess of lime is removed from the filtrate and washings by first adding ammonium hydrate and ammonium carbonate solutions in excess, and then a few drops of ammonium oxalate solution. The precipitate is filtered off, and the filtrate is acidified with HCl, and evaporated to dryness in a weighed porcelain or platinum dish.

The chlorides of sodium and potassium thus obtained are heated for a short time in the air-bath at 150° C. or upon the sand-bath, and are finally weighed after cooling in the desiccator.

In order to remove the trace of calcium which is still usually present, the residue is dissolved in water containing a little dilute HCl, and a few drops of solution of AmHO and of $Am_2C_2O_4$ added. If a precipitate forms it is filtered off, the filtrate is evaporated, and the residue is moistened with hydrochloric acid to convert any carbonate into chloride, then evaporated to dryness, ignited and weighed.

429. The Proportions of the Sodium and Potassium Chlorides which are present in this residue may be determined by either of the following methods, a or b.

(a) The weighed residue is dissolved in water, and a few drops of HCl and an excess of platinic chloride solution are added. The liquid is then evaporated on the water-bath, and the residue is treated with alcohol in which the potassium salt, K_2PtCl_6, is insoluble: the double salt is then dried and weighed as is directed in paragraph **171**. The weight of potassium chloride present is now calculated, and the weight of the sodium chloride is found by difference.

(b) The weighed residue of the chlorides is dissolved in water, and the weight of chlorine is determined by titration with standard silver nitrate solution (**373**).

The weights of sodium and of potassium present in the residue may then be calculated as follows:

If x = the weight of NaCl in the mixed chlorides;
y = the weight of KCl in the mixed chlorides;
a = the total weight of the mixed chlorides,
b = the total weight of chlorine in the mixed chlorides;

Then:

$$(1)\quad x + y = a, \text{ and}$$

$$\frac{Cl}{NaCl}x + \frac{Cl}{KCl}y = b; \text{ or } \frac{35\,45}{58\,5}x + \frac{35\,45}{74\,6}y = b; \text{ whence}$$

$$(2)\quad 0{\cdot}606\,x + 0\,475\,y = b.$$

Multiplying equation (1) by 0·606:

$$(3)\quad 0\,606\,x + 0\,606\,y = 0\,606\,a.$$

Subtracting (2) from (3)

$$0\,131\,y = 0{\cdot}606\,a - b;$$

$$\text{or } y = \frac{0\,606\,a - b}{0\,131}.$$

And from equation (1):

$$x = a - y = \frac{b - 0\,475\,a}{0\,131}.$$

From these values of x and y the weights of NaCl and of KCl in the mixed chlorides may be found, and from these the percentage weights of Na and K in the limestone may be calculated.

The weight of the oxide of each alkali metal which was present in the limestone is calculated from the weight of the metals found.

430. Limestone may also contain Phosphate, Sulphate, Chloride, and Carbonaceous Matter.—The phosphate may be estimated in the manner described under spathic iron-ore (442).

The sulphate may be estimated by dissolving 5 grams of the limestone in dilute hydrochloric acid, filtering off the residue, and precipitating the SO_4 as $BaSO_4$ (133)

The chloride may be estimated by dissolving 5 grams of the limestone in nitric acid, filtering off the residue, and precipitating and weighing the Cl as AgCl (149).

In the absence of combined water the amount of carbonaceous matter may be found by subtracting from the total loss of weight, caused by prolonged ignition to redness, the weights of moisture (420), and of CO_2 (421)

For the Results obtained by the analysis of limestone, lime and mortar refer to paragraphs 940, 941, 942.

Analysis of Spathic Iron-ore.

431. Spathic iron-ore consists essentially of impure ferrous carbonate. Its constituents are usually the same as those of limestone, but the proportion of ferrous carbonate is high, whereas the calcium and magnesium carbonates are present in small quantity only. Usually an appreciable quantity of manganese is present, and combined phosphorus and sulphur are frequently found. The phosphorus and sulphur must be carefully estimated, since the value of the ore, and the process of smelting it, are influenced by the amounts of phosphorus and of sulphur which it contains.

Preparation of the Ore.—Finely powder about 15 grams of the ore (55, 56), and keep the powder in a clean, dry stoppered bottle.

432. Estimation of Water.—Weigh out accurately about 2 grams of the powdered ore, and estimate the moisture by drying it at 200° C. in the air-oven (420).

433. Estimation of Carbon Dioxide.—The amount of carbon dioxide is then estimated in the dry ore (432) by direct weighing (421).

434. Estimation of Silicious Matter.—The hydrochloric acid solution, together with the undissolved residue from the flask (433), is evaporated with a little strong nitric acid. The residue is heated in the air-bath to 150° C. for an hour, and is then heated with a little strong HCl and some water. The residue, consisting mainly of silica, is filtered off, washed, ignited, and weighed (422).

435. Estimation of Iron and Aluminium.—The filtrate from the silica (434) usually contains an appreciable amount of manganese.

If manganese is absent refer to 423 for the method of precipitating the iron and aluminium.

If manganese is present, the iron and aluminium should be precipitated as basic acetates by carefully carrying out the following directions:

Dilute the acid filtrate (434) considerably with water; then add ammonium carbonate solution gradually, and with constant stirring, until the precipitate which forms at first is redissolved with difficulty. The solution will now be deep brown in colour. Continue the gradual addition of ammonium carbonate solution until a very slight precipitate forms, which almost disappears when the liquid is stirred, the liquid remaining slightly opalescent.

Now add a little acetic acid and a moderate quantity of strong ammonium acetate solution, and boil for a short time. Filter the liquid while it is hot (Fig. 66, p. 65), and wash the precipitate twice with boiling water. The filtrate and washings must be clear and colourless. Remove any manganese, which has been precipitated with the iron and aluminium, by redissolving the precipitate in hydrochloric acid, adding ammonium carbonate as before, and reprecipitating the iron and aluminium by again boiling the solution with acetic acid and ammonium acetate solution.

The precipitate will contain the iron and aluminium as basic acetates, and the manganese will remain in solution. Filter, and wash the precipitate without intermission with hot water. Add the first portion of the washings to the two filtrates, and treat the liquid as is described later on (438). This liquid should be perfectly colourless.

436. **Separation of the Iron from the Aluminium.**—The precipitated basic acetates (435) may be treated by either of the following methods (a, b) in order to separate the iron from the aluminium:

(a) The precipitate is dissolved in dilute hydrochloric acid, and the iron and aluminium are estimated in the solution according to the directions already given in paragraph 424.

(b) The precipitate is dissolved in hydrochloric acid, and the solution is made up to 250 c.c. with water.

100 c.c. of this liquid are mixed with excess of ammonium hydrate solution. The precipitate, thus produced, is filtered off and is weighed as is described in paragraph 423. This will give the total weight of Fe_2O_3, Al_2O_3, and P_2O_5 in 100 c.c. of the liquid. Keep this precipitate carefully.

The total amount of iron is then estimated in another part of the solution. This is effected by reducing two separate portions of 25 c.c. each (312, 313), and then titrating the ferrous salt with standard dichromate solution, or by the special procedure described in paragraph 399.

The weight of Fe_2O_3, corresponding to the Fe in the 250 c.c. of the solution,

is now calculated. By subtracting the sum of the weights of the Fe_2O_3 and the P_2O_5 (442) from the total weight of Fe_2O_3, Al_2O_3, and P_2O_5 already found, the weight of the Al_2O_3 will be obtained. The weight of P_2O_5 is usually so small as to be negligible.

437. Estimation of Iron present in the Ore in the Ferrous State.—The larger part of the iron in the ore is probably present in the ferrous state. This is estimated by dissolving 3 grams of the ore in hydrochloric acid in the apparatus shown in Fig. 84 or 85 (p. 165). The process of solution is carried out precisely as is described in paragraph 305, the ore taking the place of the steel there mentioned. By this procedure the ferrous compound present in the ore is dissolved, and its solution is diluted to a known volume, without the risk of changing any of the ferrous into ferric salt. The ferrous salt in an aliquot part of this solution is then titrated by means of potassium dichromate solution (306), or by the special procedure described in paragraph 399.

438. Estimation of Manganese.—The filtrate from paragraph 435 contains the manganese, calcium, and magnesium. Add bromine-water to this liquid until it acquires a permanent yellow colour; then add excess of ammonium hydrate solution, and warm. The manganese will be precipitated as hydrated peroxide. Filter this off, and add to the filtrate more bromine-water and AmHO in order to make sure that all the manganese is precipitated. Then wash the precipitate, dry and strongly ignite it, and weigh it as Mn_3O_4 (164).

439. Estimation of Calcium.—To the filtrate from paragraph 438 add a little ammonium oxalate solution. Allow the liquid to stand. Filter off and wash the precipitate, dry and strongly ignite it, and weigh as calcium oxide (147).

440. Estimation of Magnesium.—Evaporate the filtrate from the calcium oxalate precipitate (439) to dryness, ignite the residue, dissolve it in dilute HCl and estimate the Mg as $Mg_2P_2O_7$ (165).

441. Estimation of the Alkali-metals.—The alkali-metals may be estimated, if necessary, as is described in paragraphs 428, 429.

442. Estimation of Phosphate.—The estimation of phosphate in an iron-ore is of much importance. Two methods are described below (a, b), of which the second (b) is the more rapid and accurate.

(a) Any phosphate, which was present in the original ore, will have been precipitated with the basic acetates of iron and aluminium (435).

The precipitate of $Fe_2O_3 + Al_2O_3$, which was obtained in paragraph 435, b will therefore contain the phosphate. Dissolve this precipitate by prolonged digestion with strong hydrochloric acid. Evaporate the solution to dryness on the water-bath, and dissolve the residue in nitric acid.

Add a large excess of ammonium molybdate solution (520), and allow the liquid to stand in a warm place for a few hours. Pour off the clear liquid and warm it with fresh molybdate solution, in order to ascertain whether all the phosphate has been precipitated. Filter off the loose yellow precipitate and wash it and rinse out the beaker with very dilute nitric acid. Then dissolve the precipitate, which remains adhering to the beaker, by pouring in ammonium hydrate solution, and pour this off through the filter in order to dissolve the rest of the precipitate. Rinse out the beaker and wash the filter well. Add excess of magnesia mixture (167) to the solution and washings, and estimate the phosphate as $Mg_2P_2O_7$ (166).

(b) The phosphate may be estimated more rapidly as follows: Dissolve from 3 to 5 grams of the ore in nitric acid; boil off most of the acid; dilute, filter, and precipitate the phosphate from the filtrate by the addition of a large excess of ammonium molybdate solution (520). Treat this precipitate as is described above (a), and estimate the phosphate as $Mg_2P_2O_7$ (166).

443. **Sulphate and Chloride**, if they are present, may be estimated as is directed in paragraph 430.

For the Results obtained by the Analysis of Spathic Iron-ore refer to paragraph 943.

Analysis of Manganese-spar.

444. Manganese-spar consists mainly of manganese carbonate, but it usually contains small quantities of certain of the substances which are present in limestone (419).

Water, Carbon Dioxide, Silicious Matter, Iron, and Aluminium are estimated as is described under spathic iron-ore (432, 433, 434, 435, 436).

445. **Estimation of Manganese**.—The filtrate, from which the basic acetates of iron and aluminium have been precipitated (438), is neutralised with ammonium hydrate. A fair amount of ammonium chloride is then added, and either a slight excess of freshly prepared colourless ammonium sulphide is added, or hydrogen sulphide is passed into the liquid to saturation. The liquid is now boiled for ten minutes, more of the ammonium sulphide or hydrogen sulphide is added, and the liquid is filtered through a double filter. The precipitate is finally washed with water containing a little ammonium sulphide.

The precipitate of MnS may then be treated by either of the following methods:

(a) Dissolve the precipitate in hydrochloric acid, boil off any dissolved hydrogen sulphide gas, reprecipitate the manganese as carbonate, and weigh it after ignition as Mn_3O_4 (164).

(b) A quicker method consists in drying the precipitate of MnS in the steam-oven. The precipitate is then removed from the filter as completely as possible and placed in a crucible, and the filter is burnt in a platinum spiral (101) the ash being dropped into the crucible. The precipitate and ash are then mixed with a little sulphur, heated in a current of hydrogen gas (92, 1012, 1013) until the precipitate becomes black, and weighed as MnS.

446. **Calcium, Magnesium, Alkali-metals, Phosphate, Sulphate, and Chloride** are estimated in the filtrate from the MnS as is described in paragraphs 426–430.

Analysis of Salt-cake.

447. Salt-cake, or commercial sodium sulphate, usually contains small quantities of insoluble matter, iron, aluminium, calcium, magnesium, and chloride. For technical purposes the minor constituents are frequently determined directly, and the sodium sulphate is then estimated by difference.

448. **Estimation of Moisture.**—Salt-cake rarely contains any appreciable amount of moisture, since it has been subjected to a red-heat during its preparation; and, moreover, crystallised sodium sulphate loses its water of crystallisation by prolonged exposure to the air.

Weigh out 10 grams of the salt-cake, and heat it in the steam-oven for two hours. The loss of weight represents the adherent moisture.

449. **Estimation of Insoluble Matter.**—Treat the dried salt-cake (448) with hot water. Filter, and wash the residue with hot water until it is free from soluble sulphate. Dry the residue in the steam-oven, ignite it together with the filter (99) at as low a temperature as possible, and weigh the insoluble matter.

Make up the filtrate and washings to 500 c.c. with water, mix well by shaking, and use aliquot portions of this solution for the estimations which are described below.

450. **Estimation of dissolved Iron and Aluminium.**—Measure out 200 c.c. of the solution (449) into a beaker, and heat the liquid to boiling. Add a little ammonium chloride solution, and then sufficient ammonium hydrate to make the liquid smell faintly of ammonia after it has been well stirred. Filter, wash the precipitate, heat it to redness (99), and weigh the

$Al_2O_3 + Fe_2O_3$. This precipitate is usually so small in amount that the separate estimation of Al and of Fe (424) is not necessary.

451. **Estimation of Calcium.**—To the hot filtrate (450) add a little ammonium oxalate solution, and allow the liquid to stand. Filter, wash the precipitate, ignite it, and weigh as calcium oxide (147).

452. **Estimation of Magnesium.**—Evaporate the filtrate (451) to dryness in a platinum or porcelain dish, and drive off the ammonium salts from the residue by ignition. Dissolve the residue in dilute hydrochloric acid, dilute with water, and filter if necessary.

To the clear solution add ammonium hydrate in moderate excess, then a little sodium phosphate solution, and allow the liquid to stand for some hours. Filter, wash the precipitate with dilute ammonium hydrate solution, then ignite it, and weigh as $Mg_2P_2O_7$ (165).

453. **Estimation of Sodium.**—Measure 50 c.c. of the original solution (449) into a small beaker. Stir it with pure milk of lime, which must be added until the liquid is distinctly alkaline (428). Boil, filter off the lime with the precipitate and wash it twice. Precipitate the calcium from the filtrate and washings by adding ammonium hydrate in slight excess, then ammonium carbonate, and finally a small quantity of ammonium oxalate. Filter, and wash the precipitate.

Transfer the filtrate and washings to a platinum or porcelain dish, and evaporate the liquid after adding some sulphuric acid. As soon as nearly all the liquid is driven off, transfer it to a platinum crucible and continue the evaporation to dryness. Ignite and weigh the residual sodium sulphate (170).

Note.—The percentage of sodium is frequently estimated by difference instead of directly, the sum of the percentages of the other constituents of the salt cake being subtracted from 100.

454. **Estimation of Sulphate.**—Add to 50 c.c. of the original salt-cake solution (449) a little hydrochloric acid, and then barium chloride solution in excess. Filter; wash, dry, and ignite the precipitate, and weigh as $BaSO_4$ (133).

455. **Estimation of Chloride.**—Add to 100 c.c. of the original solution (449) a little dilute nitric acid. Then add silver nitrate solution in excess. Filter; wash, dry, and ignite the precipitate, and weigh as AgCl (149).

For the Results of an Analysis of Salt-cake refer to paragraph 944.

Analysis of Silicates, which can be Decomposed by Hydrochloric Acid.

456. Many natural silicates are completely decomposed when they are heated in a finely powdered condition for some time with strong hydrochloric acid.

Many artificial silicates, such as the slags obtained in smelting iron-ores, "stone-lime," lias-lime, cements, mortars and cement mortars, are also completely decomposed by this treatment.

Natural silicates of this class usually consist mainly of silicates of calcium and aluminium, but they may also contain silicates of iron, manganese, magnesium, and the alkali-metals. Slags frequently contain in addition sulphides and phosphates.

If the silicate cannot be completely decomposed by hydrochloric acid, it must be treated with fused alkaline carbonates (**461**, **462** *et seq.*).

For special purposes, however, the portion decomposable by acid is sometimes treated as is directed below, and only the matter left undecomposed by acid is subsequently treated by the fusion method.

Cements.—In the examination of cements and of some natural silicates (**457–459**) it will usually be necessary to determine the amount of "soluble silica" present as well as the total amount of silica. The soluble silica is that part of the total silica which was in combination with bases in the substance, and which after separation (**457**) differs by being soluble in an alkaline solution.

Mortar and Lime.—In analysing mortars and lias- or stone-lime, the following special procedure should be adopted. The matter soluble in cold dilute acid is first removed by repeatedly stirring with cold dilute hydrochloric acid containing one-tenth its volume of the strong acid: and any residue of sand or "grit" is filtered off, washed, ignited and weighed. The solution is then treated as is directed below. In the case of old mortars and of lias-lime the "soluble silica" should also be estimated after evaporation of the acid solution to dryness (**457**).

If the nature of the insoluble matter in the mortar has to be examined, the acid liquids, after standing for a minute, are poured off through a weighed filter and the matter is weighed: the "grit" which rapidly settles is then separately filtered and weighed: both forms of undissolved matter may now be microscopically examined to ascertain their nature and whether the grit particles are sharp. A paper by Dibdin and Grimwood on the "Analysis of Mortar" in the *Analyst* for August 1896 may be consulted.

457. Estimation of the Silica, Total and Soluble.—If the silicate is completely decomposable by hydrochloric acid, weigh out accurately from 1 to 1·5 gram of the finely powdered substance, and heat it with a little strong hydrochloric acid in a covered evaporating-dish. As soon as the decomposition is complete, evaporate the liquid to dryness on the water bath, with

constant stirring (210), and heat the dish in the air-bath to 150° C. for about an hour.

Then treat the residue with hydrochloric acid, and filter off, wash, and weigh the silica as is described in paragraph 210. This is the total silica present in the substance. Reserve the filtrate and washings for subsequent use.

Note.—A portion of the silica should be heated with hydrofluoric acid in a platinum dish, and the liquid evaporated to dryness. If an appreciable residue is left, a fresh portion of the silicate must be treated as is directed in paragraphs 461, 462, since complete decomposition has not been effected by the hydrochloric acid.

Soluble Silica.—In order to distinguish between "soluble silica" or the combined silica which was present in silicates which have been decomposed by the hydrochloric acid, and "insoluble silica" which was originally present in the free state in the substance, the total silica is now treated in a large platinum dish with a moderately strong solution of sodium carbonate for one hour at the temperature of boiling water. The soluble silica passes into solution and the residue of insoluble silica is collected on a filter, washed, ignited and weighed. The difference between this weight and that of the total silica is the weight of the "soluble silica."

458. **Estimation of Iron, Aluminium, and Manganese.**—The method of procedure depends upon whether manganese is present or absent.

(a) *If Manganese is Absent*, add to the filtrate from the silica (457), first some ammonium chloride solution, and then ammonium hydrate in slight excess. Filter off, and wash the precipitate twice with water. Dissolve the precipitate in hydrochloric acid, and reprecipitate this solution as is directed in paragraph 423. Determine the weight of the precipitate (423), and proceed to separate the iron from the aluminium, if necessary, as is directed in paragraph 424.

(b) *If Manganese is Present*, precipitate the iron and aluminium together as basic acetates (435), and determine the manganese in the filtrate (438).

459. **Calcium, Magnesium, Alkali-metals, and Sulphate** are estimated as is directed in paragraphs 426–430.

Phosphate is estimated as is directed in paragraph 442, and total **Sulphur** by paragraph 479.

The separation of the silica must precede each of these estimations.

For the Results obtained by the Analysis of Lime, Mortar and Cement see paragraphs 941-945.

Analysis of Insoluble Silicates.

460. Most of the common silicates, such as felspar, mica, and garnet, contain the following metallic constituents: aluminium, iron, calcium, magnesium, and the alkali-metals.

Directions for the analysis of the rarer silicates, such as beryl which contains beryllium, and petalite which contains lithium, will be found in special treatises.

Practice in the analysis of an insoluble silicate may be obtained by analysing orthoclase or potash-felspar.

461. **Preparation of the Silicate.**—Powder very finely about 5 grams of potash-felspar in the following way: Fold a small quantity of the mineral in a piece of brown paper, and strike it sharply with a hammer on an iron anvil. This will break the felspar into fragments. Next coarsely powder these fragments by means of the percussion-mortar (56) and finally triturate the particles thus obtained in the agate mortar until they are converted into an impalpable powder.

The success of the analysis largely depends upon the careful reduction of the substance to the finest powder. The powder can only be considered as suitable when it passes entirely through the finest of the brass sieves which are mentioned in paragraph 56.

462. **Treatment with Fused Alkaline Carbonates.**—Now make a fusion in the following way:

Weigh out accurately about 1·5 gram of the finely powdered felspar into a platinum crucible. Add about six times its weight of finely powdered fusion-mixture, consisting of sodium and potassium carbonates in molecular proportions, and intimately mix these powders by means of a smooth rounded glass rod.

Unless the crucible is a capacious one, it will be found convenient to introduce the mixture little by little during the process of fusion, since the substance usually froths considerably. The mixture should never more than half fill the crucible.

Now place the lid on the crucible, and heat it gently over the Bunsen flame. Gradually increase the temperature, taking care that no loss arises from the frothing which is caused by the evolution of carbon dioxide gas. As soon as the mass is fused, the crucible is kept at a bright red-heat (98) for at least fifteen minutes until effervescence ceases and the fused mass becomes tranquil.

463. **Solution of the Metals.**—Allow the crucible to cool just below

redness, then place the bottom on an iron plate or in cold water to cause the mass to separate from the crucible. Now pour about 100 c.c. of water upon it in a deep evaporating-dish or in a shallow beaker, and either boil the water for half an hour or let it stand overnight.

Then add tolerably strong hydrochloric acid gradually, keeping the vessel covered with a clock-glass and gently agitating the contents of the beaker after each addition of the acid.

When the effervescence has ceased, and the crucible is free from all adherent solid, remove the crucible and its lid by means of a glass rod, and carefully rinse them into the main portion of the liquid with a wash-bottle.

This treatment of the fused mass with acid will cause most of the silica to separate as a gelatinous mass.

If any gritty particles are felt when the bottom of the vessel is stirred with a glass rod, the decomposition of the silicate has been incomplete. This is probably due to the original substance not having been sufficiently finely powdered. In this case it is usually best to start afresh, taking care that all coarse particles have been crushed in the portion of the powdered mineral which is used for the fusion.

464. Estimation of Silica.—The acid liquid containing the gelatinous silica (463) is then transferred to an evaporating-dish, preferably of platinum, and is evaporated to dryness upon the water-bath. As soon as the contents of the dish become thick and pasty, they should be continually stirred with a rounded glass rod in order to prevent the formation of lumps (210).

When all the liquid has been driven off, the contents of the dish will be in the state of a fine powder. The dish is now placed in an air-bath (73, d), and heated to 150° C. for about an hour, or until no moisture is deposited upon a cold clock-glass when it is placed upon the dish for a few seconds.

The dish is then allowed to cool, and its contents are moistened with strong hydrochloric acid. After it has been allowed to stand for some time it is heated on the water-bath for about half an hour, a small quantity of hydrochloric acid being occasionally added.

Hot water is now added, and the acid liquid is decanted off through a filter. This operation is repeated three times. The silica is finally transferred to the filter and washed free from dissolved chloride, and is then dried in the steam-oven.

The precipitate is now transferred to a platinum crucible cautiously, since it consists of very light powder which is easily blown away, and the filter-ash is added (101). The crucible is covered with the lid and is heated very gently at first; the temperature must be only gradually raised, else the escaping steam may carry some of the fine light powder away with it. The crucible is finally heated to full redness over the Bunsen flame, and is weighed when cold (see *Note* 1, 210).

The purity of the silica should be tested as is described in paragraph **210** (*Note* 2)

465. Estimation of Iron and Aluminium.—The filtrate from the silica (464) is mixed with ammonium chloride solution, and then with ammonium hydrate in slight excess; and the iron and aluminium hydroxides, of which the precipitate consists, are filtered off and estimated (423). They may then be separated, if necessary, according to the directions in paragraph 424.

466. Estimation of Calcium.—If the volume of the filtrate (465) is very large, evaporate the liquid down to a convenient bulk. Then add a little ammonium hydrate, if necessary, to render the liquid alkaline, and then a slight excess of ammonium oxalate. Allow the liquid to stand; then filter, and weigh the calcium as oxide after ignition (147).

467. Estimation of Magnesium.—Evaporate the filtrate and washings from the calcium oxalate precipitate (466) to dryness, ignite the residue, dissolve it in dilute HCl, and estimate the magnesium as is described in paragraph 427.

468. Estimation of the Alkali-metals.—Since the silicate has been treated with sodium and potassium carbonates, the alkali-metals cannot be estimated in the filtrate from the magnesium (467). A separate portion of the felspar must accordingly be used for the determination of the alkali-metals.

Weigh accurately about 1·5 gram of the finely powdered felspar into a platinum crucible. Mix this intimately with 1·5 gram of pure recrystallised ammonium chloride (107) and 9 grams of pure calcium carbonate (109).

Now heat the crucible over a small Bunsen flame for about fifteen minutes, and then maintain the temperature at dull redness for an hour. Or inclose the crucible in a clay crucible containing a little calcined magnesia or lime at the bottom and round the sides, and heat it in a gas-furnace.

Place the cold platinum crucible in hot water in a covered platinum or porcelain dish, and boil for a time. This will dissolve out the alkaline chlorides together with some calcium hydrate. Filter, wash, and mix the filtrate and washings with ammonium hydrate and ammonium carbonate solutions in excess, and then with a few drops of ammonium oxalate solution. Allow the liquid to stand, filter into a platinum or porcelain dish, evaporate the filtrate to dryness, and heat the residue short of redness, but sufficiently strongly to drive off the ammoniacal compounds.

Dissolve the residue in water, and add a few drops of ammonium hydrate and ammonium oxalate solutions in order to precipitate any trace of calcium which may still remain in the solution. Filter, add a few drops of HCl to the filtrate, and evaporate it to dryness in a weighed dish. Ignite the residue

gently, and weigh it, repeating the ignition until the weight is constant. The weight of the residue gives the weight of the potassium and sodium chlorides.

Dissolve the residue in water; and either estimate the potassium chloride and find the weight of the sodium chloride by difference (429, a); or determine the total chlorine gravimetrically (149) or volumetrically (373), and calculate the weights of the chlorides (429, b).

The weights of the oxides corresponding to those of the chlorides found are then calculated.

Note —When very accurate results are required, and the proportion of alkali-metals present is small, it is essential to carry out a blank determination as is directed above in which no mineral is used, and to subtract the amount of alkali-metal thus found from the result obtained in the analysis of a mineral.

For the Results of Analysis of Portland Cement and Felspar refer to paragraphs 945, 946.

Analysis of Glass.

469. Glass consists essentially of the same constituents as most of the natural insoluble silicates (460). Common glass is mainly composed of silicates of sodium and calcium, but it may also contain aluminium, iron, manganese, and potassium. In flint glass the calcium is replaced by lead.

The analysis of glass is carried out in the same way as the analysis of felspar (461–468). If, however, lead or manganese is present, the following special procedure is necessary:

Separate the silica as is described in paragraph 464. Then precipitate the lead by passing hydrogen sulphide through the acid filtrate from the silica. Filter off, wash and dry the lead sulphide, and convert it into lead sulphate by heating it with strong nitric acid and adding a little dilute sulphuric acid. Dilute, filter, and ignite and weigh the $PbSO_4$ (161).

Boil the filtrate from the PbS until the excess of hydrogen sulphide is removed; then boil after adding a few drops of strong HNO_3, and precipitate the iron and aluminium as basic acetates (435), separating them, if necessary, as is described in paragraphs 424, 436.

Precipitate the manganese as hydrated peroxide, by adding bromine-water in excess and then ammonium hydrate in excess and boiling. Filter off the precipitate, ignite it, and weigh as Mn_3O_4 (438).

Then estimate the calcium and magnesium in the filtrate, as is directed in paragraphs 439, 440.

The alkali-metals must be estimated in a separate portion of the glass, according to the directions given in paragraph 468.

For the Results of an Analysis of Glass refer to paragraph 947.

Analysis of Zinc-blende.

470. Zinc-blende consists essentially of zinc sulphide, which is, however, commonly associated with galena or lead sulphide, and occasionally with calamine or zinc carbonate. The ore may also contain iron, aluminium, manganese, copper, and cadmium.

471. **Estimation of Moisture.**—The moisture is usually adherent only, and is not combined.

Weigh out accurately about 1·5 gram of the finely powdered ore into the watch-glasses and clip, and heat this in the steam-oven until the weight becomes constant. The loss gives the amount of moisture.

472. **Solution of the Ore.**—Transfer the dried ore (471) to a 500 c.c. beaker, covered with a clock-glass. Then add a little strong hydrochloric acid and heat gently for some time covering the beaker with a clock-glass, since effervescence will take place if carbonate is present.

As soon as hydrogen sulphide ceases to be evolved, add more strong hydrochloric acid and about an equal volume of nitric acid; and when the ore is completely dissolved, transfer the liquid to a porcelain dish and evaporate it to dryness on the water-bath.

473. **Estimation of Silicious Matter and Lead.**—Heat the residue for some time in the air-bath at 150° C. in order to render the silica insoluble. Then moisten the dry residue with strong hydrochloric acid, and dilute with a little water. Next add a few c.c. of strong sulphuric acid, and heat gently on the sand-bath until the hydrochloric and nitric acids are removed and white fumes of sulphuric acid are seen. Again dilute with water and filter, washing the residue on the filter with water containing a few drops of sulphuric acid, and finally with methylated spirit until all the acid is removed. Add the first washings to the filtrate and keep this liquid for paragraph 474, but reject the alcoholic washings.

The residue on the filter consists of gangue or earthy matter, silica, and lead sulphate; dry it in the steam-oven, then ignite it apart from the filter (101–105), and weigh after converting any lead, which has been reduced by the incineration of the filter, into sulphate (161).

Dissolve out the lead sulphate from this residue by boiling it with ammonium acetate solution made alkaline with ammonium hydrate. Repeat this treatment with fresh portions of the solvent until no lead can be detected in a drop of the acetate solution, when it is tested with ammonium sulphide. Again dry the residue, then ignite (99) and weigh it as silicious matter.

The loss of weight which the residue has suffered by being treated with the ammonium acetate solution represents the amount of lead sulphate which it contained.

474. **Estimation of Copper.**—To the filtrate from the first residue (473) add a little dilute hydrochloric acid, and saturate the liquid with hydrogen sulphide. Then filter at once, keeping the funnel covered with a glass plate, and washing rapidly with water containing a little hydrogen sulphide. These precautions are necessary in order to prevent the oxidation of the CuS into soluble $CuSO_4$ by exposure to the air. The filtrate and washings should be again tested with hydrogen sulphide, in order to make sure that no copper remains in solution.

If cadmium is not to be estimated (475) the copper is at once converted into cuprous sulphide, Cu_2S, and weighed as such. For this purpose the precipitate is dried in the steam-oven. The filter is burnt by itself in a Rose's crucible (92), the precipitate is added to the filter-ash, and some powdered redistilled sulphur is also mixed with the precipitate. This mixture is then heated in a current of hydrogen (1012, 1013) as long as sulphur vapour escapes, and the residue of Cu_2S is allowed to cool in the stream of hydrogen, and is weighed (496).

475. **Estimation of Cadmium.**—If any cadmium is present in the ore, the precipitate obtained by hydrogen sulphide (474) will contain both CuS and CdS. This precipitate is boiled with dilute sulphuric acid in order to dissolve out the CdS, and the copper, which remains as sulphide, is estimated as is described above. The acid filtrate, containing the cadmium, is neutralised with ammonium hydrate, and the cadmium is precipitated as sulphide by passing hydrogen sulphide gas. The CdS is then estimated as is described in paragraph 192.

476. **Estimation of Iron.**—Boil the filtrate from the CuS (474) until the hydrogen sulphide is removed, and then add barium chloride solution in sufficient quantity to precipitate the whole of the sulphate present.

The removal of sulphate is necessary in order to prevent the subsequent precipitation of basic ferric sulphate with the basic ferric acetate. The basic ferric sulphate precipitate is with difficulty converted completely into Fe_2O_3 by ignition.

Filter, and add ammonium carbonate solution to the filtrate, drop by drop,

until a very faint turbidity remains after the liquid has been well stirred, and boil after adding ammonium acetate solution containing a little free acetic acid (435).

Filter the boiling liquid, using the funnel-jacket (Fig. 66, p. 65); then wash the precipitate twice, and dissolve it in hydrochloric acid. Add ammonium carbonate in slight excess and reprecipitate the iron with ammonium acetate as is described above. Filter, wash, dry, and ignite the precipitate (99), and weigh the iron as Fe_2O_3.

The above double precipitation is necessary in order to remove small quantities of zinc and manganese which are precipitated with the iron.

477. Estimation of Manganese.—Mix together the filtrates and washings (476), which contain both the manganese and the zinc, and treat the liquid with a little bromine-water; then add excess of ammonium hydrate, and boil. Filter off the precipitate; wash, dry, and ignite it, and weigh as Mn_3O_4.

478. Estimation of Zinc.—Mix together the filtrate and washings (477), which contain the zinc, and treat the liquid in one of the three following ways (a, b, c):

(a) Make the liquid up to a known volume, and titrate either with potassium ferrocyanide (378), or with sodium sulphide solution (379).

(b) Precipitate the zinc as sulphide by adding a slight excess of colourless ammonium sulphide, and weigh it as ZnS (509, a).

(c) Instead of weighing the ZnS (b), dissolve it in hydrochloric acid, boil the solution until it no longer evolves H_2S, precipitate the zinc as carbonate, and weigh it as oxide (163).

479. Estimation of Sulphur.—Weigh out accurately about 1 gram of the finely powdered ore into a platinum or nickel crucible, and mix this intimately with six times its weight of finely powdered sodium peroxide free from metallic sodium (141). Then heat the crucible over a small Bunsen flame, gradually raising the temperature until the mass fuses, and maintaining the substance in a fused condition for several minutes.

Extract the cold mass with water, and remove lead, if it is present, by acidifying the solution with nitric acid and boiling with excess of sodium carbonate solution. Filter, wash the residue, acidify the filtrate and washings with dilute hydrochloric acid and estimate the sulphur as $BaSO_4$ (133).

The method of treatment with strong nitric acid and bromine, which is described in paragraph 142, may replace the above treatment with sodium peroxide.

480. Estimation of Carbon Dioxide.—If carbonate is present 4 grams of the finely powdered ore are heated with dilute sulphuric acid, in which some chromic anhydride (527) has been dissolved: and the carbon dioxide, which is evolved, is absorbed and weighed (175). The carbon dioxide should bubble through some solution of chromic acid before it passes into the absorption tubes.

The use of chromic acid and anhydride prevents the evolution of H_2S and its absorption by the soda-lime.

For the Results of an Analysis of Zinc-blende refer to paragraph **948.**

Analysis of Galena.

481. Galena consists essentially of lead sulphide; but it may also contain silicious matter, silver, copper, antimony, and zinc.

The estimation of the percentage of silver is frequently of great importance. The amount is not usually sufficiently great to be accurately estimated by precipitation (484), and should be found by means of the dry assay methods (572–577).

482. Estimation of Moisture.—The moisture present in galena is hygroscopic, and is usually small in amount. Weigh out accurately about 1·5 gram of the finely powdered ore, and heat it in the steam-oven until its weight becomes constant. The loss of weight represents the moisture.

483. Estimation of Silicious Matter and Lead.—Heat the dry ore (482) with strong nitric acid. This operation is best performed in a 300 c c. flask, in the neck of which a small funnel has been placed (Fig. 34, p. 36). As soon as the evolution of red fumes ceases, allow the contents of the flask to cool, add about 1 c c. of bromine, and warm the liquid until all the sulphur is oxidised and the lead is converted into lead sulphate.

Now add a small quantity of sulphuric acid and evaporate the liquid, together with the undissolved matter, in a dish. Then heat the residue on the sand-bath, until dense white fumes of sulphuric acid are evolved. This will render the silica insoluble. Dilute with water, filter, wash the residue with water containing sulphuric acid, using as little washing-water as possible, and keep the filtrate and washings after mixing them together. Finally wash the residue further with methylated spirit until all the acid is removed, and reject the alcoholic washings.

Ignite the residue apart from the filter (101–105) in a porcelain crucible, then add the filter-ash, and weigh. Now dissolve away the lead sulphate

from the gangue by means of alkaline ammonium acetate solution, as is described in paragraph 473, and weigh the residue of silica. The weight of the lead sulphate is found by difference.

484. Estimation of Silver.—To the filtrate from the silica and lead (483) add a few drops of hydrochloric acid, and allow the liquid to stand in a warm place for several hours. Filter, wash the silver chloride precipitate, and determine its weight (158).

Other methods for estimating the silver are given in paragraphs 372 and 375. If the quantity of silver chloride obtained is too small to be accurately weighed, the weight of the ore which is used for this particular determination must be increased: but it is preferable to estimate the silver together with the lead by the dry assay methods (572–577).

A percentage of silver as low as 0·001 may be profitably extracted from galena, hence great care must be taken to determine accurately even minute amounts of silver in this ore.

485. Estimation of Copper.—Into the filtrate from the silver chloride (484) pass hydrogen sulphide gas to saturation. Allow the liquid to stand, and filter off the precipitated sulphides of copper and antimony. Wash the precipitate with water containing hydrogen sulphide as expeditiously as possible, taking care to cover the funnel with a glass plate so as not to expose the precipitate unnecessarily to oxidation by the atmosphere. Keep the filtrate and washings.

Digest the precipitate on the water-bath for half an hour with sodium sulphide solution, prepared as is directed in paragraph 379, then add water and filter. Ammonium sulphide cannot be used, since CuS is slightly soluble in this reagent. The residual precipitate left upon the filter consists of copper sulphide; this is converted into Cu_2S (496), and the copper is weighed as such.

486. Estimation of Antimony.—The sodium sulphide filtrate will contain the antimony. Acidify the solution with hydrochloric acid and saturate it with H_2S: then filter off the antimony sulphide, convert it into Sb_2O_4 (198), and weigh the antimony as such.

487. Estimation of Iron and Aluminium.—Boil off the hydrogen sulphide from the filtrate and washings (485), add a few drops of nitric acid to convert the iron into the ferric state, then add ammonium chloride solution and a slight excess of ammonium hydrate. Filter, wash the precipitate twice, redissolve it in hydrochloric acid, and precipitate this solution again with ammonium hydrate. Filter off the precipitate, dry and ignite it, and weigh as $Fe_2O_3 + Al_2O_3$. The two filtrates and washings are mixed together and are used as in the following paragraph.

488. Estimation of Zinc.—To the hot filtrate add a slight excess of freshly prepared colourless ammonium sulphide, boil, and estimate the Zn as ZnS (509, a).

489. Estimation of Sulphur.—Weigh out accurately 1 gram of the finely powdered galena, fuse it with sodium peroxide (479), and estimate the sulphur as $BaSO_4$.

For the Results of an Analysis of Galena refer to paragraph 949.

Analysis of Copper-pyrites.

Copper-pyrites is the most common ore of copper. It consists essentially of a double sulphide of copper and iron, having the formula $CuFeS_2$. The ore, however, usually contains silicious matter and small quantities of lead, bismuth, arsenic, antimony, manganese, and zinc, and occasionally nickel and cobalt.

A qualitative analysis of the ore should always precede the quantitative estimations.

490. Estimation of Moisture.—The finely powdered pyrites is heated in steam-oven until its weight becomes constant; the loss of weight represents the moisture.

491. Estimation of Insoluble Matter.—Weigh out accurately about 1 gram of the ore into a porcelain evaporating-dish. Pour upon it a mixture of 3 parts of nitric acid and 1 part of hydrochloric acid, cover the dish with an inverted funnel to prevent loss by spirting, and heat it on the water-bath. As soon as all the sulphur, which separates out at first, is dissolved, evaporate to dryness twice with HCl in order to remove the HNO_3 and to render the silica insoluble.

Moisten the residue with strong HCl, then add water and heat, and filter off and wash the residue, reserving the solution and washings for **492**. The residue will consist of silica and gangue, and will probably contain some lead sulphate. Dissolve away the latter with alkaline ammonium acetate solution (473), rejecting the solution. Then wash, dry, ignite (99) and weigh the residue.

492. Estimation of Sulphur.—One of the following methods **a, b)** may be used.

(a) Add to the filtrate (491) a little tartaric acid to prevent the precipita-

tion of iron and aluminium, heat it to boiling, precipitate the sulphate with barium chloride, and filter off, wash and weigh the $BaSO_4$ (133).

(b) A more rapid method of estimating the sulphur consists in treating 1 gram of the finely powdered ore with fused sodium peroxide (141), or with strong nitric acid and bromine (142), as is described in paragraph 479.

493. **Estimation of Copper, Lead, Arsenic, and Antimony** in the hydrogen sulphide precipitate.

Dissolve 2 grams of the powdered ore in red fuming nitric acid, of 1·5 specific gravity; add a few c c. of strong sulphuric acid, and evaporate until dense white fumes appear. Treat the residue with hydrochloric acid, then add water and allow it to stand. Filter off and wash the residue, and estimate the lead sulphate as is directed in paragraph 473, adding the $PbSO_4$ found to that found below.

Pass hydrogen sulphide through the filtrate to saturation until the sulphides of copper, lead, arsenic, and antimony are precipitated. Then filter, pass H_2S again through the boiling filtrate, and pour it once more through the filter if necessary. Wash the precipitate with water containing hydrogen sulphide, and reserve the filtrate and washings for paragraph 494.

Arsenic and Antimony.—Heat the sulphide precipitate with sodium sulphide solution (379) in order to dissolve the sulphides of antimony and arsenic, then dilute and filter, reserving the residue of PbS and CuS.

Acidify the filtrate with HCl, pass H_2S and filter. Dissolve the sulphides, thus precipitated, by heating them with HCl and a little $KClO_3$. Add solutions of tartaric acid and of AmCl in order to keep the Sb in solution, and then add excess of AmHO. No precipitate will form, if sufficient $H_2\overline{T}$ and AmCl have been added. Now add magnesia mixture (167), filter off, and weigh the As as $Mg_2As_2O_7$ (169).

Acidify the filtrate from the arsenate, and precipitate the Sb as sulphide by passing hydrogen sulphide; then convert the sulphide into Sb_2O_4 (198), and weigh the oxide.

Lead.—Dissolve the copper and lead sulphides, which remained after extraction with sodium sulphide solution, in nitric acid. Evaporate the solution nearly to dryness, dilute with water, add a few drops of dilute sulphuric acid, and allow the liquid to stand. Filter, and wash the lead sulphate with a little water acidified with sulphuric acid, keeping the filtrate and washings. Finally wash out the acid from the filter with methylated spirit, rejecting the washings. Then ignite and weigh the $PbSO_4$ (161), add this to the weight found in the residue above, and calculate the weight of lead present in the ore.

Copper.—Precipitate the copper in the filtrate from the $PbSO_4$ by sodium

hydrate, and estimate it as CuO (126); or better precipitate it as CuS by hydrogen sulphide and weigh it as Cu_2S (496).

494. **Estimation of Iron, Manganese, and Zinc.**—Oxidise the original hydrogen sulphide filtrate (493) by heating it with a little nitric acid, and precipitate and estimate the metals as is directed under zinc-blende (476–478).

For the Results of an Analysis of Copper-pyrites refer to paragraph 950.

Analysis of Brass.

495. Brass is an alloy consisting mainly of copper and zinc, but small quantities of lead and iron are usually present.

Preparation of the Sample.—The sample for analysis should be removed with a drill, since if a file is employed its teeth are apt to be broken off and to increase the proportion of iron in the filings.

Solution of the Alloy.—Dissolve 2 grams of the metal in 10 c.c. of nitric acid, of 1·42 specific gravity, in a lipped beaker covered with a clock-glass. When all action has ceased remove and rinse the clock-glass, add 10 c.c. of strong sulphuric acid, and evaporate until white sulphuric acid fumes are evolved. Then cool, dilute with cold water to 150 c.c., filter off the $PbSO_4$ and weigh it if it is sufficient in quantity (498), and dilute the filtrate to 500 c.c.

496. **Estimation of Copper as Cu_2S.**—To 250 c.c. of this solution, which correspond to 1 gram of the alloy, add 40 c.c. of hydrochloric acid of 1·1 specific gravity; then dilute with boiling water to about 500 c.c. in a large beaker, pass H_2S through the boiling liquid for half an hour, and filter, washing the precipitate four times with warm H_2S water.

Remove the precipitate to a porcelain dish, and dissolve it in nitric acid to which a little bromine has been added, keeping the dish covered. Then remove the excess of nitric acid and bromine by evaporation over a steam-bath. Dissolve the residue in 40 c.c. of hydrochloric acid of 1·1 specific gravity, transfer the solution to the beaker, dilute with hot water to about 500 c.c. and reprecipitate the copper with H_2S.

This double precipitation of the copper is necessary in order to separate a small quantity of ZnS which is at first precipitated with the CuS.

Filter, and wash the precipitate with H_2S water until the washings, after being freed from H_2S by boiling, give no milkiness with silver nitrate solution.

Estimation of Cu as Cu_2S.—Dry the precipitate of CuS and detach it from the filter, burn the filter in a Rose crucible (92), then add the precipitate together with a little powdered redistilled sulphur, cover the crucible with the lid and tube, and pass a gentle stream of pure dry hydrogen (1012, 1013).

Heat the crucible gently until the flame of burning sulphur has nearly disappeared, then raise the temperature to full redness, and finally ignite strongly (98) for about five minutes. Let the residue cool in the stream of hydrogen until the crucible can be handled with comfort, then allow it to cool completely in the desiccator and weigh it. Now add a little more pure sulphur and repeat the ignition in hydrogen until the weight is constant.

From the weight of Cu_2S thus obtained, the percentage of Cu in the alloy is calculated.

An Alternative Method of determining the copper is to precipitate it as cuprous thiocyanate (408) from 50 c.c. of the original solution of the alloy (495). See also paragraphs 396, 397.

497. **Estimation of Zinc.**—Boil down the two filtrates and the washings from the CuS precipitate (496) in a large basin until all the hydrochloric acid is expelled, and sulphuric acid is the only free acid remaining. Dilute with water to about 300 c.c., add a solution of pure sodium hydrate until the acid is nearly neutralised, then add pure solid sodium carbonate in excess and boil.

Filter off the precipitate of $ZnCO_3$ and $Fe(OH)_3$, and wash it with boiling water until the washings give no trace of cloudiness with barium chloride solution even after standing. Dry the precipitate, and ignite and weigh as ZnO (163) and Fe_2O_3.

The weight of ZnO is subsequently found by deducting from this weight the weight of Fe_2O_3 found in 499, and the percentage of Zn in the alloy is then calculated.

498. **Estimation of Lead.**—Dissolve 5 grams of the alloy in 20 c.c. of nitric acid of 1·42 specific gravity, stir in gradually 15 c.c. of concentrated sulphuric acid, and evaporate the liquid with constant stirring until white sulphuric acid fumes are copiously evolved. Cool the residue, dilute it with cold water to about 225 c.c., and stir until all is dissolved except $PbSO_4$. Filter, and wash with water containing a little sulphuric acid until the copper is removed, reserving the filtrate and washings. Then wash out the acid from the filter with alcohol, rejecting the alcoholic washings.

Finally dry, ignite, and weigh the $PbSO_4$ (161), and from this calculate the percentage of Pb in the alloy.

499. **Estimation of Iron.**—Add to the filtrate and the washings from 498 a large excess of ammonia, and filter. Wash with water containing

ammonia until the washings cease to be blue. Dissolve the precipitate in the filter with hydrochloric acid, and wash the filter with cold water. Then dilute the solution and washings to about 200 c.c., add ammonia solution to the cold liquid until it is nearly neutralised, but no permanent precipitate is formed.

Now add some ammonium acetate, boil and filter, using the same filter as before, and wash the precipitate. Again dissolve the precipitate in hydrochloric acid, and precipitate the ferric hydrate by adding ammonia solution. This reprecipitation is necessary in order to remove zinc from the ferric hydrate.

Finally filter; then wash the precipitate, dry and ignite it, and weigh as Fe_2O_3 (129). From this weight calculate the percentage of Fe in the alloy.

For the Results of an Analysis of Brass refer to paragraph 951.

Analysis of Alloys containing Tin and Antimony.

Bronze is an alloy consisting chiefly of copper and tin, but other metals may be present as well.

Type-metal and the various antifriction metals consist mainly of lead, antimony, and tin, and may also contain copper and traces of iron.

Solder and pewter are alloys of tin and lead, in which traces of antimony, arsenic and copper may be present.

Note.—Provision is made in paragraphs 500–503 for the complete gravimetric analysis of these alloys, but this is a tedious process owing to the difficulty in filtering off the precipitated tin sulphide

Paragraphs 504, 505 provide for a much more rapid volumetric estimation of tin and of antimony.

500. Precipitation with Hydrogen Sulphide.—Dissolve 1 gram of the alloy in aqua regia, add 10 grams of pure tartaric acid dissolved in a little hot water, and make the solution alkaline by the addition of pure sodium hydrate solution.

Pour this liquid into a basin containing 30 grams of the pure sodium hydrate dissolved in about 500 c.c. of water. Heat the liquid until it boils gently, and pass a rapid stream of H_2S until the liquid is saturated, keeping the basin covered with a perforated glass plate. Filter, wash the precipitate with hot dilute sodium sulphide solution (379), and then once with boiling water. Reserve the filtrate and washings for paragraph 502, and treat the precipitate as follows (501).

501. Estimation of Lead, Copper, Zinc, and Iron.—Dissolve the pre-

cipitated sulphides (500) in nitric acid, evaporate until the liquid becomes syrupy, dilute with water, filter off any trace of SnO_2 which may have been originally precipitated as sulphide by H_2S, and reserve this precipitate to be added to the main quantity of SnS.

Assuming that the filtrate contains lead, copper, zinc, and traces of iron, these metals may be estimated by evaporating with sulphuric acid to separate lead (498), then precipitating the copper from the filtrate with H_2S (496), throwing down the zinc and iron with sodium carbonate (497), and estimating the iron separately (499).

502. Estimation of Antimony.—Make the alkaline filtrate (500) distinctly acid with hydrochloric acid, which must be added cautiously and with continual stirring, and allow the liquid to stand at a gentle heat until the precipitate has completely separated. Filter, and wash the precipitate four times with cold H_2S water, letting the washing-water drain away completely each time. Add a little NaCl to the water used for washing, if the precipitate shows any tendency to pass through the filter.

Now remove the precipitate from the filter by means of a platinum spatula into a porcelain basin, using hot hydrochloric acid to dissolve off the traces which adhere to the paper. Pour some more hydrochloric acid into the basin, then cover it and heat gently, adding occasionally a small crystal of potassium chlorate, seven parts of the chlorate being used for one part of tin or of antimony (*Note*). Boil the liquid gently to expel chlorine, remove the cover, rinsing it into the dish, filter into a flat porcelain dish and evaporate to about 5 c.c.

Add a clear hot solution containing 20 grams of pure oxalic acid, transfer the liquid to a tall beaker, dilute with boiling water to 300 c.c., and pass a rapid current of H_2S through the boiling solution until the Sb_2S_3 has completely separated. This usually requires about twenty minutes. Filter at once through a weighed filter-paper, wash the Sb_2S_3 thoroughly with hot water, and dry it. Reserve the filtrate and washings for the estimation of tin (503).

Digest the dry filter and precipitate in some pure carbon disulphide, contained in a very small beaker, in order to dissolve out free sulphur (193). Then place the filter in a funnel and wash it with CS_2. Dry the filter and its contents at a gentle heat, and then at 130° C. until the weight is constant, referring to paragraph 87 for a method which avoids charring the filter.

From the weight of Sb_2S_3 thus obtained, calculate the percentage of Sb in the alloy.

Note.—The $KClO_3$ is added to form double chlorides of K with Sn and Sb which are not decomposed by evaporation, the loss of $SnCl_4$ and $SbCl_5$ during evaporation is thus prevented.

503. Estimation of Tin.—Before the tin is precipitated from the filtrate

(502) it is necessary to destroy the oxalic acid. For this purpose transfer the liquid to a large porcelain basin, add hydrochloric acid in excess, heat, cover the basin, and add solid $KMnO_4$ by degrees until a small precipitate of MnO_2 remains which does not dissolve on boiling even when more hydrochloric acid is added. Redissolve the MnO_2 by adding a few drops of $FeSO_4$ solution, then pour the clear hot solution into a flask and pass H_2S to precipitate the tin.

Allow the precipitate to settle, syphon off the clear liquid, collect the precipitate on a filter, and wash it with H_2S water containing a little ammonium nitrate. After this precipitate, consisting of SnS mixed with S, has been thoroughly washed, dry it, and add to it any SnO_2 which has been previously obtained (501). Then convert the whole by ignition in an open crucible into SnO_2 (201), and weigh this.

From the weight of SnO_2 thus obtained, the percentage of Sn in the alloy is calculated.

For Results of Analyses of Bronze, Type-metal and White-metal refer to paragraphs **952, 953, 954.**

Volumetric Estimation of Tin and of Antimony in Alloys.

504. Estimation of Tin.—This metal is estimated by titration with ferric chloride solution in a solution rendered strongly acid with hydrochloric acid.

Simple alloys, like solder and pewter, which contain only traces of arsenic, antimony, and copper, may be dissolved by heating them with strong HCl, and the solution may be at once titrated: but alloys which contain the above three metals in some quantity, such as antifriction metals, must be first dissolved, and the tin must then be precipitated as metal from the solution and redissolved in hydrochloric acid for the titration.

It is obvious that suitable precautions must be taken to prevent contact with atmospheric oxygen during the process of solution and of titration: this may be most easily secured by passing a continuous stream of carbon dioxide through the flask in which the processes are carried out.

The Standard Ferric Chloride Solution is most conveniently prepared by dissolving about 180 grams of the yellow lump salt, which consists approximately of $FeCl_3.6H_2O$, in 200 c.c. of strong hydrochloric acid, and evaporating the solution just to dryness in order to remove nitric acid and arsenic. The residue is then dissolved in 300 c.c. of strong hydrochloric acid and the solution is diluted to two litres. 1 c.c. of this solution roughly corresponds to 0·02 gram of tin.

The solution is standardised by titrating it with a solution of 1 gram of pure tin in hydrochloric acid, prepared by the process which is described below for dissolving the alloy (a).

The procedure with an alloy will depend upon whether it is completely soluble in boiling strong hydrochloric acid (a), or is not completely dissolved by that acid (b).

(a) **The Alloy is completely soluble in Boiling Strong HCl.**—One gram or more of the alloy, in the form of filings or fine turnings, is weighed exactly and is placed in a 250 c.c. flask fitted with two tubes in a rubber stopper, by means of which a constant stream of carbon dioxide is passed through it. 200 c.c. of strong hydrochloric acid are then introduced, and the flask is heated until the alloy is completely dissolved; the boiling liquid is then titrated rapidly with the above standard ferric chloride solution, the conclusion of the process being indicated by the appearance of a permanent yellow colour in the liquid.

It is important that the liquid should be kept as hot as possible during the titration, since the reaction then proceeds more quickly and the colour indication is also much more delicate at the conclusion, one drop of the ferric solution sufficing to produce the yellow tint. The coloration can only be seen by daylight or white light.

Note.—The presence of the chlorides of lead, zinc, aluminium, cobalt, nickel, cadmium, or of ferrous, antimonious or cuprous chloride does not affect the quantity of ferric chloride used in the titration, although the presence of ferrous chloride in any quantity somewhat retards the process and diminishes the delicacy of the final colour indication.

(b) **The Alloy does not Dissolve Completely in Boiling Hydrochloric Acid, but a Black Powder Remains.**—The black residue consists of antimony, copper and arsenic, and contains a small amount of occluded tin.

If the amount of the residue does not exceed 5 per cent. of the alloy, a close approximation may be made in the estimation of the tin by dissolving it out of the alloy as is directed under (a), and then carefully titrating the decanted clear liquid together with the washings of the black residue with hot hydrochloric acid, with ferric chloride as under (a); but a more accurate result may be obtained by proceeding as follows.

From 1 to 2 grams of the alloy are accurately weighed and boiled gently with from 50 to 75 c.c. of hydrochloric acid in a 250 c.c. flask until action ceases, when most of the tin and lead will have passed into solution. The solution is then made complete by adding gradually a saturated solution of $KClO_3$. All chlorous fumes are then removed by further heating, and a bunch of about 5 to 10 grams of fine piano-wire is added. If the liquid is kept hot the solution

of the iron is very rapid, and the liquid quickly becomes decolorised, while the antimony and copper are also precipitated.

The last traces of antimony are then precipitated together with the arsenic by dropping in a thin strip of copper and heating, the heating being discontinued as soon as a small additional scrap of Cu remains bright when it is placed in the liquid.

The liquid is now diluted with about 40 c.c. of hot, boiled water, then boiled, and filtered as rapidly as possible into another 250 c.c. flask, covering the black precipitate as far as possible from the air, and the flask and filter-paper are washed once with hot dilute HCl.

The clear solution in the flask contains all the tin, and this is at once completely precipitated by the addition of sufficient thin strips of pure zinc, to completely neutralise the liquid and to remain in excess. As soon as the action ceases, a little of the clear liquid is poured off into some solution of hydrogen sulphide, when the formation of a white precipitate of ZnS will prove that the Sn has been completely precipitated.

The main liquid is now diluted, and when the metallic particles have subsided, it is decanted off as closely as possible through a filter-paper. The flask containing the tin is then placed under the funnel, a hole is pushed through the bottom of the filter, and any particles of metal in the filter are washed back into the flask by pouring through the filter 180 c.c. of strong hydrochloric acid. The contents of the flask are then connected with a carbon dioxide apparatus, heated to boiling until the tin is dissolved, and the boiling solution is titrated with the standard ferric chloride solution as has been described under (a).

505. **Estimation of Antimony.**—*The method depends upon the separation of iodine from potassium iodide by the antimonic chloride in the hydrochloric acid solution.* The liberated iodine is then estimated by titration with standard solution of stannous chloride.

The presence of stannic chloride and of lead chloride does not interfere with the titration: but cupric, arsenic and ferric chlorides react in the same way as antimonic chloride, and if present should be separately estimated, and their equivalent amounts in antimony deducted from the apparent amount of antimony found by the titration. This method of arriving at the true amount of antimony is not only more rapid but is more accurate than the process of separating the antimony and estimating it by itself. As a rule only traces of iron and arsenic are present in commercial alloys, but if the proportion of arsenic exceeds 1 per cent., it is advisable to precipitate the antimony and arsenic as sulphides and to separate them by the ordinary methods, else some of the arsenic will be expelled as hydrogen arsenide.

The following solutions are required:

(a) *Potassium Iodide Solution*, made by dissolving about 20 grams of the iodide in 100 c.c. of water.

(b) *Stannous Chloride Solution*, made by dissolving 10 grams of pure tin, or 20 grams of stannous chloride crystals, in 300 c.c. of strong hydrochloric acid, and diluting the solution to a litre. The solution is kept in a bottle filled with carbon dioxide and is titrated every time it is used against the standard solution of dichromate (c). Each c.c. of this stannous chloride solution corresponds approximately to 0·01 gram of antimony.

(c) *Potassium Dichromate Solution.*—Dissolve 16·34 grams of the pure, dry, recrystallised salt in water, and dilute the solution to a litre, 1 c.c. of this solution corresponds exactly to 0·02 gram of antimony. It may be standardised against pure iron (305).

(d) *Starch Solution*, prepared as is described in paragraph 333.

The Process is carried out as follows:

From 1 to 3 grams of the alloy, in the state of filings or of fine turnings, is exactly weighed and introduced into a 500 c.c. flask, and boiled gently with 150 c.c. of strong hydrochloric acid until action ceases and most of the lead and tin are dissolved. The solution is then completed by the cautious addition of potassium chlorate solution, a slight excess being ultimately added to insure the presence of free chlorine. The solution is then diluted with about its own volume of water and is boiled until it no longer smells of chlorine: boiling for half an hour should suffice, and the volume must not be reduced below 150 c.c., else antimonic chloride might be volatilised.

When the liquid in the flask is cold, fill the upper part of the flask with carbon dioxide to exclude air, add 20 c.c. of the potassium iodide solution (a), and allow the stannous chloride solution (b) to flow in at once rapidly from a burette until the brown colour of the iodine becomes very pale: then add the starch solution (d) and complete the titration by just removing the blue coloration by further addition of the stannous chloride solution.

It is well then to proceed at once to standardise the stannous chloride solution which has been used, by pouring a little of the potassium iodide and the starch solutions into a 250 c.c. flask, then filling the flask with carbon dioxide, adding 20 c.c. of the stannous chloride solution and titrating it rapidly with the standard dichromate solution (c).

Correction for the Presence of other Metals.—Since in the above estimation, cupric, arsenic, and ferric chlorides, if present, will be estimated as "antimony," it is necessary to determine these metals in a separate portion of the alloy by any of the standard methods. Their antimony-equivalents

are then deducted from the whole weight of antimony which has been found by the above titration.

It will be seen that during the titration the quantities represented by $SbCl_5$, $2CuCl_2$, $2FeCl_3$ will each furnish two atoms of chlorine during their reduction: accordingly Sb, Cu_2 and Fe_2 will be chemically equivalent quantities in the results of the estimation, or by calculation:

1	per cent.	of	arsenic	will	correspond	to	1·6	per cent.	of antimony.
1	„	„	copper	„	„	„	0·945	„	„ „
1	„	„	iron	„	„	„	1·03	„	„ „

The numbers in the last column therefore are the factors required for obtaining for the respective metals the antimony-equivalents which have to be subtracted from the total result found for antimony.

Analysis of German-silver.

German-silver is an alloy of copper, zinc, and nickel, and frequently contains traces of tin and iron.

For the estimation of these constituents, weigh out accurately about a gram of filings, or better drillings or borings of german-silver. Dissolve this in nitric acid, and evaporate the solution nearly to dryness to remove most of the acid.

506. Estimation of Tin.—Treat the residue with water, and filter off any appreciable quantity of SnO_2 which remains and weigh it (202).

507. Estimation of Copper.—Precipitate the copper from the filtrate (506) by passing hydrogen sulphide, reserving the filtrate. Dissolve the CuS in dilute HNO_3, and reprecipitate it with hydrogen sulphide, observing the precautions described in paragraph 496; then either convert the precipitate into Cu_2S, as is there directed, and weigh this, or proceed as follows:

After the original copper sulphide precipitate has been dissolved in dilute HNO_3, mix the solution with sodium carbonate in slight excess, then with excess of acetic acid, and estimate the copper by adding potassium iodide in excess and titrating with thiosulphate solution (357).

508. Estimation of Iron.—Boil off the hydrogen sulphide from the filtrate (507), and add a few drops of strong nitric acid in order to convert the iron into the ferric condition. Nearly neutralise with Na_2CO_3, add $Na\bar{A}$, boil and filter, and reserve the filtrate. Dissolve the precipitate in a little HCl and reprecipitate the iron by ammonia. Filter off and wash, reserving the filtrate and washings, and dry, ignite and weigh the precipitate as Fe_2O_3 (129).

Note.—The above preliminary precipitation of the iron by $NaC_2H_3O_2$ is necessary if the following succinic acid method of separating Zn and Ni is adopted If the cyanide method, which is described below, is used, the iron may be precipitated directly by addition of AmCl, and excess of AmOH ; but in this case it is well to dissolve the precipitate in HCl and to reprecipitate with AmCl and AmOH.

509. Estimation of Zinc and Nickel.—The zinc is separated from the nickel by adding either succinic acid or potassium cyanide to the filtrates from the precipitates caused by boiling with $NaC_2H_3O_2$, which have been mixed with the washings (508).

Succinic Acid Method.—Acidify the mixed filtrates and washings with HCl, and boil the liquid until it is free from $HC_2H_3O_2$. Add Na_2CO_3 solution in slight excess, boil, and filter off and wash the zinc and nickel carbonates. Dissolve the carbonates in boiling saturated solution of succinic acid, heat the solution to boiling, and pass H_2S to saturation. Allow the precipitate of ZnS to settle, filter off, and wash it with water containing H_2S, and determine the zinc either as sulphide (a) or as oxide (b), as is described below.

Boil the filtrate from the ZnS until it is free from hydrogen sulphide, precipitate the nickel by adding a slight excess of sodium hydrate solution and Br water, filter off and wash the nickel hydroxide, and weigh as NiO after ignition (127, *Note* 2).

Cyanide Method.—Mix the filtrates and washings from the iron precipitate, and add a clear saturated solution of potassium cyanide until the liquid assumes a brownish tint; boil until ammonia is no longer smelt, then add some sodium sulphide solution, which has been freshly made by passing hydrogen sulphide into sodium hydrate solution (379), and boil. Filter off the ZnS, adding any further quantity which may be deposited during the subsequent concentration of the filtrate, and determine the zinc either as sulphide (a) or as oxide (b), as is described below.

Concentrate the filtrate from the ZnS by evaporation, filter if necessary, and acidify it by the addition of strong nitric acid, guarding carefully against loss by effervescence. Boil for a time in a fume-closet, add KOH solution and Br water in slight excess, filter off and wash the nickel hydroxide and weigh as NiO after ignition (127, *Note* 2).

(a) Dry the precipitate of ZnS in the steam-oven, and transfer it to a porcelain crucible fitted with the Rose lid and tube (92); then incinerate the filter, and add the ash. Sprinkle a little sulphur over the contents of the crucible, and heat them in a current of dried hydrogen gas. The temperature should be low at first, but should be gradually increased to an intense red-heat (98). Weigh the ZnS which remains.

(b) Dissolve the freshly precipitated ZnS in hydrochloric acid, boil off the H_2S, precipitate the Zn as carbonate, and weigh as ZnO (163).

For Results of an Analysis of German-silver refer to paragraph 955.

Analysis of Aluminium Alloys.

510. The composition of a few typical alloys of aluminium is stated below, but alloys which are prepared for special purposes may also contain a small quantity of any of the following metals: manganese, tungsten, titanium, chromium, and cadmium.

Alloy.	Parts per 100.					
	Al	Cu	Mg	Ni	Ag	Sn
Aluminium bronze . .	5–10	95–90	—	—	—	—
Alloy for casting purposes .	85–95	—	—	15–5	—	—
Alloy for light scientific instruments . . .	75–80	—	25–20	—	—	—
For white jewellery:						
Alloy (1) . . .	30	—	—	70	—	—
Alloy (2) . . .	30	—	—	40	10	20

For the Estimation weigh out from 0·5 to 1 gram of the alloy into a 250 c.c. beaker and dissolve it in about 15 c.c. of moderately strong nitric acid. Evaporate the solution nearly to dryness on the water-bath and treat the residue with water; filter off any residue of SnO_2 and weigh it (202).

If silver is present add dilute hydrochloric acid in slight excess, and filter and weigh as AgCl (158).

Estimate the copper in the filtrate by passing hydrogen sulphide until the liquid smells strongly, then filter off the precipitated CuS, wash it quickly with H_2S-water, convert the precipitate into Cu_2S (496) and weigh the copper as cuprous sulphide.

Boil off the H_2S from the filtrate, and continue to boil after adding a little strong HNO_3, then precipitate the aluminium as hydroxide by the addition of a slight excess of solution of ammonia, filter, and weigh as Al_2O_3 (130). If iron is present in small quantity, separate the iron from the aluminium as is described in paragraph 424, a.

If the filtrate is blue, indicating the presence of nickel, add NaOH solution and Br water in slight excess, wash, filter and ignite the precipitate, and weigh the nickel as NiO (127, *Note* 2).

Finally acidify the filtrate from the nickel precipitate with hydrochloric acid, add AmOH until the liquid is alkaline, and then Na_2HPO_4 solution; then filter off, ignite and weigh the magnesium as pyro-phosphate (165).

For the Analysis of Commercial Aluminium see par. 1023.

Analysis of Iron-ores.

511. The ordinary ores of iron are the oxides, known as red and brown hæmatite, and black or magnetic oxide; the carbonate, or spathic iron-ore (431); and mixtures of oxide and carbonate, or clay iron-stone.

Iron-ores may contain the following constituents: moisture, carbon dioxide, silica, iron, aluminium, manganese, calcium, magnesium, phosphate, and sulphate. Some ores also contain organic matter.

512. **Estimation of Moisture.**—Since carbon dioxide and organic matter are usually present, the water must be estimated by heating 2 grams of the ore to dull redness, and absorbing the steam which is evolved in calcium chloride as is directed in paragraph 191.

513. **Estimation of Carbon Dioxide.**—Estimate the carbon dioxide by absorption as is described in paragraph 175, using 2 grams for the determination.

514. **Estimation of Silicious Matter.**—Weigh accurately from 5 to 10 grams of the finely powdered ore. Heat it gently with strong hydrochloric acid, add a little nitric acid, and continue the heating until it is judged that all soluble matter has been dissolved. Then evaporate to dryness on the water-bath, and heat the residue to 150° C. in the air-bath.

Treat the dry residue with strong hydrochloric acid, then dilute, heat, and decant off the clear liquid through a filter. Treat the residue again with a small quantity of hydrochloric acid, heat, and filter the solution through the same filter into the same filtrate. Continue this treatment as long as any iron can be found by ferrocyanide in a drop of the acid last used. Finally filter, wash and ignite the residue (99), and weigh it as silica and gangue.

Transfer the filtrates and washings to a half-litre flask, and dilute to 500 c.c. This liquid serves as the "original solution" which is used for the other estimations.

515. Estimation of Aluminium.—Boil 50 c.c. of the original solution (514) with a little nitric acid in order to convert the iron into the ferric state, nearly neutralise the liquid with ammonium carbonate, and precipitate by boiling with ammonium acetate solution (435).

Filter off, wash, ignite, and weigh the precipitate.

The ignited precipitate consists of Al_2O_3, Fe_2O_3, and a little ferric phosphate. The weight of Al_2O_3 is subsequently found by subtracting the weights of the Fe_2O_3 (516) and P_2O_5 (519) from the total weight of the ignited precipitate.

516. Estimation of Iron.—Reduce the iron in 50 c.c. of the original solution (514) from the ferric to the ferrous condition by one of the methods described in paragraphs 312, 313; and as soon as the iron has been completely reduced, make up the solution to 250 c.c. with air-free water, and titrate it with potassium dichromate solution (306). The iron which is present in the ferrous state may be estimated as is directed in paragraph 437.

If the procedure described in paragraph 399 is adopted, the titration may be made by means of permanganate solution.

517. Estimation of Manganese.—Treat 200 c.c. of the original solution as is directed in paragraph 515. To the filtrate from the basic acetates, which has been concentrated if necessary by evaporation, add bromine-water in slight excess and then a few drops of ammonium hydrate, and warm. Filter off and wash the manganese precipitate, reserving the filtrate and washings; then ignite the dried precipitate and weigh it as Mn_3O_4 (164).

518. Estimation of Calcium and Magnesium.—These metals are estimated in the filtrate (517) in the way described in paragraphs 426, 427, but a single precipitation with ammonium oxalate will suffice.

519. Estimation of Phosphate.—If arsenic has been found in the qualitative analysis, it must be separated by means of hydrogen sulphide (522) before the phosphate is precipitated.

To 50 c.c. of the original solution (514), or to 250 c.c. if the phosphorus is below 0·2 per cent, add a moderate quantity of ammonium molybdate solution (520), and allow the liquid to stand in a warm place for some hours. Filter, after proving that the precipitation is complete (538). Then dissolve the yellow ammonium phospho-molybdate precipitate in ammonium hydrate, precipitate the phosphate with magnesia mixture (167), and weigh it as $Mg_2P_2O_7$ (166).

520. *Preparation of Ammonium Molybdate Solution.*—Pour 10 c.c. of water into a large flask, add 50 grams of molybdic acid, and then 100 c.c. of the strongest ammonia solution; stir the liquid until all the solid is dissolved, then pour the

solution quickly into 720 c c of cold strong nitric acid, stirring constantly during the addition Keep the liquid in a warm place for some hours, and decant the clear solution for use.

521. **Estimation of Sulphur.**—Evaporate 50 c c. of the original solution (514) nearly to dryness, so as to expel almost all the free acid, then dilute and precipitate with a little barium chloride solution. Allow the liquid to stand several hours, then filter off, ignite, and weigh the $BaSO_4$ (133).

522. **Estimation of Copper, Arsenic, and Antimony.**—During the evaporation of the acid solution (514) some of the arsenic will have volatilised Therefore a fresh portion of the ore must be dissolved in hydrochloric acid, and the sulphides of the above metals precipitated by passing H_2S into the diluted solution The sulphides are then separated as is directed in paragraph 493

Estimation of Titanium.—Refer to paragraph 523 for a description of the process.

For Results of Analyses of Red Hæmatite-ores see paragraph 956

Estimation of Titanium in Titaniferous Iron-ores.

523. When silica is estimated in the usual way in ores containing titanium, a portion of the titanium is precipitated with the silica, and the rest of the titanium remains in solution.

In order to avoid this complication the ore should be decomposed by fusion with potassium bisulphate in the following manner: refer also to 1024, 1025.

Reduce the ore to as fine a powder as possible in an agate mortar, and weigh accurately about 1 gram of this powder into a large platinum crucible. Then add 10 grams of pure $KHSO_4$, carefully cover the crucible, and heat it over a small flame until the bisulphate is melted.

The mass must be kept liquid, and slight white fumes should be given off; the requisite temperature may be attained by maintaining the bottom of the crucible at a dull red-heat. Take great care to regulate the heat in such a way as to prevent the melted bisulphate from frothing over the edge of the crucible.

As soon as the ore is completely decomposed, remove the flame, take off the lid of the crucible and incline the crucible at an angle of about 45° so as to cause the fused mass to flow to one side of the crucible and to nearly reach its edge.

As soon as the crucible is cold, place it with the lid in a beaker of cold water, and pour in about 50 c.c. of strong sulphurous acid solution. Stir the pungently smelling liquid from time to time, and ultimately allow the insoluble matter to settle, transfer it to a filter, and wash it well with cold water.

Residue.—Dry the residue, then ignite it in a platinum capsule and weigh it. Then treat it with HF and a few drops of H_2SO_4, evaporate to dryness, and ignite and weigh again. The loss of weight arising from this treatment represents the amount of SiO_2 (210, *Note*). If any appreciable residue remains in the crucible, heat it with a little fused Na_2CO_3, treat the cool mass with H_2SO_4, filter if necessary, and add the clear solution to the main filtrate.

Filtrate.—The main filtrate should be colourless, and should smell strongly of SO_2. Add to it one-sixth of its volume of acetic acid of 1·04 specific gravity, and a clear solution of 20 grams of sodium acetate. Heat this liquid to boiling, and keep it boiling for a few minutes.

Then allow the precipitate to settle, filter it off, and wash it at first with hot water containing one-sixth its volume of acetic acid, then with hot water alone. Dry and ignite the precipitate, and weigh the TiO_2 which is thus obtained.

The ignited precipitate may contain traces of Fe_2O_3 and Al_2O_3, which were originally carried down as hydroxides with the titanic hydrate. In order to remove these substances, the weighed residue may be fused with Na_2CO_3. The mass thus obtained is then boiled with water, and the insoluble residue of impure sodium titanate is filtered off, washed, and dried, and is then fused again with Na_2CO_3. The cold mass is then dissolved in cold dilute H_2SO_4, and the titanic hydrate is precipitated by boiling with sodium acetate and acetic acid as is described above.

For Analysis of Bauxite refer to par. 1025 in the Appendix.

Analysis of Iron and Steel.

524. The value of a sample of iron or steel is usually determined by estimating in it the free and combined carbon, silicon, phosphorus, manganese, sulphur, and copper; but, in certain kinds of the metal, titanium, chromium, aluminium, nickel, tungsten, and arsenic (400, 523, 541, 543, 544) may also be determined.

The sample for analysis should be in the form of fine borings or drillings; and since cast-iron and ferro-manganese contain impurities in greater quantity than either wrought-iron or steel, about three times as much wrought-iron or steel is taken for analysis as is necessary in the case of cast-iron.

525. Estimation of Total Carbon.—Of the many methods which have been devised for the estimation of the total carbon present in iron, the most trustworthy are those which depend upon the separation of the carbon as such, and its subsequent conversion into carbon dioxide, the carbon dioxide being then absorbed and weighed. Two methods are described below (526, 528), of which the second (528) is the more accurate.

526. First Method for Estimating Total Carbon. — The carbon is separated by immersing the iron, in the form of crushed powder or borings, in copper sulphate solution. The iron passes into solution, and an equivalent amount of copper is deposited, the copper and carbon remaining as a residue; a minute portion of the carbon, however, usually escapes in the form of hydro carbon gases. The carbon in the residue is then converted by chromic anhydride into carbon dioxide, and this is absorbed by soda-lime and weighed.

The Process of Estimation.—Weigh out accurately about 1 gram of cast-iron, or 3 grams of wrought-iron or steel, into a 100 c.c. beaker, increasing the weight taken if the proportion of carbon is low. Pour upon the metal a solution of copper sulphate, made by dissolving one part of the crystallised salt in about six parts of water, and allow the beaker to stand in a warm place.

When the iron has been completely dissolved and no hard particles are felt by the end of a glass rod, pour off the clear liquid, and transfer the copper and carbon to a 250 c.c. round flask by means of a glass rod and a small quantity of water. Now add about 50 c.c. of strong sulphuric acid and 10 grams of chromic anhydride crystals (527). Connect the flask with the tubes shown in Fig. 68 (p. 104), of which (*f*) is weighed and (*e*) is not required, and prove the apparatus to be gas-tight.

Gradually raise the temperature of the flask, until the bubbles of gas which pass through the bulb-tube (*d*) can just be counted, and as the evolution of gas slackens, raise the temperature until white fumes are observed in the flask.

When this is the case aspirate a slow current of air, freed from carbon dioxide, through the apparatus. As soon as a volume of air equal to about six times the capacity of the flask has passed, detach the U-tube (*f*) and weigh it. Its increase in weight represents the amount of carbon dioxide produced, and from this the weight of carbon oxidised by the chromic acid may be calculated.

527. **Preparation of Chromic Anhydride.**—Make a saturated solution of potassium dichromate, and mix this with an equal volume of strong sulphuric acid in a large beaker. Allow the liquid to cool, and pour off the mother-liquor from the crystals which have formed. Drain the crystals in a covered funnel, the neck of which is plugged with glass-wool, and place them in a bottle. A further crop of crystals may be obtained by evaporating down the mother-liquor, and allowing it to cool.

528. Second Method for the Estimation of Total Carbon.—The powder or borings of the metal are digested with excess of cupric-ammonium-chloride solution. The iron is thus dissolved and an equivalent weight of copper is precipitated, while if the digestion is continued sufficiently long the copper is redissolved and a residue of carbon only remains. The carbon is then introduced into a small boat and ignited in a combustion-tube

in a current of oxygen, and the carbon dioxide thus produced is absorbed by soda-lime and weighed.

Preparation of the Cupric Ammonium Chloride Solution.—Dissolve 53 grams of pure ammonium chloride, and 85 grams of pure recrystallised copper chloride in about 500 c c. of water. Keep this solution in a stoppered bottle.

The Process of Estimation.—Weigh out accurately 1 gram of cast-iron, or 3 grams of wrought-iron or steel, and digest it with from 100 to 200 c.c. of the above cold copper solution and 7·5 to 15 c.c. of diluted (1 : 1) HCl, stirring with a glass rod until it is completely disintegrated.

Continue the digestion of the residual carbon and metallic copper at 70° C. until all the copper is dissolved, adding more of the copper solution if necessary. As soon as the residue loses its red colour, collect the carbon upon an asbestos filter, previously removing any scum of basic ferric chloride from the surface of the liquid by adding a little hot dilute hydrochloric acid.

The Asbestos Filter is Prepared by stopping the neck of a funnel with a plug of glass-wool. Asbestos, which has been ignited in a current of air, is then broken up with water in a mortar and is poured into the funnel. In this way a layer of felted asbestos fibres is formed, which serves as a filter. Before the filter is used, water is poured into it and is drawn through by an aspirator (80) as long as any asbestos fibres pass away in the liquid. The filtration is accelerated by the filter-pump.

A special funnel may be made for the purpose of the filtration in the following way: A piece of combustion-tube, about 10 cm. long and 1 cm. in internal diameter, is drawn out at one end until a small orifice only is left (Fig. 89). It will be found convenient to introduce a coiled piece of stout platinum wire into the funnel, which serves for pushing out the asbestos into the boat after the filtration has been completed. The glass-wool and asbestos are then introduced into the filter-tube above the wire-coil and are washed as is described above.

Fig. 89.



Carbon Filter.

If a small platinum filter-tube is used instead of the glass tube described above, it may be pushed with its contents into the combustion-tube: the transference of the asbestos and carbon to the boat, which is described below, is thus saved.

After the carbon has been filtered off, it is washed upon the filter until it is free from chloride. The filter is then dried in the steam-oven, the asbestos containing the carbon is transferred to a porcelain or platinum boat, and the combustion is carried out in the manner described in paragraphs 781–793.

The boat is pushed into a combustion-tube, the front part of which contains about 15 cm. of granulated copper oxide and a silver coil. The end of the tube near the silver coil is fitted with a perforated cork carrying a calcium chloride tube, with which a weighed soda-lime tube is connected (177, 178).

The calcium chloride tube absorbs any moisture which may be evolved, the soda-lime tube absorbs the carbon dioxide.

After the apparatus has been tested to ascertain that it is air-tight, the combustion-tube is laid in the furnace, and the copper oxide layer is heated to redness. A slow current of pure dry oxygen is then passed through the tube, and the heat is extended to the boat containing the carbon. After all the carbon has been burnt off, the current of oxygen is allowed to pass for a short time longer to sweep over the carbon dioxide into the absorption-tube. The soda-lime tube is then detached, and is weighed as soon as it is cold.

From the weight of CO_2 thus found, the percentage of carbon in the iron may be calculated.

It will be understood that the red-hot layer of copper oxide serves to burn any carbon monoxide which may be evolved, and the silver coil absorbs any trace of chlorine arising from the incomplete washing of the carbon; errors in the estimation of the carbon are thus avoided.

Before proceeding to the estimation, it is well to make a "blank combustion" This is carried out as is described above, but the carbon is omitted. If the absorption-tube undergoes no increase of weight in this process, all the materials which are used in the process are sufficiently pure.

529. **Estimation of Graphite.**—Weigh out 5 grams of steel, or 1 gram of grey or 3 grams of white cast-iron; heat it gently with diluted (1 : 1) HCl, using 15 c.c. for each gram of metal. Collect the insoluble residue of impure carbon on an asbestos filter, and wash it successively with hot water, potassium hydrate solution, alcohol, and ether.

Then dry the residue, and estimate the amount of graphite which it contains, by burning it in a stream of oxygen and absorbing and weighing the carbon dioxide, as is described in paragraph 528.

For Certain Technical Purposes, in which Great Accuracy is not required, the iron may be dissolved in hydrochloric acid, as is described above, and the residue may be collected on a tared filter, then washed as before, and dried and weighed. It is then transferred to a platinum crucible, the filter-ash is added, and the carbon is burnt off, with the aid, if necessary, of a stream of oxygen (92).

Since a platinum crucible suffers by the long contact with the gas-flame which is necessary to burn off the graphite, the method of combustion described in paragraph 548 may be resorted to, oxygen being used, if necessary, instead of air

The loss of weight of the residue, after allowing for the weights of the filter and of the filter-ash respectively, gives approximately the weight of the graphite. The result thus obtained is usually about 20 per cent. too high, owing to the oxidation of the Fe. It should be multiplied by the factor 0 8.

530. **Estimation of Combined Carbon in Steel, Wrought- and Cast-iron** (*Note*, p. 262) **by Eggertz's Method.**—When metallic iron contains only a small proportion of carbon, its solution in nitric acid is usually brown. The depth of this colour increases as the percentage of combined

carbon present in the iron increases. Hence by comparing the coloration of this solution with that obtained by the solution of standard iron containing a known quantity of carbon in the same condition, a rapid determination of carbon may be made.

Nitric acid of 1·2 specific gravity and free from Cl is used as the solvent. A series of standard samples of steel are first prepared, in which the amount of carbon has been accurately determined by the combustion method (528). As a rule, the standards should be prepared from the same kind of steel as that which is to be tested. The process may be carried out either as is described below, or by Stead's modified method (531). *See* Chemical News, vol. 42 (1880), p. 88.

For the estimation, weigh out accurately 0·1 gram of the sample to be tested, and the same weight of the standard steel, into two test-tubes. If the percentage of carbon is approximately known, add suitable amounts of the nitric acid, as indicated by the table below. When an insufficient amount of nitric acid has been used, the solution is slightly darker in tint than it should be; accordingly, if no knowledge of the probable percentage of carbon is obtainable, 3 c c. of the acid may be used, and the process is then repeated, if necessary, with an increased quantity of the acid.

Percentage of carbon present in steel.	Number of c c of nitric acid required for solution.
Less than 0 3 per cent.	3 c c.
From 0·3 to 0 5 ,,	4 c.c.
,, 0 5 ,, 0·8 ,,	5 c c.
,, 0 8 ,, 1·0 ,,	6 c.c.
Upwards of 1 0 ,,	7 c c.

After the first violent action has subsided, heat the test-tubes in a water-bath, until the action of the acid ceases and the solution of the sample is complete: this will usually require about 15 minutes. Then remove the tubes at once from the water-bath, and cool them by immersing them in cold water.

Now pour the standard solution into a "carbon-tube," which is a glass tube 1 cm. in diameter and closed at one end; it is capable of holding 30 c.c. and is graduated into tenths of a c.c. Rinse out the test-tube with water, until the total volume of liquid in the carbon-tube is at least twice as great as that of the acid originally used.

The volume of the standard solution should be some convenient multiple of tenths per cent. Thus, if the standard iron used contains 0·5 per cent. of carbon,

and the solution is diluted until it measures 10 c.c., each c.c. of this liquid will correspond to 0·05 per cent. of the carbon.

Now pour the solution of the sample under examination into a similar carbon-tube, rinse out the test-tube with a small quantity of cold water, and compare the intensity of the colours of the two solutions by looking across the tubes at a white surface; if the colour of the sample solution is the more intense, add water to it gradually until the colours exactly correspond, and read the volume of this solution in cubic centimetres.

The percentage of carbon will be found by multiplying the number of c.c. of liquid in the tube by the carbon-value of 1 c.c. of the standard solution. Thus, if 11 c.c. of the sample solution gave the same colour-intensity as 10 c.c. of the standard solution, each c.c. of which corresponds to 0·05 per cent. of carbon, then the percentage of carbon in the sample $= 11 \times 0{\cdot}05 = 0{\cdot}55$.

Instead of diluting the sample solution until its intensity corresponds with that of the standard solution, a graduated series of standard solutions may be employed. These are contained in sealed tubes, and successively differ by a fixed amount of carbon. Since, however, their colours are liable to fade, the method described above is more trustworthy.

Note.—The above process for wrought-iron and steel may also be used for cast-iron, but only 0·05 gram must be dissolved in the HNO_3; the liquid is then diluted to 20 c.c. and at once compared with the corresponding standard, the solution being first quickly filtered from undissolved graphitic carbon if the cast-iron was of the grey variety.

531. Stead's Modified Process for determining Combined Carbon.—It is found that the colour, which is due to the solution of the carbon, is interfered with by that of the iron nitrate present in the liquid. This interference may be prevented by adding sodium hydrate solution in excess, and removing the ferric hydroxide by filtration. The colour due to the carbon is more intense in this alkaline filtrate than it was in the original acid solution. The process is mainly used for low carbon steels. The procedure is as follows:

One gram of the steel is dissolved by heating it in a water-bath with 12 c.c. of nitric acid of 1·2 specific gravity. The standard steel is treated in a similar way. Each solution is now well mixed with 30 c.c. of hot water and with 13 c.c. of solution of sodium hydrate of 1·27 specific gravity. The liquids are then diluted to 60 c.c. and are well shaken, and after they have stood for ten minutes in a warm place they are filtered through dry filters.

The two filtrates are poured into two graduated tubes, and the intensity of their colour is compared by looking down the tubes upon a white surface. The lengths of the columns are then adjusted by removing some of the deeper-coloured liquid, until they both give equal colour-intensity. The quantities of carbon present are inversely as the lengths of the liquid columns.

Thus if the columns of liquid measure respectively 80 mm. and 100 mm., the latter corresponding to the standard steel containing 0·4 per cent. of carbon, then the percentage of carbon in the steel sample $= 0{\cdot}4 \times \frac{100}{80} = 0{\cdot}5$.

It is found that the colour which is given by steel containing a low percentage of carbon differs in character from that given by steel containing a high percentage. Hence it is necessary to prepare separate standard solutions for the two classes of steel.

532. The Percentage of Free Carbon may be found by subtracting the percentage of combined carbon (**530, 531**) from the percentage of total carbon (**526–528**).

533. Estimation of Sulphur.—Two methods are in common use for estimating sulphur in iron.

(1) The sulphur is first evolved as hydrogen sulphide and this is then converted into a suitable form for being weighed (**534**). This process is applicable to steel. If it is applied to cast-iron some of the sulphur often fails to be converted into hydrogen sulphide.

(2) The sulphur is converted into sulphuric acid, which is precipitated and weighed as barium sulphate (**535**). This method gives more accurate results than the first, and is of general application.

534. Estimation of Sulphur by conversion into Hydrogen Sulphide.—Fit into the neck of a 300 c.c. conical flask a doubly perforated rubber stopper, which has been previously boiled with sodium hydrate solution to extract the sulphur. Through one hole in this stopper push a thistle-funnel, which must nearly touch the bottom of the flask. Into the other hole fit a tube which is bent twice at right-angles, the shorter end of which just passes through the cork, while the other end passes into a tall narrow cylinder containing solution of cadmium chloride, made by dissolving 5 grams of $CdCl_2$ in 200 c.c. of strongest ammonia solution and diluting to a litre.

A second similar cylinder may be connected with the first, by means of a cork and bent tube; this, however, is rarely necessary, since the hydrogen sulphide escapes diluted with much hydrogen which facilitates its absorption.

Weigh out accurately from 5 to 10 grams of steel or wrought-iron, or 2 grams of cast-iron, into the flask, and add HCl, diluted with two-thirds its volume of water, finally boiling the contents of the flask in order to expel dissolved hydrogen sulphide gas. Filter off and wash the precipitated cadmium sulphide on a tared filter which has been previously dried at 100° C., and dry at 100° C. and weigh the precipitate (**192**).

If this method is applied to cast-iron, it is always necessary to filter off

and wash the undissolved residue in the flask; this residue is then dried, and the sulphur which remains in it is estimated by the process described in paragraph 141 or 142, and is added to that already found as CdS.

If the amount of sulphur to be estimated is very small, the hydrogen sulphide may be received in bromine-water acidified with hydrochloric acid. The excess of bromine is expelled by boiling the liquid, and the sulphur is then precipitated and estimated as $BaSO_4$ (133).

535. **Estimation of Sulphur as $BaSO_4$.**—Dissolve the weighed metal (534) in aqua regia, then add a little sodium carbonate to fix the H_2SO_4, and evaporate to dryness at a moderate heat on the iron-plate or air-bath. Moisten the residue with strong HCl, add water, heat, and filter, reserving the residue for the estimation of silicon (536). Dilute the filtrate slightly, add an excess of cold barium chloride solution, and after a time pass through a very fine filter, wash with dilute HCl and then with water, and dry, ignite and weigh the $BaSO_4$ (133).

This method gives more accurate results than that described in paragraph 534, if care is taken to remove the free nitric acid, to keep the volume of the liquid small, and to add a fair excess of barium chloride solution.

Note.—If the $BaSO_4$ precipitate is coloured red by Fe_2O_3, the precipitate is heated with dilute HCl, then washed, ignited, and weighed: or the weight of the $BaSO_4$ may be ascertained by precipitating the iron in the acid filtrate and washings, weighing it as Fe_2O_3 (129) and then subtracting this weight from that of the original $BaSO_4$ precipitate.

The reagents used in this estimation should be examined for sulphate, and if any is found to be present a blank estimation must be made, and the weight of $BaSO_4$ obtained must be allowed for.

536. **Estimation of Silicon.**—Treat the residue from the acid solution (535), as is described below, for the estimation of the silicon. Or dissolve 2 grams of cast-iron, or 5 grams of steel or wrought-iron, in about 40 c.c. of strong nitric acid, taking care to prevent loss by spirting if the action is violent, and evaporate the solution to dryness. Heat the residue, in either case, to about 200° C. in the air-bath to decompose carbonaceous matter.

The removal of this organic matter is much facilitated if a little ammonium nitrate has been added during the final stages of evaporation of the acid solution. Unless the organic matter is decomposed, the precipitation of the phosphate in the filtrate (537) will be incomplete.

Evaporate the cold residue with HCl, and heat to 150° C. Then heat with about 30 c.c. of HCl, dilute with water and filter off and wash the silica, taking care that the volume of the filtrate and washings does not exceed 100 c.c. Keep this filtrate for the estimation of phosphorus (537). Dry the silica (457), and if it is coloured red by iron oxide, digest it with strong hydrochloric acid until it is perfectly white; then wash, dry, ignite, and weigh it. (See *note* 2, 210.)

Since the silica may contain impurities, it is best to ascertain the weight of pure silica present by treating the weighed substance with pure hydrofluoric acid and a little strong sulphuric acid, as is directed in the *Note* (210).

537. **Estimation of Phosphorus.**—The phosphorus is converted by the action of strong nitric acid into phosphate, and precipitated and weighed as phospho-molybdate (539), as magnesium pyrophosphate (538), or as is directed in par. 1026.

538. *Estimation as* $Mg_2P_2O_7$.—Either dissolve 2 grams of the metal in nitric acid of 1·2 sp. gr., and remove the silica (536); or add to the filtrate from the silica (536), which measures about 100 c.c., at least twice its volume of ammonium molybdate solution (520), and allow the liquid to stand for several hours in a warm place, taking care that the temperature does not exceed 40° C. else arsenate may be precipitated together with the phosphate.

Now remove a small quantity of the clear liquid by a pipette, mix it with some more molybdate solution, and allow the liquid to stand in a warm place for some time. If any precipitate is thus produced, return the liquid and precipitate and add more molybdate solution to the whole of the liquid. Repeat these processes until the further addition of molybdate produces no precipitate.

As soon as the precipitation has been proved to be complete, filter off the loose precipitate, and wash it, as well as the precipitate adhering to the beaker, with molybdate solution diluted with an equal volume of water; test the last few drops of washing-water with K_4FeCy_6 solution for Fe, to ascertain when the washing is finished, and proceed as below, or as in par. 1026.

Dissolve the precipitate from the interior of the beaker and from the filter in 2 or 3 c.c. of strong ammonium hydrate solution, add strong hydrochloric acid until the ammonia is nearly neutralised, and precipitate the phosphate by means of magnesia-mixture (167), finally weighing it as $Mg_2P_2O_7$ (166).

539. *Estimation by Weighing as Phospho-molybdate.*—A modification of the above method consists in weighing the yellow phospho-molybdate precipitate itself. If this method is adopted, from 1 to 2 grams of the iron-sample only need be treated as is directed in paragraph 536.

After the silica has been filtered off, the volume of the filtrate is reduced by evaporation until a film forms upon the surface of the liquid. The phosphate in this solution is then mixed with excess of the molybdate solution as is directed above (538); the precipitate is filtered off, the portion which adheres to the beaker being dissolved in ammonia solution, reprecipitated by addition of nitric acid, and then added to the main portion in the filter. The precipitate is washed with water containing 1 per cent. of HNO_3. It is then dried at 120° C. on a tared filter (86, 87), and is weighed as $(NH_4)_3.12MoO_3.PO_4$, containing 1·65 per cent. of phosphorus.

540. Estimation of Manganese.—Weigh accurately from 1 to 2 grams of the iron sample, and dissolve it in 30 c.c. of nitric acid of 1·2 sp. gr. Evaporate the solution to dryness, and heat the residue to 200° C. in the air-bath to destroy carbonaceous matter. Dissolve the cold residue in 10 c.c. of dilute (1 : 1) HCl, then dilute, and filter off the insoluble matter.

Dilute this solution to about 500 c.c. with distilled water, and add ammonium carbonate solution, drop by drop, until the colour of the liquid becomes dark brown. Continue the addition of the ammonium carbonate solution very cautiously and with constant stirring, until the precipitate which is formed only just redissolves. Now add 2 grams of ammonium acetate and a little acetic acid, boil the solution for a few minutes, and filter the boiling liquid, using the funnel-jacket (Fig. 66, p. 65) and reserving the filtrate.

Redissolve the precipitate in hydrochloric acid, add ammonium carbonate solution carefully, and reprecipitate and filter as has been just described.

Mix these two filtrates which contain the manganese, evaporate if necessary, and allow the liquid to cool. Add to the cold solution bromine-water until it is of a permanent brown colour, and then add an excess of ammonium hydrate. Heat to boiling, filter off and wash the precipitate with hot water, then dry and ignite it, and weigh as Mn_3O_4. This precipitate always contains some Ni or Co, which must be separated and weighed in accurate analyses.

For Other Methods, *see* pars. **1027, 1028.**

541. Estimation of Copper and Arsenic.—Weigh accurately from 5 to 10 grams of the iron, and dissolve it in nitric acid. Add hydrochloric acid and evaporate the solution to dryness on the water-bath : repeat this process several times. Finally dissolve the residue in water, reduce the iron to the ferrous state by means of ammonium bisulphite (313), and pass hydrogen sulphide gas into the solution to saturation. Filter off the precipitate, which may contain CuS, As_2S_3, S, and possibly Sb_2S_3, and separate and estimate these substances as is described in paragraph 493. Copper may also be determined as is described in paragraph 543.

A trace of copper is more readily estimated volumetrically (636) than gravimetrically.

542. Estimation of Nickel and Aluminium.—The method is based on the fact that when ether is shaken with a solution of the chlorides of aluminium, nickel, copper and iron in dilute hydrochloric acid, it removes the ferric chloride and leaves the other chlorides in the acid solution.

543. Determination of Nickel.—Dissolve 2 grams of the steel in dilute HCl of 1·1 specific gravity, add sufficient HNO_3 to convert the iron into the ferric state, and evaporate the liquid to dryness.

Redissolve the residue in HCl and evaporate the solution until the $FeCl_3$ begins to form a skin upon the surface of the liquid. Add diluted HCl of 1·1 specific gravity in order to redissolve any basic salt, and transfer the liquid to a stoppered separating funnel 250 c.c. in capacity. Rinse out the solution into the funnel with a little of the dilute hydrochloric acid, taking care that the whole volume of the liquid does not exceed 50 c.c.

Now pour 40 c.c. of ether into the funnel and shake the liquids together for about eight minutes. The ether will remove the $FeCl_3$ from the solution, and will form an emerald green layer above the aqueous solution. Let the funnel stand for a few minutes and then allow the acid aqueous solution, containing the chlorides of Cu, Ni and Al, to flow into another separating funnel, in which 40 c.c. of ether have been previously placed.

Wash out the first funnel with a little of the dilute HCl and allow the washings to flow into the second funnel. Repeat the washings with fresh acid, and finally pour off the green ethereal solution from the first funnel into an ether-residue bottle for recovery of the ether.

Shake the contents of the second funnel for ten minutes in order to enable the ether to remove the last trace of the ferric chloride from the acid liquid. Then allow the acid liquid to flow into an evaporating-basin, and wash out the last portions with the dilute acid as before.

Evaporate the acid liquid, which contains the nickel, copper and aluminium as chlorides, to a small volume and precipitate the copper as sulphide by passing hydrogen sulphide (**1010**). Filter off the copper sulphide, add excess of H_2SO_4 and evaporate until white fumes appear. Allow the solution to cool, and add a little water and then an excess of AmHO ; filter, if necessary, and finally transfer the liquid to a platinum dish and precipitate the metallic nickel electrolytically (**219**).

The nickel may contain a very small amount of cobalt, the determination of which may usually be neglected.

544. Determination of Aluminium.—Proceed as in the determination of nickel until the acid liquid remaining after the treatments with ether has been obtained. Evaporate this to dryness, and dissolve the residue in a little hydrochloric acid. Nearly neutralise the solution with dilute ammonium hydrate solution, add a little sodium thiosulphate in order to reduce any iron, and then add 2 or 3 c.c. of a saturated solution of sodium phosphate. Finally add 5 or 6 grams of sodium acetate dissolved in a little water, boil the solution until it no longer smells of sulphur dioxide, and filter it. Then wash, dry, ignite, and weigh the precipitate of aluminium phosphate, $AlPO_4$. (See *Note* below.)

Note.—In order to make certain that the precipitate is free from traces of iron and silica, it may be redissolved in HCl. The solution is then evaporated to dry-

ness, redissolved in dilute HCl, and the solution is neutralised and mixed with a little thiosulphate and sodium acetate. The precipitate of $AlPO_4$ may now be filtered off, washed, ignited and weighed. It contains 22·18 per cent. of aluminium.

For Results of Analyses of Iron and Steel refer to paragraph **957**.

Proximate Analysis of Coal and Coke.

545. The chemical examination of coal ordinarily comprises the estimation of moisture, ash, sulphur, volatile matter, coke, and calorific power The coal must be very rapidly powdered for these estimations, as it loses water during the process: it is better therefore to use air-dried coal (**1030**).

546. Estimation of Moisture.—Powder about 2 grams of the coal rapidly, weigh the powder between two watch-glasses, and heat it in the steam-oven. Remove the coal every half-hour, allow it to cool in the desiccator and weigh it. Since the weight decreases by loss of moisture, but also gradually increases after a time by oxidation, no constant weight will be obtained, and the lowest weight which is noted must be taken as representing the completion of the drying. See also par. **1029**.

547. Estimation of Volatile Matter and Coke.—Two methods [**a, b**] for estimating the volatile matter and coke are described below.

(a) Spread out 2 grams of the rapidly powdered coal in an even layer in the bottom of a platinum crucible, which has been weighed without the lid. Cover the crucible with the lid, place it on a pipe-clay triangle, and heat it by means of a powerful Bunsen flame. In order that comparable results may be obtained in different estimations, the size of the flame and the position of the crucible in it must always be the same.

As soon as the flame of the gases, which issue from beneath the lid, is no longer seen, continue the heating for one minute longer. Then remove the gas-flame, allow the crucible to cool in the desiccator, and weigh it without the lid as soon as possible. The weight of the residue represents the weight of the coke including the ash: the loss of weight suffered by the original coal is the weight of the volatile matter. Reserve the coke.

(b) Weigh out accurately from 10 to 20 grams of the coarsely powdered coal into a weighed capacious porcelain crucible provided with a lid. The crucible should not be more than half filled with the coal. Place this crucible in a clay crucible, and surround it completely with coarsely powdered charcoal. Cover the clay crucible with its lid place it in a wind- or gas-furnace and keep

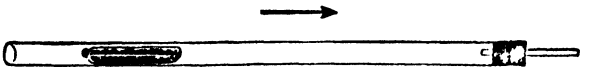
it at a red-heat for one hour. Remove the porcelain crucible when it is cold, and weigh it. The loss of weight, which it has sustained, represents the volatile matter of the coal. The residue of coke, including the ash, is reserved.

An examination of the coke obtained by this method will indicate whether the original coal is a caking, sintering, or non-caking coal.

548. Estimation of Ash.—Weigh out accurately about 2 grams of the powdered coal, or of the coke from 547, into a weighed porcelain boat about 10 cm. long and 2 cm. across. Some platinum-foil, which has been shaped upon a piece of glass rod, forms a good substitute for the porcelain boat.

Push the boat containing the coal into a combustion-tube, about 2·5 cm. in diameter (Fig. 90). Heat the tube and boat to redness in a combustion-furnace (783), while a gentle current of air is drawn through the combustion-tube by means of an aspirator (176, Fig. 68 *h*, p. 104).

FIG. 90.



ASH DETERMINATION.

The temperature should not become sufficiently high to soften the glass and cause the boat and tube to stick together, but this may be prevented by interposing a few threads of asbestos between the bottom of the boat and the glass.

As soon as the dark-coloured combustible matter is entirely removed, allow the tube to cool, then withdraw the boat and weigh it. By this method a "clean" ash, free from carbonaceous matter, is obtained in a short time.

Reserve the ash for the determination of sulphate (551).

549. Estimation of Sulphur.—It is usually necessary to ascertain the amount of sulphur which is present in the volatile matter, the sulphur contained in the coke, and the sulphur which is left as sulphate in the ash. For this purpose it is necessary to determine the total sulphur (550), the sulphur in the ash (551), and the volatile sulphur in the coke (552).

The amount of sulphur present in the volatile matter is obtained by adding the amount of sulphur found in the ash to the amount which is evolved by burning the coke, and then subtracting this from the total sulphur.

550. Estimation of Total Sulphur by Two Methods.—(a) Weigh out accurately about 1·5 grams of the very finely powdered coal, and mix it with four times its weight of finely powdered dry sodium carbonate

by adding the sodium carbonate to the coal, which is contained in a platinum crucible or capsule, and stirring the powder with a dry glass rod: the mixture must not be further stirred during the heating.

Now partially cover the crucible with its lid, and heat it for some time gently so as not to volatilise the hydrocarbons and give rise to smoke or smell. Then gradually raise the temperature nearly to visible redness, and continue the heating until the dark colour of the mixture has faded, or has become red from iron oxide. A Bunsen burner fed with spirit may be used to avoid the introduction of sulphur from the coal-gas.

Then raise the temperature to a dull red-heat, and maintain this temperature for about fifty minutes. The mass will now be almost perfectly white, owing to the complete combustion of the coal.

Now treat the cool mass with water, and filter the solution. Add a few drops of bromine to the filtrate and acidify with HCl, then boil the liquid until the bromine is removed, determine the sulphate in this solution as $BaSO_4$ (133), and calculate the corresponding weight of S.

(b) The bomb may be rinsed out with water after the calorific power determination (556). The sulphate in solution may then be determined by adding excess of HCl and of $BaCl_2$ (133). Or the free H_2SO_4 and HNO_3 in the boiled bomb-rinsings may be estimated by titrating with standard baryta-solution in presence of phenolphthalein, standard Na_2CO_3-solution being then added in excess to precipitate the barium nitrate, and the clear liquid titrated with standard acid to determine the excess of Na_2CO_3: from these results the weight of SO_4 can be found from the baryta required to precipitate it. The S is finally calculated from the SO_4.

551. Sulphur in the Ash.—The ash, which was reserved from paragraph 548, is treated with water containing a little hydrochloric acid, the solution is filtered, and the residue is washed. The sulphate contained in the filtrate and washings is determined as $BaSO_4$ (133), and the weight of sulphur which it contains is calculated.

552. Volatile Sulphur in the Coke.—The sulphur which is converted into sulphur dioxide, when the coke is burnt in the air, is determined as follows:

A quantity of coke, representing a known quantity of coal (547), is roasted in a porcelain boat, or on platinum-foil, in a slow current of oxygen (548), and the gaseous products are passed through 10 c.c. of standard solution of iodine (331) contained in a bulbed U-tube (Fig. 86, p. 188). The following reaction will take place between the sulphur dioxide, the iodine, and the water:

$$SO_2 + I_2 + 2H_2O = H_2SO_4 + 2HI.$$

The amount of free iodine which remains in the solution is determined by standard sodium thiosulphate solution (334), and the amount of iodine which has been acted upon by the sulphur dioxide is obtained by difference.

From this result the weight of the sulphur, which has been evolved by the coke, may be calculated.

553. **Estimation of Calorific Power.**—The calorific power of fuel is determined by ascertaining the number of heat-units which are evolved by the combustion of unit weight of the fuel in oxygen. One heat-unit or "calorie" is the amount of heat which is required to raise the temperature of one gram of water one degree Centigrade.

Calorific returns made in this country usually state the number of pounds of water raised one degree Fahrenheit by the combustion of one pound of coal: this result can be converted into calories by multiplying it by five-ninths.

In the methods described below the fuel is either burnt in free oxygen gas, or it is mixed with substances which are capable of yielding oxygen, such as potassium nitrate and potassium chlorate, and the mixture is kindled. The products of combustion are cooled by a known weight of water, and the increase of temperature produced in the water is noted as soon as the combustion has ceased.

The weight of the water in grams, multiplied by its rise of temperature expressed in Centigrade degrees, will then give the number of units of heat which have been evolved by the combustion of the fuel. This number, after it has been corrected for the heat absorbed by the apparatus, gives the calorific power of the fuel.

The calorific power of coal may be estimated by the Lewis Thompson calorimeter (554), using a mixture of potassium nitrate and potassium chlorate to supply the oxygen. The method is more suitable for bituminous than for anthracitic coal.

Other methods consist in burning the fuel either in a regulated stream of oxygen gas in the William Thomson calorimeter (555), or in compressed oxygen in a bomb (556).

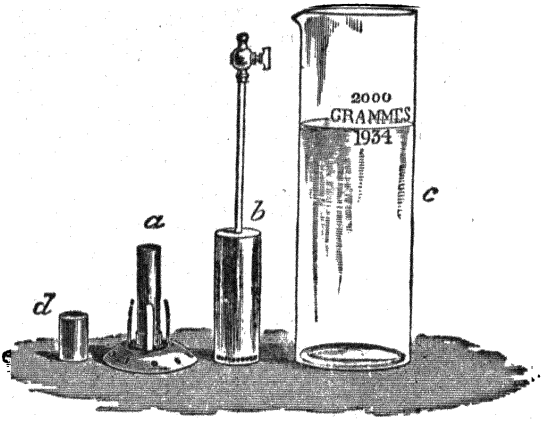
The advantage secured by using the methods of combustion in oxygen gas (555, 556) is that complete combustion is readily secured without the necessity of preparing trial mixtures with the oxidising mixtures, as is usually necessary by the Lewis Thompson method (554). When the oxygen is supplied from a holder (555) the process of combustion can be watched and is also under complete control.

554. **The Lewis Thompson Calorimeter** is shown in Fig. 91. It comprises a glass cylinder (*c*), which holds 2000 grams of water when it is filled up to the etched mark, and a suitable metal vessel and tube in which the fuel can be burnt. The procedure is as follows:

Fill the calorimeter to the mark with water which is at a temperature just below that of the surrounding atmosphere.

Weigh out accurately 2 grams of the finely-powdered and sifted coal (**1024**). Mix this intimately with ten times its weight of a mixture of one part of potassium nitrate and three parts of potassium chlorate, which has been previously well dried in the steam-oven. Then try to kindle the mixture. If it does

FIG. 91.



THE LEWIS THOMPSON CALORIMETER.

not burn steadily, the experiment must be repeated with different proportions of coal and oxidising mixture.

As soon as a mixture has been prepared which burns steadily when kindled, transfer a similar mixture to the copper tube (*a*), seen on the left in the figure, and gently press down the mass in the tube with the bottom of a test-tube. The broader tube (*d*) is intended for a mixture which does not burn readily.

When all the powder has been transferred to the tube, bury in the upper part of the powder the lower end of a little piece of fuse, which is made by steeping thin cotton-wick in potassium nitrate solution and drying it. Place the tube in the brass clips attached to the brass disc, and proceed to render the temperature of the water in the calorimeter uniform by stirring before taking the temperature carefully by means of a delicate thermometer.

Now light the fuse, rapidly push on the cover (*b*), taking care that the stop-cock is closed, and immerse the tube in the water until it stands upon the bottom of the cylinder.

The cover (*b*) consists of a copper cylinder connected with a narrow copper tube. The cylinder prevents the water from coming into contact with the mixture: it is perforated at the bottom so as to allow the products of combustion to escape.

The narrow tube attached to the cylinder is provided with a stop-cock, so that the water can be admitted into the cylinder and tube at the end of the combustion.

The mixture will burn, and the gaseous products of combustion will force their way through the holes at the base of the copper cylinder, and will pass up through the water into the air.

The whole metal apparatus is allowed to remain immersed in the water for a few seconds after the combustion has ceased, in order to allow the metal to transfer its heat to the water.

The stop-cock is then opened, so as to admit water to the interior of the metal apparatus. The metal apparatus is alternately raised and lowered several times so as to mix the water thoroughly, and the temperature of the water is once more taken carefully by a delicate thermometer.

The number of Centigrade degrees, by which the water has increased in temperature during the combustion, is added to the number of degrees corresponding to the amount of heat absorbed by the apparatus; the latter being taken as one-tenth of the rise of temperature observed. And since 2 grams of coal were used, and the glass cylinder contained 2000 grams of water, this number of degrees, when multiplied by 1000, will give the number of heat-units or calories evolved by unit weight of the fuel.

In a particular estimation the following results were obtained: The initial temperature of the water was 16° C., and the final temperature of the water was 22·7° C. Assuming that the heat absorbed by the apparatus is measured by one-tenth of the rise of temperature observed in the water, the calorific power will be equal to (6·7 + 0·67) 1000 = 7370 calories or heat-units.

A second graduation will be seen on the glass cylinder at 1934. The cylinder may be filled with water up to this mark, and the temperatures taken in Fahrenheit degrees. The number of degrees rise in temperature registered on the thermometer after the combustion, if increased by one-tenth, will then represent the number of pounds of water at 212° F. which the combustion of one pound of the coal will convert into steam at 212° F. The calculation is based on the assumption that $\frac{1934}{2} = 967$ Fahrenheit units of heat are required to convert the unit weight of water into steam.

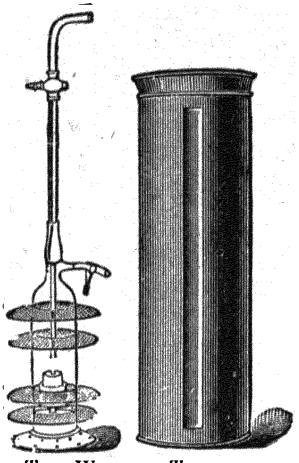
555. **The William Thomson Calorimeter.**—This apparatus is similar to the calorimeter just described, but is designed for burning a weighed quantity of fuel in a platinum crucible under water, by directing a slow stream of oxygen from a gas-holder or compression-cylinder upon it.

Several modifications of this apparatus are now obtainable; the following description applies to the form which is shown on p. 274 (Fig. 92):

The oxygen passes down the vertical tube which contains the stop-cock

Fig. 92). Wire-gauze baffle-discs are seen around the combustion-chamber; these serve to break up the escaping gaseous products into small bubbles, and thus to cause them to be more completely cooled by the water.

Fig. 92.



The William Thomson Calorimeter.

The apparatus is immersed in water contained in a glass beaker, which is again surrounded by a metal vessel with a glass slip let into its side. The fuel is then kindled by means of a small fuse, as has been already described, and the oxygen stream is started by opening the tap as soon as the chamber containing the kindled fuse has been lowered into the water.

For the Estimation 1 gram of the fuel is accurately weighed and introduced into the platinum crucible, which is then placed on the clay support; and the long narrow copper tube, which terminates in the tap and bent tube, is connected with an oxygen gas-holder by a piece of rubber tubing.

Two thousand grams of water, taken from a supply which has been kept in the room in which the experiment is to be made until it is of same temperature as the atmosphere, are then introduced into a large thin beaker of suitable dimensions. This is the calorimeter, and it is placed in the outer jacket of bright metal in order to protect it from radiated heat and later on from contact with the colder atmosphere. The water is then well mixed by stirring and its temperature is accurately noted. The thermometer may be fixed in the arm of a retort-stand so that both may be removed at once, and its height is so adjusted that the bulb and about 5 cm. of the stem will be immersed in the water of the calorimeter. Each degree measures about 1 cm. on the stem.

As soon as the temperature of the water has been noted, the thin copper tube, which slides easily through the rubber tube, should be drawn up near to the top of the bell-glass, and the upper end with the tap closed should be attached to the supply of oxygen which is under slight pressure. A fuse about 2·5 cm. in length, consisting of two strands of lamp-wick prepared as is directed on p. 272, is then placed upright in the coal in the crucible and ignited. The bell-glass is now pushed down over the crucible and fixed in position by the springs, and the whole is lifted into the beaker and sunk to the bottom of the water. At the same time the tap is opened gradually until a stream of oxygen passes through the apparatus, and the time is noted on a watch.

The coal will burn quietly at first, and the thin copper tube should not be pushed far down in the bell-glass until all fumes cease to be evolved, since plenty of oxygen must be present in the upper part of the bell-glass to insure the complete combustion of this volatile matter; when, however, the coke remains in a glowing condition, it is advisable to push the thin copper tube down until its end is immediately over the platinum crucible, in order to facilitate the combustion of the coke. A slight rotating movement may also be given to the tube, so as to cause the gentle stream of oxygen to fall on any particles of unburned coke in the bottom of the crucible.

As soon as the experiment is completed the tap is closed, and the bell is raised sufficiently to enable the side-clip to be opened and to be pushed upon the small projecting glass tube. The residual gas will now escape through this tube as the bell is again pushed downwards, and the water will come into contact with the narrow copper tube and with other parts of the apparatus, and will cool them by its contact. The bell should be moved slowly up and down in the water several times, in order to cool the parts and to mix the water.

The temperature of the water is now accurately taken again; and the duration of the experiment, which will be usually from five to ten minutes, is noted.

The Water Equivalent of the Calorimeter may be obtained by Calculation, after the weight of each part of the apparatus has been ascertained, by multiplying each weight by the specific heat of the material.

The results of this process, when applied to a particular apparatus, are tabulated below, and show a water-equivalent of 203·46 grams. A fuller statement of this method is given in the original description of the apparatus by its inventor (*Journ. Soc. Cheml. Industry*, 1886, pp. 581–84).

	Weight in grams.	Specific heat.		Water-equivalent.
Glass beaker, part in contact with the water	922 430	× 0·180	=	166 037
Glass bell	75 431	× 0 180	=	13 576
Brass base	99 853	× 0 094	=	9 377
Four copper discs	65 100	× 0 095	=	6 294
Brass over top of bell-jar	21 307	× 0 094	=	2·001
Copper tube	30 800	× 0 095	=	2·930
Rubber cork	1·578	× 0 331	=	0 552
Rubber tube	1 784	× 0 331	=	0·591
Platinum crucible	15 111	× 0 032	=	0 490
Mercury of thermometer	9·583	× 0 033	=	0 319
Glass „ „	7 350	× 0 180	=	1 323
Hence the total water-equivalent of the apparatus			=	203·460

The Direct Experimental Determination of the Water-equivalent should however be made as is described below, when the apparatus is to be applied to the determination of the calorific power of coal.

The calorimeter is carefully adjusted as it would be for working with a coal; 2000 grams of distilled water, about 5° C. warmer than the air, are then weighed and its temperature (t) is taken after it has been well mixed. The temperature (t′) of the apparatus is also noted; this will be the temperature of the laboratory in which the apparatus has been standing. The 2000 grams of water are now poured into the calorimeter beaker, the apparatus is placed in position in the water and the beaker is immersed in the metal jacket. The water is now kept well stirred for about fifteen minutes by raising and lowering the discs on the side of the bell-jar.

The temperature (t″) of the water is then taken.

The correction for radiation is obtained by continuing the above procedure for another fifteen minutes and again reading the temperature (t‴). The fall of temperature due to radiation will be $(t'' - t''') = f$.

From these data the water-equivalent, including the correction for adiation, is found from the following statement $\frac{2000\ [t - (t'' + f)]}{(t'' + f) - t'}$.

In a particular determination the following temperatures in degrees Centigrade were noted:

$t = 19{\cdot}5$
$t' = 14{\cdot}6$
$t'' = 18{\cdot}65$
$t''' = 18{\cdot}30$
$f = (18{\cdot}65 - 18{\cdot}30) = 0{\cdot}35$

Hence the water-equivalent $= \frac{2000\ [19{\cdot}5 - (18{\cdot}65 + 0{\cdot}35)]}{(18\ 65 + 0{\cdot}35) - 14{\cdot}6} = \underline{227{\cdot}22}$

The Calculation from the results of a particular experiment was made as follows: One gram of the coal raised the temperature of the 2000 grams of water and the apparatus by 6 34° F. Since the water-equivalent of the apparatus was 424 8 grams, this was equivalent to raising 2424·8 grams of water by 6 34° F, or 2424·8 × 6 34 = 15373·2 grams of water 1° F. The coal therefore gives 15373 2 British thermal units of heat by its combustion. If it is wished to express the heat-value of the coal in terms of pounds of water at its boiling-point evaporated by one pound of coal, then, since water in being converted into steam absorbs 967 units of heat, one pound of the coal will evaporate $\frac{15373\ 2}{967} = 15\ 9$ lb. of water at its boiling-point and under ordinary atmospheric pressure.

556. The Bomb Calorimeter.—A modification of the Mahler-Donkin bomb calorimeter, constructed for the determination of the calorific power of fuel, is shown in Fig. 93. It consists of the following parts:

A Bomb or suitable stout-walled combustion chamber (*a*), made of metal of great tensile strength, in which the substance is burned: the thick walls of this bomb are black in the figure.

A Calorimeter (*b*) containing water, in which the bomb is immersed and to which the bomb gives up its heat.

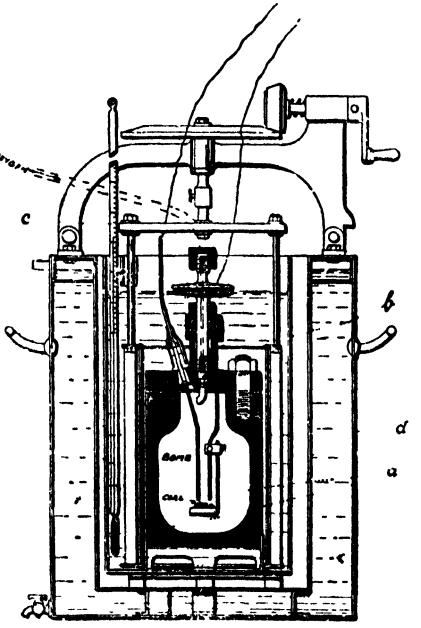
A Centigrade Thermometer (*c*) graduated in fiftieths of a degree, a hundredth of a degree Centigrade may be easily read on the scale by means of a hand-lens.

A Cylindrical Water-jacket (*d*) in which the calorimeter (*b*) is placed. Attached to this outer jacket is a bracket fitted with friction-wheels by means of which a set of paddles may be made to rotate inside the calorimeter.

A Storage Cell, Electric Battery, or other source of electricity, capable of giving a current of about 2 amperes at 10 volts for firing the fuel in the bomb (*a*).

A Pressure-gauge, which records the pressure in the bomb and connecting-tube while the bomb is being charged with oxygen from the steel cylinder. This pressure should not be less than 25 atmospheres.

FIG. 93.



THE BOMB CALORIMETER.

The interior of the bomb is protected from the corrosive effects of the acids produced during combustion, either by a heavy plating of gold, or by a lining of platinum or enamel. The bomb is fitted with a screw-valve for regulating the admission of oxygen, and with a support which carries the crucible in which the fuel is placed, and which also serves as one of the terminals required for the electrical ignition of the substance to be burned: an insulated rod forms the second terminal. The cover of the bomb can be securely bolted down by means of studs and nuts.

The Procedure is as follows: A sample of the finely powdered coal, not exceeding 1 gram, in a porcelain capsule small enough to be placed in the bomb-crucible, is dried at a temperature of 100° C. until its weight is constant

(refer to **1024**). A piece of platinum wire 0·1 mm. in diameter is looped between the two terminals, and is made to glow by passing the electric current in order to make sure that the connections are sound.

The capsule containing the dried coal is then placed in the bomb-crucible and the platinum loop is so arranged that it is well covered by the coal. The bomb-cover is then screwed down, and after the necessary connections have been made, oxygen is admitted very slowly into the bomb until the gauge indicates a pressure of 25 atmospheres. The valve of the oxygen-cylinder is then closed, and finally the screw-valve of the bomb is also secured.

The bomb is now disconnected and placed in the calorimeter containing 2500 grams of water. When it is seen that no oxygen escapes, showing the joints to be gas-tight, the paddles are kept constantly in motion until the temperature of the water remains constant as judged by thermometer readings taken at intervals of a minute.

One of the connecting-wires from the battery is then applied to any part of the bomb-cover, and the other to the insulated terminal. If this has led to a successful firing, a faint click will be heard, caused by the cracking of the capsule. The paddles are then at once restarted, and the temperature of the water is noted at intervals of a minute until the mercury begins to fall.

The difference between the maximum and the initial temperatures, when multiplied by the sum of the weight of the water and the water-equivalent of the apparatus, gives the amount of heat in calories yielded by the combustion of the weight of fuel taken.

The water-equivalent of the apparatus is determined by burning a known weight of some pure combustible substance such as cellulose, benzoic acid, or cane sugar, the calorific value of which is accurately known.

In testing ordinary fuels the following method of calculation is quite satisfactory, since careful experiments have shown that it is unnecessary to make any cooling corrections if the temperature of the water in the calorimeter is the same as that in the water-jacket before the fuel is burnt.

If the initial water-temperatures are the same as the temperature of the room when the determination is being started, then if

$t°$ C. = the initial temperature immediately before firing,
$T°$ C. = the maximum temperature after firing,
W = the weight of water in the calorimeter,
w = the water-equivalent of the apparatus,
w_1 = the weight in grams of the fuel taken,
X = the calorific value of the fuel,

$$X = \frac{(W + w) \times (T - t)}{w_1}.$$

If full corrections are to be made for losses due to cooling, and increases such as are due to the formation of nitric and sulphuric acids, the above data

must necessarily be amplified, although the method of carrying out the determination will be in no way affected. Refer for text-books to par. **1021.**

Examples of Duplicate Estimations (a, b) are given below:

	a.	b
Weight of coal dried at 100° C.	0·8135	0 7938
Initial temperature C.° of water	18·91	18 88
Maximum temperature C.° of water . . .	20 74	20 67
Weight of water in calorimeter in grams . .	2500	2500
Water-equivalent of apparatus in grams . .	712	712

Then the calorific value from (a)

$$= \frac{(2500 + 712) \times (20{\cdot}74 - 18{\cdot}91)}{0\ 8135} = 7225\ 5 \text{ calories.}$$

and from (b) the value

$$= \frac{(2500 + 712) \times (20\ 67 - 18\ 8)}{0{\cdot}7938} = 7243{\cdot}0 \quad \text{,,}$$

or the mean calorific value = 7234 2 calories.

For Results of Analyses of Coal refer to paragraph **958.**

Complete Analysis of "Superphosphate of Lime."

557. Most of the specimens of natural calcium phosphate, as well as the calcium phosphate present in bones, are insoluble in water. But when these substances are treated with sulphuric acid, the insoluble tricalcium phosphate, $Ca_3P_2O_8$, which they contain, is converted into soluble mono-calcium phosphate $CaH_4P_2O_8$. The treatment of insoluble phosphates with sulphuric acid is carried out on a large scale by manure manufacturers in order to produce the soluble phosphate or "superphosphate" of commerce.

"Superphosphate" accordingly consists essentially of mono-calcium orthophosphate. But it also contains varying proportions of free phosphoric acid, tricalcium phosphate and calcium sulphate, as well as compounds of iron, aluminium, magnesium, and the alkali-metals. Organic matter is also usually present.

In the proximate analysis of superphosphate for commercial purposes, the estimations of calcium phosphate (561) and of the alkali-metals (563) may be omitted.

558. Estimation of Moisture.—Weigh out accurately about 2 grams of the superphosphate in the watch-glasses and clip, and heat it in the steam-oven for five hours. The loss of weight represents the amount of moisture, or uncombined water.

559. Estimation of Combined Water.—The superphosphate, after having been dried as above (558), is transferred to the air-oven, and is heated to 160° C. until its weight is constant. The loss of weight represents the amount of combined water.

560. Extraction of the Portion which is Soluble in Water.—Weigh out 10 grams of the well-sampled undried superphosphate into a mortar, then add a little water and mix the whole into a paste by gently stirring it with the pestle. Now add more water, stir well, allow the undissolved matter to settle, and decant the almost clear liquid into a flask. Treat the residue again with water and once more decant, and after repeating these operations twice transfer the undissolved residue to the flask. The total volume of water used should be about 300 c.c. Then allow the flask to stand for two hours, shaking it occasionally.

Now filter the liquid into a half-litre flask, and wash the undissolved residue on the filter with water until the flask is filled up to the graduation. Reserve the residue in the filter for subsequent estimations (565-567), and proceed to use the filtrate, or "original solution," for the estimations in paragraphs 561-564.

If the superphosphate contains much free acid, the process of extraction, involving standing for two hours with the water containing acid, will probably render a larger proportion of phosphate soluble in water than was actually soluble in the original substance.

561. Estimation of Soluble Phosphates of Iron and Aluminium, and of Soluble Calcium Phosphate.—Transfer 250 c.c. of the original solution (560) to an evaporating-dish, add a little sodium carbonate in order to neutralise the free acid, and then a few small crystals of potassium nitrate. Evaporate this liquid to dryness, and remove the organic matter by igniting the residue. As soon as the dish is cold add hydrochloric acid and water, adding more acid and heating the liquid if it is not clear. Now add a slight excess of ammonium hydrate solution, and then an excess of acetic acid. Filter off the phosphates of aluminium and iron, and wash, dry, ignite, and weigh them.

Make up the filtrate to 250 c.c., and withdraw two successive portions of 50 c.c. each. Make duplicate determinations of the P_2O_5 in these by means of uranium nitrate solution, which has been standardised with calcium phosphate solution (382).

An alternative gravimetric method consists in precipitating the phosphate in 50 c.c. of the "original solution" with ammonium molybdate solution, and weighing it as magnesium pyrophosphate (538).

562. Estimation of Calcium and Magnesium.—Transfer 100 c.c. of the filtrate (561) to a beaker, add excess of ammonium oxalate solution, filter

off and wash the precipitate, and weigh the calcium either as carbonate or as oxide (146, 147).

Render the filtrate, containing the magnesium, alkaline with ammonium hydrate; the magnesium will probably be precipitated, either partially or wholly, as phosphate. Then add sodium phosphate solution, and allow the liquid to stand. Filter off, dry and ignite the precipitate of magnesium ammonium phosphate and weigh the magnesium pyrophosphate (165).

563. **Estimation of Organic Matter and Alkali-metals.**—Mix 100 c.c. of the original solution (560) in an evaporating-dish with milk of lime until the liquid is just alkaline. Evaporate to dryness, and heat the residue in the air-oven at 160° C. until its weight is constant. Then ignite over a small Bunsen flame until the dish ceases to lose in weight. The loss of weight will give the amount of soluble organic matter in the superphosphate.

Treat the residue with water, add a little more milk of lime, and heat for some time. Filter off the insoluble matter and wash it twice. Then precipitate the sulphate and the calcium from the filtrate and washings by adding barium chloride, ammonium hydrate, ammonium carbonate, and ammonium oxalate solutions in the order named. Filter, convert the alkali-metals in the filtrate into chlorides by adding hydrochloric acid, and estimate them as is described in paragraphs 428, 429

564. **Estimation of Sulphate.**—Heat 100 c.c. of the original solution (560) to boiling, add a few drops of hydrochloric acid, and precipitate with barium chloride solution. Weigh the barium sulphate (133).

565. **Estimation of Insoluble Organic Matter.**—The residue left on the filter (560) will contain the organic matter, gangue, and undissolved phosphate and sulphate. Dry the residue in the steam-oven, transfer it as completely as possible to a platinum crucible, and weigh. Then ignite the crucible until all the organic matter has been destroyed. The loss of weight will give the amount of organic matter.

566. **Estimation of Silicious Matter.**—Heat the ignited precipitate (565) with hydrochloric acid, in order to extract the portion which is soluble in acid. Filter off, wash, ignite, and weigh the residue, which consists of gangue or silicious matter.

567. **Estimation of Insoluble Iron, Aluminium, Phosphate, Calcium, Magnesium, and Sulphate.**—Make up the filtrate (566) to 250 c.c., and estimate its dissolved matter as is described in paragraphs 561, 562, 564.

568. **Estimation of Nitrogenous Matter.**—Superphosphates are occa-

sionally mixed with nitrogenous manures and ammoniacal salts, and nitrogen must then be estimated.

Nitrogen present in these forms may be determined in 2 grams of the superphosphate by the soda-lime method (804). Kjeldahl's method (807) may also be employed; but if nitrate is present, it must be removed by evaporating with ferrous sulphate and dilute hydrochloric acid before the nitrogen is estimated by this process.

The ammonia may be determined by mixing 2 grams of the substance with sufficient water, then adding sodium hydrate, or magnesia if much nitrogenous matter is present, and distilling. The ammonia gas is received in standard acid, which is then titrated as is described in paragraph 295.

For the Results of an Analysis of Superphosphate of Lime refer to paragraph 959.

Analysis of Mineral Phosphates and Bone-manures.

569. The above process for the analysis of superphosphate is applicable to the analysis of other mineral phosphates. Since, however, mineral phosphates contain little or no matter soluble in water, the treatment with water may be omitted, and the phosphate may be at once treated with acid. Carbonate, if present, is estimated by the methods described in paragraphs 175–186.

For Results of Analyses of Coprolites and of Bone-flour refer to paragraphs 960, 961.

Estimation of the Total P_2O_5 in "Basic Slag," Mineral Phosphates and Superphosphates.

570. For the estimation, 10 grams of the "Thomas' slag" are heated with 50 c.c. of strong H_2SO_4 for fifteen minutes to a temperature at which white fumes appear. The cold liquid is then diluted to 500 c.c. and filtered.

50 c.c. of the filtrate are mixed with 20 c.c. of citric acid solution, containing 500 grams of the acid per litre; and the liquid is nearly neutralised with the strongest ammonia solution diluted with ten times its volume of water.

The solution is then precipitated by adding magnesia mixture (167), and one-third of its volume of the above ammonia solution.

The precipitate is weighed as $Mg_2P_2O_7$ (166).

For Results of Analyses refer to paragraph 962.

Analysis of Guano.

571. Since guano gives off ammonia when it is heated to 100° C., its moisture cannot be estimated in the ordinary way. About 4 grams are weighed into a bent glass tube (191), which is immersed in an air-bath or oil-bath heated to 120° C.

One end of the tube is connected with a wash-bottle which contains a known volume of normal acid, and a current of air is drawn through the tube and the wash-bottle. The ammonia gas, which is given off during the heating, passes into and is absorbed by the acid in the wash-bottle. After the heating is stopped, the ammonia is estimated by titrating the free acid with standard sodium hydrate solution.

The loss of weight suffered by the guano is equal to the total weight of the water and ammonia, hence the water may be calculated by difference. The dried substance is then ignited strongly in the air, and the loss of weight represents the amount of organic matter.

The residue is treated with HCl, and the estimations which are described in paragraphs 561-564 are made in the solution.

For Results of an Analysis of Guano refer to paragraph 963.

DRY ASSAY OF ORES OF LEAD, SILVER, GOLD AND TIN.

Dry Assay of Lead-ores.

The chief ore of lead is galena, PbS. The assay by means of iron (572) includes an estimation of silver, which is always present in the ore: if much arsenic is present a lower temperature must be employed.

The oxides of lead, and oxidised lead ores which are free from sulphur arsenic and phosphorus, are readily assayed by reduction with carbon (573, 574).

The procedure described below may be substituted with advantage for that described in paragraphs 483 and 484 in the estimation of the silver.

572. Dry Assay of Galena for Lead.—The ore is reduced by heating it with iron and with a suitable flux, and the metallic lead thus separated is weighed. Either iron may be introduced into a clay crucible (a), or an iron crucible may be employed (b).

(a) *Assay of Galena in a Clay Crucible.*—Grind the sample of ore in a mortar, and pass the whole of it through a fine sieve. Also reduce some sodium carbonate and some argol or crude tartar to fine powder.

Now weigh out 25 grams of the ore, 25 grams of the sodium carbonate, 2 grams of the argol, and 2 grams of borax which is added to increase the fluidity of the flux.

Reserve one-fifth of the sodium carbonate; mix the remainder well with the ore and with the argol, and transfer the mixture to the crucible, which has been previously dried by placing it under the furnace bars. Double over a piece of hoop-iron, which is of such a length that when bent it is the same height as the interior of the crucible, and place it in the crucible with the free ends downwards. Cover the surface of the mixture in the crucible with the sodium carbonate which has been reserved for that purpose, place the crucible low down in a dull red fire, and cover it with the lid.

Now raise the temperature gradually, and at the end of ten minutes remove the furnace-cover slightly, grasp the piece of hoop-iron with the tongs and stir the mixture with it. After the lapse of another ten minutes stir again, and strike the handles of the tongs sharply on the side of the furnace, in order

to detach any beads of lead, which may adhere to the iron, and cause them to drop into the crucible.

Now heat more strongly for five minutes, remove the hoop-iron and raise the temperature by turning on the full draught, so as to render the slag fluid. Then remove the crucible from the furnace and pour the fused substance out into a smooth conical iron mould; turn the cool mass out of the mould, and hammer the button of lead found at the bottom in order to detach the slag from it. Then cleanse the button by rubbing it with a hard brush and weigh it.

(b) *Assay in an Iron Crucible.*—For the estimation weigh out 30 grams of the very finely powdered ore, and mix this with 30 grams of dry sodium carbonate and 3 grams of crude tartar. Heat a wrought-iron crucible to dull redness in a wind-furnace, remove the crucible, introduce the above mixture, and cover its surface with a sprinkling of borax.

If the crucible has been previously used, heat it and scrape off the scale from the interior before introducing the mixture.

Now cover the crucible with the lid, replace it in the wind-furnace, and surround and cover it with coke.

Heat the crucible moderately for about twenty minutes, taking care not to let the temperature rise too high; then remove it from the furnace, and scrape down any slag, which adheres to the sides, with an iron stirrer. Tap the crucible gently, and pour the melted mass into a smooth conical iron mould. When the whole has become cold, remove the mass from the mould, and break off the slag with a hammer from the metal button at the bottom; then wash, dry, and weigh the lead.

After the fused mass has been poured out, the internal surface of the crucible should be smooth, and no globules of lead or of partly fused portions of slag should be seen adhering to the interior. The slag should be homogeneous, and should contain no particles of lead or undecomposed galena.

Several assays must be made on the same ore, and the mean of the satisfactory results should be taken.

A wrought-iron crucible will serve for from ten to twenty assays.

573. **Assay of Oxides of Lead.**—The dry assay of PbO or Pb_3O_4 may be made with the following mixture:

For PbO.		For Pb_3O_4.	
PbO . .	40 grams.	Pb_3O_4 . .	40 grams.
Na_2CO_3 . .	30 ,,	Na_2CO_3 . .	30 ,,
Borax . .	10 ,,	Borax . .	10 ,,
Flour . .	8 ,,	Flour . .	10 ,,

The mixture is fused in a clay crucible in a wind-furnace, avoiding too high

a temperature which might cause loss of lead by volatilisation: the melted mass is poured into a conical iron mould as soon as it is in a state of quiet fusion. The cold lead button is then detached from the bottom of the slag, and is weighed after it has been cleaned by hammering and brushing.

By cupelling this button at a low temperature (577) the amount of silver present in the lead oxide may be found. This must be known for the correction to be applied in the silver and gold assays (582).

574. **Assay of Carbonate of Lead.**—Weigh out 30 grams of the finely powdered ore: mix this with 10 grams of sodium carbonate and 10 grams of tartar, and about 1·5 grams of finely powdered charcoal; then place the mixture in a small covered Battersea round clay crucible, and proceed as is described in paragraph 573.

Assay of Lead for Silver.

575. The button of lead (572) containing the silver is placed on a shallow vessel made of bone-ash, known as a cupel, and is heated in a muffle-furnace. The muffle is so arranged that products of combustion do not enter from the furnace, but a regulated current of air can be passed through it.

The button melts and the lead is converted into oxide, which is partly volatilised and partly absorbed by the cupel. The silver remains on the surface of the cupel as a small globule, which is detached and weighed.

576. **Preparation of Bone-ash Cupels.**—Cupels may either be purchased, or they may be prepared as follows:

Some finely powdered bone-ash is sprinkled and well mixed in a mortar with sufficient water to cause it to hold together when it is pressed with the hands, but the mixture must not be so wet as to soil the hands.

The moistened bone-ash is introduced into a suitable mould, a plug is placed upon the bone-ash and is struck sharply with a hammer several times. The cupel thus formed is detached from the mould and dried at a gentle heat in the air: it should not be used until it is at least ten days old.

577. **The Process of Cupellation.**—Place one of the cupels in the hot muffle and heat it to bright redness for about ten minutes, so as to drive off all the moisture.

Drop the button of lead (572) into the heated cupel by means of the assay-tongs, and close the muffle-door. A black crust will form on the surface of the lead, but this will disappear in a short time, leaving the button brighter than the cupel. If this "clearing" does not take place, drop a little powdered

charcoal, wrapped in tissue-paper, into the cupel, and raise the temperature of the muffle. If the clearing does not now appear, start with a fresh button, and apply a higher temperature.

As soon as the button is "clear," reduce the draught of the furnace, and allow a little air to enter by the muffle-door; also let the temperature fall somewhat, since the temperature at starting is higher than is needed during the oxidation of the lead, and might give rise to loss of silver by volatilisation. Towards the end of the process, raise the temperature again by closing the muffle-door and increasing the draught.

The final stage is easily recognised, since the thin layer of oxide is reduced to a film producing iridescent colours, and these suddenly disappear when the operation is finished. When the cupel is removed from the muffle, the globule of silver suddenly glows and solidifies.

Now remove the cupel from the muffle, and allow it to cool (*Note*). Detach the bead, hammer it out on a small anvil, and finally clean it with a hard brush. Weigh the bead carefully on a very delicate balance, and calculate the weight of silver present in the lead, stating the result in troy-ounces per ton of lead.

Note.—If the silver bead is not very small, there is risk of "spitting" taking place during its cooling, which is due to the evolution of oxygen absorbed by the liquid metal. This may give rise to serious loss of the metal It can be avoided by making the process of cooling very slow, preferably by covering the cupel with another hot cupel before removing it from the muffle and allowing the two to cool together.

Dry Assay of Gold Quartz.

578. Since the amount of gold in gold-ores rarely exceeds 2 ounces per ton, and is usually much less than this, it is necessary to extract the metal with great care. The process is divided into three parts.

(1) The ore is heated with lead oxide and a flux, and the lead thus produced extracts the gold and silver from the ore.
(2) The lead button is cupelled, and the silver and gold are left on the cupel.
(3) The gold is "parted" from the silver, by dissolving out the latter with nitric acid.

579. Concentration of the Gold.—Powder the ore and pass it through the finest brass-wire sieve (**56**). Weigh out 50 grams of the powdered ore, or 100 grams if the ore is a very poor one, or 32·7 grams for one "assay-ton" (**582, b**), and mix this intimately with the flux in the proportions stated in grams in the first two columns and for the assay-ton proportions in the third column.

Quartz-ore	50	100	32·7
Red Lead (582)	40	40	30
Na_2CO_3	75	125	40
Borax	15	25	5
Flour	4·5	4·5	4 5
Charcoal	1·5	1 5	1·5

Glass powder may also be added when mixing, if it is found necessary to increase the fluidity for "pouring."

Transfer the mixture to a smooth fire-clay crucible, which is then covered with the lid and heated in a wind-furnace. The heat at first must not be too great, but must be raised considerably before "pouring" into a warm conical iron mould. Detach the lead button from the glass-like slag, which should separate easily and must contain no particles of lead.

The slag from rich ores may contain particles of lead: if this is the case it should be crushed and mixed with 20 parts of red lead, 5 of Na_2CO_3, and 1 of charcoal, and heated once more. The lead button thus obtained is added to that already obtained.

580. Cupellation.—The lead button is now cupelled (577), a high temperature being used so as to separate the copper completely. A high temperature may be safely used, since gold is much less volatile than silver. The button of gold and silver is then cleaned and weighed.

581. Parting.—The process of "parting" consists in dissolving out the silver from the gold by means of nitric acid.

If the bead is yellow, it contains more than 50 per cent. of gold. If it contains more than 30 per cent. of gold, the gold will retain silver after the parting: but if not more than 30 per cent. of gold is present, the whole of the silver will be dissolved. The presence of too much silver causes the gold to be left as a powder which is difficult to manipulate. The most convenient proportions are 2·5 parts of silver to 1 part of gold.

If the gold does not exceed 30 per cent., flatten out he le d by carefully hammering it. If the bead is large, anneal it occasionally by heating it to redness on charcoal in the blowpipe-flame. In any case, finally anneal the flattened button before "parting" it.

Now heat a little strong nitric acid, diluted with twice its volume of water, nearly to boiling in a tube, and drop into it the weighed button. Keep the liquid at this temperature for ten minutes, then pour off the acid, and heat the button with nitric acid diluted with an equal volume of water. Boil for several minutes, then pour off the acid, and wash the residue with distilled water.

Fill up the tube with water, cover the open end with a small porcelain crucible and quickly invert the tube, carefully avoiding loss. The gold will

settle down to the bottom of the crucible. Then remove the tube and water, and drain off the water from the crucible; dry the gold, and heat it until it changes from a dark red to a yellow colour. Now cool the metal, transfer it to a watch-glass, and weigh it accurately. From this result calculate the weight of gold present in the ore, stating the result as ounces per ton.

If the button contains more than 30 per cent. of gold before "parting," it will retain silver. In such a case sufficient silver is added to raise the proportions to 2·5 parts of silver to 1 part of gold, and the parting is repeated with this alloy.

If the gold weighs only 2 or 3 milligrams, the requisite quantity of silver may be alloyed with it by simple fusion on a clean cupel before the blowpipe.

If the amount of gold exceeds a few milligrams, weigh out the required amount of silver, wrap the silver and gold together in 1 gram of sheet-lead (582), and cupel the metals; then flatten, anneal, and "part" the gold button. The gold will now be free from silver, and may be weighed on a very delicate balance, and the weight of gold calculated as ounces per ton of ore.

582. **The Silver which is introduced in the Red Lead,** and subsequently in the metallic lead, must be estimated and allowed for. The silver is usually estimated by cupellation (573, 577), but it may be determined in the nitric acid solution of the lead as is described in paragraph 484.

(a) **Example of Gold-ore Assay.**—50 grams of ore were fused with flux, and a lead button was obtained which gave on cupellation a yellow bead weighing 2·5 milligrams. Before "parting," the bead was recupelled with 2 milligrams of silver After parting, the white bead yielded 1 milligram of gold.

Bearing in mind that the number of grains in one ton = 2240 × 7000, and that there are 480 grains in 1 ounce Troy, the weight of gold present in the ore is calculated as grains and then as ounces per ton, as follows:

$$\text{The weight of gold} = \frac{2240 \times 7000 \times 0\ 001}{50} = 313\ 6 \text{ grains per ton of ore.}$$

$$= \frac{313\ 6}{480} = \underline{0\ 65} \text{ ounce per ton of ore.}$$

From the above results, the weight of Ag in the button = 3·5 milligrams.

Subtracting the weight of Ag in the red lead used 1·1
and the weight of Ag added . . . . 2 0 } = 3 1 ,,

the weight of silver from the ore = 0·4 ,,

Therefore by calculation from this result, as above:

The weight of silver = 0 26 ounce per ton of ore.

(b.) If 32·7 grams, or one "assay-ton" of ore was used for the assay, the number of milligrams of gold or of silver obtained represent at once the number of ounces of the metal in one ton of the ore. The assay ton figure is obtained by dividing the number of troy-ounces in the English ton by 1000, thus $\frac{2240 \times 7000}{480 \times 1000} = 32{\cdot}7$.

The American ton of 2000 lbs. is sometimes used, and in that case the weight of ore required would be 29 17 grams.

Dry Assay of Tin-ore

583. Cassiterite, "tinstone," or "black tin" is the ordinary tin-ore of commerce. This mineral consists mainly of SnO_2. If it is fairly free from quartz and other "gangue," it may be conveniently assayed in the following manner:

20 grams of the finely-powdered ore are boiled for about half an hour with 50 c.c. of strong HCl, 15 c.c. of strong HNO_3 are then added to the cool liquid and the mixture is again heated for about the same time. The hot liquid is then diluted with about 120 c.c. of water, the whole is stirred well, allowed to settle and filtered. The residue is well washed several times with hot water in the same way, and then several times with dilute ammonium hydroxide solution to ensure the separation of the tungsten. It is finally well washed in the filter-paper, and is then dried and ignited with the paper in a small clay crucible.

The residue is now intimately mixed with 40 grams of potassium cyanide, and after placing half this quantity of the cyanide in the bottom of the crucible, the above mixture is added and is then covered with another 20 grams of the cyanide. The crucible is now placed in a wind-furnace and is maintained at a red heat for about half an hour, and its contents are then poured into a conical iron mould and allowed to cool. The button of tin is removed from below the saline mass and is cleaned and weighed as usual.

The result furnished by the above assay is usually sufficiently accurate for commercial purposes. but if a more exact determination of tin is required, the button may be dissolved in hydrochloric acid out of contact with the air (305) and the stannous chloride titrated by iodine solution (338).

PART IV.—SECTION X.

WATER ANALYSIS.

600. Introductory Remarks.—The chemical examination of water is usually undertaken in order to ascertain the suitability of the water for drinking, or for technical purposes.

If the fitness of a particular water-supply for the purpose of washing with soap, or of raising steam, is to be ascertained, the examination may be restricted to certain determinations of its mineral constituents, such as total solid residue, permanent and temporary hardness, and acidity.

If, however, the suitability of the water for drinking purposes is to be determined, it often becomes necessary to estimate the amount of certain substances which may be hurtful to health. Some of these are of a mineral character, such as lead salts. But commonly the most serious and dangerous contamination to be anticipated is that arising from drainage or sewage. The introduction of such animal refuse is frequently indicated by the presence of an abnormal proportion of ammonium compounds, of chlorides, or of nitrites or nitrates in the water. These indications are usually valuable, but they are only of importance when no other source of these substances is possible.

The detection of more recent sewage contamination, in the form of organic matter, involves the application of certain special processes. The process of combustion, introduced by Frankland and Armstrong, estimates the absolute amounts of organic carbon and nitrogen which are present in the residue obtained by evaporation of the water, and from the absolute and relative amounts of these elements the existence and extent of recent sewage contamination are deduced.

This process, however, involves the use of special apparatus, and also requires a somewhat considerable expenditure of time and skill. Hence other processes for estimating organic matter in water, which are more simple and expeditious, have been more generally adopted by analysts. These processes are described in the text, and the student is referred to *Frankland's Water Analysis*, or to the description of this process in *Sutton's Volumetric Analysis*, for an account of the combustion method.

Reference should be made to paragraphs 646-653 for a consideration of

the results obtained by the chemical examination of water and the inferences to be drawn from them.

Collection and Inspection of the Sample.

601. Collection of the Sample of Water.—Samples of water are most conveniently collected and stored in Winchester quart bottles. These bottles are commonly made of blue glass, and are provided with accurately fitting stoppers. Each bottle holds about 2400 c.c. For an ordinary analysis one Winchester quart bottle filled with the water will be found sufficient.

Before the bottle is filled with the water-sample, it should be well washed out with water, and then allowed to drain in an inverted position. Bottles which have been used for acids should be preferred, since they are most readily cleansed.

The use of stoneware bottles and of corks in storing water-samples is to be condemned.

Before the bottles are filled, they should be rinsed out two or three times with the water. When the water is to be collected from a river or spring the bottle is totally immersed in the water, and is thus filled to within half an inch of the bottom of the stopper. If the water is supplied from a pump or tap, several gallons should be allowed to flow away before the sample is taken. A sample of a town supply must be drawn direct from the street-mains, and not from a storage-cistern.

The stopper is inserted as soon as the bottle has been filled. It should be held in its seat by drawing down tightly over it a piece of sheet rubber, or of clean calico or linen rag, the edges of which are firmly tied round just beneath the projecting edge of the neck with string or with thin copper binding-wire. The fastening should be sealed with sealing-wax. No lute or other material, which might find its way into the bottle when the stopper is removed, must be employed.

Samples of water should be stored in a cold, dark room or cellar.

602. Order of Work.—In carrying out the following estimations, the order in which they are to be started should be carefully considered, with the view of economising time as far as possible. Experience has shown that if the processes are started in the order in which they are described in the text, this end will generally be best secured.

Ammonia and organic matter should be determined as soon as possible after the sample has been collected, and immediately after the bottle has been opened, since these constituents often suffer rapid change in amount when the water is kept or is exposed to the air. The water in the bottle should be

shaken up before any portion is poured off for analysis, in order to maintain its uniformity of composition.

It is usually unnecessary to carry out the whole of the following estimations on any one sample of water, and the analyst must select those which give the necessary information in each case. Thus, water which is to be used in a steam boiler should be free from acidity, contain but little dissolved solids, and have low hardness; and in water used for washing and dyeing, low hardness and absence of iron are of special importance.

603. The Colour of the Water is observed by pouring it into a tall narrow cylinder of white glass, and looking down the cylinder upon a white surface. The tint should be compared with that of a sample of pure water. The cylinder, or tube, in which this test is made, should be about 60 cm. in length.

The Taste and Smell of the water are usually observed after it has been gently heated.

Acidity.—Pure natural water is usually slightly alkaline in reaction, and a strip of neutral litmus-paper (265) immersed in it becomes distinctly blue. Acid reaction usually indicates the presence in the water of manufacturers' waste or of mine products.

Examination of the Suspended Matter.

604. Chemical Examination of the Suspended Matter.—The presence of suspended matter in water usually indicates imperfect filtration, but it may be due to the action of the water on lead (638), and to other causes. It is not usual to filter the water before analysis unless it is distinctly turbid. If, however, much suspended matter is present, its amount may be estimated and the water may at the same time be rendered clear, by proceeding as is directed under (a) or (b) below.

(a) The necessary quantity of water is passed through an unwashed filter which has been dried at 110° C. until its weight is constant (61), and the weight of the suspended matter in the filter is determined as is directed below. The first part of the filtrate is rejected, or is used only for the determination of total solids, chloride, nitrate, hardness, or poisonous metals. The latter portion of the filtrate, or another portion of the sample which has become clear by subsidence, is employed for determining ammonia and dissolved organic matter.

The suspended matter is washed in the filter with distilled water, and is dried at 110° C. until its weight is constant.

The increase of weight of the filter will give the total weight of suspended matter in the volume of water used, which will usually be one or two litres. The weight of dry suspended matter in parts per 100,000 is therefore found by multiplying this result by 100 or by 50.

Now burn off the organic matter from the residue, and incinerate the filter in a platinum crucible (101): or if the suspended matter is small in amount and adheres to the filter, cut the filter up into strips with a clean pair of scissors, and incinerate it in the platinum crucible. As soon as all the carbon has been burnt away, recarbonate the residue by adding a few drops of ammonium carbonate solution; then ignite it again at a low temperature, and weigh it when it is cold.

This weight, less that of the filter-ash, will be the weight of inorganic suspended matter. Calculate from this the weight in parts per 100,000. The difference between this number and the one previously obtained for the total suspended matter, represents the amount of organic suspended matter.

(b) If the filtered water must be used for determining the ammonia and organic matter, pour several litres of distilled water, free from ammonia, through a 10 cm dried and weighed filter-paper. This will dissolve out the ammonia which may be present in the paper. Ascertain that the water, which passes through the filter, has ceased to dissolve out any ammonia, by adding to the last portion of it 2 c c. of Nessler solution (608): the water must remain colourless after standing for five minutes (610).

Then fit the filter into a funnel Shake up the sample of water in the bottle, and pour a measured quantity—say 2 litres—of the water through the filter, receiving the water in a clean dry Winchester quart bottle This water is used for the determination of ammonia and organic matter, and the suspended matter in the filter is weighed as is directed under (a).

605. Microscopic Examination of the Suspended Matter.—It is advisable to examine the suspended matter under the microscope. For this purpose allow the water to remain in a tall cylinder for several hours, until the suspended matter has been deposited. Carefully pour off the clear supernatant water as completely as possible; then transfer a drop of the residual liquid to a glass slide, and examine it with a one-sixth objective. Take special care to look for fibres of wool, hair, muscular tissue, or any kind of animal matter which would be indicative of sewage. The presence of organisms should be carefully noted, and the presence of chlorophyll granules and cells will indicate vegetable matter.

Estimation of the Total Dissolved Solids.

606. Rinse a clean platinum or porcelain evaporating-dish with distilled water, heat it to redness, then allow it to cool in a desiccator and weigh it

carefully. Place the dish upon a glass ring on the water-bath, or on a beaker of suitable size placed on a tripod stand (72). The bath or beaker should be about two-thirds filled with water, and a few small pieces of paper should be thrown into the water if a beaker is used, in order to prevent the water from bumping while it is boiling.

Now measure out 500 c.c. of the water in a graduated delivering-flask and fill the dish to within about 1 cm. from its edge with the water. The volume of the water used may be reduced if much dissolved solid matter is present. As the liquid evaporates, continually add more of the water, until the whole of it has been transferred to the dish. When all the water has evaporated, cleanse and dry the outside of the dish, then place it in the steam-oven, and heat it until its weight is constant.

Since the residue in the dish is often hygroscopic, the weighing must be performed rapidly and as soon as the dish is cold. It is even advisable to cover the dish with a plate of mica, which has been weighed with the empty dish.

The residue should be reserved in the dish for the estimation of nitrate (621).

For the Interpretation of the Results see paragraph 646.

Estimation of Ammonia.

607. All processes connected with this estimation must be conducted in a room which contains no ammonium salts or other sources of ammonia.

The estimation should be made as soon as possible after the collection of the sample, and immediately after the bottle has been opened.

The process depends upon the fact that when the water is distilled with a little sodium carbonate, the whole of the ammonia, which is present in the water either in the free or in the combined state, passes over in the first portion of the distillate, and may be estimated by the addition of Nessler solution.

Nessler solution gives a yellow or brown coloration with ammonia or ammonium salts, the intensity of the colour increasing with the proportion of ammonia present.

The colour produced in the distillate by the Nessler solution is accordingly exactly matched, by adding the same quantity of the Nessler solution to the same volume of pure water, to which a suitable and known amount of standard ammonium chloride solution has been added. The quantity of ammonia in the distillate is then equal to that in the ammonium chloride used.

The Following Requisites (608–613) must be provided for this estimation.

608. Nessler Solution.—Three litres of this solution may be prepared according to the following directions, but a smaller volume will usually suffice, and may be made from proportionately smaller quantities of materials.

Dissolve 180 grams of potassium iodide in 250 c.c. of water and pour this solution upon 70 grams of mercuric chloride contained in a glazed porcelain mortar; then triturate the mixture until the solid matter is dissolved, and make up the whole to 2500 c.c. by the addition of water. Now add 454 grams of caustic potash in sticks, allow the substance to dissolve, and when the liquid has cooled add saturated solution of mercuric chloride gradually in sufficient quantity to form a slight permanent precipitate. Dilute this solution to three litres, allow it to become clear by standing, and then carefully decant the clear liquid.

Keep this Nessler solution in bottles which are closed with well-fitting rubber stoppers, and decant a portion of the clear solution from time to time into a smaller bottle for use.

It will be found convenient to fit a perforated rubber stopper into the neck of the small bottle. A glass tube, with 1 c.c. and 2 c.c. marks upon it, passes through this stopper, and serves to measure out and deliver the required quantity of the solution.

609. Standard Ammonium Chloride Solution.—Weigh out accurately 3·14 grams of pure recrystallised ammonium chloride. Dissolve it in water, and make the solution up to a litre. This solution is too strong for use, but it is of convenient strength for a stock solution. When the standard solution is required, dilute 10 c.c. of the stock solution to a litre. Each c.c. of the diluted solution corresponds to 0·00001 gram of NH_3.

610. Water Free from Ammonia.—Ordinary distilled or soft water frequently contains sufficient ammonia to render it unfit for use in the estimation of ammonia. In order to ascertain whether ammonia is present, a small glass cylinder (611) is nearly filled with the distilled water, 2 c.c. of Nessler solution (608) are added, and the liquids are mixed by stirring. The cylinder is then placed on a white surface, and if no yellow coloration appears after standing for five minutes the water is sufficiently pure for use.

If, however, a yellow or brown coloration appears, proceed to distil the water in the following way: Pour the water into a large flask (612), and add about a gram of sodium carbonate prepared by the recent ignition of sodium carbonate crystals (613). Connect the flask with a condenser (1016), and then boil the water. After rejecting the first portion of the distillate, collect the remainder in a small glass cylinder (611) and test it with Nessler solution in the way which has just been described.

As soon as the distillate ceases to give a coloration with Nessler solution

collect it in a clean Winchester quart bottle, and keep the tightly stoppered bottle in a room which contains no ammonium salts or other sources of ammonia.

Instead of adding sodium carbonate to the water in order to get rid of the ammonia as is directed above, the ammonia may be retained in the water in the flask during the process of distillation by the addition of a few drops of dilute sulphuric acid; the whole of the distillate will then be free from ammonia.

611. **The Glass Cylinders** which are used in this process should be made of perfectly colourless glass: they are 15 cm in height and 4 cm. in diameter, and the capacity of 50 c c is marked upon the side It is essential that they should be uniform in size and capacity. Similar cylinders of 100 c.c. capacity are useful for other processes described later on.

612. **Distillation Flask**.—If the flask which is used for the distillation is fitted with a rubber cork, it frequently happens that the distillate is contaminated with ammonia for a long time. With some rubber corks it is impossible to obtain ammonia-free water.

A convenient flask, which does away with this source of trouble, is a round fractionating flask of not less than 2 litres capacity, with the ordinary side-tube fused upon the side of the neck (Fig 19, p. 23). Its neck is closed by a well-fitting glass stopper, which has been ground in by means of fine emery-powder and water In place of the stopper a well-fitting cork covered with tin-foil may be used The side-tube is passed to a distance of about 10 cm. down the inner tube of the condenser, and should be of such diameter as to fit into this tube precisely. By this arrangement the contact of the steam with rubber is prevented.

613 **Sodium Carbonate Crystals** do not usually contain ammonia, which is however often present in other forms of the salt. Since it is difficult to remove this impurity by ignition, and its presence renders the salt unsuitable for this estimation, the sodium carbonate should be dissolved and tested with Nessler-solution (610) before it is used

614. **The Process of Estimating Ammonia.**—The following preliminary test is made for the purpose of ascertaining what amount of water should be used for the more exact determination of the ammonia.

50 c.c. of the water under examination are measured into a glass cylinder (611), and the cylinder is placed upon a white tile. 2 c.c. of Nessler solution (608) are added to the water, and the liquid is then well stirred.

50 c.c. of the distilled water free from ammonia (610) are now poured into a second cylinder, 0 5 c.c. of the dilute standard ammonium chloride solution (609) is added, and the liquid is mixed with 2 c.c. of Nessler solution.

If the intensity of colour in both cylinders is about the same, after they have been allowed to stand for about five minutes, half a litre of the water may be used for the determination of the ammonia.

If the coloration produced by the water-sample is less or greater than that of the standard, a proportionately larger or smaller quantity of the water must be used. A little experience will render it possible to judge the amount of water to be used for the distillation, after merely inspecting the colour which is obtained in the preliminary experiment.

It should be remembered that the coloration, which corresponds to that given by about 2 c.c. of the standard ammonium chloride solution, is most suitable for accurately determining ammonia by this process.

(a) *Process of Distillation.*—Now adapt the distillation-flask to the condenser (612), and proceed to free the apparatus from ammonia as follows: Pour into the flask about 250 c.c. of water free from ammonia (610), and add a gram of recently ignited sodium carbonate (613). Heat the flask with an Argand burner (95), or with a Bunsen burner which is raised to within about 1 cm. from the bottom of the flask so as to flatten out the flame.

When the liquid boils briskly, allow the steam to blow through the whole apparatus for a few minutes. Then continue the distillation, condensing the steam, until about 50 c.c. of water have been collected in one of the glass cylinders (611), and test this for ammonia by adding 2 c.c. of the Nessler solution. If any coloration is seen, distil over about 50 c.c. more of the water into a fresh cylinder and test again with Nessler solution. Continue this procedure until no ammonia can be found in the last portion of the distillate. The apparatus has now been freed from ammonia.

Pour the requisite quantity of the water under examination into the flask, and distil over three separate portions of about 50 c.c. each into three cylinders. Reserve these in the order in which they have been collected. Then allow the apparatus and its contents to stand by undisturbed for the subsequent determination of the "albuminoid ammonia" (615).

(b) *Process of "Nesslerising."*—Add to the contents of the second of the test-cylinders which contain the distillate, 2 c.c. of Nessler solution, stir well, and place the cylinder on a white tile. Now make a comparison-test by dropping into a clean empty cylinder 1 c.c. of the standard ammonium chloride solution from a burette, adding 50 c.c. of ammonia-free water and 2 c.c. of Nessler solution, and mixing the liquids by stirring. Allow both the cylinders to stand for five minutes before their tints are compared.

If the intensity of colour in the two cylinders is not the same, throw away the contents of the comparison-cylinder and rinse it out with water. Drop into the cylinder either more or less of the ammonium chloride solution, as may be considered necessary, and pour in 50 c.c. of the ammonia-free distilled water. Now mix the liquid with 2 c.c. of Nessler solution, allow the cylinder to stand for five minutes, and compare the coloration with that in the test-cylinder.

These operations are repeated, if necessary, until the colour in the test-cylinder matches that in the comparison-cylinder: the volume of the ammonium chloride solution which has been required is then noted down.

The process may usually be hastened by preparing four standard cylinders containing 0·5. 1, 2 and 3 c.c. respectively of the ammonium chloride solution, together with the ammonia-free water and Nessler solution, and judging the value of any slight variation of colour-intensity from any one of these.

The addition of the ammonium chloride solution to the water must always precede that of the Nessler solution, else the liquid will become turbid and an accurate comparison of the colours will be impossible.

The distillate in the third cylinder may now be tested in the same way with the Nessler solution. It will usually be found to contain no ammonia. But if it requires more than 1 c.c. of the standard ammonium chloride solution, the distillation must be continued, and a fourth cylinder must be collected and tested.

If the colour given by the second cylinder does not require more than 1·5 c.c. of the ammonium chloride solution to match it, the first cylinder may be tested at once in the same way as the second.

If more than 1·5 c.c. of the ammonium chloride solution is required to match the second cylinder, the whole of the first distillate must not be mixed with the Nessler solution, else the colour produced would be too intense to allow of accurate judgment. In this case the volume of the first distillate is ascertained, and 25 c.c. or even less of the distillate are then diluted to 50 c.c. with ammonia-free water, and are tested with the Nessler solution in the manner already described. The total amount of the ammonium chloride solution, which would correspond to the ammonia in the distillate in the first cylinder, is then calculated.

The separate amounts of ammonium chloride required by the different portions of the distillate are now added together, the weight of ammonia present in the chloride is calculated, and from this the weight of ammonia contained in 100,000 parts of the water is found.

Example.—The first cylinder of the distillate from 500 c c of the water required 3 c c, and the second 1·5 c c. of the ammonium chloride solution; the total amount used was therefore 3 + 1 5 = 4 5 c c Hence it follows that half a litre, or 500 grams, of the water contains 4 5 × 0 00001 = 0 000045 gram of NH_3, and the water contains 0 000045 × 200 = 0 009 part of NH_3 per 100,000.

For Interpretation of the Results refer to paragraph 647.

Estimation of Albuminoid Ammonia.

615. Estimation of Albuminoid Ammonia.—When an organic substance containing nitrogen is mixed with alkaline potassium permanganate solution and the liquid is boiled, either a portion or the whole of its nitrogen is evolved as ammonia. The ammonia thus generated has been termed "albuminoid ammonia."

The fraction of the total nitrogen, which is thus converted into ammonia, appears to be definite for any one organic substance; but the fractions of the total nitrogen evolved as ammonia from different substances vary greatly. Hence this method would be of no value for estimating the amount of sewage contamination in a water, if the nitrogenous organic matter in sewage were not fairly uniform in its character. It is maintained that in ordinary water containing sewage, "the disintegrating animal refuse is pretty fairly measured by ten times the albuminoid ammonia which it yields."

Sewage or sewage effluents, and liquids which contain much nitrogenous organic matter, may be acidified and evaporated, and the residue may be treated by the Kjeldahl process (807) The total nitrogen is thus estimated as ammonia

For the estimation of albuminoid ammonia, an alkaline solution of potassium permanganate is required, in addition to the requisites for the process of estimating ammonia (608–613).

616. Preparation of Alkaline Potassium Permanganate Solution.—Pour about 44 c.c. of distilled water into a flask, add 10 grams of potassium hydrate and 0 5 gram of potassium permanganate. While the distillation of the water for the estimation of ammonia is proceeding (614), boil the above liquid vigorously in the open flask. As soon as the liquid has been boiled down to about half its original volume, it is free from ammonia and is ready for use in estimating the albuminoid ammonia.

617. The Process of Estimating "Albuminoid Ammonia."—Add the alkaline potassium permanganate solution (616) to the liquid which is left in the distillation-flask after the estimation of the ammonia (614, a); then pour in sufficient ammonia-free water (610) to bring up the volume to about half a litre.

Boil the contents of the distillation-flask over an Argand flame (95), or over a naked Bunsen flame flattened against the bottom of the flask, until at least four 50 c.c. portions have been collected in separate cylinders (611). Test each of these portions with Nessler solution, starting with the last one, and reject any portions of the distillate which are practically free from ammonia.

If the quantity of ammonia in the distillate is believed to be small, the cylinders may be "Nesslerised" in the manner described in paragraph 614, b. If much NH_3 is present, either proceed as is there directed, or mix the several portions of the distillate together, measure the volume of the mixture, and estimate the ammonia in 50 c.c. of it with the Nessler solution: then calculate the amount of ammonia present in the whole of the mixture.

From the whole amount of "albuminoid ammonia," which has been found in the distillate, the weight which is present in 100,000 of the water is found, as is shown in the Example (614).

For the Interpretation of the Results refer to paragraph 648.

Estimation of the Organic Matter.

618. Estimation of the Oxygen Consumed by the Organic Matter, by the Forschammer or Oxygen Process.—This process enables a judgment to be formed as to the total amount of oxidisable matter present in water. In the absence of nitrite and of other inorganic reducing substances, the amount of oxygen which is required for the oxidation of the organic matter can be accurately determined by this process.

The process consists in mixing a known volume of the acidified water with a known volume in excess of standard potassium permanganate solution. The mixture is allowed to stand for a definite time at a definite temperature, and the organic matter in the water is thus oxidised. The excess of the permanganate remaining after the oxidation is then estimated, and is subtracted from the amount originally added. The result is the amount of permanganate which has been required to oxidise the organic matter.

It is best to mix two samples of the water with the permanganate, and to expose them to a temperature of 27° C. The first is maintained at this temperature for fifteen minutes, and the second for four hours. This procedure gives some indication of the nature of the reducing substance, since nitrites, ferrous salts or sulphuretted hydrogen will effect reduction immediately, whereas a relatively large amount of ordinary organic matter will only reduce the permanganate after a considerable time.

The Following Solutions are required for this process:

(a) *Solution of Potassium Permanganate.*—Dissolve 0·395 gram of pure potassium permanganate in 1000 c.c. of water. Each c.c. of this solution contains 0·0001 gram of oxygen available for oxidation.

(b) *Sodium Thiosulphate Solution.*—Dissolve 2·5 grams of pure recrystallised sodium thiosulphate in a litre of water.

(c) *Dilute Sulphuric Acid.*—Dilute 1 volume of pure strong sulphuric acid with 3 volumes of water, and add $KMnO_4$ solution to the liquid until a very faint but permanent pink coloration is obtained.

(d) *Potassium Iodide Solution.*—Dissolve 1 part of pure recrystallised potassium iodide in 10 parts of water.

(e) *Starch Solution.*—Dissolve 1 part of starch in 100 parts of boiling water (333), and use the clear cold solution.

The Process of Estimating the Oxygen required by the Organic Matter.—Rinse out two 500 c.c. stoppered flasks (A, B), first with strong sulphuric acid to destroy organic matter, and then with distilled water. Measure into each flask 250 c.c. of the water under examination. Place the flasks in a water-bath or air-bath which is kept at a temperature of 27° C. by means of a suitable regulator. When the contents of the flask have attained the temperature of 27° C. measure into each of them 10 c.c. of the standard potassium permanganate solution (a), and 10 c.c. of the dilute sulphuric acid (c), and mix the liquids by shaking them round in the flask. Then restopper the flasks and place them again in the bath.

If the pink colour at any time disappears from the water in the flask, start the process afresh with 20 c.c. of the permanganate solution; and if the pink colour is seen to be diminishing rapidly, add a further 10 c.c. of permanganate solution.

At the expiration of fifteen minutes take flask (A) out of the bath and add a little potassium iodide solution (d). The pink colour of the permanganate will change to yellow, since the oxygen of the permanganate liberates its equivalent of iodine. Now add the thiosulphate solution (b) from a burette, until the colour of the liquid in the flask fades to a pale straw tint. At this stage add 1 c.c. of fresh starch solution (e). A deep blue colour will appear: proceed to add more thiosulphate solution gradually until this colour entirely disappears.

After the other flask (B) has been kept for four hours at 27° C. take it out of the bath and titrate its contents in a similar way.

Then proceed to titrate the standard thiosulphate solution (b), since although the solution may retain its strength for a few days, it is subject to rapid change. To 250 c.c. of pure recently distilled water (1015) add 10 c.c. of the sulphuric acid (c), 10 c.c. of the permanganate solution (a), and a few drops of the potassium iodide solution (d), and titrate this liquid as is directed above.

The Process of Calculation.—Let x represent the number of c.c. of thiosulphate solution which have been used in the titration of the permanganate in the distilled water, and y the number of c.c. used in the titration of

the permanganate in the water under examination. Then $x - y$ is the number of c.c. of thiosulphate solution which are equivalent to the permanganate reduced by the organic matter in the water.

Further, if the amount of available oxygen in the 10 c.c. of permanganate originally added is represented by a, then the weight of oxygen required to oxidise the organic matter in 250 c.c. of the water will be $\frac{(x-y)a}{x}$. But $a = 0{\cdot}001$ gram of oxygen, and 250 c.c. of water were used, therefore the amount of oxygen consumed by 100,000 parts of the water

$$= \frac{(x-y) \times 0{\cdot}001 \times 100{,}000}{x \times 250} = \frac{(x-y)0{\cdot}4}{x}.$$

Example.—In a particular estimation 15 c.c. of the standard thiosulphate solution were required for the distilled water, and 10 c.c. for the water under examination. The amount of oxygen consumed by 100,000 parts would accordingly be in this case $\frac{(15-10)0\,4}{30} = 0\,067$.

Factors for Calculation of the Organic Matter.—Attempts have been made to calculate the amount of organic matter in the water, from the quantity of oxygen which it consumes. It has been shown that no constant relation exists between the amount of oxygen consumed and the amount of organic matter present, except in the case of waters from a similar source, which have been oxidised at the same temperature. By employing a proper factor under these conditions, however, the approximate amount of organic carbon can be calculated from the oxygen consumed.

Thus when oxidation has been effected at about 27° C., the weight of organic carbon is equal to that of the oxygen consumed multiplied by 2 38, in the case of river-waters: in the case of deep well-waters the factor is 5 8, and factors have been determined for waters from other sources.

For the Interpretation of the Results refer to paragraph 649.

Estimation of Chloride.

619. Estimation of Chlorine present as Chloride.—Chlorine is usually present in water in the form of sodium chloride, and its proportion is frequently reported in terms of that salt. The process of estimating chloride in water is identical with that described in paragraph 373, standard solution of silver nitrate being added to the water, which has been mixed with potassium chromate solution to serve as an indicator. Accordingly the solutions required for the estimation are the following:

(a) *Standard Solution of Silver Nitrate.*—Dissolve 2·3944 grams of pure

recrystallised silver nitrate in distilled water, and make the solution up to a litre. If 50 c.c. of water are used for the titration, 1 c.c. of this silver nitrate solution will represent 1 part of chlorine per 100,000 of the water.

(b) *Solution of Potassium Chromate.*—Dissolve 1 part of potassium chromate in 10 parts of water. The chromate solution must be freed from chloride by adding solution of silver nitrate until a permanent red precipitate is obtained, and then filtering the liquid.

The Process of Estimating Chloride.—Pour the silver nitrate solution (a) into a burette, which is graduated into tenths of a c.c. Measure 50 c.c. of the water into a porcelain dish, and add three drops of the potassium chromate solution (b). Now add the silver nitrate solution, drop by drop, until a faint but permanent red colour is imparted to the liquid. This colour is due to the formation of silver chromate, after the whole of the chlorine has been precipitated as silver chloride.

It will be found convenient, until experience has been gained, to prepare a similar dish containing 50 c.c. of water mixed with three drops of the potassium chromate solution, to which silver nitrate solution has been added but not in excess. The faintest appearance of a reddish tint in the test-dish will then be easily seen, if the two dishes stand side by side for comparison.

The number of c.c. of the silver nitrate solution which have been used, represents the weight of chlorine present in 100,000 parts of the water, if 50 c.c of water were used.

For the Interpretation of the Results refer to paragraph **650.**

Estimation of Nitrite.

620. Estimation of Nitrite.—When an acid solution of metaphenylene-diamine is brought into contact with a weak solution of nitrous acid, a reddish brown coloration is produced. A process for the estimation of nitrite is based upon this reaction. The following solutions are required for the estimation.

(a) *Solution of Metaphenylene-diamine.*—Dissolve 5 grams of this substance in a litre of water, to which a little sulphuric acid has been previously added.

(b) *Dilute Sulphuric Acid.*—Add 1 volume of strong sulphuric acid to 2 volumes of distilled water.

(c) *Standard Solution of Sodium Nitrite.*—Dissolve 0·406 gram of pure

silver nitrite in boiling distilled water. Add an excess of pure sodium chloride solution, so that the silver is completely precipitated as chloride. Now make up the liquid to a litre with distilled water. Allow the precipitate to subside, and make up each 100 c.c. of the clear liquid to a litre.

Since the solution undergoes change when it is exposed to the air and to daylight, it should be kept in small stoppered bottles, each of which is completely filled and is then stored in the dark.

One c.c. of this solution corresponds to 0·00001 gram of N_2O_3, and to 0·000006 gram of the nitrite radicle NO_2.

The Process of Estimating Nitrite.—Measure 100 c.c. of the water into a perfectly colourless glass cylinder, similar to those used for the ammonia determination (611). The liquid should fill about three-fourths of the cylinder, and a file-mark should be made upon the side of the cylinder denoting the level of the liquid surface when 100 c.c. are present.

Add 1 c.c. of the dilute sulphuric acid (b), then 1 c.c. of the metaphenylene-diamine solution (a), and stir well with a glass rod. If a coloration is produced at once, a smaller quantity of the water must be taken and diluted to 100 c.c. with pure distilled water. When the coloration only appears after the liquid has stood for one minute, the dilution will be sufficient.

An approximate measurement of the quantity of nitrous acid present is now made, by introducing different fractions of 1 c.c. of the standard sodium nitrite solution (c) into similar separate glass cylinders. Each is then made up to 100 c.c. with distilled water, and 1 c.c. of the acid and 1 c.c. of the metaphenylene-diamine solution are added to each, as is described above.

It must be remembered that the colour develops only slowly, and that the comparison-cylinders will not have had so long a time for the development of colour as the original test-cylinder has had.

Hence, as soon as the approximate matching of colour has been effected, it will be necessary to make a fresh series of tests with the water and with the comparison-cylinders, all of which must be started at the same time. The colours of these liquids should be compared after they have been standing for twenty minutes.

For the Interpretation of the Results refer to paragraph 651.

Estimation of Nitrogen in Nitrite and Nitrate.

621. Three methods are described.

According to the first method (622) the nitrogen is converted into nitric

oxide by the action of strong sulphuric acid and mercury, and the nitric oxide gas is measured.

In the second method (623) the nitrogen is converted into ammonia by the action of the copper-zinc couple (*Note*), and the ammonia is estimated by the Nessler colorimetric process (614).

Note.—A more rapid method for the reduction of the nitrate consists in acidifying its solution with dilute sulphuric acid, and then treating it with iron which has been recently reduced from its oxide by hydrogen The liquid should be kept just boiling for about ten minutes: it is then made alkaline and the ammonia is distilled over, and is estimated either by Nessler solution (614) or by standard acid (295). Fuller details are given in paragraph 623

In the third method (624) the nitrate is caused to form ammonium picrate, and this is estimated colorimetrically. This process estimates nitrate only and not nitrite.

622. Reduction of Nitrate and Nitrite to Nitric Oxide, and Measurement of this Gas: Crum's Method.—The most accurate means of estimating nitrate and nitrite was devised by Crum. According to this method, the solution which contains the nitrate and nitrite is shaken with strong sulphuric acid and mercury in a closed tube. The nitric oxide, which is thus evolved, is measured; and the weight of nitrogen which it contains is calculated. In the absence of other gas apparatus, the nitric oxide may be measured in a carefully calibrated Lunge nitrometer (890).

The Process of Estimation.—Add a small quantity of sulphuric acid, diluted with four times its volume of water, to the residue which was obtained in determining the total solids (606). Warm the dish on the steam-bath to remove CO_2 from any carbonate present, and if the volume of the liquid exceeds 2 c.c. evaporate it down to that volume.

Fill the Lunge nitrometer (890, 892) completely with mercury, pour the liquid from the dish into the cup (*f*) of the nitrometer, and finally rinse out the dish with a very small quantity of the dilute sulphuric acid. Allow the liquid to pass through the stop-cock by gently turning the tap, taking care that no air enters. Then pour about double the volume of pure strong sulphuric acid into the cup, allow this to flow through the stop-cock, and at once shake the measuring-tube in such a way as to cause part of the mercury to mingle in small globules with the hot liquid. This is most readily effected by giving a rotatory as well as a vertical movement to the tube.

After the tube has been shaken for about two minutes, nitric oxide gas will be given off. The agitation must be continued until the evolution of gas ceases, which will usually be the case in about five minutes.

Now allow the liquid to cool down to the temperature of the air, and adjust the levels of the mercury columns as is described in paragraph 892. Note down the atmospheric temperature and pressure, and proceed to calculate the weight of nitrogen in the volume of nitric oxide obtained as is shown in the following example:

Example.—In an estimation of nitrate and nitrite, 500 c.c. of the water yielded 3 3 c.c of nitric oxide gas.

The atmospheric temperature was 20° C, and the atmospheric pressure 766 mm.

Therefore, the volume of the nitric oxide under normal conditions of temperature and pressure $= \frac{3\,3 \times 273 \times 766}{293 \times 760} = 3\,3 \times 0{\cdot}939$ (838, 984).

Now nitric oxide contains half its volume of nitrogen, and the weight of 1 c c. of hydrogen = 0 0000899 gram; therefore, the weight of nitrogen in the nitric oxide $= \frac{1}{2}(3\,3 \times 0\,939 \times 0\,0000899 \times 14) = 0\,00195$.

And since 500 c c. of water were used, the weight of nitrogen in 100,000 parts of the water = 0 00195 × 200 = 0 39.

623. Reduction of Nitrate and Nitrite to Ammonia by means of the Copper-Zinc Couple, and Estimation of the Ammonia.—Zinc, upon which copper has been chemically deposited as a black film, constitutes a "copper-zinc couple." When this is immersed in the solution of a nitrate or nitrite it converts the nitrogen completely into ammonia, which can then be estimated by means of Nessler solution. (See also *Note*, 621).

The following substances should be prepared:

(a) *Pumice.*—Clean pumice is broken into pieces about the size of large shot, and is sifted free from powder; it is then heated to redness for some time, and is kept in a well-stoppered bottle.

(b) *Hydrochloric Acid.*—Strong hydrochloric acid is tested for ammonia, by mixing 0 5 c c. of it with water free from ammonia in a Nessler cylinder (611), and adding 2 c.c of Nessler solution. If it is practically free from ammonia, 10 c.c. are diluted to 100 c c. with ammonia-free water, and the liquid is preserved in a well-stoppered bottle.

The strong acid is freed from ammonia, if necessary, by distillation: that part of the distillate being collected separately which comes over free from ammonia.

(c) *The Copper-Zinc Couple* is prepared by pouring a 3 per cent. solution of crystallised copper sulphate upon pieces of zinc. The zinc may either be in the granulated condition, or it may be prepared by cutting thin zinc sheet or foil into strips and folding these up. The deposition is allowed to go on until the zinc is covered with a firmly adherent black film of copper. This film must not be so copious as to be detached when the zinc is subsequently washed by gently shaking it several times with fresh quantities of water. About 5 grams of zinc should suffice for one estimation, and an immersion of fifteen minutes in the copper solution usually causes a satisfactory film of copper to be deposited upon it.

Process of Estimation.—The process must be conducted in a room which contains no ammonium salts or other sources of ammonia; and before proceeding to make a determination of nitrate, a blank experiment should be made by the process described below. Any amount of ammonia which is obtained in this blank experiment must be subtracted from the ammonia which is found in an estimation.

The process may be carried out either with the water itself, or with the water extract of the solid residue (606). The latter is commonly used when the amount of nitrate present is small.

The ammonia which is produced from the nitrate by the following process may frequently be estimated directly without distillation (2); but distillation (1) is necessary when the water is coloured, or when the amount of nitrate present is small.

(1) *Estimation of the Ammonia by Distillation.*—The copper-zinc couple is prepared, as is directed above (c), in a 300 c.c. stoppered fractionating-flask (612). After the metals have been washed in the flask, finally with ammonia-free water, the tubulure of the flask is connected with a U-tube filled with the pumice (a) moistened with the hydrochloric acid (b); one hundred c.c. of the water, or the equivalent extract of the water-residue (606), are now measured into the flask, which is at once stoppered, and is then allowed to stand for at least an hour.

If any doubt is felt as to the completion of the reduction, a small quantity of the liquid may be tested for nitrite by mixing it with dilute sulphuric acid and with metaphenylene-diamine (620). As soon as no nitrite can be detected the reduction is complete.

Then add to the liquid about a gram of recently ignited sodium carbonate crystals (613), and rinse in the pumice moistened with hydrochloric acid from the U-tube. Connect the tubulure of the flask with a condenser (1016), and proceed to distil over 50 c.c. Mix the distillate well, and measure 5 c.c. into a Nessler cylinder (611). Dilute this with ammonia-free water, and add 2 c.c. of Nessler solution. Proceed in this way to estimate the whole amount of ammonia which has been produced by the reduction of the nitrate, using more than 5 c.c. of the distillate if necessary (614, b)

The amount of ammonia which has been found in the original water must be subtracted from the result thus obtained, unless the ammonia was removed before the reduction by the copper-zinc couple, and the weight of nitrogen which is contained in the ammonia is then calculated as parts per 100,000 of the original water.

(2) *Direct Estimation of the Ammonia without Distillation.*—A volume of 200 c.c. of the original water, or the equivalent volume of the extract of the water-residue, is mixed with a small quantity of oxalic acid solution. The

whole is made up to 250 c.c. with ammonia-free distilled water (610) and is then allowed to stand in a well-stoppered flask until the precipitate of calcium oxalate has completely subsided. Two separate portions (A, B) of the clear liquid are then transferred to Nessler cylinders.

The copper-zinc couple is allowed to act upon one portion (A) for an hour, as has been just described (1), and as soon as the reduction to ammonia is complete, the clear liquid is decanted into another cylinder and 2 c.c. of Nessler solution are added to it. The comparison-test is made by adding the requisite quantity of standard ammonium chloride solution to the other portion (B), and then stirring it with 2 c.c. of Nessler solution (614, b).

The amount of ammonia present in 250 c.c. is then calculated from each result. The difference between these two amounts will represent the amount of ammonia which has been formed by the reduction of the nitrate and nitrite which were originally present in 200 c.c. of the water. From this result the weight of nitrogen present in the nitrate and nitrite is calculated.

By the above procedure allowance is made for the ammonia which was originally present in the water, or was contained in the oxalic acid. The production of turbidity by the addition of Nessler solution is prevented by the previous precipitation of calcium salts by the oxalic acid.

624. Conversion of Nitrate into Ammonium Picrate, and Estimation Colorimetrically.—When phenol-sulphonic acid solution is poured upon a nitrate, and sulphuric acid is added, picric acid is formed:

$$C_6H_4.OH.SO_3H + 3HNO_3 = C_6H_2(NO_2)_3OH + H_2SO_4 + 2H_2O$$

and the addition of ammonia in excess then produces ammonium picrate, the yellow colour of which is easily seen even in a very dilute solution. The degree of intensity of the colour serves to estimate the picrate, and hence the nitrate from which it has been produced.

This process estimates nitrate only, and not nitrite. If nitrite is present in the water, it must be separately determined (620).

The following solutions are required:

(a) *Phenol-sulphonic Acid.*—55·5 c.c. of strong pure H_2SO_4 are added to 4·5 c.c. of water containing 9 grams of phenol. The liquid is shaken and is preserved in a tightly stoppered bottle.

(b) *Standard Potassium Nitrate Solution.*—Some KNO_3 is heated just sufficiently to fuse it; 0·722 gram of the salt is then dissolved in water and the solution is diluted to a litre. Each c.c. of this solution contains 0·0001 gram of nitrogen.

The Process of Estimation.—A measured volume of the water, usually 25 c.c., is evaporated to dryness in a small porcelain dish.

Five c.c. of the standard KNO_3 solution (b) are evaporated in another similar dish.

One c.c. of the phenol-sulphonic acid solution (a) is added to the liquid in each dish as soon as it is cold, and the contents of each dish are thoroughly mixed with small glass rods. One c.c. of distilled water is then added to each dish, followed by 3 drops of strong sulphuric acid, and after the liquids have been well stirred, the rods are rinsed into the dishes with a little distilled water.

The dishes are now heated on the water-bath for five minutes; each dish is then removed from the water-bath and its contents are diluted with 25 c.c. of distilled water and mixed with ammonium hydrate in excess. A deep yellow colour will appear in the standard solution, and also in the water-sample if it originally contained nitrate.

The liquids are now transferred from the dishes to graduated 250 c.c. closed cylinders, and each is diluted to 100 c.c. with distilled water. 50 c.c. of that solution, which shows the lesser intensity of colour, are then placed in a Nessler cylinder (611), and the more intensely coloured liquid is diluted with water and is well mixed by shaking. The dilution is continued until 50 c.c. of the liquid, when poured into a Nessler cylinder, exactly matches in intensity the tint of the originally paler liquid. The total volume in c.c. of the diluted liquid is then noted down, the volume of the other being 100 c.c.

The Formula for Calculating the weight of nitrogen (N) present as nitrate in 100,000 of the water is

$$N = \frac{50 \times \text{Number of c.c. of the sample after dilution}}{\text{No. of c.c. of the water used} \times \text{No. of c.c. of standard after dilution.}}$$

Example.—In a particular case 25 c.c. of the water-sample were used. In the process of matching the colours the yellow liquid from the water was made up to 100 c.c., while the yellow liquid from the standard nitrate solution was made up to 250 c.c. Hence N, the weight of nitric nitrogen present per 100,000 of the water $= \frac{50 \times 100}{25 \times 250} = 0.8$.

For the Interpretation of the Results obtained refer to paragraph **652**.

Estimation of Hardness.

625. The "Hardness" of Water, or its soap-precipitating power, depends upon the amount of calcium and magnesium salts which it contains, since these salts act chemically upon soap and precipitate it from solution. Other salts are occasionally present in water which act in a similar way upon soap; and if much sodium chloride is present, it precipitates the soap from its solution in an unaltered state.

Hardness is of two kinds: "temporary hardness," which can be removed

by boiling the water; and "permanent hardness," which cannot be removed in this way.

Two processes for the estimation of hardness are described.

Clark's Method (626) is the older process; it does not yield accurate results if a large quantity of magnesium salts is present.

Hehner's method (631) gives on the whole better results, since the presence of magnesium salts does not materially affect the process.

For the Interpretation of the Results of Analysis refer to paragraph 653.

Estimation of Hardness by Soap Solution.

626. Clark's method depends upon the fact that when solution of soap is mixed with solution of a calcium or magnesium salt, an insoluble calcium or magnesium soap is produced. Accordingly no lather will form when the water is shaken with soap solution, until the soap solution has been added in excess and some soap therefore remains unaltered in the liquid.

The solution of soap in methylated spirit, which is used in this process, is first titrated by means of a standard calcium chloride solution, and is then brought to the requisite strength. The water is tested with this standard soap solution, and the number of "degrees of hardness" of the water are obtained from the amount of soap solution which is required to precipitate the hardening salts. Each degree of hardness corresponds to one part of $CaCO_3$ per 100,000 of water, and the result is therefore expressed in these terms.

The following solutions are required for the estimation:

(a) *Standard Solution of Calcium Chloride.*—Weigh accurately 0·2 gram of pure iceland-spar, and dissolve it in dilute hydrochloric acid, taking care to keep the vessel covered so as to prevent loss by spirting. Evaporate this solution to dryness on the water-bath; then add water and again evaporate to dryness, and repeat these processes, once at least, in order to remove all free hydrochloric acid. Now dissolve the residue of neutral calcium chloride in water, and make the solution up to a litre.

(b) *Preparation of Soap Solution.*—Potassium oleate soap is prepared by rubbing in a mortar 150 parts of lead plaster (Plumbi Emplast., *B.P.*) with 40 parts of dry potassium carbonate. When these substances have been thoroughly mixed a little methylated spirit is added, and the process of mixture in the mortar is continued until a creamy mass is formed. This is stirred with more spirit, and is decanted after the sediment has subsided.

(c) *Titration and Dilution of Soap Solution.*—This strong soap solution now requires to be diluted, until 14·25 c.c. of it just produce a permanent lather when they are shaken with 50 c.c. of the standard calcium chloride solution.

Mix the strong soap solution with methylated spirit which has been diluted with half its volume of water, and pour some of this solution into a burette. Measure 50 c.c. of the calcium chloride solution (a) into a stoppered bottle of 250 c.c. capacity, allowing the liquid to flow out of the pipette without blowing any carbon dioxide from the lungs into the bottle (*Note* p. 313).

Now allow 1 c.c. of the soap solution to flow from the burette into the bottle, and close the bottle and shake it vigorously for a short time. If no permanent lather is produced, add another c.c. of the soap solution and shake again.

Continue the addition of the soap solution, shaking the water well after each addition, until a lather is formed which remains for a short time when the bottle is laid upon its side on the bench. The process is finished when the lather remains upon the surface as an unbroken layer for five minutes.

Towards the end of this operation, the amount of soap solution which is added should be lessened, and it should finally not exceed one-fifth of a c.c. Experience renders it possible to detect the approach of the end of the reaction by the sound and sensation produced during shaking, since the sound and shock become much more gentle when a lather begins to form.

The soap solution can now be diluted from calculation (287), and its strength must be ultimately adjusted so that exactly 14·25 c.c. are required to produce the lather with 50 c.c. of the calcium chloride solution.

The strength of the soap solution should be checked after it has stood for about twenty-four hours, since a sediment usually forms which reduces its value. It is on this account preferable to defer the final dilution and titration of the solution until no further sediment is deposited.

Another Method of Preparing the Soap Solution is to dissolve 80 grams of chemically pure oleic acid in alcohol. A few drops of phenol-phthalein are mixed with this solution, and a strong solution of potassium hydrate in alcohol is then gradually added until the oleic acid is exactly neutralised and saponification is therefore complete. This is indicated by the liquid retaining a faint purple coloration. The solution is then titrated with the standard calcium chloride solution (a), and is diluted to standard strength (c).

627. Estimation of the Total Hardness.—Measure 50 c.c. of the water into a stoppered bottle of 250 c.c. capacity. Shake the water well, and remove any carbon dioxide, which has been evolved, by sucking out the air from the upper part of the bottle by means of the pipette; repeat these processes once at least (*Note*). Then proceed to titrate the water with the standard soap solution in the manner already described (626, c).

If more than 16 c.c. of soap solution are required by the water, dilute a

suitable measured quantity of the water to 50 c.c. with boiled distilled water (*Note*), and titrate again.

The number of degrees of hardness in the water, expressed as parts of calcium carbonate per 100,000, may now be obtained from the number of c.c. of soap solution used, by reference to the Hardness Table (630).

If much magnesium salt is present, it will be difficult to ascertain the end of the process. This is partly due to the formation of a permanent scum upon the water, but also to the fact that the soap solution acts much more slowly upon magnesium salts than it does upon calcium salts. When magnesium salts are present, it is best to dilute the water until not more than 7 c.c. of the soap solution are required for the titration, and after the titration is finished the bottle should be allowed to stand for at least ten minutes, in order to make certain that the lather is of a permanent nature.

Note.—Various precautions are mentioned in the above description of the process for determining the hardness, with the object of preventing the introduction of carbonic acid Carbonic acid acts chemically upon soap in such a way as to prevent it from giving a lather when its solution is shaken Hence, before any soap solution is added to a measured sample of water, the sample should be repeatedly shaken vigorously in the bottle, and the CO_2 which is liberated should be sucked out by a tube after each shaking For the same reason all distilled water, which is used for dilution or for making solutions, should have been recently boiled and quickly cooled.

628. Estimation of the Permanent Hardness. — The method consists in boiling the water until all the hardening salts, which are precipitable by boiling, are thrown out of solution. The liquid is then made up to its original volume with air-free distilled water, and is filtered if necessary. The hardness is determined in the clear filtrate.

Measure about 250 c.c. of the water into a flask, and weigh the flask with the water. Boil the water gently for half an hour, adding boiled distilled water from time to time, in order to replace the water which evaporates. Now cool the water quickly, and make up the flask and water to their original weight (*Note*) with cold recently boiled distilled water (627, *Note*). Mix well, pour the water through a dry filter, and titrate a suitable volume of the filtrate with soap solution as was described in paragraph 627.

The degrees of Permanent Hardness are then obtained by reference to the Hardness Table (630).

Note.—Instead of weighing the water, an exactly measured volume of the water may be taken, and the water may be made up to the same volume again after it has been boiled and filtered. This procedure is, however, less rapid in practice than weighing.

629. Temporary Hardness.—The difference between the Total Hardness

and the Permanent Hardness gives the Temporary Hardness of the water.

HARDNESS TABLE.

630. Parts of $CaCO_3$ per 100,000.

c c of Soap Solution	Parts of $CaCO_3$	c c of Soap Solution	Parts of $CaCO_3$	c c of Soap Solution	Parts of $CaCO_3$	c c. of Soap Solution.	Parts of $CaCO_3$	c c of Soap Solution.	Parts of $CaCO_3$	c.c of Soap Solution	Parts of $CaCO_3$
0 7	00	3 3	3·64	5·9	7 29	8 5	11 05	11 1	15 00	13 7	19 13
·8	·16	·4	·77	6·0	·43	6	20	2	16	8	·29
·9	·32	·5	·90	·1	·57	·7	·35	·3	·32	9	44
1·0	·48	·6	4 03	·2	·71	8	·50	·4	·48	14 0	60
·1	63	·7	·16	·3	86	9	·65	·5	63	·1	·76
·2	·79	8	29	·4	8 00	9 0	80	6	79	·2	92
3	95	9	43	·5	·14	·1	95	·7	95	3	20 08
·4	1 11	4 0	57	6	·29	2	12 11	·8	16 11	4	24
5	27	1	71	7	·43	3	26	9	27	·5	40
·6	43	2	86	8	·57	·4	·41	12 0	43	6	56
·7	56	·3	5 00	9	71	·5	·56	1	59	7	71
8	69	·4	·14	7 0	86	6	71	2	75	8	87
9	82	5	29	1	9 00	7	86	·3	90	·9	21 03
2 0	95	6	43	2	14	8	13 01	4	17 06	15 0	19
1	2 08	7	57	3	·29	9	16	·5	22	·1	35
2	21	8	71	·4	43	10 0	31	6	38	2	·51
3	·34	9	86	5	57	1	46	7	·54	·3	68
4	47	5 0	6 00	6	71	2	61	8	·70	4	85
5	·60	1	14	7	86	3	76	9	·86	5	22 02
6	·73	2	29	8	10 00	4	91	13 0	18 02	6	18
7	86	·3	43	9	15	5	14 06	1	·17	7	35
·8	·99	4	57	8 0	30	6	21	2	33	8	·52
9	3 12	·5	71	·1	45	7	37	3	·49	9	69
3 0	25	6	86	·2	60	8	52	4	65	16 0	86
1	38	7	7 00	3	75	9	68	5	·81		
2	·51	8	14	·4	90	11·0	84	6	·97		

Estimation of Hardness by Standard Acid.

631. The calcium and magnesium carbonates, which cause the temporary hardness, are first determined by titration with standard acid in a portion of the water (632).

The sulphates and other soluble salts of calcium and magnesium are then removed, together with the carbonates, from another portion of the water, by adding a known volume of standard sodium carbonate solution in excess, and boiling for half an hour, or evaporating to dryness if magnesium is present; the unchanged sodium carbonate is then estimated by means of standard acid (633). The amount of sodium carbonate which has been

decomposed by the above soluble salts is thus found, and from this the permanent hardness is calculated.

The hardness is expressed as parts of $CaCO_3$ per 100,000.

The following solutions are required:

(a) *Decinormal Sulphuric Acid.*—Dilute 100 c.c. of normal sulphuric acid (285) to a litre.

(b) *Decinormal Sodium Carbonate Solution.*—Dissolve 5·305 grams of pure dry sodium carbonate (284) in water, and make this solution up to a litre. The solution may also be prepared by diluting 100 c.c. of normal sodium carbonate solution (283) to a litre.

(c) *Methyl-orange* (268) is used as an indicator in these titrations, because it is not affected by carbonic acid.

632. Estimation of the Temporary Hardness.—Add to 500 c.c. of the water, or less if it is very hard, a few drops of methyl-orange (c). Then add the decinormal sulphuric acid (a) from a burette, until the colour of the solution just changes to the pink tint. From the number of c.c. of acid used, the corresponding amount of $CaCO_3$ is calculated, and this is converted into parts per 100,000.

Note.—The end of the reaction is somewhat difficult to determine by the gradual change of the yellow colour of the methyl-orange to pink, and a sharper change may be obtained by using decinormal hydrochloric acid with lacmoid solution as indicator. It is best to add a few drops of the lacmoid solution to the boiling water, and to titrate while the water is actually boiling.

The lacmoid solution is prepared by dissolving 2 grams of lacmoid in dilute alcohol and making this solution up to a litre.

633. Estimation of the Permanent Hardness.—To 250 c.c. of the water add 50 c.c. of the decinormal sodium carbonate solution (b), and boil for about half an hour. If magnesium salts are present, evaporate to dryness and extract the residue with water. Filter, and wash the precipitate or the insoluble matter with boiled distilled water, and make the cold filtrate up to 250 c.c.

Titrate 50 c.c. of the filtrate with the decinormal acid (a), using methyl-orange (c) as an indicator (632, *Note*).

From the number of c.c. of acid which have been used, the weight of Na_2CO_3 used in precipitating the hardening salts may be found, and from this the permanent hardness is calculated in terms of $CaCO_3$ and is then converted into parts per 100,000.

The Total Hardness may be obtained by adding together the temporary and the permanent hardness.

Example—In an estimation of temporary hardness in a water, 500 c c. of the water required 8 4 c c of decinormal sulphuric acid. Now 1 c c of this acid corresponds to 0 005 gram of $CaCO_3$, therefore the weight of $CaCO_3$, which would neutralise the acid used in the titration, is 8 4 × 0 005 = 0 042 gram. Hence the temporary hardness as parts of calcium carbonate per 100,000 = 200 × 0 042 = 8 4.

In estimating the permanent hardness, 250 c c of the water were boiled with 50 c c. of decinormal sodium carbonate solution, and after filtration the filtrate was made up to 250 c c Fifty c c of this liquid required 8 6 c c of decinormal sulphuric acid for neutralisation Hence the permanent hardness in the 50 c c. used corresponds to 10 – 8 6 = 1 4 c c. of decinormal sodium carbonate solution, since 10 c c. of Na_2CO_3 solution were present in every 50 c c of the solution. Therefore the number of c c of Na_2CO_3 solution corresponding to the permanent hardness in the 250 c c of the water used = 1 4 × 5 = 7. And since 1 c c of the sodium carbonate solution corresponds to 0 005 gram of $CaCO_3$, the permanent hardness in 100,000 parts = 7 × 0 005 × 400 = 14

Hence the total hardness = 14 + 8 4 = 22 4

634. Estimation of Sodium Carbonate.—When the water contains sodium carbonate, it will be distinctly alkaline in reaction and no permanent hardness will be present. The amount of sodium carbonate present in the water can be easily estimated by means of the standard acid (a), since the sodium carbonate will remain in solution after the water has been boiled. It can therefore be titrated in the filtrate after the carbonates of magnesium and calcium have been precipitated by boiling the water for the determination of the permanent hardness.

For the Results of Analyses of Water refer to paragraph **964**, and to paragraphs **646** **654** for the consideration of the results of analysis.

ESTIMATION OF OTHER SUBSTANCES IN WATER.

For ordinary purposes the estimations described above are sufficient. But other processes are appended for the detection and estimation of poisonous metals, for certain estimations which are required for technical purposes, and for the estimation of dissolved oxygen.

Refer to paragraph **654** for the limiting amounts of poisonous substances allowable.

Detection and Estimation of Poisonous Metals.

635. Copper and lead are the most commonly occurring poisonous metals in water: arsenic, barium, and zinc may be tested for in exceptional cases.

Copper and lead may often be detected by placing 200 c.c. of the water in a glass cylinder (**611**), and adding 10 c.c. of acetic acid and 10 c.c. of saturated solution of hydrogen sulphide. The tint of the well-mixed liquids will be darker in tint than that of the same water similarly mixed with 10 c.c. of acetic acid only, if lead or copper or both should be present.

Small traces of these metals, which cannot be found directly in the water, may be detected by evaporating a measured quantity of the water down to a small volume, rendering it just acid with a few drops of acetic acid, then dividing this liquid into two parts and testing as is directed above.

The quantity of metal present may be estimated colorimetrically (**636, 637**), or the metal may be estimated gravimetrically if an appreciable quantity of sulphide is precipitated.

636. Estimation of Copper.—Prepare a standard copper sulphate solution containing 0·3929 gram of crystallised copper sulphate per litre. Each c.c. of this solution corresponds to 0·0001 gram of copper.

Evaporate 500 c.c. of the water to 50 c.c., add 5 c.c. of decinormal acetic acid, and transfer the liquid to a glass cylinder (**611**). Then add a few drops of very dilute potassium ferrocyanide solution. If copper is present, a reddish brown tint will appear (*Note*).

Match the intensity of this colour by mixing a suitable measured volume of the standard copper solution in a similar cylinder with 50 c.c. of distilled water, which has been acidified with 5 c.c. of decinormal acetic acid and mixed

with the same quantity of potassium ferrocyanide solution as has been already used.

The weight of copper present in 100,000 parts of the water = $n \times 0{\cdot}0001 \times 200 = n \times 0\,02$, where n represents the number of c.c. of the standard copper solution which correspond to the copper in 500 c.c. of the water.

Note.—If iron is also present in the water the coloration produced on adding the ferrocyanide will be altered by the formation of Prussian blue. The iron should therefore be removed from the water by adding a few drops of nitric acid, evaporating considerably and precipitating by an excess of ammonium hydrate. The precipitate should be filtered off and dissolved in nitric acid, then precipitated once more by ammonium hydrate, filtered off and washed. The precipitate may be used for the estimation of iron (641) and the filtrate and washings may be neutralised with HNO_3 and used for the estimation of copper.

637. Estimation of Lead.—If copper is absent (*Note*), lead may be estimated by the following method:

Prepare a standard lead acetate solution containing 0·1831 gram of normal lead acetate per litre, and a little free acetic acid which is added to keep the solution clear. Each c.c. of this solution corresponds to 0·0001 gram of lead.

A direct estimation may often be made by mixing with 200 c.c. of the water in a glass cylinder (611) 10 c.c. of normal acetic acid and 10 c c. of hydrogen sulphide solution. The intensity of the dark coloration thus produced is matched in a similar cylinder, containing 200 c.c. of distilled water 10 c c. of normal acetic acid and 10 c.c. of hydrogen sulphide solution, by adding the appropriate volume of the standard lead acetate solution. This may be effected by dropping in the lead solution gradually from a burette and mixing well: but a second experiment must be made in which the whole volume of the lead solution is added to the acidified distilled water at once and then the hydrogen sulphide solution is added and well mixed.

It may be found advisable to use only 100 c.c. of water if the dark coloration is too strong, and if the coloration is too slight it is well to evaporate 500 c.c. down to 50 c.c. and to use this for the estimation.

Note.—If both copper and lead are present in the water, estimate the copper (636) and then add a corresponding amount of the standard copper solution (636) to 50 c c of distilled water before introducing the standard lead acetate solution for the comparison test. In this way the coloration due to the presence of copper may be allowed for.

638. Action of Water on Lead.—Rain-water, many natural soft waters, and waters containing natural vegetable acids, act upon lead or a lead-alloy if they remain in contact with it during storage or conveyance. It is therefore advisable to ascertain whether water, which is to be used for drinking purposes, has any action upon lead.

Hard waters do not as a rule act upon lead unless they contain much carbonic acid. This is due to the fact that the hardening constituents rapidly form an insoluble coating upon the surface of the lead, and this prevents the further action of the water.

The behaviour of a sample of water towards lead may be tested as follows: Cut off two strips of sheet-lead; scrape one of these so as to expose the bright surface of the metal, and leave the other in its tarnished condition. Immerse the lead strips in separate beakers of the water, and allow them to stand undisturbed for twenty-four hours. Then note the appearance of the lead and of the water.

If the surface of the lead has remained unchanged in appearance, and the water is perfectly clear and bright even after it has been shaken, the water has probably not acted upon the lead, since a white insoluble basic lead carbonate is usually formed by the action. To make sure whether any solvent action has occurred, however, it is best to remove the lead strips, and to test the water for lead in solution by adding a little saturated solution of hydrogen sulphide, as has been described above (637).

The Relative Action of Samples of Different Waters on lead may be estimated as is described below. The procedure is given for bright lead, but it would be precisely similar for tarnished lead, the preparatory scraping of the surface only being omitted.

A strip of sheet lead, 1·5 cm. wide, is scraped bright, and is cut into lengths of 2·5 cm.

10 c.c. of each of the different water-samples are introduced into separate test-tubes, 15 cm. long and 2 cm. in diameter, and a piece of the bright freshly scraped lead, which has been rubbed with a clean cloth and has not afterwards been touched with the fingers, is dropped into each tube. The tubes are then shaken to detach any air-bubbles from the lead, and are allowed to stand for three, seven or fourteen days, as may be decided upon.

The water is then poured off from each tube into a glass cylinder with a mark at 100 c.c. capacity (611). The lead is rinsed in the tube by shaking it with about 10 c.c. of distilled water, and this water is poured into the cylinder; the lead is then removed and is rinsed, if necessary, by the jet of water from the wash-bottle to remove any adherent lead compound into the cylinder. 10 c.c. of decinormal acetic acid are now poured into the test-tube, from which the lead-strip has been removed, in order to dissolve any lead compound adhering to the glass: this acid is poured into the cylinder and the test-tube itself is finally rinsed out into the cylinder. The liquid in the cylinder is then stirred, if necessary, until all lead compounds are dissolved and the liquid is quite clear: it is then made up to the 100 c.c. mark and is well mixed by stirring.

This liquid, or an aliquot portion of it, is now used for estimating the lead in a manner similar to that described in paragraph 637; the dark coloration yielded by a measured volume of hydrogen sulphide solution being matched in intensity by the coloration produced by a known volume of standard lead solution and the same volumes of hydrogen sulphide solution and of acetic acid being present in the same liquid volume in each case.

For Limiting Amounts of Poisonous Substances refer to paragraph 654.

Estimation of Mineral Constituents.

639. Estimation of Iron.—If the quantity of iron present is small, it may be most readily estimated colorimetrically as follows. If the quantity is large, the iron may be estimated with greater accuracy gravimetrically (640, 641).

For the colorimetric estimation prepare a standard iron solution by dissolving 0·861 gram of iron alum, $Fe(NH_4)(SO_4)_2\ 12H_2O$, in a litre of water. This solution contains 0·1 gram of iron per litre.

Evaporate 500 c.c. of the water to dryness, after adding a few drops of nitric acid free from iron. Dissolve the residue in 50 c.c. of water, pour the solution into a glass cylinder (611), and add 1 c.c. of very dilute potassium ferrocyanide solution.

If a blue colour appears at once, or develops in the liquid after it has been allowed to stand, iron is present. Match the intensity of colour of this liquid by adding to 50 c.c. of distilled water in another cylinder a known volume of the standard solution of ferric salt, a few drops of nitric acid, and 1 c.c. of the ferrocyanide solution.

The amount of iron present in 100,000 parts of the original water is equal to $n \times 0{\cdot}02$, where n represents the number of c.c. of the standard iron solution which correspond to the iron in 500 c.c. of the water.

640. Estimation of Silica.—Acidify a litre of the water with hydrochloric acid, and evaporate it to dryness. Dry the residue in the steam-bath, and finally at 150° in the air-bath; then moisten it with hydrochloric acid, add water, and heat. Filter off any insoluble residue of silica, and wash, ignite, and weigh it. Preserve the filtrate.

641. Estimation of Iron and Calcium.—If the quantity of iron present is too large to be estimated colorimetrically by the above directions (639), add a few drops of strong nitric acid, free from iron, to the filtrate from the silica (640), and boil. Then add a little ammonium chloride solution,

and a slight excess of ammonium hydrate. Filter off and ignite the ferric hydroxide, and weigh the iron as Fe_2O_3 (129).

Add excess of ammonium oxalate solution to the filtrate, allow the liquid to stand, filter off and ignite the calcium oxalate, and weigh the calcium as oxide (146, 147).

642 **Estimation of Magnesium.**—Evaporate the filtrate from the calcium oxalate to dryness, expel the ammonium salts from the residue by ignition, dissolve the residue in hydrochloric acid, add water, and filter if necessary. Then add a moderate excess of ammonium hydrate, and then sodium phosphate solution. Filter, wash and ignite the precipitate, and weigh the magnesium as pyrophosphate (165).

643. **Estimation of Sulphate.**—Acidify 500 c.c. of the water with hydrochloric acid, and evaporate to about 50 c.c. Add barium chloride solution in excess. Filter off, ignite, and weigh the precipitate of barium sulphate (133).

644. **Estimation of the Alkali-metals.**—Concentrate a litre of the water by evaporation to about 100 c.c. Precipitate the sulphate completely from this liquid by adding barium chloride solution. Filter, and boil the filtrate with milk of lime in order to precipitate the iron and magnesium. Filter, and precipitate the barium and calcium from the filtrate by adding excess of ammonium hydrate, then ammonium carbonate solution and a few drops of ammonium oxalate solution. Filter, evaporate the filtrate to dryness, and expel the ammonium salts from the residue by ignition.

Extract the residue with water, filter if necessary, and add one drop of ammonium oxalate solution in order to ascertain that all the calcium is precipitated. Filter again if necessary, acidify with hydrochloric acid, evaporate to dryness in a weighed dish, ignite the residue of alkaline chlorides gently, and weigh it (428). The amounts of potassium chloride and of sodium chloride in this residue may then be estimated if necessary (429).

Estimation of Dissolved Oxygen.

645. The amount of dissolved oxygen which a water contains originally, and especially the amount which it loses when kept, is a most important criterion of what may be termed active organic pollution. An average potable fresh-water supply should contain from 6 to 7 c.c. of oxygen per litre (973, 974), and this amount should not be reduced when the water is stored.

A simple method of determining the dissolved oxygen which can, if

necessary, be applied at the place where the sample is collected, is described below. Two gasometric methods, which can only be carried out in the laboratory on samples previously collected, are subsequently described in paragraphs 896, 897.

The Method consists in absorbing the dissolved oxygen, which is contained in a measured volume of the water, by adding to the water an excess of a mixture of solutions of ferrous sulphate and of ammonia in a vessel which is completely filled with the liquids and is closed from the air. Sulphuric acid is then added in excess, and the acid mixture is transferred to an open dish and titrated with either permanganate or bichromate standard solution (306, 319). The dichromate solution is generally to be preferred, and especially for impure water and sewage effluents.

The process is comparable in regard to accuracy with gasometric methods and is much more readily carried out. The presence of nitrite in the water does not affect its accuracy unless the amount of nitrous nitrogen exceeds 0·07 parts per 100,000.

The Following Standard Solutions and Apparatus will be required:

(a) *Ferrous Sulphate Solution.*—About 12 grams of the crystallised salt are dissolved and made up to 250 c.c. with distilled water. 12·444 grams would give a solution, each c.c. of which is equivalent to 1 c.c. of oxygen under normal conditions. But nothing is gained by preparing a solution of exactly this strength, since it becomes turbid after some days, and when it is cleared by filtration before using it for a series of determinations, its strength is altered and must be redetermined. It is best to treat the solution as one which varies in strength by being kept, and which therefore requires frequent titration.

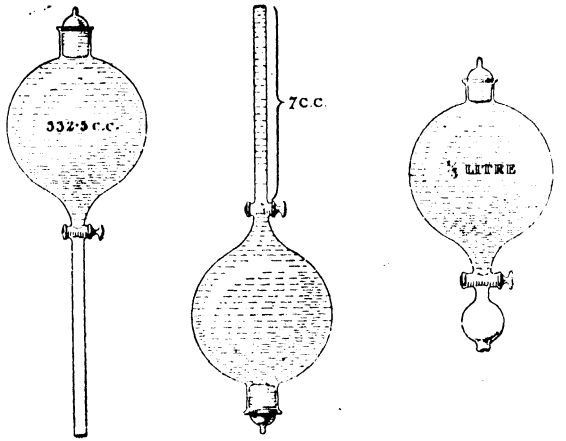
(b) *Standard Permanganate Solution.*—A solution of such strength that 1 c.c. is equivalent to 1 c.c. of oxygen under normal conditions of temperature and pressure is obtained by dissolving 5·6538 grams of the pure crystallised potassium salt and making the solution up to a litre with distilled water. A decinormal solution is also suitable, 1 c.c. of which corresponds to 0 56 c.c. of oxygen under normal conditions.

For the estimation of the dissolved oxygen in distilled water, or in ordinary water, a solution of one-tenth the first-mentioned strength may be used; but for all practical purposes the stronger solution will be found to give sufficiently accurate results, especially if a narrow burette of 10 c.c. capacity is employed, with which readings may be made accurately to 0 025 c.c. The stronger solution keeps well in the dark, but the weaker one should be prepared freshly from the former for each series of experiments.

(c) *Standard Dichromate Solution*, of a strength corresponding with that of the permanganate, may also be used, and in the case of sewage effluents and of sea-water is undoubtedly to be preferred. When dichromate solution is used, potassium ferricyanide must be employed as an indicator (306); and as the ferrous sulphate solution is highly diluted by the water under examination, a strong dichromate solution should be employed. This is prepared by dissolving 8·7906 grams of the pure crystallised potassium salt and making the solution up to a litre with distilled water. Each c.c. of this solution corresponds to 1 c.c. of oxygen measured under normal conditions.

(d) *Dilute Sulphuric Acid.*—A mixture of equal volumes of the strong acid and water is prepared.

FIG. 94.



ESTIMATION OF DISSOLVED OXYGEN.

(e) *The Absorbing vessel.*—The vessel in which the water under examination is mixed with the solutions of ferrous sulphate and of ammonia, and in which the mixture is afterwards acidulated with sulphuric acid, may be an ordinary stoppered separating-funnel of the shape and capacity shown in the diagram (Fig. 94, A). Its exact capacity and dimensions are immaterial if the vessel holds a sufficient volume of water, and if the tube forming its lower extremity is wide enough to contain, when inverted (B), the quantity of sulphuric acid which is required to acidify the ammoniacal mixture before titration.

Since an ordinary separating-funnel is, however, somewhat unwieldy for the purpose of these determinations, owing to the length of its tube, a special form of apparatus (Fig. 94, C) which contains exactly one-third of a litre will

be found very convenient. This can be purchased, together with the whole of the necessary apparatus and reagents for the determinations, suitably packed in a portable box.

The Process.—The absorbing-vessel (e) is completely filled with the water under examination, which has been collected and stored in a Winchester-quart bottle filled to the brim and then stoppered. One limb of a glass siphon-tube is dipped almost to the bottom of this bottle, while the other and longer limb is connected with a piece of rubber tube provided with a screw-clamp.

A little of the water is first drawn off and the absorbing-vessel is rinsed with it. The end of the rubber tube is then passed to the bottom of the vessel, the clamp is opened, and the water is allowed to flow in until it has filled the vessel and a fair quantity has overflowed. In this way the possibility of error arising from the absorption of atmospheric oxygen by the upper layer of the water, as it flows into the wide part of the vessel, is avoided.

The stopper is now inserted and the excess of water is drained off. The stopper is then removed and about 7 c.c. of the water are taken out by a pipette and thrown away. If the vessel is of about the capacity specified, 5 c.c. of the clear ferrous sulphate solution (a) are carefully measured off into a graduated pipette and are allowed to flow into the absorbing-vessel, the nozzle of the pipette being dipped just below the surface of the water: the ferrous sulphate solution, owing to its higher density, will flow at once to the bottom of the water. Strong ammonia solution is then cautiously poured upon the top of the water until the vessel is just full, and the stopper is at once inserted.

If a few drops of the ammonia solution is lost when the stopper is being inserted, no harm is done, since the ammonia solution floats on the surface and does not appreciably mix with the contents of the vessel. But no air-bubble must be inclosed, and a little dexterity is necessary to prevent this while the stopper is being pushed in.

There is now a layer of ferrous sulphate solution at the bottom of the absorbing-vessel, above this is the sample of water, and above this again the ammonia solution. These are mixed together by inverting the vessel once or twice with a swinging motion. A greenish turbid mixture is thus produced, which contains ferrous hydroxide partly in solution and partly in suspension, and this rapidly darkens as it absorbs the dissolved oxygen from the water. Fifteen minutes may be allowed for the completion of this absorption.

The stoppered vessel is now inverted (Fig. 94, B), and its tube or lower extremity, which is now uppermost, is filled with the dilute sulphuric acid (d). The stop-cock is then opened and the acid is allowed to flow down into the alkaline mixture. In the course of a few minutes the iron hydroxides will

be dissolved, and a clear liquid will be produced; this may be hastened, if necessary, by applying a gentle heat.

An air-bubble, if present in the bore of the stop-cock, will prevent the flow of the acid, but a few sharp taps will cause it to be displaced and to rise through the liquid and escape into the air.

The acidified solution is then allowed to flow into a porcelain dish, and is titrated with either the permanganate or the dichromate solution.

It still remains to determine the value of the ferrous sulphate solution under conditions similar to those present in the estimation itself. The absorbing-vessel is filled with the water under examination, 7 c.c. are removed, and the remainder is poured into a porcelain dish, where it is mixed with the same volumes of the dilute sulphuric acid (d) and of the ferrous sulphate solution (a) as were employed in the estimation, and the mixture is then titrated. In this way, the error arising from the oxidisable substances present in the water is eliminated, even when their amount is considerable.

It is convenient to determine the value of the iron solution in this way during the interval required for the absorption of the dissolved oxygen, and consequently as a preliminary to the latter process to fill the absorbing-vessel with the water under examination, and to transfer the latter, after removing 7 c.c., to a porcelain dish ready for the addition of the ferrous sulphate solution and the dilute sulphuric acid.

Calculation of Results.—When the stronger solution of either the permanganate or the bichromate is used, the number of c.c. of dissolved oxygen at 0° C. and 760 mm. pressure, which were present in the volume of water, are equal to the difference between the burette reading for the blank experiment and that for the actual determination. This is on the assumption that the 7 c.c. of mixed reagents contained the same proportion of dissolved oxygen as the water under examination, which is practically true.

Thus in a particular determination, 332·5 c.c. of the water were taken, and the difference between the burette readings for the blank and for the dissolved oxygen determination was 2·35 c.c.

Assuming that the 7 c.c. of reagent added contained the same amount of dissolved oxygen as the water under examination, then a litre of the water contained $\frac{2{\cdot}35 \times 1000}{332{\cdot}5} = \frac{2350}{332{\cdot}5} = 7{\cdot}067$ c.c. of dissolved oxygen at 0° C. and 760 mm.

For the Results of Estimation of Oxygen in Water refer to paragraphs **971-974.**

GENERAL REMARKS ON THE RESULTS OF THE CHEMICAL EXAMINATION OF WATER.

Note.—The results of the above estimations are expressed in parts per 100,000; they can be converted into grains per gallon by being multiplied by 0·7.

646. Total Dissolved Solids (606).—Water which leaves a large residue on evaporation is not suitable for manufacturing purposes, since its use leads to waste of soap in washing, and produces scale in steam-boilers. Such water is not, however, necessarily undesirable for use as drinking-water.

The amount of dissolved solids present in water depends mainly upon the nature of the soil through which the water has percolated. River-water usually contains from 10 to 30 parts of dissolved matter per 100,000. Shallow well-water may contain from 30 to 200 parts or even more, the variation in this class of waters being very great. Deep well-waters may contain from 20 to 70 parts, but the proportion varies even beyond these limits in some cases.

The weight of total solids found should be approximately equal to the sum of the weights of all the constituents estimated separately.

647. The Ammonium Salts (607) present in water are almost invariably of animal origin. Their presence usually points to recent sewage contamination, since ammonia is one of the first products of change of nitrogenous animal refuse. When ammonia is present in water which contains calcium or magnesium carbonates, it is readily oxidised to nitrite and nitrate; hence its amount is reduced by keeping the water, and it should therefore be estimated as soon as possible after the water has been collected.

The amount of ammonia which is present as ammonium salts in water varies greatly.

Upland Surface-water usually contains about 0·002 per 100,000, but the amount may exceed 0·008. If the land through which the water passes is manured, the amount of ammonia may rise to 0·03 or even higher.

Shallow Well-water may be free from ammonia, or may contain any amount not exceeding about 2·5.

Deep Well-water may contain as much as 0·1, but frequently contains no ammonia at all. The presence of a high proportion of ammonia in a deep well-water casts suspicion on the water if the albuminoid ammonia rises above a mere trace, or if any appreciable amount of oxygen is required in the permanganate test.

Spring-water contains but little ammonia, seldom more than 0·01; the average amount is about 0·001.

Sewage may contain as much as 10 parts.

As a rule, it may be stated that the quality of the water must be considered suspicious, if the water contains as much as 0·01 of ammonia per 100,000.

648. Albuminoid Ammonia, as has been already explained (615), gives an indication of the amount of organic nitrogenous matter present in the water. It should not exceed 0·008 part per 100,000, although in special cases a larger proportion may not be condemnatory.

649. Oxygen Consumed by the Organic Matter (618).—The relative freedom from organic impurity may be judged from the results of the permanganate process, by the following standards. The weight of oxygen required for 100,000 parts of the water is stated in the Table.

	Upland Surface-water	Water from other sources.
Water of		
Great purity . .	Not exceeding 0·1.	Not exceeding 0·05.
Medium purity .	From 0·1 to 0·3	From 0·05 to 0·15.
Doubtful purity .	From 0·3 to 0·4.	From 0·15 to 0·2.
Impure . . .	Exceeding 0·4	Exceeding 0·2.

650. Chloride (619) is usually present in water as sodium chloride, occasionally as chloride of calcium or of some other metal. Sodium chloride may occasionally be derived from the soil. It may also be derived from sea water, which has been either mixed with the water or introduced as sea-spray. If no such source of the chloride can be traced, and its quantity exceeds 2 parts per 100,000, it is considered to be derived from urine.

Rain-water usually contains sodium chloride, which has been derived from the air.

Spring- and River-water, if they are unpolluted with animal refuse, usually contain less than 1 part of chlorine as chloride per 100,000.

Shallow Well-water may contain almost any amount of chloride, the proportion depending on the extent to which sewage has percolated into the well.

651. Nitrite (620), if it is present in any appreciable quantity, should

be regarded as an indication of comparatively recent sewage contamination. Nitrite is readily oxidised to nitrate. Both nitrate and nitrite are innocuous, but they are usually oxidation products of objectionable organic matter which has previously been present in the water (652).

Nitrite in *Deep Well-water* has probably been produced by the deoxidation of nitrate. When nitrite is found in deep well-water, it is therefore not looked upon with as much suspicion as when it is found in *Shallow Well-water* or in *Upland Surface-water*, unless albuminoid ammonia or organic matter is also present in appreciable quantity.

652. **Nitrogen as Nitrite and Nitrate** (621).—The estimation of the nitrogen present as nitrite and nitrate is of importance for the following reason:

When nitrogenous organic matter is fully oxidised, its nitrogen remains chiefly in the form of nitrate; but nitrite is also occasionally present if the oxidation is incomplete. Thus, the presence of a large amount of nitrogen as nitrite and nitrate points to past sewage contamination. This implies that, if the filtration and aeration which have caused the oxidation of the organic matter should fail, there will be the risk of recent unoxidised sewage-matter being present in the water. Such a risk is, however, practically absent in the case of water drawn from well-constructed deep wells.

Upland Surface-water, if uncontaminated, should not contain more than 0·03 of nitrogen as nitrate and nitrite per 100,000, although in cultivated districts the amount may reach 1 part per 100,000.

In Shallow Well-water the amount of oxidised nitrogen varies greatly.

In Deep Well-water the amount of oxidised nitrogen may rise to 5 parts, but the average is only 0·5.

653. **The Degree of Hardness** of water (625) is chiefly of importance, when the water is used with soap for cleansing or for manufacturing purposes, or when it is used for generating steam in steam-boilers.

If water is required for drinking purposes, its hardness may vary from 2 to 50 parts per 100,000. Hardness within these limits seems to have no effect upon the health of the consumers, but a very hard water is not suitable for technical purposes. The character of the hardness will depend upon the nature of the soil with which the water has been in contact.

Water may be Softened by the removal of its temporary hardness. This is usually effected by Clark's process. The process consists in adding sufficient milk of lime to neutralise the carbonic acid which is in the water. The

calcium hydrate thus added is precipitated as carbonate, together with the dissolved calcium and magnesium carbonates. Since calcium carbonate is soluble to a small extent in water free from carbonic acid, a slight degree of hardness remains after the treatment with slaked lime.

It has been found that by adding to 700 gallons of the water one ounce of quicklime for each degree of temporary hardness per 100,000 a good result is obtained.

For technical purposes, both the temporary and permanent hardness may be removed by the addition of a mixture a sodium hydrate and sodium carbonate. The removal of calcium salts is more complete if solution of an alkaline oxalate is added in slight excess.

654. Objectionable Metallic Constituents (635).—Opinions differ as to the limits allowable for certain metals in water, but probably those stated below will be generally accepted.

Iron.—Not more than 0·1 part of iron per 100,000 should be present in water to be used for domestic and technical purposes: when as much as 0·3 part per 100,000 is present, the water has a distinct chalybeate taste. The amount is reducible by aeration or filtration.

Copper is very rarely found unless the water has been stored in copper vessels: not more than 0·1 part per 100,000 of water is permissible.

Zinc has been found as a normal constituent of certain mineral waters; quantities varying from 0·0015 part of $ZnCO_3$ to 13 parts of $ZnSO_4$ per 100,000 have been found. It may also be introduced by contact of the water with galvanised iron pipes or tanks. Its presence in a drinking-water is undesirable.

Lead has more often caused serious or fatal disturbances to health when taken in drinking-water than any other metal. It is not a normal constituent of natural water, but is generally derived from contact of soft water with lead pipes or with lead-lined tanks. Its action will vary with different individuals, but generally speaking not more than 0·025 part per 100,000 of water may be present without producing an effect when the water is drunk: 0·05 is considered decidedly dangerous, while 0·095 part has proved fatal in drinking-water. Drinking-water should undoubtedly be free from lead, as its physiological action is increased by the fact that lead accumulates in the organism and is not constantly voided.

PART IV.—SECTION XI.

ANALYSIS OF FOOD-MATERIALS, SOAP AND OILS

662. Introductory Remarks. — In this Section certain processes are described for the chemical examination of food. Those which are most frequently in use, and are more or less typical, have been selected, and a few analyses of Technical Products are appended.

Analysis of Milk.

663. The constituents which are usually estimated in milk are the total solids, the ash, and the fat. From the results thus obtained the amounts of water and of "solids not fat" are deduced. The casein and the milk-sugar, which are included in the latter term, are rarely estimated separately.

The examination may frequently be curtailed by determining the specific gravity of the milk and the percentage of total solids, and then calculating the percentage of fat present by the formula given in paragraph 673 (c). If any doubt is thus raised as to the due proportion of fat being present, the fat may then be directly estimated by one of the four methods described in paragraphs 666–672.

664. Estimation of the Total Solids.—Mix the sample of milk well by shaking it, and measure 5 c.c. into a small flat-bottomed platinum dish, whose weight together with about 7 cm. of stout platinum wire is known. Then weigh the dish with the milk quickly, in order to ascertain the weight of the 5 c.c. of milk.

Evaporate the milk to dryness upon the steam-bath, occasionally drawing aside the film from the surface by the platinum wire. Transfer the dish with the residue to the steam-oven, and continue to heat it until its weight is constant. About three hours is usually necessary to complete this process of drying.

665. Estimation of the Ash.—Ignite the residue in the platinum dish

(664) over a Bunsen or Argand flame, at a temperature which never reaches visible redness, since if the temperature of ignition is too high part of the chloride will be volatilised. Continue the ignition until all the volatile matter has been driven off, and the carbon has been completely burnt; then allow the dish to cool, and weigh it.

666. First Method for Estimating Fat.—The fat is extracted from the dry residue of the milk (664) by ether, the ether is removed by distillation, and the residue of fat is weighed.

The Process.—Mix the milk well by shaking it, and weigh 10 c.c. in a stoppered weighing-bottle; then pour it upon about 20 grams of dry clean silver-sand or of anhydrous plaster of Paris, contained in a porcelain evaporating-dish about 7 cm. in diameter. The sand should have been freed from soluble matter by treating it with hydrochloric acid and washing it with water, and should then have been dried by heat.

Place the dish on the water-bath, and heat it until the mass is dry, stirring continually in order to prevent the formation of lumps. Then remove the fat from this residue by extracting it with ether in the Soxhlet apparatus (671), or by the following method, which is however more tedious:

Transfer the residue from the dish to a wide-mouthed 250 c.c. round flask, detaching the last portions if necessary by using a little ether and a glass rod.

Heat the residue in the flask with about 50 c.c. of anhydrous ether. For this operation the flask should be connected with a reflux condenser, so that the ether, as it is boiled off, may be condensed and caused to flow back again into the flask.

After the ether has been boiled for about half an hour, pour off the ethereal extract of the fat through a dry filter into a weighed flask. Repeat these operations with 50 c.c. more ether, and pour the ether off through the filter into the same flask as before.

Finally wash the residue, which still contains a little fat, with more ether, until no fat is left when the last drops of ether are evaporated to dryness on a watch-glass. Add these washings to the ether-extract which is already in the flask.

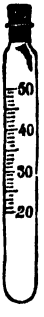
Distil off the ether from the fat-extract, as far as possible, condensing the ether-vapour by means of a condenser. Remove the flask to the water-bath, and heat it for some time; finally heat it in the steam-oven, until its weight is constant.

It will probably be found convenient to distil off the ether from the first ethereal solution of fat, as soon as it has been filtered into the tared flask. The subsequent extracts and washings are then poured into the same flask, and are subjected to distillation later on.

667. The Werner-Schmidt Method for Estimating Fat.—The milk is mixed with hydrochloric acid and heated. The acid attacks the casein, which incloses the fat-globules, and thus renders the fat easily soluble in ether. Ether is now added and the liquid is vigorously shaken. The volume of the ethereal solution is noted after it has risen above the acid liquid. An aliquot measured part of this ethereal solution is removed into a small weighed dish, and the ether is evaporated. From the weight of fat which is thus obtained the amount of fat which is in solution in the whole of the ether can be calculated.

The Process.—Mix the milk well by shaking it, and weigh accurately about 10 grams into a Schmidt tube (Fig. 95), which is graduated into 50 c.c. Add 10 c.c. of strong hydrochloric acid, close the bottle with a cork, and heat it in the water-bath for about ten minutes, shaking it occasionally. The liquid will become dark brown in colour, owing to the chemical action of the acid upon the casein.

FIG 95.



SCHMIDT TUBE.

Now cool the liquid rapidly by holding the tube in a stream of cold water. When it is perfectly cold, fill the tube to the 50 c.c. graduation with ether, which has been freed from alcohol by washing it repeatedly with water. Then insert the cork, and shake the liquid vigorously for one minute.

When the ether has again risen to the surface, a small layer of undissolved matter will be seen between the ethereal and the acid portions of the liquid. Read off the volume of the ether from the middle of this layer of undissolved matter to its upper surface.

Transfer rapidly two 10 c.c. portions of the ether solution, by means of a dry pipette, into separate tared porcelain dishes. Evaporate these to dryness on the water-bath. Then remove each of the dishes to the steam-oven, and heat it until its weight is constant.

The percentage of fat in the milk is calculated from the mean of the weights of fat which are obtained in these two estimations.

Example—In an actual estimation, 10 grams of milk were used.
After agitation with ether, the ethereal solution measured 28 c.c.
The evaporation of 10 c.c. of solution yielded 0·124 gram of fat.
Hence 10 grams of the milk contained $\frac{0{\cdot}124 \times 28}{10} = 0{\cdot}347$ gram of fat.
Therefore the milk contains 3·47 per cent. of fat.

668. Richmond's Modified Gotlieb Method.—Accurately weigh or measure about 5 grams of the milk into a narrow 50 c.c. stoppered cylinder 25 cm. in height, and standing on a foot. Add 0·5 c.c. of ammonium hydrate

solution and shake the liquids, then add 5 c.c. of alcohol of about 0·83 specific gravity and shake the liquids again. Now add about 12·5 c.c. of methylated ether of 0·720 specific gravity, and mix the liquids by shaking the vessel; finally add 12·5 c.c. of petroleum ether, and shake the whole two or three times. The above directions for mixing the liquids after each addition must be carefully followed.

Then draw off as much as possible of the ethereal layer into a flask, shake up the residual liquid with a mixture of about 25 c.c. each of ether and petroleum ether, and remove as much as possible of the ether layer into the flask, repeating this treatment twice in a similar way with fresh ether. Distil the ether from the flask and dry the flask in the steam-oven until its weight is constant. Then dissolve out the fat with a little petroleum ether, and subtract the weight of the very slight dried residue from the total weight of fat already obtained.

If the milk is sour, lumps are sometimes seen after the ether has been added, but these will disappear if the tube is placed in warm water for a few minutes and is then well shaken.

669. Adams' Method for Estimating Fat.—According to this method, a known weight of the well-mixed milk is absorbed by a strip of filter-paper. The filter-paper is then dried, and the fat is subsequently removed by means of ether in an extraction-apparatus. The resulting ether solution is distilled in order to remove the ether, and the residual fat is weighed.

The milk-residue thus obtained presents a very large surface to the solvent action of the ether, and the removal of the fat can therefore be quickly and completely effected. The filter-paper and the extraction-apparatus, which are required for this process, are described below.

670. *The Filter-paper Strip.*—The strip is 58 cm. long, and about 6 cm. wide. Its exact width will be determined by the dimensions of the reservoir of the Soxhlet extraction-apparatus (Fig. 94, *b*). The strip should be of such a width that when it is coiled up and placed in the reservoir of the Soxhlet apparatus, it reaches nearly to the upper bend of the syphon-tube (*b*).

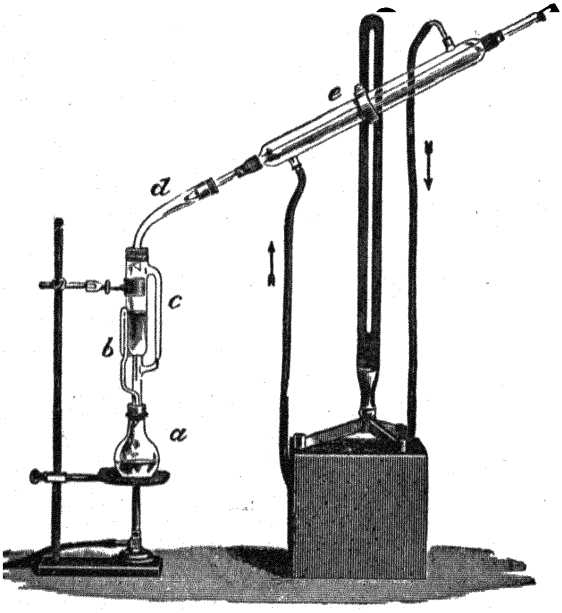
Paper practically free from fat, and from other matter soluble in ether, may be purchased for use in this process. A strip of such paper may, however, contain from four to five milligrams of matter soluble in ether, and this should be either removed or allowed for in accurate analyses, as is described below.

If Ordinary Filter-paper or Blotting-paper is used, it will contain matter soluble in ether. This is either extracted from each strip of paper by the following treatment before it is used in the process, or the soluble matter is estimated and allowed for.

If the paper-coil is to be freed from fat, soap, and resin, treat it as follows: Place the coil in the extractor (Fig. 96). Half fill the flask (*a*) with ether, and boil the ether for about half an hour by heating the flask in an evaporating-dish containing water. Then extinguish the heating flame, and take out the paper-coil. The coil will now be free from all matter soluble in ether, and will be ready for use.

If the fatty matter is to be estimated and allowed for, the loss of weight which five similar strips of the paper suffer when they are treated with ether in the Soxhlet apparatus (671) is ascertained in the above way. From this result the average weight of the soluble matter in one strip is calculated, and this weight, which usually amounts to from 10 to 12 milligrams, is subtracted from the weight of the milk-fat which is subsequently found.

FIG. 96.



THE SOXHLET EXTRACTOR.

671. *The Soxhlet Extraction-apparatus.*—A suitable extraction-apparatus is shown, ready for use, in Fig. 96.

The flask (*a*) contains the solvent liquid. The neck of this flask is connected with the Soxhlet extractor (*b*, *c*) by means of an ordinary cork, the lower end of the extractor being pushed through a perforation in the cork. Into the upper end of the extractor another cork is fitted, through a perforation in which the end of the adapter (*d*) passes. The adapter is a conical piece of glass tube, bent as is shown in the figure; it enables the Liebig condenser (*e*) to be attached to the extractor at a convenient angle.

Instead of using the adapter and Liebig condenser, one of the forms of condensers described in paragraph 1016 may be fitted directly into the cork of the extractor.

The corks which are used in this apparatus must have been previously extracted with ether, in order to remove all matter soluble in that liquid.

The requisite quantity of ether or other solvent is poured into the flask (*a*), and the paper, or other substance which is to be treated with the solvent, is placed in the broad central tube of the extractor (*b*, *c*). The substance should not reach higher than the shaded portion in the figure: it is usually placed in a bag made of filter-paper, so that no solid matter can find its way into the reservoir and thence through the side-tube (*b*) into the flask (*a*).

Note.—An "Extractor-thimble" may be purchased, which is made of fat-free paper in a size and shape suitable for insertion in the extractor. It may be used repeatedly for the process of extraction.

When the liquid in the flask (*a*) is boiled, its vapour passes up through the lower central tube, and thence through the side-tube (*c*) since there is no direct communication between the reservoir and the lower central tube. The vapour then passes into the condenser, and the condensed liquid drops back from the adapter (*d*) upon the substance in the reservoir, and accumulates in the reservoir.

As soon as the liquid reaches the level of the upper bend of the narrow syphon-tube (*b*), which communicates with the bottom of the reservoir, it fills that tube and syphons over and thus finds its way back again to the flask (*a*). This process will repeat itself as often as the liquid collects in the reservoir in sufficient quantity to reach the necessary level. In this way the substance is constantly brought into contact with the pure warm solvent; and the matter thus extracted is carried by the solvent into the flask (*a*), where it will gradually accumulate.

672. The Process of Extracting the Fat.—The following method of preparing the paper-coil for the extraction of fat may be adopted: Pin the end of one of the paper-strips (670) to the edge of the bench, so that the strip hangs vertically in the air. Then allow 5 c.c. of the well-shaken milk to drop slowly upon the paper and to be absorbed by it, removing the last portions of the milk from the pipette by rubbing the point against the dry part of the paper. Now allow the strip to hang until it is quite dry, hastening the drying process, if necessary, by holding the strip near the side of a steam-oven.

Then roll the paper into a coil, and place it in the Soxhlet extractor (Fig. 96); pour about 100 c.c. of anhydrous ether into the weighed flask, and heat the flask in a small dish of water sufficiently to keep the ether boiling. Maintain the heat until the ether has syphoned over from the extractor at least twelve times.

If any suspended matter is present in the tared flask, the ethereal solution must be filtered into a second tared flask; the filter is then washed with ether, and the washings are added to the flask before distilling off the ether. If the paper-coil is placed in an "extractor-thimble" (671, *Note*) no solid particles will pass into the flask.

Then distil off the ether as far as possible, and dry the fat-residue by heating the flask upon the water-bath, and finally in the steam-oven. As soon as the weight of the flask containing the fat is constant, the amount of the fat is found by subtracting the weight of the flask. Since the weight of the 5 c.c. of milk, which contained this weight of fat, is known (664), the percentage of fat may be calculated from these results.

673. **The Other Principal Constituents of the Milk** are not estimated directly, but their amounts are calculated from the results already obtained, as is described below:

(a) **Estimation of Water.**—The water in the milk is estimated by difference. The percentage of milk solids (664), when subtracted from 100, gives the percentage of water:

(b) **Estimation of the "Solids not Fat."**—The percentage of "solids not fat" is obtained by subtracting the percentage of fat (665–672) from the percentage of milk solids (664).

(c) **Estimation of Fat by Calculation.**—The results which have been obtained by the direct analysis of the milk may be checked by an indirect method of calculation. This is based upon the following considerations:

The specific gravity of milk is influenced by the amounts of fat and of "solids not fat" which are present, the former tending to lower the specific gravity, and the latter to raise it. Several formulæ, expressing the relation of the quantity of fat to the specific gravity and the amount of total solids, have been proposed.

The following formula, which is adapted to the Adams process of fat-extraction, has been given by Hehner and Richmond:

$$F = \frac{T}{1{\cdot}2} - \frac{0{\cdot}219\,[(G \times 1000) - 1000]}{G}$$

in which F represents the percentage of fat, T the percentage of total solids, and G the specific gravity of the milk.

In the case of a poor skimmed milk a correction must be made, by subtracting from the result obtained by the above formula the following amount:

$$0{\cdot}05 \times \left[\frac{(G \times 1000) - 1000}{T} - 2{\cdot}5\right].$$

Example.—A milk which yielded 12·5 per cent. of total solids, and had a specific gravity of 1·030, would contain $\frac{12\cdot5}{1\cdot2} - \frac{0\cdot219 \times 30}{1\cdot03} = 4\cdot1$ per cent of fat.

674. Remarks on the Results of Milk Analysis.—The results of the analysis of milk may either be returned as grams per 100 c.c., or as percentage weights. If the percentage weights are to be given, the specific gravity of the well-mixed milk at 15·5° C. is taken (33-38); the weights of the volumes of milk which have been used are then calculated from the specific gravity, and the analytical results are converted into percentage weights. The separate portions of the milk which are used in the analysis may however be weighed instead of being measured, and this will render the determination of the specific gravity unnecessary.

The most common adulterant of milk is water; and this "watering," or addition of water, reduces the percentage of total solids in the milk. But the quality of the milk may also be reduced by "skimming," or removal of fat in the form of cream, which only reduces the amount of fat.

The "solids not fat" in genuine whole milk should not be less than 8·5 per cent. This number, however, is only obtained from a milk of poor quality, and 9 per cent. is sometimes the minimum limit accepted.

The amount of fat present in milk should not be less than 3 per cent. but it varies with the season and with the method of feeding the cows.

Taking the above minimum percentages of "fat" and of "solids not fat" as standards, the extent of adulteration with water, and of impoverishment by the removal of fat, may be calculated as follows:

If a is the percentage of "solids not fat" in a sample of watered milk, then the percentage of pure milk present will be $\frac{100}{8\cdot5} \times a$, and the percentage of added water will be $100 - \frac{100}{8\cdot5}a$.

Also if b is the percentage of fat, the number of grams of fat which have been removed by skimming 100 grams of the milk, whether it has been watered or not, will be $\frac{3a}{8\cdot5} - b$; and the percentage deficiency due to skimming only will be $\left(\frac{3a}{8\cdot5} - b\right) \times \frac{100}{3}$. The whole deficiency of fat due to both skimming and watering, stated as a percentage of the fat which is present in the accepted standard milk, will be $\frac{3-b}{3} \times 100$.

A useful criterion as to whether milk has been skimmed is furnished by determining the amount of protein matter present. This may be effected

by estimating the amount of nitrogen contained in 10 c.c. of the milk by the Kjeldahl process (807): this amount when multiplied by 6·37 gives the weight of proteins present.

General experience proves that in "whole" or unskimmed milk the amount of fat present is at least as great as the amount of protein matter.

This criterion is of special value in judging condensed milks.

674. Preservatives in Milk.—Certain substances are occasionally introduced into milk, more especially during hot weather, in order to prevent it from undergoing change. Those which have been most commonly detected are borax or boric acid, and formaldehyde introduced as the aqueous solution termed "formalin."

675. Borax and Boric Acid may be tested for by adding a few drops of alcoholic extract of turmeric to a little milk acidified by oxalic or citric acid, and evaporating to dryness in a flat porcelain dish: a bright red coloration of the residue, which changes to bluish green on the addition of ammonia solution, indicates the presence of borax or boric acid.

If this coloration is obtained, the amount of the preservative may be estimated by titrating the boric acid as is directed below:

To 100 grams of the sample add from 1 to 2 grams of potassium hydroxide and evaporate to dryness in a platinum dish. Char the residue thoroughly at a low temperature, and when it is cool boil it with 20 c.c. water, adding HCl drop by drop until all is dissolved except carbon. Filter into a 100 c.c. flask, taking care that the filtrate with the washings does not exceed 50 or 60 c.c. in volume.

Remove the phosphates from this liquid by adding to it 0·5 gram of calcium chloride, and then making it slightly alkaline to phenol-phthalein by adding a few drops of 10 per cent. potassium hydroxide solution and then 25 c.c. of lime-water.

Now make up the liquid to 100 c.c. with water and filter it through a dry filter. To 50 c.c. of this filtrate add just enough normal sulphuric acid to destroy the pink colour, then add methyl-orange, and continue adding the normal acid until the liquid just gives the red acid indication with the methyl-orange. After boiling to expel carbon dioxide, add decinormal potassium hydroxide solution cautiously until the reaction just becomes neutral: then add an equal volume of glycerol, and titrate the boric acid with decinormal KOH solution until a permanent pink colour is produced with the phenol-phthalein. Each c.c. of the decinormal alkali corresponds to 0·0062 gram of H_3BO_3, to 0·0035 gram of B_4O_3, or to 0·00955 gram of $Na_2B_4O_7.10H_2O$.

676. Formaldehyde may be tested for by a reagent consisting of a

mixture of 0·1 c.c. of pure nitric acid, or 1·6 c.c. of normal nitric acid, with 100 c.c. of strong hydrochloric acid.

10 c.c. of this freshly made reagent are added to 5 c.c. of the milk in a test-tube, and the mixture, after being vigorously shaken, is kept for ten minutes in a water-bath at the temperature of 50° C.: the liquid is then cooled rapidly to about 15° C. A violet coloration of the liquid indicates the presence of formaldehyde in the milk.

The proportion of formaldehyde in the milk may be estimated by comparing the intensity of this coloration with that furnished by each of several standard tubes containing milk with known amounts of formaldehyde, which have been treated in precisely the same way. The reaction is most delicate when from 0·2 to 6 parts of formaldehyde are present in a million of milk, and if the colour is deeper than that corresponding to 6 parts per million, the sample should be diluted with pure milk down to that proportion.

Another method of estimation consists in adding to 100 grams of the milk, 1 c.c. of dilute sulphuric acid made by mixing the strong acid with three times its volume of water, and distilling over 20 c.c. of this liquid. The amount of formaldehyde in the distillate is then estimated by the iodometric method (346), and is multiplied by three, since the distillate contains about one-third of the formaldehyde which was originally present in the milk.

For the Average Results of Analyses of Milk refer to paragraph 965.

Analysis of Butter.

677. It is usual to estimate in butter, the water, curd, salt and fat. If preservatives are detected, it may also be necessary to estimate the amount of boric acid which is present either as such or as producible from borax. In case the butter is to be tested for foreign fats, a further examination is necessary, such as is described in paragraphs 685–689.

678. **Estimation of the Water.**—Weigh out accurately about 5 grams of the butter into a tared dish; heat it in the steam-oven, or better in an air-oven to a temperature of 110° C., until no globules of water can be seen below the fat, and until the weight becomes constant. The loss of weight represents the water.

679. **Estimation of the Curd and Salt.**—Melt the dry butter (678), and treat it with about 10 c.c. of ether, pouring off the ether solution through a tared filter. Then treat the residue again with ether, transfer it to the filter, and continue to wash it with ether until the last few drops of the ether give

no residue when they are evaporated to dryness on a watch-glass. Then dry the filter and its contents in the steam-oven, until their weight becomes constant. The weight of the residue represents the amount of curd and salt in the weight of butter taken (678).

The ether solution may be reserved for the direct estimation of the fat (682).

680. Estimation of the Ash.—Transfer the dried filter and its contents (679) to a weighed platinum crucible, and ignite them at as low a temperature as possible, until the residue is white in colour and its weight is constant.

The residue should consist almost wholly of salt, but it may contain boric acid or borax introduced into the butter as a preservative. The ash may be dissolved in water, and half the solution may then be titrated for salt by silver nitrate (373), while the other half is tested for boric acid (675). If boric acid is found it may be estimated as is directed in paragraph 681.

681. Estimation of Boric Acid.—10 grams of the butter are heated gently in a small evaporating-dish, and the melted fat is washed into a small stoppered separating-funnel with about 40 c.c. of boiling water. The whole is then well shaken and allowed to stand until the fat has separated completely from the water, when the water is allowed to flow off through the tap into a 100 c.c. flask.

This treatment is repeated three times, not more than 20 c.c. of boiling water being used on each occasion. The four washings are then cooled in the flask and are made up to the 100 c.c. mark with distilled water. This solution is filtered through a dry filter, and 50 c.c. are rendered alkaline to phenol-phthalein by being mixed with a few drops of KOH-solution, and are then titrated as is directed in the last paragraph of 675.

682. Estimation of the Fat.—The fat may be estimated either by difference or directly. The estimation by difference is the more exact method.

If the fat is to be estimated by difference, its percentage is found by subtracting the sum of the percentages of water, curd and salt (678, 679) from 100.

If the fat is to be estimated directly, the ethereal solution and washings from paragraph 679 are transferred to a weighed flask, and the ether is distilled off as far as possible. The flask containing the residue of fat is then heated for some time on the water-bath, and is finally dried in the steam oven until its weight is constant.

683. Remarks on the Results of Butter Analysis.—Hehner states that the percentage of water present in well-made butter of good

quality is not as a rule greater than 13, nor less than 11. A proportion exceeding 16 per cent. indicates either careless making or intentional adulteration.

The percentage of curd and salt should amount to about 2·5, and although the weight may be considerably higher it should never reach 8 per cent.

The percentage of fat, which averages from 85 to 87, should never fall below 80.

For the Results of Analyses of Butter refer to paragraph **966.**

Detection of Foreign Fats in Butter.

684. Four methods are given for detecting and estimating foreign fats in butter. They are Reichert's method (**685-687**), Hehner's method (**688**), Koettstorfer's method (**689**), and Blichfeldt's method (**1031**).

The degree of rancidity of butter may also be estimated by the Koettstorfer method, as is explained in paragraph **690**.

685. Reichert's Method of Detecting Foreign Fats in Butter.—This method is based upon the fact that genuine butter-fat furnishes more than 4 per cent. of volatile fatty acids, whereas other fats either furnish no volatile acid or else a very much smaller proportion.

This method is now employed either in the modified form described in paragraph (**686**), or as a second modification (**687**) which will be found to be more simple and rapid in execution. A standard process, known as the Reichert-Wollney method, is also described in paragraph **760**.

686. The First Modified Reichert Process requires the following preliminary preparations:

(a) *Caustic Soda Solution.*—Dissolve 50 grams of caustic soda in 50 c.c. of water, let the liquid stand until it is clear and then decant it. This solution will be free from carbonate, since sodium carbonate is quite insoluble in a solution containing 50 per cent. of sodium hydrate.

(b) *Dilute Sulphuric Acid* of such strength that 5 c.c. are more than sufficient to neutralise 1·5 c.c. of the above caustic soda solution.

(c) *Decinormal Solution of Barium Hydrate.*—This solution is preferred for the final titration of the volatile fatty acids because it can contain no soluble carbonate, and any carbonate which was present would evolve carbon dioxide during the titration with acid, which would seriously interfere with the accuracy of the process.

(d) *Preparation of "Butter-fat."* — Prepare some butter-fat, free from moisture, salt, and curd, in the following way:

Melt some of the butter in a small beaker on the water-bath. When the fat is clear, pour it off through a dry filter-paper which is supported, without a funnel, in another small beaker upon the water-bath. Care must be taken that none of the water, from beneath the fat, is poured upon the filter, and the filtered liquid fat must be perfectly clear and transparent. The butter which has been prepared in this way will be termed "butter-fat," in order to distinguish it from the unclarified butter.

Process of Estimation.—Weigh out 2·5 grams of the cold "butter-fat" (d) into a dry flask, which is capable of holding about 200 c.c. Add about 10 c.c. of alcohol, and then 1·5 c.c. of the solution of caustic soda (a). At once close the flask with a rubber stopper, and gently shake the contents until they have become quite clear; then allow the mixture to stand at a gentle heat for about ten minutes in order to complete the saponification.

Now remove the rubber stopper, and replace it by a perforated cork, bearing a short piece of narrow glass tubing open at both ends. Then heat the flask upon the water-bath, so as to evaporate the alcohol. The narrow glass tube will prevent the entry of any carbon dioxide from the air, the absorption of which would ultimately lead to the result obtained being too high.

When the alcohol has been driven off, add 70 c.c. of boiling distilled water which has been freed from carbon dioxide by being boiled for at least twenty minutes, and once more close the flask by the rubber stopper. As soon as the soap has been dissolved by the hot water, add 5 c.c. of the dilute sulphuric acid (b). Then shake the contents of the flask well, drop a few pieces of broken clay-pipe into the flask, and distil through a condenser (1016) at such a rate that 50 c.c. of distillate are collected in about a quarter of an hour. It is important that this distillation should not actually begin until the fatty acids in the flask have been melted to a clear yellowish oily fluid.

Now filter the acid distillate through a filter-paper, which has previously been washed with distilled water freed from carbonic acid by boiling. Then wash the filter until it is free from acid, and titrate the well-mixed filtrate and washings with the decinormal baryta solution (c), using phenol-phthalein as an indicator.

If the butter-fat is genuine, the 50 c.c. of distillate will usually require for neutralisation about 13 c.c. of the decinormal barium hydrate solution and the quantity will rarely be less than 12·5 c.c. Butter made from the milk of individual cows not unfrequently gives lower results, especially when the cows are near the end of their period of lactation. On the other hand, butters produced in Egypt, Australia, and New Zealand usually require from 15 to 16 c.c.

Every sample of market-butter, which has been made from the mixed milk of a number of cows and requires less than 12·5 c.c., should therefore be looked upon with suspicion; and if the suspicious result obtained by this method is confirmed by other means, the adulteration of the sample may be considered to have been proved.

The volatile acid contained in the 50 c.c. of distillate represents almost accurately 83 per cent. of the total quantity of volatile fatty acids contained in the butter-fat. Hence if the number of c.c. of decinormal solution used for 2·5 grams of butter-fat is multiplied by the factor 0·424, the percentage of total volatile acids present, calculated as butyric acid ($C_4H_8O_2$), is approximately obtained.

The above factor is derived thus: Since the molecular weight of butyric acid is 88, each c c of decinormal baryta solution corresponds to 0 0088 gram of butyric acid; and since 2 5 grams of butter-fat were used, the percentage of butyric acid $= n \times \left(0\ 0088 \times \frac{100}{83} \times 40\right) = n \times 0\ 424$, where n is the number of c.c. of baryta solution used.

687. The Second Modified Reichert Process is described below. It is much more rapid in execution, but requires a special solution of caustic soda.

Caustic Soda Solution.—Dissolve 50 grams of caustic soda in water, dilute the solution to 100 c.c., and filter it through a toughened filter. Add this to 500 grams of pure glycerine, and stir well.

Process of Estimation.—Weigh 5 grams of the butter-fat into a wide-mouthed flask, add 10 c.c. of the glycerine solution, and heat it by means of a small flame until frothing ceases and the solution becomes clear. Allow the liquid to cool somewhat, and then add very gradually 95 c.c. of freshly boiled distilled water, constantly shaking the liquid in order to prevent loss by frothing.

Now add 50 c.c. of normal sulphuric acid, drop in about 0·1 gram of powdered pumice, connect the flask with a condenser, and commence the distillation as soon as the layer of fatty acids has become quite clear. The process of distillation has been already described on page 342.

Collect 110 c.c. by distillation; filter off 100 c.c. of the distillate through a dry filter, and titrate the acid in this filtrate by decinormal barium hydrate solution (c), using phenol-phthalein as an indicator. Add to this result one-tenth of the number of c.c. of barium hydrate solution used.

Process of Calculation.—Let N represent the number of c.c. of the barium hydrate solution used for the neutralisation of the distillate from the butter-fat, and n the volume in c.c. of the barium hydrate solution required by the distillate in a blank estimation in which no butter-fat has been used; then, since 5 grams of normal butter-fat require 26 c.c.,

(1) The percentage of foreign fats $= \frac{26 - (N - n)}{26} \times 100.$

This formula does not allow for the presence of volatile fatty acids in margarine. But if y represents the number of c.c. of standard barium hydrate solution required to neutralise the volatile fatty acids in 5 grams of margarine, then

(2) The percentage of foreign fats $= \frac{26 - (N - n)}{26 - y} \times 100.$

According to the statement given below, y varies between 0·0 and 4·0, but unless butter-fats are present the value does not exceed 1·0. Accordingly if first the value 0·0 and then 1·0 is substituted for y in the above formula, the extreme quantities of foreign fats which can be present will be found. The higher figure, 1·0, alone is usually taken for the calculation.

Adulteration with Foreign Fats.—The following statement shows that the volatile fatty acids, which are derived from equal weights of other ordinary fats, require a far smaller volume of the standard alkali to neutralise them than is the case with butter-fat.

The volume in c.c. of decinormal barium hydrate solution, which is required for neutralising the volatile fatty acids from 5 grams of the following fats, is for

Genuine butter-fat	26·0 to 34·0
Cocoa-nut fat	7·2
Beef-fat	0·5
Lard	0·6
Margarine	0·0 to 4·0

Note.—The value, 4·0, given for margarine corresponds to a mixture which contains 10 per cent of butter-fat, this is the largest proportion allowed by law, and a value of 1·0 may be taken as the average for oleo-margarine mixtures.

The number for butter-fat is seen to differ so widely from the numbers obtained for all other fats, that it furnishes a means not only of detecting the admixture of foreign fats with the butter, but of calculating its amount as is described above.

In calculating the percentage amount of adulteration in the butter-fat, it is usual to take the lowest number of c.c. required by 5 grams of genuine butter, 26·0, and the highest number, 1·0, required by margarine. This has been done in drawing out the above formulæ.

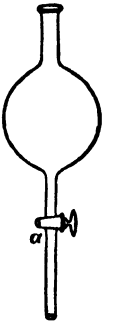
688. Hehner's Method of Detecting Foreign Fats in Butter.—This method depends upon the fact that butter-fat contains a smaller proportion of fatty acids insoluble in water than other fats do. Hence, by estimating the amount of insoluble fatty acids in a sample of butter, the

presence of foreign fats may be detected, and the proportion in which they are present may be calculated.

The Process.—Prepare from the butter some "butter-fat" free from moisture, curd, and salt (686, d). Then weigh accurately about 4 grams of this butter-fat into an evaporating-dish, about 15 cm. in diameter. Melt the fat on the water-bath, and add from 5 to 10 c.c. of a saturated solution of potassium hydrate in alcohol. The fat will be rapidly saponified. Now add a few drops of water, and if any fat separates out, add more alcohol and continue the heating.

Dilute the soap-solution thus formed with water, and then boil it down until the smell of alcohol is no longer perceptible. Dissolve the soap, which will have partly separated out, in water; and add dilute hydrochloric acid until the solution strongly reddens litmus-paper. Then heat the dish for about half an hour on the water-bath. The fatty acids will form an oily layer above the aqueous solution, which should itself be almost clear.

FIG. 97.



BUTTER-FLASK.

Separation and Washing of the Fatty Acids.—Now rinse out a "butter-flask" (Fig. 97), about a litre in capacity, with hot water, and transfer the fatty acids together with the liquid to the flask, reserving the dish. Allow the aqueous liquid to flow away by opening the stop-cock (*a*), leaving the melted fatty acids in the flask. Pour hot water into the flask, and shake it well with the fatty acids; then allow the water to flow away again. Repeat this process of washing until the washing-water is no longer acid in reaction.

Now carefully open the stop-cock, allow the fatty acids to just reach the lower end of the tube (*a*), and remove the drop of water from beneath the fat by touching it with filter-paper.

Then allow the whole of the fat to flow into a weighed glass dish. Rinse out the dish, which was used for the saponification, with a little ether. Pour this liquid into the butter-flask, and after shaking it round in the flask, allow it to flow through the tube (*a*) into the weighed dish. Rinse the butter-flask twice with fresh small portions of ether, and add these to the liquid in the glass dish. Evaporate the ether by gentle heat, heat the dish containing the residue in the steam-oven for a short time, and then cool it.

If a drop of water is seen beneath the fat, cut out a circular piece of fat with a sharp penknife, so as to be able to reach the water and absorb it by a piece of filter-paper. Then place the dish in the water-oven, heat it for two hours, and weigh it when it is cold. Repeat these processes, until the difference between two consecutive weighings amounts to 1 or 2 milligrams

only; the fat may then be considered as dry, and the final weighing may be taken as correct.

The Presence of Admixed Foreign Fats may be ascertained, and their amount may be found, from the percentage of insoluble fatty acids which is thus obtained:

Since animal fats contain on the average 95·5 per cent. of insoluble fatty acids, and butter-fat contains on an average only 87·5 per cent. (*Note*), 100 parts of foreign fat contain 8 parts of insoluble fatty acids more than 100 parts of butter do. Hence if (a) represents the percentage of insoluble fatty acids found, then the amount of foreign fat present in 100 parts of the butter-fat $= \frac{100(a - 87{\cdot}5)}{8} = 12{\cdot}5\,(a - 87{\cdot}5)$.

Note.—Although the percentage of insoluble fatty acids in butter is, as a rule, 87 5, genuine butter has been found to contain 88 5, and even 89 per cent

Example—In a particular estimation the butter-fat contained 93 5 per cent. of insoluble fatty acids; hence the amount of adulteration in 100 parts of the fat $= 12\,5(93\,5 - 87\,5) = 12{\cdot}5 \times 6 = 75$. But the butter-sample contained 15 per cent of water, curd, and salt, and 85 per cent of butter-fat: therefore the percentage of adulteration in the sample $= \frac{75 \times 85}{100} = 63\,75$, and the percentage of real butter present $= 36\,25$.

689. Koettstorfer's Method of Detecting Foreign Fats in Butter.—This method depends upon the great difference between the molecular weights of certain fatty acids. This difference is made evident when the weight of potassium hydroxide which is required to saponify a given weight of the different fats is determined.

The Koettstorfer "saponification value" is the weight in milligrams of potassium hydroxide which is required for the complete saponification of 1 gram of the fat.

The molecular weights of the fatty acids derivable from most natural fats are high and do not differ widely one from another, but the fatty acids present in butter are of comparatively low molecular weight since they contain not more than ten atoms of carbon in their molecules.

Hence the saponifying power of a certain weight of butter will be greater than that of an equal weight of any other natural fat, and the saponifying power of equal weights of different samples of butter will be diminished by the presence of foreign fats in the butter-fat.

The method founded on the above facts is simple and may be rapidly carried out. The solutions required are the following:

(a) *Alcoholic Solution of Potassium Hydrate.*—About 35 grams of caustic

potash are dissolved in a litre of 94 per cent. alcohol. Since this solution is subject to change, it should be prepared in small quantity only and should not be stored for any length of time. It must be titrated with standard acid each time it is used.

(b) *Seminormal Hydrochloric Acid Solution*, made by diluting normal hydrochloric acid solution (290) with its own volume of water.

(c) *Phenol-phthalein Solution:* very dilute solution in alcohol (269).

The Process of Estimation.—The butter is first clarified by fusion and filtration (686, d).

About 1·5 grams of this "butter-fat" are accurately weighed into a flask holding about 250 c.c.; 25 c.c. of the potassium hydrate solution (a) are then added, and the contents of the flask are heated for about fifteen minutes under a reflux-condenser until the solution is perfectly clear. Complete saponification is thus effected. One cubic centimetre of the phenol-phthalein solution (c) is then added, and the free alkali is titrated with the hydrochloric acid solution (b) with as little exposure to air as possible. The change of colour to yellow sharply indicates the end of the reaction.

Meanwhile 25 c.c. of the alcoholic potash solution (a) are treated in precisely the same way as is described above, and are finally titrated with the standard acid.

The difference between the number of c.c. of acid which have been required in these two titrations is taken as representing the volume of seminormal potassium hydrate solution, which has been neutralised by the fatty acids of the butter-fat used in the experiment. This number of c.c. is multiplied by 0·028, in order to obtain the weight of potassium hydrate which has been neutralised by the butter-fat. From this result the "Koettstorfer value," or the number of milligrams of potassium hydrate which would be saponified by 1 gram of the butter-fat, is calculated. It will be seen that this number represents the parts of KOH required to saponify 1000 parts of butter-fat.

When pure butter-fat is treated in this way, it gives a number between 221·5 and 233. Both oleo-margarine and lard, the common adulterants of butter, give about 195·5.

If the number which is yielded by a sample of butter-fat is below 221·5, the butter has been adulterated.

The probable percentage amount of adulteration

$$=\frac{100\,(227{\cdot}25-n)}{227{\cdot}25-195{\cdot}5}=\frac{100\,(227{\cdot}25-n)}{31{\cdot}75}=3{\cdot}15\,(227{\cdot}25-n),$$

where n is the number obtained from the sample analysed, 227·25 is the mean number for pure butter-fat, and 195·5 is the mean number for adulterants.

Example—In a particular estimation, 1·76 grams of the butter-fat were used.

The blank titration of 25 c c of the KHO solution required 20·4 c c. of the standard acid.

The titration of 25 c c of the KHO solution, which had been heated with the butter-fat, required 6·0 c c of the acid.

Therefore the fatty acids were equivalent to 20·4 - 6·0 = 14·4 c c of semi-normal acid, and would therefore neutralise 14·4 c c. of seminormal KHO solution

One gram of the butter-fat would therefore neutralise $\frac{14{\cdot}4}{1{\cdot}76} = 8{\cdot}18$ c c of semi-normal KHO solution, which would contain $8{\cdot}18 \times 0{\cdot}028 = 229{\cdot}04$ milligrams of KHO

And since 1 gram of pure butter-fat neutralises from 221 to 233 milligrams of KHO, the sample of butter under examination was not adulterated with foreign fats

690 **Estimation of Rancidity in Butter.**—A modification of the above method offers a means of determining the degree of rancidity in butter, by estimating the amount of free acid present in it From 3 to 10 grams of the "butter-fat" (686, d) are weighed into a flask of about 100 c c capacity. Some ether is then freed from acidity, by adding first some phenol-phthalein solution (689, c), and then the alcoholic caustic potash solution (689, a) until the pink colour is just permanent. This ether is shaken with the butter-fat in quantity sufficient to dissolve it. The acid in the butter-fat solution is then titrated with the alcoholic potash solution, the value of which has been ascertained by means of the seminormal hydrochloric acid (689, b).

The number of c.c. of semi-normal potash solution required by 100 grams of palatable rancid butter-fat varies from 1 to 8, giving an average of 4 In exceptional cases 15, 26, and even 41·6 c c. have been required, but this last number corresponds to an intolerable degree of rancidity.

Partial Analysis of Beer, Wine, and Spirits.

691. The estimations which are usually made in the chemical examination of a sample of beer are those of alcohol, acidity, and of total solid matter in solution.

The nitrogen present in the albuminoid matters may be determined by means of the Kjeldahl process (807) in the residue left on evaporation; if the weight of nitrogen thus found is multiplied by 6·25 the approximate weight of albuminoids will be obtained.

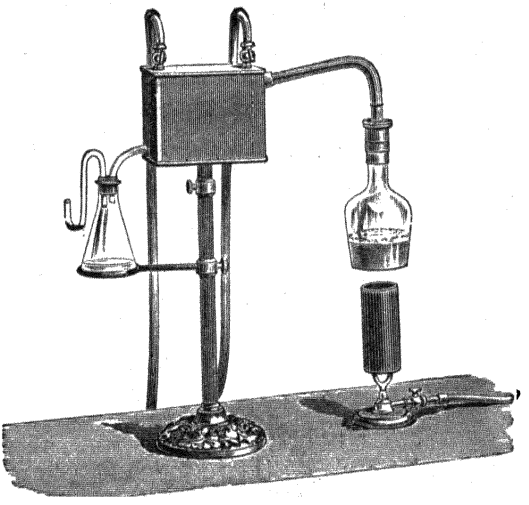
For excise purposes it is necessary to ascertain the "original gravity" of the beer. This indicates the relative amount of solid matter which was in solution in the "wort" before it was fermented.

In examining spirits it is usually only necessary to estimate the amount of alcohol present, in order to detect dilution with water. The estimation

of alcohol in spirits is simplified by the fact that they contain very little dissolved matter. In the case of beer and wine the presence of much dissolved matter renders distillation advisable, as is explained below (693).

692. Estimation of the Alcohol in Spirits.—Take the specific gravity of the spirit at 15·5° C. (33–38). Then boil down a measured volume of the spirit to one-third to remove the alcohol. Cool the residue and make it up to its original volume with distilled water. Mix this liquid well, and then take its specific gravity at 15·5° C. The specific gravity which the spirit would possess, if it were deprived of its dissolved matter, can then be calculated by adding 1 to the specific gravity of the spirit, and subtracting from this the specific gravity which has been found for the diluted residue. From the

FIG. 98.



ALCOHOL STILL FOR BEER OR WINE.

result thus obtained the proportion of alcohol in the spirit can be found by reference to the Alcohol Tables (985, 986).

Example.—A sample of brandy gave a specific gravity of 0·95528; the residue which was left after boiling down a measured volume of the brandy to one-third its volume was made up to its original volume with distilled water, and gave a specific gravity of 1·00328. Hence the specific gravity of the brandy, if it were deprived of its dissolved solid matter, would be 1·95528 – 1·00328 = 0·95200. From the Alcohol Tables it is found that this specific gravity indicates the presence of 33 per cent. by weight of alcohol in the brandy.

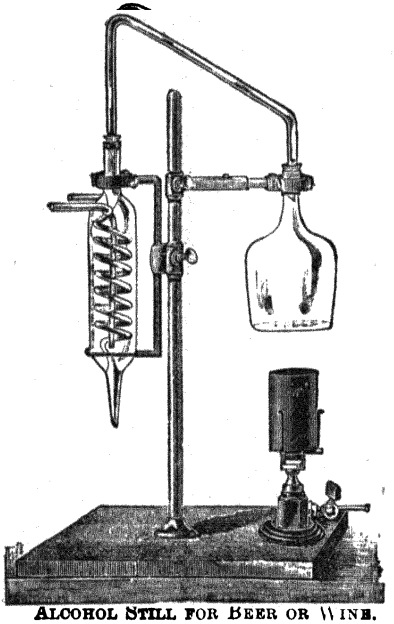
693. Estimation of the Alcohol in Beer and Wine.—A volume of about 750 c.c. of the liquid is freed from the greater part of the carbon

dioxide which is dissolved in it. For this purpose the liquid may either be filtered, or it may be "tossed" by pouring it backwards and forwards from some height out of one vessel into another.

The liquid is then distilled in an ordinary flask attached to a condenser (1016), or in the special apparatus which is shown in Fig. 98. A vertical condenser with a glass spiral inner tube sealed into a broad glass jacket (Fig. 99) is now frequently used in place of the older metal still, shown in the preceding figure.

The apparatus with metal condenser (Fig. 98) consists of a flask about a litre in capacity, upon the neck of which is cemented a brass tube bearing a screw-thread on its outside. This fits into a screw, which is on the interior of a brass

FIG. 99.



ALCOHOL STILL FOR BEER OR WINE.

cap connected with the condensing-tube. A rubber washer, which is inserted between the top of the flask and the under surface of the cap, causes the connection of the flask with the condensing-tube to be perfectly air-tight when it is screwed up.

In the centre of the figure is seen the metal condensing-box, and to the left the flask for receiving the distillate. A cork, pierced with two holes, is fitted into the neck of this flask. Through one hole passes the tube conveying the distillate; into the other is fitted a doubly bent tube, the lower bend of which is closed by a globule of mercury in order to prevent the loss of alcohol vapour by diffusion. The cold water-supply for condensing the spirit, and the overflow of heated water, are conveyed by tubes which are seen at the back of the condenser

The Process of Estimation.—Measure 250 c.c. of the "tossed" liquid into the distillation-flask, and connect the flask with the condenser and receiver; then heat the flask with the flame of an Argand burner, until it boils gently.

When about two-thirds of the liquid have distilled over, transfer the distillate to a measuring-flask, make it up to the original volume of the liquid with distilled water, and mix well. Then take the specific gravity of this liquid at 15·5° C., either by direct weighing, or by means of a delicate hydrometer (33–38).

The amount of proof-spirit or of absolute alcohol, which is present in the liquid, may then be ascertained by reference to the Alcohol Tables (985, 986) in which the specific gravity of water is taken as 1000.

The residual liquid in the distillation-flask is allowed to cool; it is then diluted to the original volume of 250 c.c., and its specific gravity is taken at 15·5° C. The number thus obtained is used in calculating the "original gravity" of the beer.

694. Estimation of the "Original Gravity" of Beer.—As has been already explained, the "original gravity" of a beer is the gravity of the wort from which the beer has been prepared.

During the process of fermentation of the wort, a portion of the saccharine matter is converted into alcohol with evolution of carbon dioxide. Consequently the beer has a lower specific gravity than the wort from which it has been brewed.

In order to determine the original gravity of the wort, the alcohol is separated from the beer by distillation, and the specific gravity of the distillate is determined as is directed above (693). The gravity of the wort, which would be required to produce a liquid of this specific gravity, is then ascertained by reference to Table I. below, in which the degree of "spirit indication" is the difference between 1000 and the specific gravity of the alcoholic distillate, the specific gravity of water being taken as 1000.

The number thus obtained is then added to the specific gravity of the liquid, which was produced by diluting the residue left in the distillation-flask (693) to 250 c.c. The resulting number represents the original specific gravity of the wort.

The acidity which has been produced during fermentation is estimated and allowed for as follows:

The acidity of the tossed beer is ascertained by titrating 100 c.c., or more correctly 100 grams, of the beer with seminormal sodium hydrate solution, using litmus-paper as an indicator. From this result the amount of acetic acid present is calculated, assuming that each c.c. of the seminormal sodium hydrate solution corresponds to 0·03 gram of acetic acid; 0·1 per cent.

which represents the average acidity of the unfermented wort, must be subtracted from the result thus obtained.

TABLE I.—*Spirit Indication, with corresponding Degrees of Gravity lost in Malt Worts by the "Distillation Process."*

Degrees of Spirit Indication	0 0	0 1	0 2	0 3	0 4	0·5	0 6	0 7	0 8	0 9
0	—	0 3	0 6	0 9	1 2	1 5	1 8	2 1	2 4	2 7
1	3 0	3·3	3 7	4 1	4 4	4 8	5 1	5 5	5 9	6 2
2	6 6	7 0	7 4	7 8	8 2	8 6	9 0	9 4	9 8	10 2
3	10 7	11 1	11 5	12 0	12 4	12 9	13 3	13 8	14 2	14 7
4	15 1	15 5	16 0	16 4	16 8	17 3	17 7	18 2	18 6	19 1
5	19 5	19 9	20 4	20 9	21·3	21 8	22 2	22 7	23 1	23 6
6	24 1	24 6	25 0	25 5	26 0	26 4	26 9	27 4	27 8	28 3
7	28 8	29 2	29 7	30 2	30 7	31 2	31 7	32 2	32 7	33 2
8	33 7	34 3	34 8	35 4	35 9	36·5	37 0	37 5	38 0	38 6
9	39 1	39 7	40 2	40 7	41 2	41 7	42 2	42 7	43 2	43 7
10	44 2	44 7	45 1	45 6	46 0	46 5	47 0	47 5	48 0	48 5
11	49 0	49 6	50 1	50 6	51 2	51 7	52 2	52 7	53 3	53 8
12	54 3	54 9	55 4	55 9	56 4	56 9	57 4	57 9	58 4	58 9
13	59 4	60 0	60 5	61 1	61 6	62 2	62 7	63 3	63 8	64 3
14	64 8	65 4	65 9	66 5	67 1	67 6	68 2	68 7	69 3	69 9
15	70 5	71 1	71 7	72 3	72 9	73 5	74 1	74 7	75 3	75 9
16	76 5	—	—	—	—	—	—	—	—	—

TABLE II.—*For Ascertaining the Value of the Acetic Acid.*

Excess per cent of Acetic Acid in the Beer	Corresponding Degrees of "Spirit Indication"									
	0 00	0·01	0 02	0 03	0 04	0 05	0 06	0 07	0 08	0 09
0 0	—	0 02	0 04	0 06	0 07	0 08	0 09	0 11	0 12	0 13
0 1	0 14	0 15	0 17	0 18	0 19	0 21	0 22	0 23	0 24	0 26
0 2	0 27	0 28	0 29	0 31	0 32	0 33	0 34	0 35	0 37	0 38
0 3	0 39	0 40	0 42	0 43	0 44	0 46	0 47	0 48	0 49	0 51
0 4	0 52	0 53	0 55	0 56	0 57	0 59	0 60	0 61	0 62	0 64
0 5	0 65	0 66	0 67	0 69	0 70	0 71	0 72	0 73	0 75	0 76
0 6	0 77	0 78	0 80	0 81	0 82	0 84	0 85	0 86	0 87	0 89
0 7	0 90	0 91	0 93	0 94	0 95	0 97	0 98	0 99	1 00	1 02
0 8	1 03	1 04	1 05	1 07	1 08	1 09	1 10	1 11	1 13	1 14
0 9	1 15	1·16	1 18	1 19	1 21	1 22	1 23	1 25	1 26	1 28
1 0	1 29	1 31	1 33	1 35	1 36	1 37	1 38	1 40	1 41	1 42

The following statement illustrates the method of calculating the "original gravity" of a sample of beer:

Example.—If the specific gravity of water be taken as 1000, the gravity of the distillate will be less than 1000; suppose it to be 989·33. This number is deducted from 1000 and furnishes the "spirit indication," which in this case is 10·67. On referring to Table I. it will be seen that the corresponding number is 47·35. This represents the number of degrees of gravity which were lost in the production of the spirit during the fermentation of the wort

If the specific gravity of the diluted residue from the distillation was 1023·42, and no acid was detected in the beer, the original gravity of the beer would be 1023·42 + 47·35 = 1070·77.

Suppose however that the acidity was such that 100 grams of the beer required 11 c.c. of semi-normal NaHO for neutralisation; then the percentage of acid, calculated as acetic acid, would be 11 × 0·03 = 0·33. But the average percentage of acidity in unfermented wort amounts to 0·1 per cent, therefore only 0·23 of the acid will be due to oxidation of the alcohol Referring to Table II, it is seen that the spirit indication corresponding to 0·23 of acid is 0·31, therefore the total spirit indication will be 10·67 + 0·31 = 10·98. On referring to Table I it will be seen that the gravity lost by the formation of alcohol in the beer corresponding to this number is 48·9. Hence the original gravity would be 1023·42 + 48·9 = 1072·32.

695. Estimation of Salt in Beer.—Sodium chloride is a normal constituent of beer and its average amount is about 50 grains per gallon: it is rarely added as an adulterant. Its amount may be found as follows:

Evaporate 25 c.c. of the beer to dryness in a platinum dish with 0·1 gram of pure calcium hydroxide, and ignite the residue gently over an Argand burner (95) until a grey ash remains. Triturate this residue in the dish with a little boiling water and heat on the water-bath for half an hour. Then transfer the whole with the washings to a 100 c.c. flask, make up to 100 c.c., shake well and allow the liquid to clear by settling.

Add a few drops of phenol-phthalein solution to 50 c.c. of the clear liquid and neutralise it with decinormal nitric acid, leaving only a faint pink colour in the liquid. Now add a few drops of potassium chromate solution and estimate the chloride by titration with standard silver nitrate solution (373).

The weight of salt is stated as grains per gallon, that is as parts per 70,000.

Analysis of Sugar.

In the chemical examination of sugar, the estimations usually made are those of moisture, ash, cane-sugar, and invert-sugar or glucose. Moist brown sugar will be found the most suitable kind of sugar to use for practice in the methods of analysis.

696. Estimation of Moisture.—Weigh out accurately about 4 grams of the sugar in the watch-glasses with clip and heat this in the steam-oven until its weight becomes constant.

697. Estimation of Ash.—Transfer the dried sugar (696), little by little, to a platinum crucible; and incinerate each part, as it is added, at as low a temperature as possible. The mass will fuse and swell as the heating proceeds, and care must be taken that it is not allowed to pass over the edge of the crucible.

When the charred mass has assumed the appearance of coke, gently stir it from time to time with a thick platinum wire or spatula, or with a thin glass rod, so as to assist the combustion of the carbon; adding finely powdered ammonium nitrate, if necessary, in order to facilitate the process. As soon as the ash is free from black particles, allow the crucible to cool, and weigh the ash.

698. Estimation of the Sugar.—The process which is described below depends upon a chemical reaction. It should be stated, however, that the most accurate estimation of sugar is made by means of the polariscope.

Before the cane-sugar, $C_{12}H_{22}O_{11}$, is estimated chemically, it is usually converted into glucose, $C_6H_{12}O_6$, by digesting it with a dilute acid:

$$C_{12}H_{22}O_{11} + H_2O = 2C_6H_{12}O_6.$$

The glucose is then estimated by heating it with an alkaline solution of copper, known as Fehling solution. The blue colour of this solution disappears during the reaction, while red cuprous oxide is precipitated. The process is sometimes made a volumetric one, by adding the sugar solution in quantity just sufficient to remove the blue colour and to completely precipitate the copper from the Fehling solution (700). Another method consists in causing the sugar to act upon an excess of Fehling solution, and then either weighing the Cu_2O as such, or after oxidation to CuO or reduction to Cu (702).

Allowance must be made, in calculating the result, for the increase in weight which the cane-sugar has undergone by its hydrolysis, which involves combination with the elements of water.

In practice the glucose which was originally present in the sugar is first estimated. The total amount of glucose, including that derived from the conversion of cane-sugar and that which was originally present in the sugar, is then determined. The difference between these two estimations gives the amount of glucose which has been derived from the conversion of the cane-sugar.

Precautions.—It should be noted that solutions containing about 0·25 per cent. of glucose give the most consistent and accurate results in this process of estimation. If the preliminary analyses show that the solution is much weaker or much stronger than this, the amount of sugar in solution should be altered accordingly.

Estimations of sugar by the Fehling solution only yield constant results, or

become comparable with one another, when the process is carried out under precisely similar conditions; hence it is necessary that the Fehling solution should be standardised under exactly the same conditions as those under which the estimations are made. It must also be remembered that the reducing powers of various kinds of sugar are different even if the conditions of estimation remain the same. Thus, taking the reducing value of dextrose as 100, the value of the reducing power as determined by experiment of levulose and invert sugar are respectively,

Dextrose	100 0
Levulose	93 5
Invert sugar	96 8

the above numbers being based on the usual amount of each sugar, from 0 15 to 0 2 gram, being employed for the determination.

It is evident therefore that in accurate analyses the values of the Fehling solution must be adjusted to agree with the above results.

Air should be excluded throughout the process else some cuprous oxide may be redissolved.

699. Preparation of the Fehling Solution.—Weigh out 69 28 grams of pure recrystallised copper sulphate and dissolve this in water, adding a few drops of H_2SO_4 if the solution is not perfectly clear. Add to this a solution containing 350 grams of Rochelle salt and 100 grams of sodium hydrate, and make the mixed solutions up to a litre. Use 25 c.c. of this Fehling solution for each estimation.

The Fehling solution, as thus prepared, gradually undergoes chemical change and alters in strength when it is kept. This change may be obviated by dissolving the copper sulphate in a litre of water, and dissolving the Rochelle salt and the sodium hydrate in another litre of water. These liquids are kept in separate bottles, and 25 c.c. of each of the solutions are mixed together immediately before they are used.

As a rule 25 c.c. of the original Fehling solution, or 50 c.c. of the mixed solutions, correspond to 0 25 gram of dextrose; but it is always necessary to standardise the solution in order to ascertain its exact sugar-value, unless one of the gravimetric methods described in paragraph **702** is used.

700. Standardisation of the Fehling Solution.—In order to standardise the solution, weigh out 5 grams of pure crystallised cane-sugar. Place it in a flask with about 100 c.c. of water and 10 c.c. of strong hydrochloric acid, and heat to 70° C. for ten minutes in order to convert the cane-sugar into glucose. Then neutralise the cold liquid with sodium hydrate solution, and make it up to 500 c.c. with distilled water.

Now fill a burette to the zero mark with this sugar solution, and measure 25 c.c. of the Fehling solution into a 500 c.c. conical flask; or, if the copper and caustic soda solutions are kept in separate bottles, mix together 25 c.c.

of each of them in the flask. Make up the Fehling solution to 200 c.c. with water, heat it to boiling, and add the sugar solution from the burette in portions of about 5 c.c., heating the liquid by immersing the flask in boiling water for two minutes after the addition of each portion of the sugar solution. As soon as the deep blue colour of the copper solution begins to fade, add the sugar solution cautiously while still heating the liquid, and place the flask upon a white surface in order to judge the colour.

As the final disappearance of the blue colour approaches, the red precipitate of Cu_2O somewhat obscures the colour of the copper solution. If, however, a few seconds are allowed for the subsidence of the precipitate, and the flask is slightly tilted, the colour of the solution will be readily seen.

The exact point of complete precipitation of the copper is readily ascertained, even if the liquid is coloured by the precipitate, by placing two drops of it upon a white tile by means of a glass rod, and adding to one of them a drop of potassium ferrocyanide solution which has been mixed with about thirty times its volume of acetic acid diluted with six times its volume of water. If any copper is still present in the solution, the colour of the drop will become more brown. The cautious addition of the sugar solution, followed by boiling, must be continued until this coloration is not produced by the ferrocyanide, and the two drops remain of the same tint.

Now ascertain the strength of the Fehling solution with greater accuracy by repeating the titration, and adding nearly the whole of the requisite quantity of the sugar solution at once within about half a c.c. Heat the liquid in boiling water for two minutes, and finally add the sugar solution very cautiously to this, heating again after each addition. Two such titrations should not differ by more than one-fifth of a c.c. It is necessary to carry out this final titration rapidly, in order to minimise the oxidation which occurs by contact with the air; and it is always preferable, if great accuracy is required, to arrange for a final titration, in which practically the whole of the sugar solution is added at once.

The strength of the solution is stated in terms of glucose.

The whole operation may be conducted while the liquid is kept boiling in a flask closed by a doubly perforated cork, the delivery-jet of the burette passing through one perforation of the cork, and a tube with a Bunsen valve (Fig. 85, page 165) in the other perforation permitting the escape of the steam. Oxidation is thus easily and entirely prevented.

701. Estimation of the "Invert Sugar," or Glucose, originally present in the Sugar.—Dissolve 10 grams of the sugar in water, make the solution up to 200 c.c., and fill a burette to zero with this solution. Then measure out either 25 c.c. of the Fehling solution, or 25 c.c. of each of the separate solutions (699) into a flask, dilute to 200 c.c., and proceed to add the sugar solution to the Fehling solution (700).

If the amount of glucose present is very small, only 5 c.c. of Fehling solution, or 10 c.c. of the mixed solutions, should be used, the precautions on page 354 being duly observed.

The percentage weight of glucose present in the sugar can be readily calculated from the result thus obtained, since the glucose-value of the Fehling solution is known.

702 Gravimetric Methods —Instead of titrating the sugar, its amount may be estimated by adding the Fehling solution in excess to a portion of the sugar solution containing not more than 0 25 gram of glucose, and then heating the liquid in boiling water for ten minutes and filtering. The cuprous oxide is then weighed as such (1), or it is reduced to metallic copper by heating it in a stream of dry hydrogen and the copper is weighed (2), or the cuprous oxide is oxidised and weighed as cupric oxide (3). The process of weighing as cuprous oxide is the most rapid one of these three.

The analyst should first determine the relation between the weight of sugar and the weight of cuprous oxide which it can precipitate This will involve making preliminary experiments on the process with a known weight of pure cane-sugar which has been inverted. The generally accepted factors for dextrose, levulose, or galactose are 0 5045 for Cu_2O; 0 4535 for CuO; and 0 5634 for Cu The result of the determination when multiplied by the appropriate factor should give the corresponding weight of glucose, but these factors vary somewhat with differences in manipulation and are therefore best determined by each analyst.

In carrying out this gravimetric method, 30 c c of the copper solution are mixed with 30 c c of the tartrate solution (699) and with 60 c c of water in a beaker, and this liquid is heated by immersing the beaker in boiling water Twenty-five c c. of the sugar solution, which must not contain more than 0 25 gram of glucose, are then heated to boiling and added to the liquid in the beaker, and the beaker is heated in the boiling water for ten minutes longer. The liquid is then quickly filtered through a weighed asbestos filter (*Note*), using the filter-pump (80), the cuprous oxide is well washed on the filter with boiling water, and is either weighed as such (1), or after reduction (2) or oxidation (3)

(1) If the cuprous oxide is to be weighed as such, it is washed at once with alcohol, then with ether, and is finally dried in the steam-oven and weighed in the filter-tube.

(2) If the cuprous oxide is to be reduced, t is treated as above (1) but is finally heated in the filter-tube in a stream of dry hydrogen or of coal-gas, and the residual copper is allowed to cool in a stream of the gas and is weighed in the tube.

(3) If the cuprous oxide is to be oxidised, it is heated in the filter-tube in a stream of air or of oxygen before it is weighed.

Note.—The asbestos filter is prepared in a hard glass tube (Fig 89, p 259) by passing down to the bottom of the broader part a tightly fitting disc of fine platinum gauze, or a disc of platinum foil which has been perforated by a pin or needle all over its surface. Some asbestos is broken up into a creamy mass in water, and is poured into the tube after it has been connected with the filter-pump. A felted layer of asbestos, about 0 5 c m. thick, is thus formed on the platinum. The asbestos-film is treated successively with dilute acid and with caustic alkali solution. It is then well washed with hot water, with a little alcohol, and finally with a little ether; the tube and filter are then dried in the steam-oven

and weighed. An ordinary filter-paper always retains some copper derived from the solution.

703. Estimation of the Cane-sugar.—Weigh out 1 gram of the cane-sugar accurately, and dissolve it in water in a flask. Dilute the solution to about 100 c.c. with distilled water, and add 2 c c. of strong hydrochloric acid. Then heat the liquid to 70° C. for ten minutes, neutralise it, filter if necessary, make it up to 200 c c., and estimate the glucose by means of the Fehling solution, as is described above (**700, 701**).

By subtracting the percentage of glucose already found (**701**) from the percentage calculated from the present estimation, the percentage of glucose derived from the cane-sugar is obtained.

From this the percentage weight of cane-sugar can be calculated. For since the relative weights of cane-sugar, and of the glucose which it furnishes by inversion, are as 342 : 360, it follows that, if the weight of the glucose found is multiplied by $\frac{342}{360}$, or by 0 95, the weight of the cane-sugar from which the glucose has been derived will be obtained.

An Alternative Method is to add a measured volume of the inverted solution containing less than 0 25 gram of sugar to the Fehling solution, and to weigh the precipitated cuprous oxide as is described in paragraph **702**.

Example.—In a volumetric estimation of the amount of glucose and cane sugar in a sample of moist sugar, the following results were obtained :

For the estimation of the original Invert Sugar 10 grams of the sugar were dissolved in water, and the solution was made up to 200 c c.

Twenty-five c c of Fehling solution, equal to 0 25 gram of glucose, required 60 c.c. of the sugar solution.

Hence the percentage of the invert sugar $= \frac{200 \times 100 \times 0\ 25}{10 \times 60} = 8\ 33$

For the estimation of the Total Sugar, the solution of 2 grams of the sugar was inverted, then neutralised and made up to 200 c c.

Twenty-five c c. of Fehling solution required 27 5 c c. of this sugar solution

Therefore the total percentage of sugar, as glucose, $= \frac{200 \times 100 \times 0\ 25}{2 \times 27\ 5} =$ 90 91.

Hence the percentage of glucose equivalent to the cane-sugar = 90 91 - 8 33 = 82 58 ; and the percentage of cane-sugar = 82 58 × 0 95 = 78 45.

Partial Analysis of Tea.

The value of tea depends upon its natural quality, and upon its freedom from adulteration. The following estimations should be made in order to enable a judgment to be formed on these points :

704. Estimation of Water.—Weigh out accurately about 3 grams of the powdered tea in the watch-glasses with clip, and heat this in the steam-oven until its weight is constant.

705. Estimation of Ash.—Incinerate the dried tea (704), little by little, in a weighed platinum capsule or crucible (Fig. 57, page 57) at as low a temperature as possible, and weigh the ash. The total amount of ash thus obtained should not exceed 6 per cent.

Now add water to the ash and boil; then filter, and wash, dry, ignite and weigh the residue.

From these two determinations, the relation between the soluble and the insoluble matter in the ash may be calculated. This relation furnishes a valuable indication of the adulteration of tea with spent tea-leaves, since fresh tea-leaves contain a large proportion of soluble mineral matter, and this is dissolved out of the leaf during the "mashing." The ash of fresh tea-leaf always contains more than 50 per cent. of soluble matter.

706. Estimation of Tannin.—Extract about 10 grams of the tea by boiling it repeatedly with fresh portions of water. Make up the clear extract to a litre, and estimate the tannin which it contains as is described under the assay of sumach (713). The amount of tannin usually varies from 12 per cent. in black tea to 18 per cent. in green tea, but higher proportions occur in tea from certain sources.

707. Estimation of Theine.—The value of tea depends largely upon the amount of theine which it contains. Proceed to estimate the theine as follows:

Extract 5 grams of the tea with successive small portions of boiling water, allowing ten minutes for each "mashing," and mix these extracts. A Soxhlet extractor (671) may be used for the extraction. Dilute the liquid with water to 600 c.c., heat, add about 4 grams of powdered lead acetate, and boil the liquid with a reflux-condenser for ten minutes. Filter off 500 c.c. through a dry filter, evaporate to about 50 c.c., add a little sodium phosphate solution, and filter. Transfer the filtered liquid to a small flask, add chloroform, connect the flask with a reflux-condenser, and extract for two hours.

Then separate the chloroform solution, pour it through a dry filter into a tared flask, and wash the residue with a little fresh chloroform. Distil off the chloroform, dry the residue at 100° to 106° C., and weigh the resulting theine. The amount of theine may vary from 1 to 3 per cent. according to the variety of the tea.

Valuation of Tanning Materials.

708. The exact estimation of tannin in natural tanning materials is complicated by the fact that there is often present in the same substance a mixture of different tannins. These are also always accompanied by other bodies which affect the accuracy of the determination. Probably no process of estimation gives results of scientific accuracy, but two methods which are employed for technical purposes are described below. The first is a gravimetric method, the second volumetric.

One of these methods (**711**) depends upon causing the tannin, which is contained in the water-extract of a known weight of the tanning material, to combine with hide-powder which has undergone a preliminary treatment of "chroming" The loss of weight, which the dissolved material suffers, gives the weight of the tannin. It is necessary for this purpose to evaporate a portion of the extract or infusion of the tanning substance and ascertain the total amount of matter in solution: then to remove by hide-powder the tannin from another portion of the extract and again determine the matter in solution: the loss of weight caused by the removal of tannin is thus found and the amount of the tannin is estimated.

Thus four samples of oak-wood furnished the following results:

Percentage of	A	B	C	D
Total soluble matter . .	41·3	35·0	37·8	38·1
Soluble non-tanning matter .	14·1	4·7	14·0	4·8
Soluble tanning matter . .	27·2	30·3	23·8	33·3

This method is the more suitable one for the tanner, since it directly estimates the amount of tannin which is concerned in tanning a skin. It is generally adopted for the valuation of tanning materials.

The other method (**712**), proposed by Lowenthal, estimates the tannin by its deoxidising effect upon standard potassium permanganate solution under suitable conditions. It is now mainly employed for the control of tannery liquors.

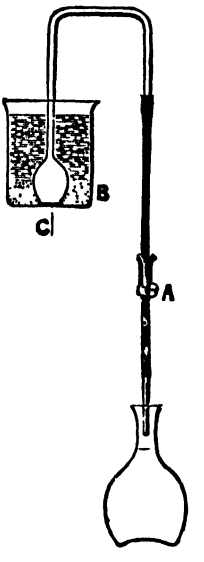
709. The Procter Extractor, which is used for extracting solid tanning materials with water, is shown in Fig. 100. The beaker (B) is used as the extracting-vessel. A common thistle-funnel (C), with its stem bent twice at right angles, serves as a siphon to draw off the extract; the mouth of the funnel has muslin tied over it and is placed on the bottom of the beaker,

and the funnel is held in position by a clamp. A 1·5 cm. layer of sand, which has been purified by treatment with hydrochloric acid, is then poured upon the bottom of the beaker so as to cover the mouth of the funnel, and the prepared and dried tanning material is mixed with the water in which it is to be digested and is poured upon the sand.

After the digestion with water has continued for some hours, either at the ordinary temperature, or at a higher temperature which is secured by immersing the beaker in the water-bath, the extract is siphoned over.

This is accomplished by attaching to the shorter arm of the funnel a narrow glass tube about 15 cm. long, connecting it by means of a short piece of narrow rubber tube provided with a pinch clamp (A). The tube is filled by suction, and the clear extract is allowed to drop into a flask as it is siphoned over. The extraction of the tanning material is finished by pouring successive quantities of fresh water into the beaker and siphoning them over. The process may be considered to be completed when the water is no longer coloured.

Fig. 100.



The Procter Extractor.

710. General Directions for the Preparation of the Extract or Solution.—The tanning material is either supplied in its natural state, or the soluble matter which has been already extracted by water is supplied as a liquid extract, or as a "solid extract," which is the solid residue remaining after the water-extract has been evaporated.

The infusion of the tanning material, which is to be used for the hide-powder process, must contain as nearly as possible 4 grams of tanning matter per litre, and not less than 3·5 or more than 4·5 grams. The weights of different tanning materials to be extracted by a litre of water, or diluted to a litre, in order to obtain an infusion of suitable strength, are tabulated below:

Barks, &c.	Grams	Extracts.	Grams.
Algarobilla	8–9	Oak-wood, sp. gr. 1·2 or over	16
Canaigre	15–18	Chestnut (liquid)	14
Divi-divi	9	Chestnut (solid)	7
Hemlock-bark	32–36	Quebracho (solid)	6
Mimosa-bark	11	Quebracho (liquid)	9–13
Myrobalans	15	Mimosa D.	10–12
Oak-bark	30–36	Gambier (block)	12–14

Barks, &c.	Grams.
Oak-wood	50–100
Quebracho-wood	20–22
Sumach	15–16
Pistacia lentiscus	20–22
Pine-bark	32
Willow-bark	36
Chestnut-wood	45
Mangrove-bark	10
Valonia	14–15
Valonia-beard	10–11
Spent tans	50–100

Extracts.	Grams.
Gambier (cube)	7
Mangrove (liquid)	9
Mangrove (solid)	7
Cutch	7
Myrobalans (liquid)	16
Hemlock	10–14
Pine-bark	16

A Natural Solid Tanning Material must first be well sampled (55) and then suitably broken up and ground until it will pass through a wire sieve of 5 strands per centimetre. The soluble matter is then removed from a suitable weight (see Table above) in a Procter extractor (Fig. 100, page 361) by treatment with 500 c.c. of water at a temperature not exceeding 50° C., and the extraction is continued with boiling water until the filtrate amounts to a litre. The best temperature for extraction differs materially with different samples. When this temperature is not known, it is generally best to begin at about 35° C. and then to raise the temperature to 100° as the operation proceeds. It is desirable to allow the material to soak for some hours before the percolation commences, and the percolation should occupy not less than three hours in order to extract the maximum amount of tannin. Any soluble matter remaining in the material is neglected, or is reported separately as "difficultly soluble" matter. The volume of cold liquid in the flask is made up accurately to a litre.

A Liquid Extract is weighed in a basin or beaker and is washed with boiling distilled water into a litre flask; the liquid is then filled up to the mark with boiling water, is well mixed, and is then rapidly cooled to a temperature of 17·5° C.; after which it is accurately made up to the mark, again well mixed, and then filtered if necessary as is directed below. Sumach and myrobalans extracts should be dissolved at a lower temperature.

A Solid Extract is dissolved by stirring it in a beaker with successive quantities of boiling water, the dissolved portions being poured into a litre flask and the undissolved matter being allowed to settle and being then treated with further portions of boiling water. After the whole of the soluble matter is dissolved the solution is treated similarly to that of a liquid extract.

Filtration.—Solutions of tanning materials, whether they are made from the original substance or from extracts, frequently become turbid on

cooling even if they were clear while hot, and they will then require careful filtration. This is usually effected by passing the liquid through a special Berkefeld candle arranged in connection with a vacuum-pump. After the vacuum has been formed in the flask, the connection between it and the pump must be closed in order to avoid loss of liquid by evaporation. At least 200 to 300 c.c. of the first part of the filtrate should be rejected, and more if necessary, in order to obtain an absolutely clear and brilliant filtrate. The infusion must be filtered repeatedly if necessary until it is optically clear; it must not be merely transparent, but must show no opalescence when the vessel is placed on black paper in a good light.

Part of the filtered infusion is reserved for evaporation (*Note*) and another part is subjected to treatment with the chromed hide-powder.

Note.—If it is desired to estimate the total solids and indirectly the moisture in an extract, and the solution obtained is of uniform turbidity, it is frequently convenient to draw off 50 c c. of the well-mixed and unfiltered solution with a pipette, place it in a basin, and then determine the total solids by evaporation and drying.

Correction for Absorption of Tannin-matter by the Filter is not needed for the Berkefeld candle, or for the Schleicher and Schull No. 590 filter-paper, if from 250 to 300 c.c. are rejected before the portion is collected for the evaporation. But if other methods of filtration are employed the average correction necessary is determined in the following manner:

About 500 c c. of the same or a similar tanning solution are filtered until they are perfectly clear, and 50 c.c. of the well-mixed filtrate are evaporated to determine "total soluble No 1." A further portion is now filtered, the time of contact with the filter and the volume at first rejected being the same as in an actual filtration, and 50 c c are evaporated to determine "total soluble No. 2." The difference between Nos. 1 and 2 is the correction sought, and this must be added to the weight of soluble matter found in an estimation.

An alternative method for determining the correction, which is as accurate and often more convenient, consists in filtering a portion of the tanning solution through the Berkefeld candle until it is optically clear, which can generally be accomplished by rejecting from 200 to 400 cc. and returning the remaining filtrate repeatedly. 50 c.c. of this filtrate and 50 c c. of the clear filtrate obtained by the method for which correction is required are then separately evaporated: the difference between the weights of the two dried residues will be the correction sought.

An average correction should be obtained from at least five determinations. It will be found that this is approximately constant for all materials, and amounts to about 5 milligrams per 50 c.c. in the case of Schleicher and Schull's No. 605 filter-paper when the first 150 c c of the filtrate have been rejected, and to 7·5 milligrams when 2 grams of kaolin are employed in addition for clarification. The kaolin should have been previously washed with 75 c c. of the same liquor, which has been allowed to stand for fifteen minutes and has then been poured off.

Preparation of the Hide-powder by "Chroming."—The hide-powder should be of woolly texture, and should be thoroughly delimed by treatment with hydrochloric acid. After this treatment not more than 5

c.c. or less than 2·5 c.c. of decinormal solution of NaOH or KOH should be required to produce a permanent pink colour with phenol-phthalein when 6·5 grams of the dry powder are suspended in water. If the remaining acidity does not fall within these limits, it must be reduced before "chroming" by soaking the powder for twenty minutes in from ten to twelve times its weight of water, to which the requisite calculated quantity of standard alkali has been added.

The hide-powder must not swell during the "chroming" process to such an extent as to render difficult the necessary squeezing in a press which is described below, and it must be sufficiently free from soluble organic matter to render it possible to reduce the total soluble matter by ordinary washing with distilled water below 5 milligrams per 100 c.c. in a blank experiment.

The moisture in the air-dried powder is determined if necessary, and the weight of powder corresponding to 6·5 grams of the dry hide-powder is then calculated: this will remain practically constant if the powder is kept in an air-tight vessel. Any multiple of this quantity is taken according to the number of analyses to be made, and is wetted with approximately ten times its weight of distilled water. Two grams per hundred of dry powdered crystallised chromic chloride ($Cr.Cl_3.6H_2O$) are now dissolved in water, and are made basic by the gradual addition of 11·25 c.c. of normal sodium carbonate solution containing 0·6 gram of Na_2CO_3: this makes the compound correspond to the formula $Cr_2Cl_3(OH)_3$. The solution is now added to the powder and the whole is mixed by churning it slowly for an hour.

In laboratories where analyses are continually being made, it is more convenient to keep a 10 per cent stock-solution of the chroming liquid. This is made by dissolving 100 grams of $CrCl_3\,6H_2O$ in a little distilled water in a litre flask, adding very slowly a solution containing 30 grams of anhydrous sodium carbonate with constant stirring, and finally making up to the mark with distilled water and mixing well. 20 c.c. of this solution should be used per 100 grams, or 1·3 c.c. per 6·5 grams of the dry powder.

At the end of an hour the powder is squeezed in linen to free it as far as possible from the residual liquor, and it is then washed repeatedly with distilled water and squeezed, until the addition to 50 c.c. of the last filtrate of a drop of 10 per cent. K_2CrO_4 solution and two drops of decinormal $AgNO_3$ solution produces a brick-red coloration. Four or five squeezings are usually sufficient, but more may be necessary. Such a filtrate cannot contain more than 0·001 gram of NaCl in 100 c.c. The powder is then squeezed in a press until it contains from 70 to 75 per cent. of water, and the whole is weighed.

711. The Process of Estimation.—The detannisation of part of the tannin extract is effected by weighing out a quantity (Q) of the chromed

powder which contains 6·5 grams of the dry powder; this is added immediately (*Note*) to 100 c.c. of the unfiltered tannin infusion, together with 20·5 – Q grams of distilled water, and 1 gram of kaolin freed from soluble matter. The whole is agitated for fifteen minutes in a corked bottle, which is caused to rotate not less than 60 revolutions per minute, and the contents are then squeezed immediately through linen, stirred, and filtered through a folded filter of sufficient size to hold the entire filtrate: the filtrate is returned to the filter until it is clear, and 60 c.c. are then evaporated and reckoned as 50 c.c., and the weight of the dried residue is ascertained. Another 50 c.c. of the original extract is then similarly evaporated and the weight of the dried residue is ascertained.

These evaporations are rapidly carried to dryness at steam-temperature in flat-bottomed porcelain, Jena glass, or platinum basins of not less than 6·5 cm. diameter; and the residue is subsequently dried at from 98° to 100° in vacuo, or in a water- or steam-oven with small compartments, until it is of constant weight; it is subsequently cooled in a small air-tight desiccator over dry calcium chloride for at least twenty minutes. Not more than two basins are placed in one desiccator, and the basins must not be wiped after removal from the desiccator. The basins must be weighed rapidly to avoid absorption of moisture. As has been already stated (**708**) the difference in weight between these two residues is the weight of tanning matter present in the volume of extract taken, and from this the percentage weight of tanning matter in the sample can be calculated.

The Analysis of Used Liquors and of Spent Tans should be made by the same methods as are employed for fresh tanning materials, the liquors or infusions being either diluted, or concentrated by boiling in vacuo or in a vessel so closed as to restrict access of air, until the amount of "tanning matter" is if possible between 3·5 and 4·5 grams per litre, but in no case must the amount of "total solids" present exceed 10 grams per litre. The weight of hide-powder to be used is 6·5 grams.

Note.—The moist hide-powder should not be kept for more than a few hours before it is used, without special precautions. The non-tannin filtrate must give no turbidity when it is mixed with a drop of solution containing 1 per cent of gelatin and 10 per cent. of salt.

712. The Lowenthal or Permanganate Method.—This method can only be used for the estimation of the relative tanning-value of different specimens of the same tanning material; it is useless for comparing the relative tanning-values of different kinds of tanning materials.

The principles upon which the method depends, are the following:

Solution of potassium permanganate is readily reduced by solution of tannin, and the relative reducing powers of the different varieties of tannin have been determined. Accordingly if the tannin could be extracted from the various tanning materials, unaccompanied by other oxidisable matter,

its amount could be readily estimated by titrating the extract with standard permanganate solution.

But an extract of a tanning material invariably contains other substances, besides tannin, which reduce permanganate. Hence it becomes necessary to titrate a portion of the extract with permanganate, and then to titrate in a similar way a second portion of the extract from which the tannin has been removed. The difference between the volumes of permanganate solution which are required in the two titrations represents the volume of the permanganate solution which has been required for the oxidation of the tannin.

In order to limit and make definite the oxidising action of the permanganate on the oxidisable matter, a known volume of indigo-carmine solution is added, and the permanganate solution is added to the extract until the blue colour of the liquid changes to a clear yellow.

The following solutions and other chemicals are required for the Löwenthal process:

(a) *Standard Potassium Permanganate Solution.*—Half a gram of pure permanganate crystals is dissolved in water and the solution is made up to a litre; but if many titrations have to be made, it is better to dilute 100 c.c. of a solution containing 5 grams per litre when it is required, since weak permanganate solutions undergo change when they are kept.

The actual tannin-value of the permanganate solution is then determined, if necessary, by titrating with it a solution of pure tannin, under exactly the same conditions as those under which the extract of the tanning material is to be subsequently titrated (713).

For this purpose the amount of moisture present in 1 gram of pure tannin is estimated by drying it at 100° C.; two grams of the undried tannin are then dissolved in water and the solution is made up to a litre, and this solution is used for the titration with the permanganate.

Assuming that the sample of tannin contains 86·8 per cent of dry tannin, the 2 grams of tannin will contain $2 \times 0{\cdot}868 \times 1{\cdot}05 = 1{\cdot}8228$ grams of pure dry tannin, and this weight of tannin is contained in a litre of the solution.

The result obtained by the titration is multiplied by the factor 1·05 in order to make allowance for oxidisable impurities in the tannin, and the tannin-value of each c.c. of the permanganate solution is then calculated.

This process evidently only fixes the tannin-value of the permanganate when it is used for estimating the same kind of tannin as that which was employed for standardising the solution, but a method for extending the method of titration to other forms of tannin is described in paragraph 714.

It is however more simple to use a solution of 0·1 gram of pure crystallised gallic acid in 100 c.c. of water as a standard, and to calculate by the factor in the Table on page 370 the kind of tannin which is required. Thus 1 gram of pure gallic acid is equivalent to 1·34 gram of pure gallotannic acid.

(b) *Solution of Pure Indigo-carmine.*—This is prepared by dissolving 5 grams of pure dry sodium or potassium sulphindigotate (Carminum cærul. opt.) in distilled water, 50 grams of pure sulphuric acid are added, the solution is diluted to a litre, and is then filtered if necessary.

(c) *Solution of Gelatin* is made by allowing 2 grams of the purest gelatin in thin sheets to soak in cold distilled water for a few minutes, rejecting the washing-water, and finally dissolving the gelatin by heating it upon the water-bath after adding enough water to make up to about 100 c.c. This solution should be made shortly before it is required for use, since it is liable to undergo change.

(d) *Kaolin*, purified by washing and levigation.

(e) *Sodium Chloride Solution.*—Good table-salt in saturated solution containing 50 c.c. of concentrated sulphuric acid per litre.

713. The Process of Estimation.—The estimation of the value of a sample of sumach is made as follows :

An extract of from 15 to 16 grams of the sumach is prepared according to the directions already given (710).

Five c.c. of the filtrate, or less if necessary, are measured into a beaker about a litre in capacity, together with 25 c.c. of the indigo solution (b), and 750 c.c. of distilled water or of good tap-water. The amount of the indigo solution added should require, when it is titrated alone, from 25 to 30 c.c. of the permanganate solution in order to change its colour to pure yellow.

The permanganate solution (a) is now dropped from a burette, furnished with a glass stop-cock, into the mixture in the beaker until the blue colour of the solution begins to change to green. The addition must be made at a constant rate, and the liquids must be well mixed by vigorous stirring during the whole titration.

As soon as a green tint appears, the permanganate is dropped in much more slowly until the solution assumes a dirty greenish yellow colour. It is best at this stage to allow the liquid to stand for a moment or two, and then to drop in the permanganate, one or two drops at a time, and to stir vigorously after each addition. This procedure is continued until the liquid in the beaker assumes a clear yellow colour.

This titration should then be repeated, and the two results thus obtained should not differ by more than 0·1 c.c. The correspondence of the results is made more certain if the liquid from the first titration is kept, and care is taken that the tint finally obtained in subsequent titrations exactly matches it; this insures all titrations being carried to the same stage. A constant error may still be introduced, but this will not affect the final result.

The titration can be made by artificial light diffused by passage through ground glass or tissue-paper; but as the end-point is slightly different with different lighting, the whole of an analysis must be made under the same conditions of illumination.

The result of this titration corresponds to the total amount of oxidisable matter, both tannin and non-tannin, which is present in the sumach.

It is now necessary to remove the tannin from a portion of the solution, in order to determine the non-tannin matter separately and the tannin by difference. For many purposes the use of hide-powder, as is described under *Detannisation* in paragraph **711**, may be adopted to remove the tannin; but this may also be effected by means of gelatin as is described in the following paragraphs. See also *General Remarks* on page 369.

50 c.c. of the original filtered solution of the sumach are introduced into a 100 c.c. stoppered measuring-cylinder, 25 c.c. of the gelatin solution (c) and 25 c.c. of the acidified salt solution (e) are added, and the mixture is shaken to insure perfect mixture; a teaspoonful of kaolin (d) is then added to facilitate the filtration, and the liquid is filtered.

10 c.c. of the filtrate, corresponding to 5 c.c. of the original solution, are now titrated with the permanganate as is described above, and the process is repeated until corresponding results are obtained. Since the gelatin, in the presence of salt and sulphuric acid, precipitates the tannin-matter, it is evident that the difference between the result of this titration and of that already carried out on the untreated extract will give the amount of permanganate solution which has been reduced by the tannin-matter itself. From this result the percentage of tannin may be calculated, if necessary, as is described hereafter.

The Following Precautions must be attended to in carrying out the Lowenthal Process.

(1) If the gelatin, kaolin, or salt, which are used to precipitate the tannin, contain any soluble oxidisable impurities such as sulphites, these would render the titration-result of the oxidisable non-tannin matter too high When very accurate results are desired, it is well to ascertain whether this source of error exists.

This is done by mixing together the same quantities of indigo solution, distilled water, kaolin, and acidified salt solution as are used in a titration The mixture is made up to 100 c c , then filtered, and 20 c c. of the filtrate are titrated with the permanganate. If the amount of permanganate reduced exceeds by more than 0 1 c c. that required by the indigo solution alone, one-half of this excess must be deducted from the result obtained by the titration of the oxidisable non-tannin matter, before this is subtracted from the result representing the total oxidisable matter present in the extract.

(2) The indigo solution in this method serves not only as an indicator, but it also controls the oxidising action of the permanganate by keeping it within certain definite limits In order to insure a uniform limiting action, the volume of the permanganate solution which is used in a titration must never much exceed one

and two-third times that which is required by the indigo alone; if this quantity is exceeded, the tannin solution must either be diluted or a smaller volume of it must be taken and the titration must be repeated.

(3) If the titrations are not carried out in a strictly similar manner, as regards stirring and rate of addition of the permanganate, comparable results cannot be obtained, since the procedure during titration considerably affects the ultimate result.

Calculation of Löwenthal Analysis of Sumach.—Fifteen grams of sumach per litre were used as for the gravimetric analysis. 25 c c. of the indigo solution with 2 5 c c. of the sumach infusion required in two titrations 41 35 and 41 25 c c of permanganate, or an average of 41 3 c.c. 25 c c. of the indigo solution alone required 26 7 c c. Accordingly 2 5 c c. of sumach-extract required 14 6 c c., and 10 c c. of the original sumach solution would require 58·4 c.c. After detannising the extract, 10 c c. if the precipitation by gelatin was used, or 6 c c. = 5 c.c of original solution if the gravimetric method with wet powder was used, were mixed with 25 c c. of the indigo solution and required 28 7 c c. of permanganate, and after deducting 26 7 c c. for the indigo, the sum of two such determinations was 4 c.c. This corresponded to 10 c.c. of the original liquor. The volume of the permanganate solution required for the tannin in 10 c c. is therefore 58 4 - 4 0 = 54 4 c c.

Similarly two 5 c c portions of the gallic acid solution, which are together equal to 10 c c. of the 1 gram per litre solution, required 19 4 c.c. of the permanganate Now 1 gram of gallic acid is shown by the Table (714) to be equivalent to 1 5 gram of sumach-tannin, and the gallic acid solution is therefore equivalent to a solution containing 1 5 gram per litre of sumach tannin. Accordingly

$$19\,4 : 54\,4 \times \frac{100}{15} : : 1\,5 : 28 \text{ per cent.}$$

The gravimetric analysis of the same sumach gave 27·5 per cent. of tannin, and substituting this in the above equation, we obtain

$$\frac{27\,5 \times 19\,4 \times 15}{54\,4} = 1{\cdot}47 \text{ gram,}$$

the amount of the tannin of this particular sumach as determined gravimetrically which is equivalent to 1 gram of gallic acid. Substituting this for the factor 1 5 actually employed in the Löwenthal analysis, the result obtained by the method would exactly correspond to that yielded by the gravimetric method.

General Remarks on Detannisation —Shaking with chromed hide-powder is generally to be preferred to precipitation with gelatin, since the results of the former method can be calculated, by multiplication by a suitable factor, with very considerable accuracy into those of the gravimetric method by which materials are usually bought. Such a factor may be obtained from the Table (714), but it is always more safely found by direct estimation made on an average sample of the tannery liquors

Great simplification may be made in the method of detannisation when no gravimetric determination is required, since the Lowenthal titration is unaffected either by the salts present in the chroming liquor or by traces of dissolved hide-substance, so that washing is superfluous and the powder needs only to be chromed and squeezed, and the necessary water added as is described in the gravimetric method.

A still further shortening of the manipulation is obtained by using Professor Paessler's "lightly chromed" dry hide-powder, obtainable from the Research Institute for Leather Industries, Freiberg-in-Sachsen, or even by using fine freshly air-dried chrome-leather shavings from the machine as suggested by Kopecky. 7 grams of the dry powder and a little kaolin are well mixed with 100 c.c. of the diluted liquor, and are shaken in a suitable machine for fifteen minutes; the liquid is then filtered and 5 c.c. are titrated. It is uncertain whether the small amount of hygroscopic water contained in such an air-dried powder, not exceeding in this case 1 gram, really acts as water of dilution when the powder is shaken with a liquor; but in any case the error thus introduced cannot exceed one-hundredth part of the total tannin present, and as it is constant in all analyses, and these are only required for comparative purposes, it may be neglected without hesitation.

714. Determination of the Absolute Percentage present of any Form of Tannin.—If it is desired to determine the actual percentage weight of any form of tannin other than gallotannic acid in a sample of tanning material by the Lowenthal method, it is necessary to resort to the gravimetric process already described (**711**) in order to standardise the permanganate solution.

5 c.c. of the original extract (**710**) is titrated as is directed above (**713**). 6 c.c. representing 5 c.c. of the same extract after detannisation (**711**), is similarly titrated in order to estimate the amount of non-tannin matter present. 50 c.c. of the original extract and 60 c.c. of the filtrate from the hide-powder are then evaporated separately, and the residues are dried as directed and weighed. The actual weight of the tannin matter, which corresponds to the gallic acid equivalent of the permanganate reduced, can then be calculated and a factor obtained.

This method is obviously useless for a single estimation, but when a number of titrations of similar tanning solutions are being made it is often very convenient. In some cases the proportion of oxidisable non-tannin matter can be assumed to be constant, and the tannin-strength of a liquor is then obtained by a single titration.

Table of Average Factors for Lowenthal's Method.

Material.	Tannin value of 1 gram of gallic acid.
Chestnut-wood tannin	1·65
Oak-wood tannin	1·89
Myrobalans tannin	1·73
Quebracho-wood tannin	1·69
Valonia	1·58
Sumach	1·50
Oak-bark	1·71
Mimosa-bark	1·88
Mangrove-bark	1·46
Gambier cube	1·78
Average of all above materials	1·69

SOAP ANALYSIS

715. In an ordinary analysis of soap, it is not necessary to estimate all the constituents. The determination of water, free and combined alkali, fatty acids, and insoluble matter will commonly suffice.

The first scheme described below (**716–721**) is rapid, and is sufficient for ordinary technical analyses.

A more complete chemical examination of the soap would include the estimation of the amount of free fat, resin, glycerine, and of certain other substances. In many cases also an investigation is required into the nature of the fatty acids present.

Two schemes for more complete analysis are drawn out below. That described in paragraphs **722–728** includes the estimation of all the constituents of an ordinary soap, while that described in paragraph **730** may be used for toilet or other special soaps.

Scheme for Partial Analysis of Soap.

716. An Average Sample of hard or soda soap is obtained by cutting out a slice at about one-third the length of the bar; either the whole of this slice or a half or quarter may be taken as representing the soap, and this is thoroughly mixed by cutting it up, and is at once placed in a stoppered bottle.

A soft or potash soap should be well mixed before taking the sample.

Moisture.—One gram of the average sample, in fine shavings, is dried in the water-oven for six hours or more, and is weighed when cool; the drying is then repeated for an hour and the soap is again weighed, and these processes are repeated until two consecutive weighings closely agree with one another.

717. Ash.—Place 2 grams of the average soap (**716**) in a small platinum dish and ignite it at a moderate heat. If any difficulty is experienced in burning off the carbon, treat the mass with water and filter, then dry and ignite the filter in the dish: now add the filtrate to the incinerated filter, evaporate to dryness, and gently ignite the residue.

718. Insoluble Matter.—Dissolve the ash (**717**) in water, and filter if there is any appreciable residue; reserve the filtrate, and wash, dry, ignite and weigh the insoluble matter.

719. **Total Alkali.**—Titrate the aqueous solution of the ash (718) with seminormal hydrochloric acid, using methyl-orange as an indicator. Then calculate the weight of alkali, using 0·775 as the factor for the conversion of HCl into Na_2O, and 1·27 as the corresponding factor for K_2O in a potash soap.

720. **Free Alkali.**—Dissolve 3 grams of the average soap in fine shavings by warming it with 150 c.c. of methylated spirit, which has been made neutral to phenol-phthalein by the addition of NaOH solution.

(a) Titrate 50 c.c. of this solution with decinormal hydrochloric acid, using phenol-phthalein as an indicator, to obtain the amount of NaOH or KOH present.

(b) Boil 50 c.c. of the alcoholic solution with 5 c.c. of decinormal hydrochloric acid to decompose any carbonate present, then cool the liquid and titrate it with decinormal caustic soda solution, using phenol-phthalein as an indicator.

The amount of HCl neutralised by the Na_2CO_3 or K_2CO_3 will be equal to the difference between the amounts of the acids which have been neutralised in (b) and (a).

721. **Fatty Acids.**—Dissolve 10 grams of the average soap in 250 c.c. of water contained in a beaker, and heat with excess of dilute H_2SO_4 until the fatty acids separate out as a clear layer. Then cool, and filter the aqueous solution through a plug of glass-wool, rejecting the filtrate. Remelt the mass of fatty acids several times with boiling water, stirring vigorously each time, and finally introduce the mass into a glass basin; melt the fatty acids in the basin, pour off the clear part into a weighed beaker, and heat this in the water-oven until its weight remains constant.

Now wash the vessels and the glass plug with cold water until they are free from acid; then dissolve the fatty acids from them with boiling methylated spirit, collecting the liquid in a weighed beaker. Evaporate the alcoholic solution on the water-bath, and dry the residue in the steam-oven until its weight is constant.

The sum of the two weights thus obtained gives the total weight of the fatty acids, and this is multiplied by 0·97 to obtain the weight of the fatty anhydrides.

Note.—In case the fatty acids are fluid or very soft proceed as is directed in the *Note* (726).

Scheme for more Complete Analysis of Soap.

722. Preparation of an Average Sample for Analysis.—The following special method for preparing an average sample for analysis is described because soap contains a large proportion of water which is differently distributed throughout the mass, the outside of the sample usually containing much less moisture than the inside.

Cut out a slice of the soap through the middle of the bar, and at right-angles to its long axis. This slice must either weigh exactly 50 grams, or else the volume to which the soap solution is diluted must be adjusted accordingly. Warm the soap with air-free distilled water until it is dissolved. Then dilute the solution, and filter it if necessary through a dried tared filter.

Any insoluble matter thus obtained is dried on the filter and weighed.

The warm solution is cooled in a half-litre flask to about 60° C.; it may gelatinise if its temperature is further reduced. It is then made up to the mark with air-free water at 60° C., and the liquid is thoroughly though gently mixed by inverting the flask, since if the liquid is violently agitated it will froth seriously. Several portions of 50 c.c. and 100 c.c. each are then at once measured off by heated measuring-flasks into separate vessels for analysis.

An alternative method consists in making the solution up to 500 c.c. at 60° C., then allowing it to cool and set, and bringing it to the liquid state in the stoppered measuring-flask, when necessary, by warming the contents of the flask to 60° C. If the soap-solution has been allowed to stand aside, it must always be thoroughly mixed before any portion is measured off for analysis.

723. Estimation of Moisture.—50 c.c. of the above solution of the soap, corresponding to 5 grams of the soap, are evaporated to dryness in a weighed platinum or porcelain dish upon the water-bath. The soap residue is dried in the steam-oven, or in an air-bath at 120° C., until the weight is constant, and the weight of the dry residue is subtracted from 5, in order to obtain the weight of water which was originally present in 5 grams of the soap.

724. Estimation of Matter Insoluble in Alcohol.—Transfer the dried soap from the dish (723) as completely as possible to a 15 cm. filter, which has been previously treated with alcohol and then dried at 100° until its weight is constant. Ascertain the amount of soap, which has been removed to the filter, by reweighing the dish. Then press the filter round the soap so as to enclose it in a bag, and place the filter containing the soap in the Soxhlet extractor (671). Pour absolute alcohol into the flask and drop in a few pieces of platinum-foil to prevent the alcoholic solution of soap from

bumping; then boil the spirit, and allow the extraction to continue for two hours.

The filter will now contain any matter which was present in the soap and was insoluble in alcohol, such as starch and alkaline silicate and carbonate. Dry the filter with its contents in the steam-oven until its weight is constant, and subtract the weight of the filter in order to obtain the weight of the insoluble matter.

The amount of mineral matter, which is present in this residue, may then be found by incinerating the residue and filter at the lowest temperature possible, weighing the residue and subtracting the weight of the filter-ash.

725 Estimation of the Alkali which is present as Hydroxide, Carbonate, and Silicate.—Since the evaporation of the soap solution would convert the alkaline hydroxide into carbonate, it is necessary to dissolve a slice of the soap (722), weighing 20 grams, in 200 c.c. of absolute alcohol. This solution is filtered, and 50 c.c. of the filtrate are titrated with normal sulphuric acid, using phenol-phthalein as an indicator. This titration gives the amount of sodium hydroxide present (*Note*).

The residue on the filter is dissolved in water, and the solution is titrated with standard acid in the presence of methyl-orange in order to estimate the amount of Na_2O present as carbonate and as silicate.

Note.—The above separation of sodium hydroxide from sodium carbonate by means of absolute alcohol is frequently not complete. If the alcohol is quite absolute some NaOH remains undissolved, while if water is present some Na_2CO_3 may pass into solution. A qualitative test for free alkali may be made by placing a drop of phenol-phthalein solution on the freshly cut surface of the soap; if no red coloration appears, free alkali is absent and absolute alcohol may be satisfactorily used.

726. Estimation of the Fatty Acids.—The fatty acids in the soap may either be determined in the alcoholic solution, which has been neutralised with the normal acid as is described above (725), the solution being diluted with water and then boiled until all the alcohol is removed; or 50 c.c. of the original soap solution (722), corresponding to 5 grams of the soap, may be used for the determination.

In either case, a measured quantity in excess of normal sulphuric acid is added to the soap solution contained in a beaker, a dish, or a conical flask. The vessel is then heated on the water-bath, or gently boiled, until the fatty acids form a transparent layer, free from white spots, on the top of the liquid, and a clear solution remains below.

The fatty acids are most conveniently separated from the liquid in a dish and are then washed by using the "butter-flask" as is directed in paragraph 688. The aqueous liquid and washings are reserved for the estimation

of the alkali (728), and the weight of fatty acids found is multiplied by 0·97 in order to obtain the weight of the fatty anhydrides.

Another method consists in decomposing the soap solution by the acid in a beaker, and cooling the hot liquid until the fatty acids set into a solid cake. The aqueous solution is then filtered through a wetted filter, and the fatty acids in the beaker are washed by shaking them with hot water, cooling, and pouring off the aqueous portion again (*Note*). This washing process is repeated until the washing-water no longer affects blue litmus-paper. If the washing is carefully performed, very little fatty acid will be present on the filter.

The funnel containing the filter is placed in a small beaker and dried in the steam-oven. The fatty acids are dissolved from the beaker and the filter by means of alcohol, and the solution is added to the fatty acids in the beaker. The beaker and its contents are then heated on the water-bath and then in the steam-oven until the weight becomes constant. The weight of fatty acids thus found is multiplied by 0 97 in order to obtain the weight of the fatty anhydrides.

Note.—Instead of washing the fatty acids upon the filter, they may be removed as a cake, which is washed with cold water, this becomes a necessity if the fatty units are liquid or very soft For this purpose from 5 to 7 grams of white wax are accurately weighed out, and are kept in a melted state with the fatty acids in the beaker on the water-bath, after the normal acid has been added, until all water separates from the melted layer. The beaker is then cooled, and a firm cake is obtained which can be removed, rinsed with cold water, drained, dried with filter-paper, and weighed: any fatty matter which remains adhering to the inside of the beaker is scraped off, washed, dried in a desiccator, and weighed with the cake. From the total weight thus obtained the weight of the wax is subtracted, and the result is the weight of the fatty acids.

727. Twitchell's Process for estimating Resin Acids in mixture with Fatty Acids.—The process depends upon the conversion of the fatty acids by suitable treatment into their ethylic esters, the resin acids under the same treatment remaining unaltered. The resin acids are then either separated and weighed as such, or are estimated by titration.

About 2 grams of the dry fatty acids (726) are accurately weighed into a suitable flask, 25 c.c. of absolute alcohol are added, and the flask is gently warmed to dissolve the acids.

Dry hydrochloric acid gas is then passed rapidly through the alcoholic solution for about half an hour, the flask being cooled meanwhile by immersion in running water.

The hydrogen chloride may be generated by slowly dropping strong sulphuric acid from a tap-funnel into strong solution of hydrochloric acid, and drying the gas by passing it through strong sulphuric acid.

It is advisable to introduce a stop-cock or screw-clip between the drying-flask and the alcoholic solution, so as to be able to prevent any back-rush of the alcoholic solution when rapid absorption is taking place. With this object the rate of evolution of the hydrogen chloride may be increased while the first rapid absorption of gas continues, and diminished when the

absorption and esterification approaches completion. The excess of the gas may be absorbed by passing it up a tower filled with marbles down which water is allowed to flow.

As soon as the action is complete, which is known by the dark colour of the liquid and the escape of unabsorbed HCl, the flask is removed from the cooling-bath and is allowed to stand for half an hour.

The fatty acids will now have been converted into their ethylic esters while the resin acids will be present in a practically unchanged condition. The estimation of the resin acids can now be made by separating and weighing them (A), or by titrating them in the mixture of fatty and resin acids (B).

(A) **Estimation by Direct Weighing of the Resin Acids** —The liquid is diluted with about five times its volume of cold water and is heated on the water-bath until it becomes practically clear, the mixed resin acids and ethylic esters forming an upper oily layer.

The flask is then cooled, 40 c.c. of petroleum ether are added, and the whole is transferred to a stoppered separating-funnel, the flask being rinsed out into the funnel with 10 c.c. of petroleum ether. The separator is now gently shaken, and the lower acid layer is allowed to flow off after the liquids have had time to separate. The residual ethereal solution is washed once in the funnel with water to remove most of the remaining hydrochloric acid, and is then mixed with 50 c.c. of an alcoholic solution of potash, which is made by dissolving 10 grams of pure potassium hydroxide in water, adding 85 c.c. of absolute alcohol and diluting to a litre with distilled water. The mixing is best effected by rolling the separator round gently on the bench so as to avoid the formation of an emulsion.

The liquids are now allowed to separate completely, and the lower layer containing the resin soap is transferred to another separator, while the upper layer may be reserved for the isolation of the fatty acids if necessary.

The lower alkaline liquid in the separator is then mixed with 25 c.c. of dilute sulphuric acid, and the liberated resin acids are dissolved out by shaking the liquid with 50 c.c. of methylated ether. The lower layer is allowed to flow away, and the ethereal solution is washed three times with water in the separator, and transferred to a weighed beaker or flask; after the ether has been removed by evaporation, the resin acids are dried in the steam-oven until their weight is constant.

The resin which is thus obtained should be transparent and hard; if it remains slightly soft and sticky after being dried, it probably retains a small amount of fatty acid.

(B) **Estimation of the Resin Acids by Titration.**—The esterification is carried out as has been described above. After the dark liquid thus obtained

has been transferred to the separator, it is well shaken and allowed to separate completely into two layers; the acid layer is allowed to flow away, and the ethereal solution is washed thoroughly with successive amounts of water, until the washing-water is perfectly neutral to litmus.

50 c.c. of neutral alcohol are then added to the ethereal solution of the esters and resin acids, and the liquid is titrated with standard caustic alkali, using phenol-phthalein as an indicator. The alkali immediately combines with the resin acids, whilst the aliphatic esters remain practically unaltered.

The average combining equivalent of resin acids is usually taken as 346, so that 1 c.c. of the normal alkali solution corresponds to 0·346 gram of resin acids.

The volumetric method is somewhat more rapidly carried out than the gravimetric. It is, however, less accurate, since its results depend upon the correctness of the combining equivalent of the resin acids which varies in different samples, whereas the gravimetric method directly determines the actual weight of these acids. Even the gravimetric process must not be considered to give results which are absolutely accurate, and the error may amount to as much as 5 per cent. of the amount of resin present: this method is, nevertheless, the most accurate one known for the determination of the amount of resin present in soap

728 Estimation of the Total Alkali.—All the alkali will be contained in the aqueous filtrate (726), if the original soap solution was employed for the estimation of the fatty acids. If, however, the alcoholic solution (725) was used for the estimation of the fatty acids, the filtrate (726) will contain the total alkali, less that which is present in the insoluble residue (725).

In either case the excess of standard acid is measured by titrating the filtrate with standard sodium hydrate solution. Since a known volume of standard acid was originally added to the soap solution (726), the quantity of acid corresponding to the total alkali in the soap can now be obtained by difference, and from this result the amount of the combined alkali, Na_2O, or K_2O, may be calculated.

729. Potash Soap or Soft Soap.—Since the alkali present in this soap is potassium oxide, the alkali must be calculated as K_2O instead of as Na_2O. If both sodium and potassium are to be estimated, a measured volume of the soap-solution (722) is decomposed by hydrochloric acid instead of sulphuric acid (726), and the alkali metals are determined in the filtrate from the fatty acids by proceeding as is directed in paragraphs 428, 429.

For the Results of Analyses of Soaps refer to paragraphs 967, 968.

730. Complete Analysis of Soap

Measure 50 c c of the Soap Solution (722) and evaporate this on the water-bath, or weigh tracted from 5, gives the **Weight**

Remove this residue to a tared filter, which has been extracted with petroleum ether, and treat

Ether Extract. Distil off the ether, and dry the flask at 100° C, until its weight is constant. The residue is **Uncombined Fat.**

Note. — Essential oils and certain adulterants may be present in this residue.

The Residue in the filter consists of soap and other

The Alcoholic Extract contains soap (fatty anhydride and combined alkalis), resin, and glycerine Add a few drops of phenol-phthalein, and exactly neutralise with dilute H_2SO_4 if free alkali is shown to be present by the colour of the phenol-phthalein

Free Alkali For this estimation refer to par. 725.

Add a large excess of water, and boil off all the alcohol Decompose the soap by adding a measured volume in excess of normal H_2SO_4; boil, separate the free fatty acids (726), filter and wash

The Filtrate contains combined alkali and glycerine Titrate it with normal sodium hydrate solution

From the volume of sodium hydrate solution used, the H_2SO_4, which corresponds to the **Combined Alkali**, is known The amount of the combined alkali is calculated as Na_2O

After titration, evaporate the liquid to dryness on the water-bath Heat the residue with 1 part of chloroform and 2 parts of absolute alcohol, evaporate the clear alcoholic solution to dryness in a tared dish, and weigh the residual **Glycerine**

Note.— The residue should be incinerated, and the weight of any ash thus found must be deducted from that of the glycerine.

The Residue on the filter-paper consists of **Fatty Acids and Resin.** Dry it at 110° C, and weigh Dissolve an aliquot part in 20 c c. of strong alcohol, saponify by heating with sodium hydrate solution added in slight excess, using phenol-phthalein to ascertain when excess is present Boil, cool, transfer to a stoppered cylinder, and add ether until the volume is 100 c c Add a fair quantity of $AgNO_3$ in fine powder, shake well for ten minutes, and allow to settle

The Precipitate, which consists of stearate, palmitate, and oleate of silver is rejected.

The Solution consists of resinate of silver Filter off 50 c c from the total 100 c c Decompose this with 20 c c dilute HCl (1 of acid : 2 of water) Measure the volume of the liquid, allow the AgCl to settle, and evaporate an aliquot portion of the clear solution in a tared dish. Dry the residue at 110° C., and weigh **The Resin.** For each 10 c.c of solution evaporated, subtract 0 00236 gram, to correct for dissolved oleic acid

Subtract the weight of resin in 5 grams of soap from the corresponding weight of the fatty acids + resin, and multiply the weight of the fatty acids thus obtained by 0·97 (726).

[Modification of Leeds' Scheme).

5 grams of the average soap and dry at 100° C. The weight of the dried substance, when sub- of Water in 5 grams of the soap.

the soap, wrapped up in the filter-paper bag, with petroleum ether in the Soxhlet apparatus (671).

constituents. Treat this with alcohol in the Soxhlet apparatus.

The Residue consists of Na_2CO_3, NaCl, Na_2SO_4, sodium silicate, starch, and insoluble matter Wash with 60 c c. of cold water

The Filtrate consists of Na_2CO_3, NaCl, Na_2SO_4, and sodium silicate Make the solution up to 100 c c, and use separate portions of 20 c c. each for the following estimations

Na_2CO_3 Titrate with normal H_2SO_4, and calculate the result as **Na_2CO_3**. This will include any Na_2O originally present in the residue as silicate and as hydrate (725)

NaCl Titrate with $AgNO_3$ (373), or precipitate as AgCl, and weigh (149) Calculate the result as **NaCl**.

Na_2SO_4 Acidify with HCl, precipitate with $BaCl_2$ solution, and weigh the $BaSO_4$ (133) Calculate as **Na_2SO_4**.

SiO_2. Decompose with HCl, evaporate down to dryness, heat the residue at 150° in the air-oven, and determine the **Silica** in the residue (210).

The Residue consists of starch and insoluble matter. Dry at 100° C, and weigh the **Starch + Insoluble Matter**

Boil the residue with about 100 c c. of water. Place the solution in a small bottle, and add 1 c c. of strong H_2SO_4 Cork the bottle, and wire down the cork tightly. Heat the bottle and its contents on the water-bath for several hours Then neutralise the excess of acid, titrate the glucose thus formed with Fehling solution (701), and calculate the weight of the **Starch**

The weight of the **Insoluble Matter** is found by difference.

PART IV.—SECTION XII.

EXAMINATION OF OILS, FATS AND WAXES.

Introductory.

740. The following is a general description of the characters of Oils, Fats, and Waxes, and of the chemical methods suitable for their identification These subjects have not been treated exhaustively, and special books (**1021**) should be consulted if fuller information is required.

When they are chemically considered, the majority of the vegetable and animal oils and fats are glycerides of the fatty acids, whereas the waxes are esters of monhydric or dihydric alcohols. This natural division has been adopted in the description of the constitution and properties of these substances.

741. Constitution of Fats and Oils.—The natural fats and oils are usually mixtures of the triglycerides of fatty acids of high molecular weight.

Thus olive oil consists mainly of glyceryl oleate or "triolein," and is represented by the formula $C_3H_5(O.C_{18}H_{33}O)_3$. Similarly mutton fat contains the triglycerides of palmitic and stearic acids, which have the formulæ $C_3H_5.(O.C_{16}H_{31}O)_3$ and $C_3H_5(O.C_{18}H_{35}O)_3$ respectively, and are shortly named tripalmitin and tristearin.

The pure triglycerides are only prepared with difficulty from the natural products, but they have been prepared synthetically and their properties have been ascertained.

742. Chemical Properties of the Natural Oils and Fats.—As has been already stated, most of the common fats and oils contain tripalmitin, tristearin or triolein: but even the purified oils usually contain colouring and mucilaginous matter, together with fragments of vegetable and animal tissue which are derived from organisms in which the fats were present. These foreign substances constitute the "unsaponifiable matter," the amount of which rarely exceeds 2 per cent. of the oil or fat.

The most important of these unsaponifiable matters are cholesterol and phytosterol, which respectively indicate the animal or the vegetable origin of the fat or oil.

The amount of free fatty acids present is at first small, but it increases with the length of time during which the sample has been exposed to the air.

When the oils and fats have been prepared by synthesis they are colourless, odourless, and tasteless; but the purest natural products frequently possess characteristic colour, taste, and smell. Their solutions should be neutral to indicators.

The natural glycerides are either liquid at atmospheric temperatures or they melt when a moderate heat is applied. The solid glycerides separate out more or less completely from mixtures when the liquids are cooled.

The natural oils and fats are practically insoluble in water, and while they are only slightly soluble in cold alcohol their solubility is increased when the alcohol is heated. They are freely soluble in most other organic liquids such as ether, petroleum ether, carbon tetrachloride and chloroform.

Their densities vary from 0·910 to 0·970.

When they are heated to 260° C. little change occurs, but in the case of drying oils polymerisation takes place. At higher temperatures the fats decompose, and at and above 300° C. the characteristic penetrating odour of acrolein is perceived; at higher temperatures fatty and aromatic hydrocarbons are given off in considerable amount.

Exposure to dry air has no effect upon oils and fats, but ordinary damp atmospheric air in daylight exerts a marked influence on the composition of these glycerides. The chemical change is most marked in the case of drying oils such as linseed oil, oxygen being absorbed in large amount and the oil thickening and finally setting. The semi-drying oils absorb less oxygen and the ordinary solid fats least of all.

Exposure of the non-drying oils of low molecular weight, such as butter and cocoa-nut oil, to moist air and daylight gives rise to rancidity which is due to the formation of free fatty acids. This effect is less marked in the case of the fats, such as tallow, which contain the higher fatty acids.

When these glycerides are heated with water to 150° C. they remain unchanged, but at and above 200° C. hydrolysis occurs, water being assimilated and glycerol and fatty acids being formed: thus if R represents a fatty acid radicle, $C_3H_5(O.R)_3 + 3H_2O = C_3H_5(OH)_3 + 3R.OH$. This process of hydrolysis is greatly accelerated by the presence of strong acids or bases, such as strong hydrochloric acid and alcoholic potash. When the action occurs in the presence of caustic alkali the change is commonly termed "saponification," since one of the products is an alkali-salt of the fatty acid, and these salts are soaps or analogous bodies.

Strong sulphuric acid acts upon oils and fats at ordinary temperatures causing a rise of temperature, which is utilised in the Maumené test (754), and evolution of sulphur dioxide. At temperatures exceeding 100° C. the acid

reacts energetically, hydrolysing the fat and forming sulpho-compounds of the fatty acid together with glycerol.

Nitrous acid converts the non-drying oils into solids of a buttery consistency. The consistency varies with the amount of triolein present, since the thickening is due to the conversion of the triolein into a solid isomeride known as trielaidin. Drying oils remain liquid under this treatment.

Iodine does not yield substitution products when it is mixed with an oil or fat. The iodine is absorbed slowly at ordinary temperatures by the glycerides of the unsaturated fatty acids, but at higher temperatures the absorption is irregular and secondary reactions take place. Theoretically one molecule of iodine should be absorbed by each pair of doubly linked carbon atoms: and Hubl has shown that when an alcoholic solution of iodine and mercuric chloride is allowed to act upon the fat or oil this change takes place quantitatively, every pair of doubly linked carbon atoms present in the unsaturated compound absorbing one molecule of iodine mono-chloride (758).

743. Constitution of Waxes.—While the fats and oils are all glyceryl esters of the fatty acids, the waxes proper are esters of the fatty acids containing a radicle of a mono- or di-hydric alcohol. Thus the cetin or cetyl palmitate present in spermaceti may be considered as a product of the action of cetyl alcohol, $C_{16}H_{33}OH$ upon palmitic acid, $C_{15}H_{31}.CO.OH$, and the formula of this ester is accordingly $C_{13}H_{31}.CO.OC_{16}H_{33}$.

Similarly, the myricin or myricyl palmitate present in beeswax has the composition represented by the formula $C_{15}H_{31}.CO.OC_{18}H_{37}$.

The alcohol radicles present may belong to alcohols of the saturated or unsaturated aliphatic series, or to the aromatic series.

The liquid waxes in sperm oil contain compounds of the unsaturated alcohol radicles of the series $C_nH_{2n}O$ in combination with the radicles of the unsaturated fatty acids.

744. Properties of the Natural Waxes.—The properties of the waxes have not been as thoroughly investigated as those of the oils and fats. In beeswax and Canauba wax free fatty acids and free alcohols have been found. Since the alcohols are of high molecular weight and are insoluble, notable amounts of unsaponifiable matter are found which are due to the presence of these alcohols.

The liquid waxes and spermaceti are neutral in reaction. In their physical properties these substances resemble the fats and oils, and they behave similarly with reagents.

The liquid waxes are of lower density than the fats, the density varying between 0·875 and 0·881. They do not emit the odour of acrolein when they

are heated, since glyceryl is absent; but when they are heated to a high temperature the esters are converted into hydrocarbons. They do not become rancid as fats and oils do when they are exposed to similar conditions.

Preparation of the Fatty Matter for Examination.

745. A fat or oil must be carefully "sampled," so as to secure a truly average and representative portion for examination.

If the substance is a liquid, some of the constituents may possibly have separated more or less completely from the mass, and it is then necessary to mix the whole thoroughly by stirring immediately before the removal of any portion for examination.

If the fat is solid, a suitable amount is removed by an auger or other suitable tool. Before this fat is used for examination, it is melted upon the water-bath at a temperature not exceeding 60° C. and is then removed from the water-bath and stirred vigorously in order to prevent the separation of water and impurities.

Estimation of Water.

746. Weigh accurately about 5 grams of the fat or oil in a small tared beaker containing a thin glass rod, and heat the beaker with its contents in the air-oven to a temperature of from 100° to 110° C. until the weight is practically constant.

The drying should be stopped as soon as two successive weighings agree within 1 or 2 milligrams. This will usually be secured in about two or three hours. If the heating is further continued, some of the lower fatty acids may be volatilised, or possibly an increase of weight may take place owing to absorption of oxygen from the air: these opposite effects may in certain cases, however, chance to balance one another.

While the fat is being dried it should be stirred from time to time, since any water which collects below the melted fat will evaporate through the fat very slowly unless it is brought near the surface.

In the case of drying oils, which absorb oxygen readily from the air, it is advisable to displace the air and steam by passing a constant stream of carbon dioxide over the surface of the heated fat.

Estimation of Foreign Substances.

747. Matters other than fat, such as animal and vegetable tissues and certain fraudulent admixtures, are determined by removing the fat by a solvent. The solvents usually employed are petroleum ether and ordinary ether.

Weigh out accurately into a flask 10 to 20 grams of the dried fat (746) and shake this with petroleum ether, then pour the solution through a tared filter, and wash with fresh solvent until a few drops of the washing-liquid when evaporated on paper does not leave a grease spot.

Then dry the filter with its contents at 100° C. and weigh them. The proportion of mineral matter may be estimated by incinerating the filter and its contents at a red heat and weighing the ash: the amount of organic matter may then be found by difference.

Starch may be detected, in the residue left from the extraction of the fat, by the iodine test.

The Mineral Residue may contain salt, chalk, clay, lime and alumina: the two latter substances being derived from the admixture of the fat with mineral soaps.

The Substances Soluble in Water may be removed by shaking from 50 to 100 grams of the original fat with warm water: the water-layer which separates out on standing may be tested for alkali, salt, or soluble acid, and any substance thus detected may then be estimated volumetrically.

Determination of the Fat and the Foreign Substances.

748. The direct determinations of fat and of foreign substances may be combined by using a Soxhlet extractor (671) as is described below:

Weigh out accurately from 10 to 20 grams of the fat into a "Soxhlet thimble," or into a cartridge made by rolling a strip of filter-paper round a wooden cylinder and folding it in at one end. Introduce the weighed fat into the cartridge and place the whole in the extractor (Fig. 96, page 334). The top of the paper may be pinched together to prevent any solid matter from getting out of the cartridge.

Now pour 50 c.c. of the solvent into the lower flask, which should have a capacity of about 150 c.c., and pour the solvent also into the Soxhlet apparatus until it begins to syphon over; then at once attach the reflux condenser and heat the flask by means of a water-bath. The amount of liquid which condenses will be sufficient to cause the syphon to empty the reservoir of the Soxhlet apparatus from twenty to thirty times in the hour.

The extraction of the fat, which will require about an hour, is known to be complete when a few drops of the solvent, taken as they come from the siphon, leave no grease-spot when they are evaporated on filter-paper. As soon as this is the case separate the flask from the condenser and extractor, distil the solvent on the water-bath, and dry the residual fat at 100° C. to 110° C. until its weight is approximately constant.

Detection and Determination of Inorganic Substances Dissolved in the Fatty Matter.

749. Oils and fats have the property of dissolving small quantities of metals and forming metallic soaps: and soaps of lead and manganese are often introduced into "boiled oils" in this way. The presence of metals in this condition may be detected by incinerating about 5 grams of the fat in a platinum dish, or if lead is present in a porcelain crucible, and testing the residue for alkalis, lime, alumina, lead, manganese, iron, copper, and zinc.

The alkalis may be dissolved from the residue by water and will give an alkaline solution. The other metals are detected by the ordinary methods of analysis, and their separation and estimation is described in the earlier part of this book.

DETERMINATION OF CERTAIN PHYSICAL CHARACTERISTICS.

750. Methods for determining certain physical characteristics of fats and waxes are described in paragraphs **752–754**. Some of the reference-books which are mentioned in paragraph **1021** must be consulted if the refractive index and the viscosity are to be ascertained.

Separation of the Fat or Wax for Physical and Chemical Examination.

751. The fat may be prepared for examination by keeping it in a melted condition on the water-bath until the water and dirt have settled out, and then filtering it through a dry filter-paper.

This "prepared fat" is used for any physical determinations which may be made, such as those of the density and melting-point, and for determining the heat generated with sulphuric acid. Various characteristics and other experimental data for the oils, fats, and waxes will be found in the Table (993).

Determination of Density at 15·5° C. and at 100° C.

752. The density of an oil may be determined by the hydrometer (38), but for accurate work the density-bottle (34, 35) or the Sprengel tube (36, 37) may be used. The temperature of 15·5° C. is usually selected for the determination.

The density of a solid fat or wax is generally taken at a temperature at which the fat is liquid, and 100° C. is usually selected for this purpose.

The Sprengel tube may be used in the following way at 100° C.: After the melted fat has been sucked up into the tube, the body of the tube is placed in a vessel of boiling water with the capillary ends protruding. As soon as the volume of the liquid has been adjusted exactly to the mark and the boiling has continued for about twenty minutes, the glass caps are placed on the ends, the outside of the tube is dried, and the tube is weighed as soon as it is cool.

The weight of the fat is then referred to the weight of the same measured volume of water either at its boiling-point or at 15·5° C. The temperature of the water-unit which is chosen must be carefully entered.

Determination of the Melting-point and the Solidifying-point.

753. The determination of the melting- and solidifying-point of fats and oils is not generally of much value, since these changes in condition take place so gradually that it is difficult to decide upon any definite temperature. Thus the criterion for the melting-point varies with different operators, some selecting the point at which the fat begins to soften, and others the point at which the fat becomes perfectly transparent. Since the size and shape of the vessel in which the fat is melted gives rise to considerable differences in the melting-point of the same fat, the determinations must always be made under precisely similar conditions in order to be comparable.

For determining the melting-point of natural fats, the open-tube method (39, 40) may be employed; but since a fat does not again attain its normal melting-point for some time after it has been melted, twenty-four hours at least must be allowed to elapse after a sample has been melted before its melting-point is determined.

Heat of Reaction with Sulphuric Acid (Maumené Test).

754. When Strong Sulphuric Acid is mixed with Drying Oils, a greater Rise of Temperature occurs than when it is mixed with Non-drying Oils.

In applying this test comparable results can only be obtained when the experiments with different oils are conducted under exactly similar conditions It is essential that the acid should always be of the same strength, which must be not less than 95 per cent. of acid, and that it shall in every case be at the same initial temperature; the vessels which are used should also be similar and of the same size.

For the application of this test prepare a "nest" of cotton-wool for a beaker of 200 c.c. capacity, by placing cotton-wool or wadding in a larger beaker.

Then weigh accurately 50 grams of the oil in the smaller beaker, and place this beaker and the bottle of strong sulphuric acid in cold water. As soon as the oil and the acid have acquired the same temperature, take out the beaker of oil, dry the outside, and place it in the nest of cotton-wool. Then stir the oil well with a thermometer, take its temperature accurately, and allow 10 c.c. of the strong acid to flow in slowly from a pipette. The acid must take one minute to flow into the oil, and during this time the oil must be continuously stirred. The highest temperature recorded by the thermometer during this process is recorded.

In order to eliminate the error due to the use of different strengths of acid the temperature may be referred to that given by 50 c.c. of water when they are treated in exactly the same manner.

The rise of temperature in an experiment is termed the "temperature reaction," and this is referred to that of water as 100. Thus the temperature reaction of the oil will be given by the formula:

$$\frac{\text{Rise of temperature with oil} \times 100}{\text{Rise of temperature with water}} = \text{Specific temperature reaction.}$$

CHEMICAL EXAMINATION OF OILS, FATS AND WAXES.

Methods are described below for identifying and valuing oils, fats and waxes for technical purposes, and for detecting admixture or adulteration. The processes for the separation of the various fatty acids and bases present in these complex bodies have not been described, but the methods here given will serve for general technical examination.

Determination of the Acid Value.

755. The Acid Value is expressed by the Number of Milligrams or Potassium Hydroxide which are required to neutralise the Free Fatty Acids present in One Gram of the Fat or Wax.

This test indicates the age and quality of an oil or fat. Freshly prepared animal oils and fats contain practically no free fatty acid, and vegetable oils usually contain only a small amount, but the amount of free acid is increased on keeping by hydrolytic change and oxidation.

For the estimation about 10 grams of the fat or oil (*Note* 1), more or less according to its degree of acidity, are weighed accurately into a flask which is fitted with a glass stopper, and 50 c.c. of purified methylated spirit are added (*Note* 2).

The flask is now immersed in boiling water, and is shaken for a time to dissolve the fatty acid. A few drops of phenol-phthalein are then added, and seminormal sodium hydroxide solution is allowed to flow in from a burette until a pink colour remains in the liquid after it has been well shaken. Decinormal alkali solution may be used if the acidity is very small in amount.

The Method of Calculating the Acid Value from the above result is indicated by the following example:

3·254 grams of a particular sample of tallow required 3 5 c c of decinormal potassium hydroxide solution: hence the free fatty acids present neutralised 3 5 × 5 61 = 19 63 milligrams of KOH, and since the acid value (A) is the amount of KOH required to neutralise 1 gram of tallow, $A = \frac{3\,5 \times 5\,61}{3\,254} = 6\,03$.

If the nature of the fatty acid is known, its percentage may be calculated from the following data.

1 c.c. of	Normal	KOH	= 0·256	gram of	Palmitic Acid.
,,	,,	,,	= 0 284	,,	Stearic ,,
,,	,,	,,	= 0·282	,,	Oleic ,,

In this country the percentage of free acid is usually returned as if it were all oleic acid, and the acid in the above sample would be returned as equivalent to $\frac{3{\cdot}5 \times 0\,0282}{3{\cdot}254} \times 100 = 3{\cdot}03$ per cent. of oleic acid.

Note 1.—The presence of mineral acid may be detected by shaking the fat or oil with a little hot water and seeing whether the water is reddened by a drop of methyl-orange solution. Mineral acid, if present, should be removed before proceeding by washing the fat repeatedly with fresh portions of boiling water, and its amount is then titrated in the washings as is described above.

Note 2.—The spirit is purified by allowing it to stand with solid sodium hydroxide and then distilling it. Before it is used, any acidity must be neutralised by adding a few drops of phenol-phthalein and then cautiously dropping in decinormal potassium hydroxide solution until a permanent faint pink colour is produced.

The Saponification Value, or Koettstorfer Value.

756. The Saponification or Koettstorfer Value is the Number of Milligrams of Potassium Hydroxide which are required for the Complete Sponification of One Gram of an Oil, Fat or Wax.

The following solutions are required for the process of estimation:

(a) *Standard Hydrochloric Acid.*—A seminormal solution (290).

(b) *Alcoholic Solution of Potassium Hydroxide.*—Dissolve 35 grams of potassium hydroxide, which has been purified from alcohol, in a little water, and make up the volume of this solution to a litre with alcohol of 0·81 specific gravity, or with purified methylated spirit (*Note* 2, 755). Allow the alcoholic solution to stand for twenty-four hours, then filter it into a litre bottle. This bottle should be closed by a perforated rubber stopper in which is fitted a 25 c.c. pipette, and a piece of rubber tube closed by a piece of glass rod is pushed upon the upper end of the pipette.

For the Determination weigh accurately about 2 grams of the purified and filtered fat (751) into a 200 c.c. flask. Then add 25 c.c. of the alcoholic potash solution (b) by means of the pipette attached to the rubber stopper. Now attach a reflux-condenser, or a long cooling-tube, to the neck of the flask and heat it on the water-bath for about thirty minutes. The contents of the flask should just simmer and should be shaken from time to time.

As soon as saponification is complete, and the fat has passed into clear solution, add 1 c.c. of a 1 per cent. solution of phenol-phthalein and titrate the excess of alkali with the standard hydrochloric acid (a).

Carry out at the same time a blank experiment, in which the same amount of alcoholic potash is heated in the same way as in the actual determination, and is finally titrated by the same process. This is necessary in order to eliminate all sources of disturbance, such as that due to the presence of carbon dioxide. The difference between the amounts of potash used in the two titrations is the quantity which is required to saponify the fat. From this the number of milligrams of potash which would be required for 1 gram of the fat is then calculated.

In an Actual Estimation with Olive oil, the following results were obtained Twenty-five c c of the KOH solution were added to 1 532 grams of olive-oil After saponification 12 c c. of seminormal hydrochloric acid were required for neutralisation. In the blank test 25 c.c. of the alkali solution required 22 5 c c. of the acid for neutralisation. Hence the volume of potash solution required for the saponification is 22 5 − 12 = 10·5 c.c., which contain a weight of KOH in milligrams of $\frac{10{\cdot}5 \times 56{\cdot}1}{2} = 294{\cdot}5$; and 1 gram of the oil would therefore require $\frac{294\,5}{1{\cdot}532} =$ 192·2 milligrams of KOH for its saponification.

The Saponification Value varies with the nature of the fatty acid, the lower the molecular weight of the fatty acid-radicle present the greater will be the weight of potash required for the neutralisation of a given weight of the acid, and the higher the saponification value.

The saponification value does not vary greatly for the same substance, but it is affected by the presence of free fatty acids which tends to slightly increase the value, and by slight differences in the composition of the fats which may arise from differences in locality and soil and from other natural causes.

The Table in paragraph 993 shows the saponification values of the common oils, fats and waxes. It will be seen that waxes are characterised by low saponification values, and this fact furnishes a ready means of distinguishing waxes from oils and fats.

It will also be noticed that the majority of oils and fats have a saponification value which approximates to 193. Deviations from this number are characteristic of certain oils, thus while rape-oil and castor-oil have low saponification values, some of the fish-oils and butter possess relatively high values.

Determination of Unsaponifiable Matter.

757. The term "Unsaponifiable Matter" is applied to Substances which are Insoluble in Water and which cannot be saponified by Caustic Alkali with production of Soluble Soaps.

Since oils and fats usually contain only small quantities of unsaponifiable matter, larger amounts of the samples must be used for this estimation than for the determination of the Koettstorfer value.

The method described below is only suitable for oils and fats, since although waxes are completely saponified by alcoholic potash, they yield insoluble alcohols together with hydrocarbons which interfere with the results. After fats and oils have been saponified, the unsaponifiable matter usually remains dissolved in the soap solution, and it only causes turbidity when it is present in large amount. This matter may be extracted from the solution by shaking it with common ether.

For the Estimation weigh out accurately about 5 grams of the sample, add 25 c.c. of a solution of potassium hydroxide in alcohol containing 80 grams of KOH in a litre of alcohol, and evaporate to dryness on a water-bath. Dissolve the resulting soap in 50 c.c. of hot water, and transfer the liquid to a separating-funnel or to a butter-flask (Fig. 97, p. 345) of two litres capacity, using not more than 30 c.c. of hot water for washing out the dish. Cool this liquid, then pour in from 25 to 50 c.c. of ether and mix the

liquids well by vigorous shaking, adding a little alcohol if the layers do not separate readily.

Then allow the soap solution to flow out from below into another separator, and shake it again with ether. Now mix the two ethereal solutions, wash them well by shaking with a little water to dissolve away any dissolved soap, and transfer the ethereal solution to a tared flask. Now distil off the ether on the water-bath, and weigh the residue after it has been dried at 100° C. The Table (993) gives the amounts of unsaponifiable matter which are found in a number of normal fats and oils.

Determination of the Iodine Value.

758. The Iodine Value is the Percentage of Iodine Chloride which is absorbed by a Fat or Wax, expressed in terms of Iodine.— The process described below is Wijs' modification of the Hubl method. It depends on the fact that unsaturated aliphatic compounds are capable of forming additive compounds with the halogens, the extent of this combination depending on the degree of unsaturation. Thus oleic acid, which has two doubly linked carbon atoms, absorbs two atoms of a halogen.

It was found, however, that in practice iodine is not itself absorbed by such compounds to the extent corresponding to the unsaturation, but that iodine in conjunction with chlorine is quantitatively absorbed to the full extent. Iodine chloride can therefore be used as a means of estimating the "saturation value" of an unsaturated fatty substance. In the case of oleic acid, for example, the reaction which takes place is thus represented:

$$C_{17}H_{33}.COOH + ICl = C_{17}H_{33}ICl.COOH.$$

The following solutions are required:

(a) *Wijs' Iodine Solution* is prepared by introducing 13 grams of powdered iodine into a litre flask and shaking it with about 750 c.c. of 99 per cent. acetic acid, free from SO_2, until solution is complete, and diluting the liquid to a litre by the addition of more acetic acid.

The exact amount of iodine present in the solution is then ascertained by titrating 5 c.c. with the standard thiosulphate solution (b). A slow stream of washed and dried chlorine, free from hydrogen chloride, is then passed into the iodine solution, until the 5 c.c. require twice the volume of the thiosulphate solution which was originally required by the iodine solution alone. The exact time at which this point is reached may be known by the change in colour of the liquid from brown to red, which indicates that the iodine is entirely converted into monochloride.

(b) *Standard Sodium Thiosulphate Solution* is made by dissolving 25 grams of the pure thiosulphate in water and diluting the solution to a litre. This solution is approximately decinormal (332), but requires to be titrated from time to time.

(c) *Approximately Normal Potassium Iodide Solution* is made by dissolving 166 grams of the iodide in water and diluting the solution to a litre.

(d) *Carbon Tetrachloride*, which must be of such purity that no green coloration develops when the liquid is mixed with potassium dichromate and strong sulphuric acid and is allowed to stand. The formation of a green colour would indicate the presence of oxidisable substances.

For the Estimation the quantity of the sample stated below is dissolved in 10 c.c. of the carbon tetrachloride (d), and the solution is placed in a stoppered bottle about 500 c.c. in capacity.

From 0·15	to 0·18	gram of a	drying or marine animal oil.
„ 0·2	„ 0·3	„ „	semi-drying oil.
„ 0·3	„ 0·4	„ „	non-drying oil.
„ 0·8	„ 1	„ „	solid fat.

25 c.c. of the Wijs' solution (a) are then poured into the bottle, and the mixture is allowed to stand for an hour in a dark place. In order to avoid loss of iodine the stopper of the flask is wetted with the solution of potassium iodide (c).

At the end of the hour the amount of iodine in the liquid is determined by adding 15 c.c. of the potassium iodide solution (c), 150 c.c. of water and 20 c.c. of the standard thiosulphate solution (b), and then finishing the titration with thiosulphate from a burette, using starch solution as an indicator.

Note.—It is essential to the success of the estimation that not less than half of the iodine introduced into the bottle should remain in the free state and be found in the final titration.

A blank titration should now be made at once by introducing into a similar stoppered bottle 10 c.c. of carbon tetrachloride, 25 c.c. of the Wijs' solution, 15 c.c. of the potassium iodide solution, 100 c.c. of water, and 45 c.c. of the standard thiosulphate solution, and then completing the titration by adding the thiosulphate solution from a burette in the presence of starch solution. The amount of iodine solution used in the blank experiment may require to be considered in connection with the statement in the preceding *Note*.

In an Estimation of the Iodine Value of a sample of lard, the following results were obtained: 0·312 gram of the lard was dissolved in 10 c.c. of carbon tetrachloride, and 25 c.c. of the iodine solution were added. After standing for a time 33·4 c.c. of the thiosulphate solution were required by the free iodine. In a blank titration, 25 c.c. of the iodine solution required 49·2 c.c. of the thiosulphate solution. Now since each c.c. of thiosulphate solution

correspond to 0 0127 gram of iodine, 0 312 gram of the lard had absorbed (49 2 - 33 4) × 0 0127 gram of iodine, and 100 grams would therefore absorb $\frac{15\,8 \times 0\,0127 \times 100}{0\,312} = 64\,3$ grams. Accordingly the iodine value of the lard was 64 3.

The Iodine Value of an Oil, Fat, or Wax is a constant quantity, but it varies with different kinds of fatty substances. It is therefore of great importance as a means of identifying the substance. The value does not materially alter with the age of an oil, unless some important chemical change has taken place such as oxidation in the case of drying oils and of certain fish-oils.

The Table (993) gives various iodine absorption values and affords a ready means of indicating the class or group in which an unknown substance should be placed.

The Reichert, Reichert-Meissl and Reichert-Wollney Values.

759 This Value is measured by the Number of Cubic Centimetres of Decinormal Potassium Hydroxide Solution, which are necessary for the Neutralisation of that part of the Volatile Soluble Fatty Acids, which distils over when 2.5 or 5 grams of the Fat or Wax are heated under the Specified Conditions.

The Reichert and Reichert-Meissl processes have been already described in the section on butter-analysis (686, 687). The third process is the standard one now adopted in this country for determining the volatile fatty acids in margarine and butter on the recommendation of a Joint Committee of the Government Laboratory and the Public Analysts.

760. Standard Reichert-Wollney Process —The standard apparatus, with the dimensions recommended by the Committee, is shown in Fig. 101, page 394.

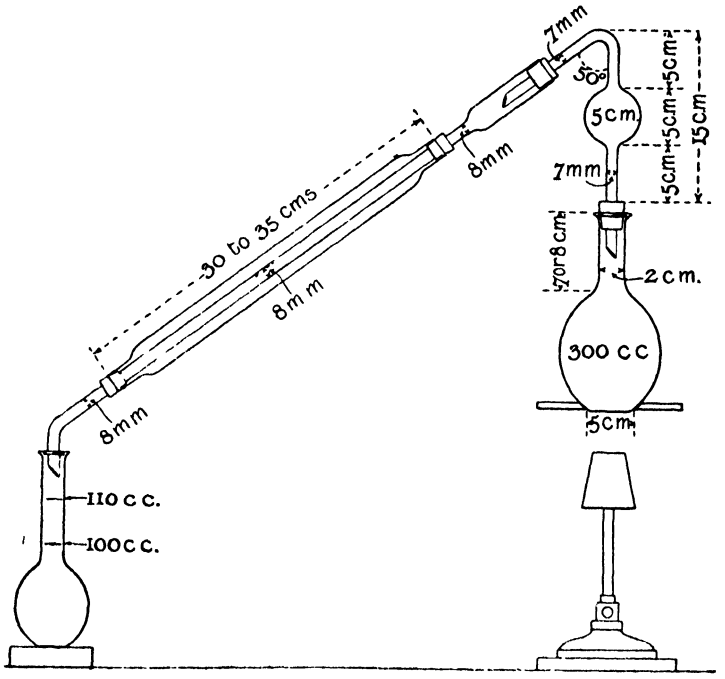
Five grams of the liquified fat are introduced into the 300 c.c. flask; two c.c. of caustic soda solution, prepared by dissolving 98 per cent. sodium hydroxide in an equal weight of water, and 10 c.c. of 92 per cent. alcohol are added; and the mixture is heated under a reflux-condenser, connected with the flask by means of a T-piece, for fifteen minutes over a bath containing boiling water.

The alcohol is then evaporated on the water-bath, the heating being continued until the residual soap is dry. 100 c.c. of water, which have been recently boiled for at least ten minutes, are then poured into the flask, and the flask

is heated until the soap is dissolved. A few fragments of pumice or pipe-stem and 40 c.c. of normal sulphuric acid are then introduced into the flask, which is immediately connected with the condenser by means of a bulbed glass tube 7 mm. in diameter.

The flask is supported on a circular piece of asbestos-board 12 cm. in diameter, which has a hole in its centre 5 cm. in diameter, and is heated with

Fig 101.



Standard Reichert-Wollney Apparatus.

a small flame so as to melt the fatty acids. The temperature is then gradually raised, and as soon as fusion is complete 110 c.c. are distilled over at such a rate as to require thirty minutes for the operation.

After this distillate has been mixed by shaking, 100 c.c. of it are filtered into a beaker, then mixed with 0·5 c.c. of a phenol-phthalein solution containing 1 gram dissolved in 100 c.c. alcohol, and titrated with decinormal solution of caustic soda or baryta.

A blank experiment is now at once carried out in precisely the same way, for which the amount of decinormal soda required should not exceed 0·3 c.c. The volume of the decinormal alkali used in the first titration, less that

required for the blank experiment, when multiplied by 1·1 gives the Reichert Wollny number for the fat.

The number obtained from 5 grams of a fat is not always double that obtained from 2·5 grams of the same fat, still for most practical purposes the numbers may be assumed to stand in that relation to one another. In the Table (993) the lower number is shown as R, and the higher number as RM.

Most of the natural oils and fats contain but small quantities of volatile soluble fatty acids, therefore the Reichert number is usually below 0·5 and the Reichert-Meissl number below 1.

The high values shown in the table for substances like butter-fat are due to the presence of acids of comparatively low molecular weight.

The Hehner Value.

761. The Hehner Value is the Percentage of Insoluble Fatty Acids and Unsaponifiable Matter present in the Fat or Wax.

For the Estimation about 3 or 4 grams of the filtered fat (751) are accurately weighed and introduced into a porcelain basin 13 cm. in diameter; 50 c.c. of strong alcohol and from 1 to 2 grams of solid potassium hydroxide are then added, and the whole is heated on the water-bath with constant stirring until a clear solution is obtained and the fat is completely saponified Saponification is known to be complete when the addition of a drop of water to the liquid no longer produces a turbidity.

The liquid is now evaporated until it is pasty; it is then made clear again by adding from 100 to 150 c.c. of water, and is acidified by adding dilute sulphuric acid. It is then heated until the fatty acids form a clear oily layer, and is filtered through a 10 cm. filter which has been dried at 100° and weighed. The filter should be stout enough to prevent the fat from running through and rendering the filtrate turbid, and should have been previously half filled with hot water. The fatty acids are finally washed on the filter with hot water, until the last washing-water does not redden blue litmus-paper.

The filter with its contents is now placed in a weighed beaker and heated at 100° C. for two hours, and is then cooled and weighed. It is again heated for an hour and cooled and weighed, these processes being repeated until the difference between two consecutive weighings is not greater than 1 milligram.

The final result is in any case only an approximation, since the continued heating drives off a portion of the more volatile fatty acids and hence causes loss of weight, whereas any unsaturated fatty acids present absorb oxygen and give rise to increase in weight.

Since all natural glycerides contain small quantities of unsaponifiable

matter which is insoluble in water, the Hehner value is somewhat greater than the proportion of insoluble fatty acids. The amount of unsaponifiable matter however is usually so small as to be negligible, and the value obtained for fats and oils is therefore almost identical with the amount of insoluble fatty acids.

The insoluble fatty matter in waxes may consist of insoluble fatty acids and insoluble alcohols, this fact and the assimilation of water during saponification may cause the value to exceed 100. The Hehner value therefore is not usually determined for waxes, other characteristics being of greater value.

The Hehner value of most oils and fats approximates to 95, butter-fat and some other fats being notable exceptions to this general statement as is shown in the Table (993).

Determination of the Neutralisation Value, or Mean Molecular Weight.

762. The Neutralisation Number is the Number of Milligrams of Potassium Hydroxide which are required to saturate One Gram of the Mixed Fatty Acids.

It is sometimes desirable to obtain information respecting the composition of the esters present in fatty bodies. By the following process the mean molecular weight of the fatty acids present may be determined.

When the saponification value does not exceed 195 (756) the mixed fatty acids obtained in estimating the Hehner value (761) may be considered to represent the total fatty acids present in an oil or fat.

If the saponification number exceeds 200, it is best to determine the mean values of the molecular weights of the soluble and insoluble acids separately (763. 759).

The neutralisation number is obtained as is described under the determination of the acid value (755), not less than 5 grams of the fatty acids being used for the purpose.

The Method of Calculation is as follows:

If M represents the molecular weight in grams of the fatty acids, and A the number of grams of KOH required to neutralise 1 gram of the fatty acids,

Then M grams of the fatty acids will require 56 grams of KOH for neutralisation, or $M : 56 :: 1 : A$, and $M = \frac{56}{A}$

Or if B = the neutralisation number, or the number of milligrams of KOH required to neutralise 1 gram of the fatty acid, then $M = \frac{56}{B \times 1000}$

Determination of the Potassium Hydroxide Equivalent of the Volatile or Soluble Fatty Acids.

763. If the saponification number exceeds 200, and consequently the Reichert-Meissl result is above 5, the volatile fatty acids are present in fair quantity; and since their amount cannot be obtained from the distillate, as only a portion is distilled over even in the Reichert process, one of the following methods (A, B) may be adopted for estimating the amount of volatile fatty acids. It is assumed that the volatile and soluble acids are identical, and this is true of ordinary fats.

(A) **Saponify 5 grams** of the sample with 60 c.c. of deminormal alcoholic potash, and determine the excess of potassium hydroxide by deminormal hydrochloric acid as is described in the process for determining the saponification value (756). The amount of alkali used in the saponification is thus found and this represents the saponification value.

Now remove the alcohol by evaporation, dissolve the residual soap in water, add excess of hydrochloric acid to liberate the fatty acids, and wash these acids with water to remove the soluble fatty acids as is described under the determination of the Hehner value (761). Then dissolve the insoluble fatty acids in neutral alcohol, and determine their neutralisation value by means of deminormal potash. The difference between this value and the saponification value will give the amount of potassium hydroxide required to neutralise the soluble or volatile fatty acids, and if the mean molecular weight of the butter-fats is known the absolute amount of the volatile acids may be calculated.

Thus in an estimation made with butter-fat, 5 grams of the butter-fat require 1130 milligrams of KOH for saponification, and the insoluble fatty acids required 920 milligrams. Hence 1130 – 920 = 210 milligrams of KOH were required to neutralise the volatile fatty acids.

(B) **Saponify 5 grams** of the sample in a flask with 60 c.c. of seminormal alcoholic potash, and distil off the alcohol. Dissolve the residual soap in boiled water and add sufficient seminormal sulphuric acid to exactly neutralise the whole of the alkali taken. The requisite amount of acid should be determined by a blank experiment in which alkali alone is used, the blank being carried out simultaneously with the saponification of the fat.

Now remove the soluble fatty acids by filtration and subsequent washing, as in Hehner's process; the aqueous filtrate and washings should contain the whole of the soluble fatty acids in the free state together with potassium sulphate and glycerol.

The amount of potash required to neutralise these soluble acids can be

determined by directly titrating this liquid with standard alkali, using phenolphthalein as an indicator, and the usual precautions being taken against the presence of carbon dioxide.

The Acetyl Value.

764. The Acetyl Value is the Number of Milligrams of Potassium Hydroxide which are required to neutralise the Acetic Acid obtained by the Saponification of One Gram of the Acetylated Fat or Wax.

The acetyl value is a measure of the number of alcoholic hydroxyl groups which are present in the original fatty substance. In the case of oils and fats, which consist of glycerides of the fatty acids, only those fatty acids which contain hydroxyl groups in addition to the hydroxyl present in the carboxyl group can have the hydroxylic hydrogen replaced by the acetyl group.

Ordinary fats and oils contain little or no hydroxy-acid, and they accordingly give acetyl values which are rarely higher than 10, unless they have been exposed to atmospheric oxidation. Castor-oil, however, gives the very high value of about 100.

Waxes, on the other hand, contain free alcohols which assimilate the acetyl group, and the acetyl number of a wax is mainly due to the presence of this alcoholic hydroxyl.

Lewkowitsch finds that free fatty acids react upon one another in such a way as to increase the acetyl value, and he accordingly acetylates the original fat or wax instead of the fatty acids. He directs the following procedure:

Boil 10 grams of the substance for two hours with twice its weight of acetic anhydride in a round-bottomed flask connected with a reflux-condenser. Pour the resulting mixture into a large beaker containing 500 c.c. of hot water, and boil for half an hour, passing a slow current of carbon dioxide through the solution to prevent bumping. Then allow the mixture to stand and separate into two layers, draw off the water by means of a syphon, and boil the oily layer with three successive portions of fresh water.

All the free acetic acid should be removed by this treatment, and this is proved by the last portion of washing-water giving no acid reaction to litmus.

Now separate the acetylated fat from the water, and remove the last traces of water by passing the liquid fat through a dry filter-paper, and then heating it in a drying-oven.

Weigh accurately from 2 to 5 grams of this acetylated fat and saponify it by treatment with a measured volume of standard alcoholic potash as is described in the estimation of the saponification value (756). Evaporate the soap solution nearly to dryness to expel the alcohol; then dissolve the

residual soap in water and add an amount of standard sulphuric acid which is exactly equivalent to the alkali used for saponification.

Now warm the liquid gently until the fatty acids separate as an upper layer. Syphon off the aqueous solution through a wet filter, and wash the fatty acids with hot water until the washing-water is no longer acid. Finally titrate the filtrate and washings with decinormal alkali, using phenol-phthalein as an indicator. From the number of c.c. of alkali used, the number of milligrams of KOH which were required for the removal of the acetyl from 1 gram of the fat may be calculated.

If the fat or oil contains volatile or soluble fatty acids, the value obtained by the above procedure would include the alkali value of the volatile fatty acids. In order to find the true acetyl value in such a case, it is necessary to determine the amount of alkali which is required to neutralise any soluble fatty acids which were present in the original substance (763), and to deduct this from the quantity obtained above.

Estimation of Mineral Oil in the Presence of Saponifiable Oil.

765. The separation of mineral oil depends upon the treatment with caustic alkali which saponifies only the fatty oils, the unsaponified mineral oils can then be extracted by treatment with petroleum spirit.

Weigh out accurately 10 grams of the oil into a 200 c.c. Jena or Bohemian glass flask. Add 10 c.c. of a 50 per cent. solution of NaOH and 50 c.c. of alcohol, boil the mixture for thirty minutes in a flask connected with a reflux-condenser and then allow it to cool. Now transfer the solution to a separator, and shake it with petroleum spirit which boils below 80° C.

Allow the lower aqueous solution to flow off into another separator and again extract it with fresh petroleum spirit. Mix the two spirit solutions and wash them with 50 per cent. alcohol to extract any dissolved soap: then pour the washed petroleum spirit into a beaker, allow it to stand covered for a few minutes to allow any water to settle, and decant the spirit into a tared flask.

Finally distil off the spirit, dry the residual mineral oil at 100° C., and weigh it.

Estimation of Sulphur in Fuel Oil

766. The presence of sulphur in oils used for internal combustion engines is objectionable. The sulphur may be determined in the oil by the bomb-calorimeter (550, b), but excess of bromine-water must be added to the rinsings from the bomb to convert some H_2SO_3 into H_2SO_4 before the liquid is boiled or precipitated.

REMARKS ON THE SCHEME AND THE RESULTS OF THE EXAMINATION OF OILS, FATS AND WAXES

767. The scheme for the examination of a specimen of an oil, fat, or wax by the preceding processes varies somewhat with the object for which it is undertaken.

If the quality and freshness of the sample are under consideration the acid value should be determined, and this number, together with the smell and taste, enables an opinion to be formed.

If adulteration by the admixture of cheaper oils or of mineral-oils is suspected, the saponification and iodine values should be determined.

If a mixture of several oils is being dealt with, however, the problem is more difficult and is sometimes not capable of being solved.

A few hints are given below as to procedure, and are illustrated by some simple examples.

The observation of the consistency, colour, odour, and taste of a fatty substance will in many cases assist in the formation of an opinion. The smell is developed when the substance is gently warmed. Many kinds of oil possess a distinct colour and smell, and the sample under examination should be compared in these respects with a fairly representative sample.

In ascertaining the nature of the less valuable adulterating oil, which has been introduced for the purpose of lowering the cost of a high-priced oil, the following table compiled by Lewkowitsch will be of assistance. The most costly oil, fat, or wax is placed at the head of the table, and those which follow are placed in the order of their decreasing value. The relative order, however, is liable to be disturbed by the alterations in market price.

Oils, including Liquid Waxes.

1. Almond.
2. Sperm.
3. Olive.
4. Neat's-foot.
5. Lard
6. Cod-liver.
7. Arctic sperm.
8. Arachis.
9. Poppy-seed
10. Sesamé.
11. Seal.
12. Rape.
13. Castor.
14. Cotton-seed.
15. Maize (corn).
16. Linseed.
17. Whale.
18. Cod.
19. Japan fish.
20. Mineral.
21. Rosin.

FATS AND WAXES.

1. Cacao butter.	7. Cocoa-nut-oil.
2. Butter-fat.	8. Palm-nut oil.
3. Beeswax.	9. Tallow.
4 Carnauba wax.	10 Paraffin wax.
5. Chinese wax.	11. Palm-oil.
6 Lard.	12. Bone-fat.

If a substance under examination is a known fat or oil, the properties and values given in the Table (993) should be consulted, and the values obtained in the examination should then be compared with those given in the Table. The fatty acids are then examined if necessary.

A few examples are appended to help the beginner.

EXAMPLES OF EXAMINATIONS OF OILS AND FATS.

768 Estimation of Saponifiable and Unsaponifiable Oils in Machinery Oil.

Ascertain first the proportion of each class of oils present by the method described in paragraph 765, which will determine the percentage of mineral oil directly and the saponifiable oil by difference.

Since the amount of saponifiable oil will be small, it is probably better to determine the saponification value (756) and to calculate the amount of oil from the assumption that the fatty acids have mean molecular weight of 193.

The saponification value in an oil was found to be 20 2. Hence the percentage of fatty oil is found by the statement 193 . 20 2 : : 100 : x,

whence $x = 10\ 46$ per cent. of fatty oil.

In order to determine the character of the oil, the unsaponifiable oil was removed (765), and the fatty acids were liberated and weighed (761) 10 06 per cent. of fatty acids were found, corresponding to 10 03 of fatty glycerides. The mixed fatty acids gave the following results :

Iodine value	78 8
Neutralisation value by KOH . . .	199

Both the iodine and the neutralisation values (993) indicate the presence of an animal oil, probably lard-oil, and therefore the absence of vegetable oils such as colza-, cotton-seed-, or castor-oil.

769. Estimation of Neutral Fat and of Free Fatty Acids in a Sample of partly saponified Tallow.

In the technical saponification of fats by superheated steam, it is frequently necessary to ascertain the extent to which saponification has proceeded.

A specimen of an autoclaved tallow gave the following results :

Saponification value of the tallow .	203 0
Acid value	162 2

The difference, 203 - 162 2 = 40 8, corresponds to the neutral fat left un-

saponified Hence, assuming that 195 is the saponification value of neutral tallow, the percentage of neutral fat is found by the following statement:

$$195 : 40\,8 :: 100 : x, \text{ whence } x = 20{\cdot}92, \text{ or } 21.$$

Hence the percentage of neutral fat in the treated tallow is 21. and the percentage of free fatty acids is 100 – 21 = 79.

770 Estimation of Free Fatty Acids and Neutral Fat in a Mixture of Fatty Acids derived from one kind of Fat and mixed with Neutral Fat of another kind

In this case the fatty acids must be determined gravimetrically. About 5 grams of the sample are accurately weighed and dissolved in hot alcohol, phenolphthalein solution is added, and the fatty acids are neutralised by adding deminormal standard alkali solution until the liquid just becomes of a pink colour. The liquid is now allowed to cool, and is then diluted with an equal volume of water and shaken with petroleum ether as is described in paragraph **757**. The aqueous layer is now drawn off. The remaining ether solution is repeatedly washed with water, the ether is distilled and the residue of neutral fat is weighed

The fatty acids are now separated from the above aqueous layer by means of mineral acid, and their weight is determined as is described under the Hehner value (**761**) Their mean molecular weight may then be calculated (**762**), and the mean molecular weight of the fatty acids in the neutral fat may be found after saponifying the fat and isolating the liberated fatty acids

If the mean molecular weight of the free fatty acids is known, their quantity could be found, without weighing them, by calculation from the known quantity of deminormal KOH solution which was used to neutralise the free fatty acids.

771 Examination of an Edible Oil —The following numbers were found by analysis

Acid value	3 2
Saponification value	196 1
Iodine value	109 3
Unsaponifiable matter, percentage	0 82

As the sample is practically completely saponifiable it cannot belong to the rape-oil group of oils. Its iodine value points to the presence of cotton-seed-oil, and the free fatty acids correspond to 1·6 per cent, taking the mean molecular weight as 182 (**762**).

772 Examination of a Mixture of Two Oils —The following example, sold as olive-oil, gave on analysis the following numbers:

Acid value	3·2
Saponification value	196·1
Unsaponifiable matter, percentage	0 82
Iodine-value	93

The iodine value is too high for olive-oil, and the oil is probably a mixture. Oils of the rape-oil class are excluded by the saponification value (**993**). Almond-oil is excluded by its higher price. The iodine value suggests the presence of cotton-seed-oil, and its percentage may be calculated from the iodine values. If x, y = the percentages of olive-oil and of cotton-seed-oil, then $x + y = 100$.

Taking the iodine value of cotton-seed-oil as 109, and the iodine value of olive-oil as 85, we have $\frac{85\,x}{100} + \frac{109\,y}{100} = 93$, whence $x = 66\,6$ per cent. of olive-oil

PART V.

ORGANIC ANALYSIS.

SECTION XIII.

CARBON AND HYDROGEN BY COMBUSTION. NITROGEN BY COMBUSTION AND BY KJELDAHL PROCESS. OTHER ELEMENTS BY COMBUSTION.

780. Introductory Remarks.—This section treats of the general and typical methods employed for the ultimate analysis of organic substances and for the determination of their molecular weights.

Carbon and hydrogen, the most common constituents of an organic compound, are estimated by burning a known weight of the organic substance, and determining separately the weights of carbon dioxide and of water which are thus produced. There is no simple method for directly estimating with accuracy the proportion of oxygen present, but this is usually calculated by difference after the percentages of all the other constituents have been found.

Several methods for determining nitrogen are described. The estimation is an important one, not only for scientific purposes but also in connection with the analysis of manures and of agricultural products.

Methods for estimating the halogen elements, as well as sulphur and phosphorus, are also described.

A large number of other elements may be present in organic compounds. As a rule the ordinary methods of estimating these elements in their inorganic compounds, which are described in the earlier part of this book, are directly or indirectly applicable to their determination in organic substance.

Estimation of Carbon and Hydrogen in a Solid Organic Substance.

781. Organic Combustion Process.—The method pursued is a modification of that first described by Liebig. It consists in heating the

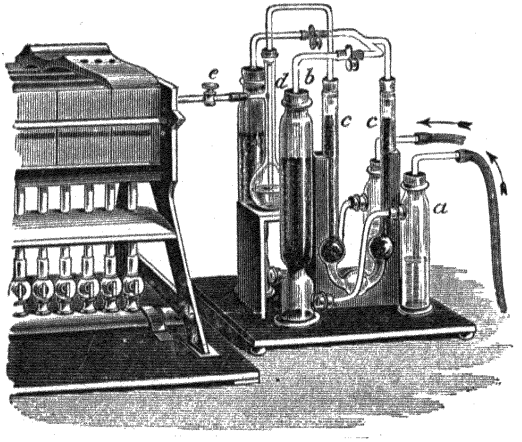
organic substance to redness with copper oxide, whereby its hydrogen is converted into water and its carbon into carbon dioxide. These products are absorbed by calcium chloride, and by soda-lime or potassium hydrate solution respectively.

In the method now commonly in use, the "combustion" of the organic substance, and the removal of the products of combustion, are assisted by passing a current of air or of oxygen through the combustion-tube.

The following apparatus and materials are required for an organic combustion:

782. Apparatus for Purifying the Air and Oxygen used in the Combustion.—This apparatus (Fig. 102) is in duplicate, with the exception of the U-tube (*c c*) and the flask (*d*). The front wash-bottle (*a*) and the eprouvettes (*b*) are used for purifying air, and the corresponding vessels behind them are used for purifying oxygen. The wash-bottles (*a*) are connected respectively with supplies of air and of oxygen under pressure.

FIG. 102.



ABSORPTION APPARATUS.

Either air or oxygen, or a mixture of both, may therefore be passed in a purified condition into the combustion-tube, by suitably adjusting the clamps between the eprouvettes and the U-tube (*c c*).

Both the air and the oxygen finally pass through the U-tube (*c*) and the flask (*d*) on their way to the combustion-tube. The air is usually passed from a gas-holder. The oxygen may be transferred to a gas-holder from a steel cylinder charged with the compressed gas and provided with a regulator for reducing the pressure: the gas will be moist, but will be more under control than if it is supplied directly from the steel cylinder.

The two wash-bottles (*a*) contain strong sulphuric acid, and serve to dry

the gas passing through them: the eprouvettes (*b*) contain granular soda-lime, which absorbs the carbon dioxide. Any trace of moisture is subsequently removed during the passage of the gas through the calcium chloride in the U-tube (*c c*). The flask (*d*) contains strong sulphuric acid and indicates the speed of the current of gas which is regulated by the stop-cock (*e*).

The apparatus is fitted up as is shown in Fig. 102. Either rubber stoppers or sound corks are used; the tops of the corks are cut off level with the tube, and the ends are brushed over with melted paraffin wax. The wash-bottles (*a*) and the flask (*d*) are one-third filled with pure strong sulphuric acid. The lower chambers of the eprouvettes (*b*) contain broken glass, and the bodies of these vessels are charged with granular soda-lime. The U-tube (*c*) is filled with granular calcium chloride, a plug of glass-wool being inserted in the top of each limb.

783. A Combustion-furnace.—Of the many forms of gas combustion-furnace in use, Erlenmeyer's (Fig. 108, p. 422) is perhaps the most convenient. Part of a Glaser furnace is shown in Fig. 102 (p. 404). A sheet-iron or fire-clay trough, lined with a thin layer of asbestos, should extend down the interior of the furnace, and the combustion-tube is laid in this trough.

784. The Combustion-tube.—Cut off a piece of combustion-tubing, about 1·5 cm. in internal diameter, and long enough to project about 2·5 cm. from each end of the furnace. Round off the sharp edges at each end of this tube by fusing them in the blow-pipe flame. As soon as the glass is cold, cleanse the interior by washing it with a long-stemmed tube-brush in a stream of water, or by attaching a plug of cotton-wool to the middle of a piece of string about 5 feet in length, and drawing the wetted plug up and down the tube; then rinse the tube well in a stream of water from the tap, and dry it by heat.

785. A Glass Plug to prevent Diffusion is shown at *d* in Fig. 103 (p. 407). This is made by drawing off about 2 cm. of a glass tube or rod, which just passes into the combustion-tube (*Note*). The narrow portion is cut off about 1·5 cm. from the shoulder, and the end is bent round into the form of a loop, or a loop of platinum wire is fused into the end. This loop enables the plug to be withdrawn from the combustion-tube by means of a piece of hooked wire. The partial closure of the tube by this plug during the process of combustion causes the air-stream to move with greater velocity at this point, and thus prevents the backward diffusion of the products of combustion into the purifying-tubes (**782**).

An additional method for preventing diffusion consists in admitting air and oxygen into the combustion-tube through a tube which is only one millimetre in bore.

Note.—An 8 cm cylinder of tightly coiled copper gauze may take the place of the glass plug. The cylinder should fit the combustion tube, and should have been repeatedly heated in the blow-pipe flame and cooled in the air so as to be superficially oxidised. It is placed in the tube and maintained at a red heat to burn any organic vapour which may diffuse backwards during the combustion.

786. A Platinum or Porcelain Boat is shown at *e* (Fig. 103, p. 407); this boat must be of such dimensions that it can be readily pushed into the combustion-tube. A platinum boat may either be purchased or may be made from platinum-foil.

787. Copper Oxide.—The copper oxide must be prepared by the direct oxidation of metallic copper; it is usually made by roasting short lengths of copper wire in a current of air. If the oxide has been prepared by the ignition of copper nitrate it often evolves oxides of nitrogen when it is heated, and such oxide is quite unsuitable for use in organic combustion.

788. A Silver Coil and Copper Coil.—A cylinder 8 cm. in length, which just passes into the combustion-tube, is made by tightly coiling the metal gauze or sheet (Fig. 103, *g*).

The copper coil (809, d) should always be used if the substance to be burnt contains nitrogen, and the silver coil when the substance contains a halogen element.

At a red heat the copper deoxidises any nitrogen oxide, and the silver retains any halogen which is evolved during the combustion. These gases would otherwise be retained in the absorption-tubes, and would give rise to error in the carbon and hydrogen determinations.

789. Calcium Chloride Absorption-tube.—The tube *h* (Fig. 103), which is intended to absorb the aqueous vapour evolved during the combustion, contains granular calcium chloride (177), through which CO_2 has been passed if necessary until its solution is neutral to test-paper (*Note*, p. 107).

The bulb nearest to the combustion-tube is empty, and serves to condense much of the water-vapour which is produced (*Note*).

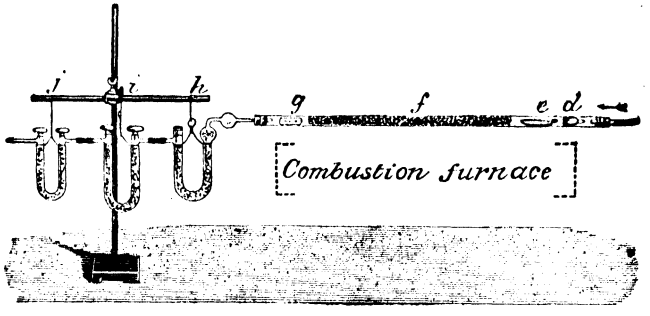
The other bulb and the two limbs of the U-tube are nearly filled with the calcium chloride, after a small plug of glass-wool has been placed at the top of the second bulb in order to prevent the calcium chloride from passing into the narrow tube above.

A second plug of glass-wool is then placed in the other limb of the tube, in order to prevent particles of calcium chloride from entering the small side-tube. The straight limb is either closed with a well-fitting cork, which is cut off level with the top of the tube, and is then brushed over with melted paraffin wax; or the ends of the tube are drawn off in the blow-pipe flame and are thus permanently sealed (*a*, Fig. 104, p. 408).

Note.—The greater part of the water which is produced during the combustion collects in the empty bulb, and is emptied out after each combustion as soon as the tube has been weighed. The calcium chloride in the tube is thus prevented from becoming rapidly saturated with water, and serves for many combustions without being renewed.

790. Soda-lime Tubes.—These tubes (*i*, *j*, Fig. 103) are intended to absorb the carbon dioxide which is formed during the combustion. Three-quarters of each tube from one end is filled with granular soda-lime, the remainder of the space being filled with granular calcium chloride. The inlet- and outlet-tubes are loosely closed by plugs of glass-wool. The preparation

FIG. 103.



ORGANIC COMBUSTION WITH OXYGEN.

of similar absorption-tubes, which has been already described in paragraphs **177**, **178**, should be referred to.

All tubes and vessels containing absorbent material must be closed from the air except when they are in actual use or are being weighed.

Potash-bulbs.—Thirty-three per cent. potassium hydrate solution may be used instead of soda-lime as an absorbent for the carbon dioxide. The solution may be introduced into a bulb-tube of the Liebig or the Geissler pattern. The liquid absorbent presents the advantage over soda-lime of serving as a gauge, since the rate at which the current of gas is passing may be ascertained by counting the bubbles as they pass. A guard-tube containing granular calcium chloride must be attached to the further end of the bulb apparatus, and must be weighed with it. This tube prevents moisture from being carried away from the potash-bulbs during the combustion.

The Geissler bulbs with their calcium-chloride tube are shown in Fig. 104 (*b*): they take the place of the U-tubes (*i* and *j*) in Fig. 103. A second larger calcium-chloride tube (*c*) is attached to the small tube in order to prevent its contents from absorbing moisture from the atmosphere, this is removed during the weighing. The potash-bulbs should as a rule be recharged after they have been used twice.

791. The Combustion Apparatus is fitted up as follows: About two-thirds of the combustion-tube (**784**) are filled with granular copper

oxide (787), the oxide being compactly shaken together (*f*, Fig. 103). The oxide may be kept in its place by means of coiled cylinders of copper-gauze placed before and behind it; each of these cylinders is made by tightly coiling a strip of copper-gauze, and is about 2·5 cm. in length and of such diameter that it just passes into the combustion-tube.

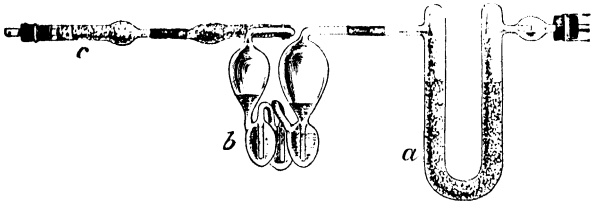
Sufficient space must be left in the tube for the insertion of the coil (*g*), the boat (*e*), and the diffusion-plug (*d*).

The tube is now laid on the asbestos in the iron trough of the combustion-furnace, with its ends projecting about 3 cm. from the furnace, and perforated discs of sheet-iron or of asbestos millboard are pushed upon the ends of the tube in order to protect the corks from the heat of the furnace.

The metal coil (788) is then introduced (*g*).

Two rubber corks are now selected to fit the ends of the combustion-tube. One cork is perforated to receive the glass tube of millimetre bore (785), it

FIG. 104.



POSTASH-BULBS AND DRYING-TUBE.

is then inserted into the empty end of the combustion-tube, and the glass tube is connected by means of rubber tubing with the purifying apparatus (782).

The other cork is perforated to admit the bulbed tube at the end of the calcium-chloride tube (789), and this tube (*h*) is inserted so as to project through the cork about 0·3 cm.; the cork is then pushed into the other end of the combustion-tube.

The soda-lime tubes (*i*, *j*) are then connected in succession with one another, and with the calcium-chloride tube, by means of rubber joints, the soda-lime in each of these tubes being in the limb which is nearer to the tube (*h*). The glass tubes are made to touch one another within the rubber joints, and are bound with copper binding-wire if the joints are not air-tight. As has been already explained, the potash-bulbs with guard-tube (Fig. 104) may take the place of the soda-lime tubes.

792. **Now proceed to heat the Combustion-tube,** containing the copper oxide and the metallic coil, to redness for at least half an hour with a current of purified air passing through it, in order to remove all combustible matter and moisture; and if the copper oxide has not been recently

used in the tube for a combustion, it is best to prove that its contents are no longer evolving carbon dioxide or steam, by attaching the weighed absorption-tubes (*h*, *i*, *j*) and continuing the process of heating the oxide in the air-current for another half-hour. The tubes are then reweighed, and should have undergone no increase in weight during the process.

For this purpose weigh the tube (*h*) without its rubber caps or connections. As soon as the weighing is finished, slip a little rubber tube closed with a piece of glass rod upon each of its ends, so as to prevent access of atmospheric air. Then weigh the tubes (*i*) and (*j*) separately, and immediately close them with similar caps, unless they are so constructed that by turning their stoppers contact of the soda-lime with the air can be prevented (178).

Now connect these tubes with one another, and with the combustion-tube as is shown in Fig. 103, and regulate the speed of the current of air passing through the apparatus until the bubbles follow one another through the sulphuric acid (*a*, Fig. 102, p. 404) at such a rate that they can be easily counted.

Remove the absorption-tubes after they have been in connection with the combustion-tube for half an hour, and again weigh them. If any one of them is found to have increased in weight more than a few milligrams, the above test must be repeated.

It will be understood that the above process of preparing and testing the combustion-tube and copper oxide need only be applied when a new combustion-tube and its contents are used, or when the tube has been laid aside for some time. A series of combustions may ordinarily succeed one another without any such testing being necessary.

793. For Practice in the Combustion Process weigh out accurately into the boat about 0·25 gram of pure crystallised cane-sugar, which has been recently dried in the steam-oven.

Then connect the parts of the apparatus together (791), push in the boat containing the sugar and the diffusion-tube, and ascertain that the whole is air-tight (180).

The silver and the copper coils (*g*) may be omitted in this case, since sugar contains no nitrogen or halogen.

Now heat the copper oxide (*f*) to redness, being careful to avoid heating the boat and to protect it from radiated heat by a small screen. Start a slow current of air through the tube, allowing the bubbles to pass at such a rate that they can be easily counted. Then extend the heating to the boat very gradually, so as to avoid a rapid evolution of gas and vapour from the sugar. The sugar will be slowly burnt away.

A current of oxygen may be made to mingle with or replace the air-current, either throughout or towards the end of the process, in order to facilitate the complete burning of the substance, but a current of air must finally be used to replace the oxygen from the absorption-tubes before they are weighed.

As soon as the whole of the sugar is burnt, the current of air is allowed to pass slowly for fifteen minutes in order to sweep out the carbon dioxide and steam from the combustion-tube, and to reoxidise the metallic copper which has been formed by the reduction of the copper oxide.

If any water condenses in the end (*g*) of the combustion-tube, it may usually be removed by shifting the screen on the end of the combustion-tube, so as to allow the tube to become gently heated while the air-current is passing. The water must be all transferred by evaporation in the air-current to the calcium-chloride tube in this way.

The absorption-tubes are then detached from the combustion-tube and from one another, and their contents are at once shut off from contact with the atmosphere. After they have stood for half an hour near the balance-case, in order to gain the temperature of the air, each tube is weighed separately.

The increase of weight of the calcium-chloride tube (*h*) gives the weight of water which has been produced by the combustion of the sugar, and from this the weight of hydrogen in the sugar can be calculated. The increase of weight of the soda-lime tubes (*i*, *j*), or of the potash-bulbs with their guard-tube, gives the amount of carbon dioxide which has been produced by the combustion of the sugar, and from this the weight of carbon in the sugar can be calculated.

The smaller soda-lime tube (*j*) serves as a "guard-tube" If its weight increases during the combustion, either the contents of the first tube (*i*) are not absorbing carbon dioxide satisfactorily and require to be replaced by fresh soda-lime, or the combustion has been carried on too rapidly. In either case the guard-tube will probably have prevented the loss of any carbon dioxide which has passed through the first soda-lime tube.

794. The Method of calculating the Results from the weights which have been obtained by an organic combustion is shown below:

Example.—In a particular combustion, 0·4739 gram of pure sugar was burnt.

The calcium-chloride tube, which weighed 48·769 grams before the combustion, gained 0·2763 gram in weight by absorbing the water formed during the process.

The soda-lime tube, which weighed 58·4891 grams before the combustion, gained 0·731 gram in weight during the process.

Therefore the weight of hydrogen in the sugar $= \frac{0{\cdot}2763}{9} = 0{\cdot}0307$ gram:

And the weight of carbon in the sugar $= \frac{0{\cdot}731 \times 3}{11} = 0{\cdot}1994$ gram.

Accordingly the percentage weight of hydrogen $= \frac{0\ 0307 \times 100}{0\ 4739} = 6\ 47$:

And the percentage weight of carbon $= \frac{0\ 1994 \times 100}{0\ 4739} = 42\ 08$.

Calculating the weight of oxygen by difference, and comparing the percentage results found with those calculated from the formula for cane-sugar, $C_{12}H_{22}O_{11}$, the following statement is the result:

	Theoretical.	Found.	Error.
Carbon	42 10	42 08	− 0 02
Hydrogen . . .	6 43	6 47	+ 0 04
Oxygen	51 47	51 45	− 0 02

Note.—It may be remarked that, owing to the difficulty of removing moisture entirely from the substance and from the apparatus and the materials used for the combustion, the percentage of hydrogen which is obtained is usually somewhat too high: whilst the imperfect drying of the substance and a slight loss of carbon dioxide tend to make the percentage of carbon too low.

795. **Any Incombustible Mineral Matter** which is present in an organic substance will remain as ash in the boat. Its weight may be determined by weighing first the boat containing the ash, and then the empty boat.

796. **The Presence of Nitrogen** in the organic substance leads to the formation of nitrogen oxide, which would be taken up in the absorption-tubes. To obviate this source of error, a copper-coil (809, d) is kept at a red heat in the front of the combustion-tube (Fig. 103, *g*, p. 407), and decomposes any nitrogen oxide which is produced. The copper oxide and the copper-coil are first heated to redness, a slow current of air is then passed as soon as the combustion is started, and the combustion of the charred substance is finally completed in a current of oxygen.

A more satisfactory method consists in absorbing any nitrogen oxide by the following mixture: A strong solution is prepared from K_2CrO_4 mixed with one-tenth its weight of $K_2Cr_2O_7$; this is made into a thick paste with precipitated manganic hydrate, and the mixture is heated until it is dry. About 13 cm. of the front of the combustion-tube is filled with this granulated mixture; it is always heated to redness while the preliminary current of air is passing through the tube, and is maintained at a temperature of about 200° C. during the process of combustion.

797. **The Halogen Elements** present in an organic substance are also evolved during the combustion in a condition in which they may remain in the absorption-tubes. They should be completely absorbed by causing them to pass over a red-hot silver coil (788) placed in the tube (Fig. 103, *g*). The halogens may also be dealt with as follows:

Substances which contain Cl, Br, I, S, and P are usually mixed with powdered lead chromate which has been fused, instead of with copper oxide, and the front part of the combustion-tube is filled with granulated lead chromate instead of granular copper oxide (791). In the fore-part of the tube a reduced copper coil (809, d) is placed, and in the hinder portion an oxidised copper coil (785, *Note*). The tube and its contents are dried by heating them only to dull redness while a current of dried air is passing; the chromate must not be fused in this process.

The powdered substance, mixed with about six times its bulk of recently heated powdered chromate, is introduced into the cold tube. The oxidised copper coil is then inserted, the reduced copper coil is placed in the fore-part of the tube, and the combustion is carried out in a slow current of air. The main portion of the chromate is heated to dull redness, while about 10 cm. of it nearest to the front copper coil are kept comparatively cool. As soon as the substance is completely charred, a current of oxygen may be passed to complete the combustion.

798. **A Volatile Solid Organic Substance** requires to be burnt much more carefully than a non-volatile body like sugar. A check against backward diffusion of vapour (785) should be used, and the substance must only be introduced into the rear of the combustion-tube after the front part of the tube has been heated to redness, and must then be heated very slowly.

Combustion of a Liquid Substance or Gas.

799. **A Liquid Organic Substance** which is not very volatile or hygroscopic may be weighed in the boat and burnt in the usual way. Or it may be weighed in a small glass tube which is sealed at its lower end, and this may be loosely closed by a stopper consisting of a small piece of glass rod flattened out at the top (Fig. 127 *b*, p. 483): this tube is placed in the boat, and the boat is pushed into the combustion-tube.

800. **A Volatile Organic Liquid** is weighed in a little tube with a capillary opening, and this is introduced into the combustion-tube.

The little tube is made by drawing out a short piece of glass quill-tubing into capillary bore in two parts about 0·6 cm. apart. One of the capillaries is then drawn off close to the short piece of tube so as to seal it, and the other capillary-tube is broken off about 3 cm. from the sealed tube (Fig 127 *a*, p. 483).

Before the capillary-tube is broken off, the little piece of closed quill-tube into which it opens may be expanded into a bulb by heating it to redness while it is being constantly rotated in the flame and blowing down the open tube.

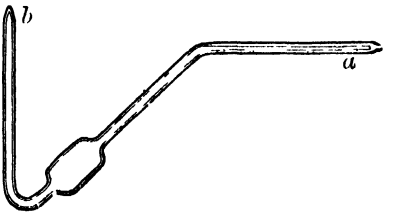
The empty tube is first weighed. The liquid is then introduced into it in suitable quantity, by heating the tube and allowing it to cool with the end of the capillary immersed in the liquid. The end of the capillary-tube is then sealed in the flame, and the tube is weighed again. Its gain in weight will give the weight of liquid which has been taken.

A slight scratch with a file is made near the end of the capillary in order that it may be easily broken off, and the end is broken off and placed together with the bulb in the boat just before the boat is pushed into the combustion-tube. Backward diffusion must be specially guarded against (785, 798).

801. A very Volatile Substance should be weighed in a special tube, from which it may be allowed to escape as vapour into the combustion-tube while the liquid is itself outside the furnace.

A convenient form, which is readily made from a piece of ordinary glass tubing, is shown in Fig. 105. The tube is first weighed, and is weighed again after the liquid has been introduced and both ends have been sealed. It is then placed either in a dish of cold water, or in ice and salt, according to the degree of volatility of the liquid.

FIG. 105.



WEIGHING-TUBE FOR VOLATILE LIQUID.

When the combustion-tube has been heated to redness the horizontal end (*a*) of the bent tube is opened, and is at once pushed through a hole in the cork of the combustion-tube into which it must fit tightly.

The liquid is then allowed to rise in temperature and evolve its vapour, which will pass into the combustion-tube and be burnt. As soon as the liquid has volatilised, the upright end (*b*) of the tube is snapped off, and air or oxygen is passed through the tube (793).

802. Gaseous Organic Substances are burnt by passing them in known volume through the combustion and absorption apparatus which has been described for solids (791).

ESTIMATION OF NITROGEN IN AN ORGANIC SUBSTANCE.

803. Three methods for the estimation of nitrogen in an organic substance are described.

The Soda-lime Method (804), which consists in heating the substance with soda-lime and estimating the ammonia which is evolved, is suitable for many organic substances.

The Kjeldahl Method (807) depends on converting the nitrogen into ammonium sulphate by heating the substance with strong sulphuric

acid, and then estimating the ammonia contained in the sulphate. This process can be rapidly carried out and is used for the estimation of nitrogen in organic substances generally, and especially in manures and vegetable products, and in liquid or moist bodies.

The Dumas or Absolute Method (809) provides for the measurement of the nitrogen which is evolved when the substance is burnt under suitable conditions with copper oxide. This process of estimation is applicable to all nitrogenous substances.

Estimation of Nitrogen by the Soda-lime Method.

804. This process cannot be applied to the estimation of nitrogen in nitro-compounds and in certain other bodies.

The substance is mixed with soda-lime, and the mixture is heated to dull redness. The nitrogen in the organic body is thus evolved as ammonia gas, which may be estimated in one of the two following ways. The second is the more exact, but it is more tedious in execution than the first.

(1) The ammonia is absorbed in a known volume of standard acid, and the amount of acid which remains unneutralised is afterwards determined by standard sodium hydrate solution (805).

(2) The ammonia is absorbed in excess of dilute hydrochloric acid, and the ammonium chloride thus produced is precipitated as the double chloride of ammonium and platinum and is weighed as such (806).

805. The Ammonia is absorbed in an Excess of Standard Acid and is Estimated Volumetrically.

The following materials are required for the process:

(a) *A Combustion-tube* about 50 cm. long and 1·5 cm. in internal diameter, which has been closed at one end and has had the sharp edges of the other end rounded in the flame for the reception of a rubber cork.

(b) *A Will and Varrentrapp Bulb-tube*, which is fitted into the open end of the combustion-tube by means of a tightly fitting perforated cork (Fig. 106). The end of the bulb-tube projects about 0·3 cm. through the cork.

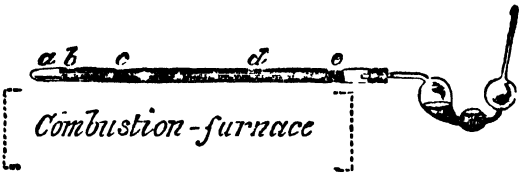
(c) *Soda-lime* both in a state of fine powder and in a granular condition (177). The soda-lime must be heated in a dish over a sand-bath until it is perfectly free from moisture and from ammonia, and the powder and the granular substance are then kept in separate well-stoppered bottles.

(d) *Fibrous Asbestos*, which has been ignited in a porcelain or platinum crucible.

(e) *Oxalic acid*, which has been heated in the steam-oven until all its water of crystallisation has been expelled.

For Practice in the Process, weigh out carefully about 0·3 gram of pure dry urea, CON_2H_4, or of pure dry acetanilide, C_8H_9ON. Hold the perfectly clean and dry combustion-tube in a vertical position, with its closed end resting on a square of glazed paper. Introduce into the tube a layer of the dried oxalic acid about 4 cm. in depth (Fig. 106, *a*). and then 4 cm. of the dry powdered soda-lime (*b*).

Fig. 106.



Soda-lime Combustion Apparatus.

Then turn out the weighed quantity of urea into a clean dry porcelain mortar, reduce it to powder, and add sufficient finely powdered soda-lime to fill about 10 cm. of the combustion-tube. Thoroughly mix the urea with the soda-lime in the mortar, and pour the mixture into the tube through a funnel made by rolling round a piece of glazed paper. When all the mixture has been transferred to the tube, rinse out the mortar with a little fresh soda-lime powder, and pour this also into the combustion-tube. The mixture and rinsings should fill the part of the tube shown by special shading (*c*).

Now fill in about 25 cm. of the granular soda-lime (*d*), and finally push in a loose plug of the ignited asbestos (*e*). After the introduction of the asbestos, about 2 cm. of the tube should remain clear.

Finally hold the tube in a horizontal position and tap its whole length upon the bench, to make sure that there is a free passage along its upper part for the gases which will be evolved.

Note —If the substance to be burnt is hygroscopic or volatile it should be mixed with the powdered soda-lime in the combustion-tube instead of in the mortar. The mixing may be effected by a long wire shaped at its end like a cork-screw.

Now measure out 15 c.c. of normal sulphuric acid (285) into the bulb-tube by means of a fine pipette, and add a little water to make up the liquid to the level shown in the figure. Then connect the bulb-tube with the combustion-tube by means of the cork and make sure that the joint is gas tight.

The tube is now ready to be heated. Lay it upon the asbestos in the trough of a combustion-furnace, with the end (*e*) extending about 2 cm. beyond the end of the furnace. Slip upon this end of the tube a circular piece of sheet-iron or asbestos cardboard about 8 cm. in diameter and perforated in its centre so as to fit the combustion-tube. This will shield the cork from the direct heat of the furnace, and will prevent it from being charred.

Now light the burners under the portions (*d*) and (*e*) of the tube, and heat them to dull redness. Then gradually extend the heat along the mixture (*c*). The intervention of the powder (*b*) will prevent the oxalic acid (*a*) from being heated but it is better to insure this by screening the acid with a piece of sheet-iron or asbestos millboard.

When the portions (*c*), (*d*), and (*e*) are at a dull red heat, and all evolution of gas has ceased, heat the oxalic acid at (*a*) gently. The gases thus evolved will drive out any ammonia gas which is still present in the tube, and will insure its absorption by the standard acid.

Instead of sweeping the ammonia out of the combustion-tube by heating some oxalic acid, the tube may be drawn out to a narrow sealed end: when the combustion is finished this sealed tip is then broken off and a stream of air is drawn through the combustion-tube by applying suction at the open end of the absorption vessel.

Care must be taken that no drops of liquid remain between the asbestos (*e*) and the cork, since ammonia would be dissolved by this liquid. If drops are seen, gradually push the tube further into the furnace so as to evaporate the liquid.

Now pour the acid from the bulb-tube into a beaker, and rinse out the bulbs several times into the beaker. Titrate the acid, which remains unneutralised by ammonia, with normal sodium hydrate solution (289), using methyl-orange as an indicator: and ascertain by difference the amount of acid which has been neutralised by the ammonia. Each c.c. of acid which has been neutralised by the ammonia corresponds to 0·014 gram of nitrogen.

It must be remembered that ammonia may have passed unabsorbed through the bulbs, unless some free acid remains at the end of the combustion. The addition of a small quantity of methyl-orange solution (268) to the acid in the bulbs before the combustion is started will serve to indicate whether any acid remains unneutralised after the combustion is finished.

806. The Ammonia is absorbed in Excess of Dilute Hydrochloric Acid, and is precipitated as $(NH_4)_2PtCl_6$.

The preparation and heating of the combustion-tube is carried out precisely as is described above (805), but hydrochloric acid diluted with four times its volume of water, instead of normal sulphuric acid, is introduced into the absorption-bulbs.

After the combustion is finished, the acid solution of ammonium chloride

is transferred from the bulbs to a dish, and is mixed with excess of pure platinum chloride solution; the ammonium platini-chloride is then estimated as is described in paragraph 173.

The weight of nitrogen contained in the double chloride, and the percentage of nitrogen in the organic substance are then calculated (173, *Note*).

Instead of weighing the double chloride as such, the salt may be ignited and the residual platinum weighed: the weight of nitrogen originally present in the double chloride is then calculated from the weight of platinum found. This method may follow the weighing of the double chloride, and its result may serve as a check upon the result already obtained from weighing the salt.

Estimation of Nitrogen by Kjeldahl's Process.

807. This process is suitable for dry or moist solids, and for liquid bodies.

The substance is first heated with strong sulphuric acid, free from nitrogen compounds. The nitrogen of the organic body is thus converted into ammonium sulphate.

The acid solution is then heated with excess of sodium hydrate; and the ammonia thus evolved is either absorbed in a known volume of standard acid and determined volumetrically, or is precipitated as ammonium platini-chloride and then determined gravimetrically.

Any nitrate present in the original substance must be removed, by evaporation to dryness with hydrochloric acid and ferrous sulphate, before the substance is heated with the strong sulphuric acid.

Strong Sulphuric Acid free from ammonium sulphate and from oxides of nitrogen is required for the process. The freedom of the acid from these substances can be ascertained by making a blank experiment as is described below (808), using sugar instead of urea. This experiment should yield no ammonia.

808. **For Practice in the Estimation,** weigh out 0·7 gram of pure dry urea or acetanilide into a round-bottomed flask of about 500 c.c. capacity, and pour in 20 c.c. of the sulphuric acid. Heat the liquid nearly to boiling for an hour. Then add 8 grams of dry powdered potassium sulphate and continue the heating.

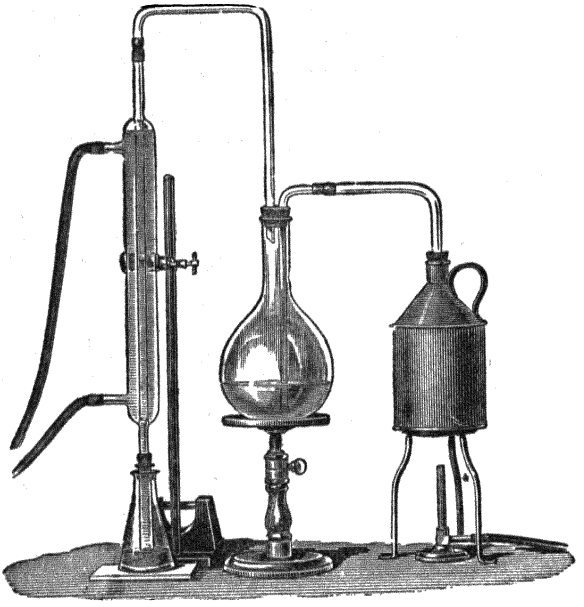
The presence of the potassium sulphate in the acid raises the temperature to which the acid may be heated without boiling, and renders it possible to heat the liquid sufficiently to complete the necessary change in the organic substance. Many organic substances cause the liquid to become dark coloured before the sulphate is added, but the liquid almost loses its colour as the reaction advances after the addition of the sulphate.

The addition of a small crystal of copper sulphate expedites the reaction.

By this treatment all the nitrogen of the urea is converted into ammonium sulphate. The ammonia is then expelled from this ammonium sulphate and is absorbed in either of the following ways (1) or (2):

(1) The cold acid liquid in the flask is diluted with water. A decided excess of sodium hydrate, dissolved in three times its weight of water, is then added, the flask is fitted with the absorption apparatus described in paragraph **173**, and the ammonia is expelled and absorbed as is there described.

FIG. 107.



AMMONIA DISTILLATION IN STEAM.

(2) The sodium hydrate solution described above (1) is added in excess to the cold sulphuric acid in the large flask (Fig. 107), and the bent delivery-tube from the flask is connected with a vertical condenser (**1016**). The lower end of the condenser-tube is then attached by means of a perforated cork to a test-tube, in the bottom of which an opening has been blown while the glass is heated to redness. The bottom of the test-tube just dips into the absorbent acid in the receiving-flask.

The ammonia is then driven over into the acid either by simply boiling the alkaline solution, or by passing a current of steam from a separate vessel through the alkaline liquid as is shown in Fig. 107.

For the latter procedure the acid liquid should be poured from the digestion-flask into a flask of greater capacity. 100 c.c. of sodium hydrate solution,

containing 357 grams of sodium hydrate per litre, are then carefully poured down the inside of the flask, without being allowed to mix with the acid liquid The alkaline solution, thus introduced, is more than sufficient to neutralise the acid. The apparatus is then connected together (Fig. 107), and steam is blown through the liquid in the large flask. The steam mixes the acid and the alkaline liquids together, raises the temperature of the mixture, and carries over the ammonia into the condenser and thence into the absorbent acid.

The ammonia may either be received in a known volume of standard acid, the unneutralised excess of which is titrated after the absorption (295); or it may be absorbed in an excess of dilute hydrochloric acid, and then estimated by conversion into the double chloride of ammonium and platinum, as is described in paragraph 173.

Example—The following are the particulars of an estimation:

0 788 gram of urea was weighed out, and was treated as is described above, and the resulting ammonia was absorbed in 100 c c of normal sulphuric acid.

This solution was made up to 250 c c, and was then added from a burette to neutralise 10 c c of a sodium hydrate solution, corresponding to 10 03 c c. of a normal sodium hydrate solution; 34 c c. of the acid solution were required to neutralise this alkali.

Therefore the volume of acid not neutralised by the ammonia =

$$\frac{10\ 03 \times 250}{34} = 73\ 76 \text{ c c.}$$

And the volume of acid neutralised by the ammonia = 100 - 73 76 = 26·24 c.c.

Now since each c c. of the normal acid corresponds to 0 017 gram of NH_3, containing 0 014 gram of N, the weight of nitrogen in the urea = 26 24 × 0 014 = 0·36736 gram.

And the percentage of nitrogen in the urea = $\frac{0\ 36736 \times 100}{0\ 788} = 46\ 61.$

Estimation of Nitrogen by Dumas' Method.

809. This Method depends upon the Measurement of the Volume of the Nitrogen, which is evolved by the Combustion of the Substance.

The method is applicable to the analysis of all organic compounds containing nitrogen.

The organic substance is heated with copper oxide in an atmosphere of carbon dioxide gas. The constituent elements, nitrogen, carbon, and hydrogen, are then evolved as nitrogen, carbon dioxide, and steam respectively. These products are passed through cold strong potassium hydrate solution into the measuring-vessel, in which the nitrogen alone collects in the gaseous condition. The volume of gas thus obtained is corrected for temperature and pressure, and its weight is then calculated.

The following materials are required for the process:

(a) *A Combustion-tube*, from 1·3 to 1·6 cm. in diameter, and 70 cm. in length. The tube is cleansed and dried, and is then sealed at one end by drawing it out in the blowpipe flame; the other end has its edges rounded in the flame for the reception of a cork.

(b) *Magnesite* in pieces the size of a pea, or pure dry *sodium bicarbonate* which has not been prepared by the ammonia-soda process.

(c) *Copper Oxide* in both the powdered and the granular condition. The oxide must have been prepared by the oxidation of metallic copper, since when it has been prepared from copper nitrate it frequently contains nitrogen. It must have been ignited shortly before it is used.

(d) *A Copper Spiral*, or *a Roll of Copper Gauze*, about 8 cm. in length, and of such diameter as just to fit the combustion-tube. Before using the coil, its surface should be freed from organic matter and rendered metallic by being ignited first in a current of air and then in a stream of hydrogen gas.

This result may be more readily attained by holding the copper-roll with crucible-tongs in the tip of a large blowpipe flame until it is heated to redness, and then dropping it while red-hot into a little methyl alcohol contained in a large test tube.

For Practice in the Process, weigh out 0·15 gram of pure dry urea. Introduce first into the end of the combustion-tube (Fig. 106, p. 415) a layer of magnesite (b) about 10 cm. in length, then about 8 cm. of the granulated copper oxide (c), and make each layer settle down compactly by tapping the tube while it is in a vertical position.

Now mix the urea intimately with some of the finely powdered copper oxide (c) in a glazed mortar, and introduce the mixture into the tube by means of a wide-stemmed funnel. Rinse out the mortar with a little fresh copper oxide, and pour this also into the tube. The mixture and rinsings should occupy about 12 cm. of the tube after they have been rendered compact by tapping the tube.

The mixing of the substance with the powdered copper oxide is more easily effected in the tube than in the mortar, by using a long wire bent into a corkscrew shape at its end.

Next add a layer of about 25 cm. of the granular copper oxide, and then push in the recently deoxidised copper roll. Tap the whole length of the tube, held in a horizontal position, upon the bench, so as to form a free passage along the upper part for the evolved gases. Attach a bent delivery-tube by means of a perforated rubber cork (Fig. 108, p. 422), and slip upon the end of the combustion-tube a perforated piece of asbestos cardboard in order to

prevent the overheating of the cork. The tube is now ready for the combustion process.

Lay the combustion-tube in the trough of the combustion-furnace, and proceed to heat the granular layer of copper oxide in the front of the tube, gently heating at the same time the front half of the magnesite.

When the evolution of carbon dioxide has continued for some time, test the gas by collecting it in a vessel containing solution of potassium hydrate, in order to see if it is free from air.

For this purpose the gas may be passed into the special collecting apparatus, the construction and use of which are described in paragraph 810. If this apparatus is not at hand, the end of the delivery-tube is dipped just beneath the surface of mercury contained in a trough, and a small test-tube or the graduated tube mentioned below, one-third of which is filled with mercury and the remainder with potassium hydrate solution, is supported over the end of the delivery-tube.

In filling this tube introduce the necessary quantity of mercury into the inverted tube, and remove any air-bubbles which adhere to the interior. Then pour in the potash solution until it reaches to 0·5 cm. of the top, and carefully add water until the tube is quite full. Now slide a glass plate over the mouth of the tube, invert the tube with its mouth under the mercury in the trough, withdraw the glass plate, and support the tube securely over the end of the delivery-tube. In this way contact of the potash solution with the fingers may be avoided, since the lower specific gravity of the water causes it to float on the potassium hydrate solution.

When each bubble of gas from the combustion-tube is completely absorbed by the potassium hydrate solution, all the air has been expelled from the tube. If the bubbles are not completely absorbed, continue to heat the magnesite until the carbon dioxide has entirely expelled the air. Not more than half the magnesite must be heated for this purpose, and when the air has been completely removed one burner only should be left to heat the magnesite.

Now proceed to arrange the apparatus for the collection of the nitrogen, which is evolved during the combustion.

If the special form of apparatus, just referred to, is employed, it will be already in position, and it will only be necessary to remove any air from the interior, and to proceed as is directed in paragraph 810.

As a substitute for this apparatus a graduated tube of 150 c.c. capacity may be used. Two-thirds of this tube are filled with mercury and the remainder with a concentrated solution of potassium hydrate by the procedure described above, and the tube is securely clamped over the end of the delivery-tube in the mercury trough (Fig. 108, p. 422). The tube may have a stop-cock at its end, which must be accurately ground and made air-tight with vaseline, and this stop-cock facilitates the removal of any air which has been already collected in the tube.

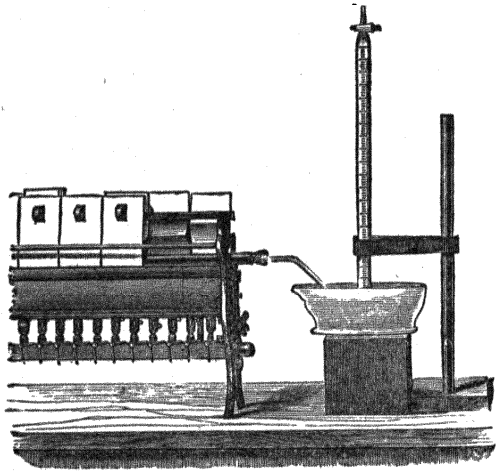
As soon as the collecting apparatus has been duly arranged, and the front part of the combustion-tube containing the copper oxide and the copper coil

has been heated to redness, gradually heat the mixture containing the substance from the front backwards.

When the evolution of gas from the delivery-tube has altogether ceased, heat the remainder of the magnesite. The carbon dioxide thus evolved will sweep out the nitrogen which remains in the combustion-tube. Now shake the gas collected in the tube, in order to bring it into contact with the caustic potash solution and to remove any carbon dioxide which may have escaped absorption.

When the volume of the gas undergoes no further decrease it is read off

Fig. 108.



Combustion for Nitrogen.

with the following precautions, and represents the nitrogen evolved from the organic substance:

If the special collecting apparatus has been used, the process of reading off the volume of nitrogen is conducted as is directed in paragraph 810.

If the gas has been collected as is shown in Fig. 108, the measuring-tube is removed by means of a small porcelain dish filled with mercury, and is placed in a large cylinder of water which should be at the temperature of the laboratory. The mercury and caustic potash solution are allowed to fall out of the measuring-tube into the water, and the measuring-tube itself is then entirely immersed.

As soon as the nitrogen has gained the temperature of the water, the measuring-tube is raised until the water is at the same level both outside and inside the tube, and the volume of the gas is read off.

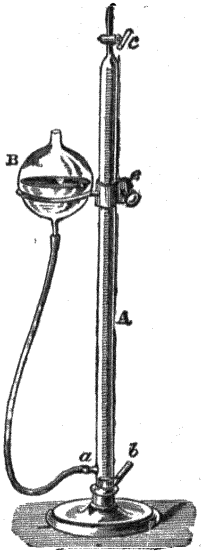
As soon as the volume of the nitrogen has been read, take the temperature of the surrounding water and the barometric pressure, and calculate the weight of the nitrogen from these data by means of the following formula (835-839):

$$\text{Weight of N} = \frac{v \times (p - w) \times 273 \times 0{\cdot}001257}{760 \times (273 + t)} \text{ gram.}$$

where v = volume of nitrogen in c.c.;
t = temperature of the water;
p = barometric pressure, reduced to 0°;
w = the tension of aqueous vapour at $t°$;
0·001257 = the weight of 1 c.c. of nitrogen under normal conditions.

In order to be able to correct the result thus obtained for unavoidable errors, a blank experiment should be carried out with an organic substance which contains no nitrogen. Pure sugar may be used for the purpose. The volume of gas which is obtained represents the amount of nitrogen which is introduced during the process, and should not exceed 1 c.c.; it must be deducted from the volume of nitrogen obtained in each estimation before the percentage weight is calculated.

FIG. 109.



COLLECTION OF NITROGEN.

810. A Special Form of Apparatus, in which the nitrogen may be both collected and measured, is represented in Fig. 109. It consists of a graduated 100 c.c. burette (A), which is supported in a heavy foot and is furnished at the top with an accurately fitting stop-cock (*c*) lubricated with vaseline. The burette is connected by a side-tube (*a*) with a reservoir (B) by means of a flexible rubber tube which has been soaked in melted paraffin wax. A second side-tube (*b*) is connected with the burette, at a point about an inch and a half lower down than the first (*a*), and is inclined upwards.

Mercury is poured in through the lower side-tube (*b*) until it rises about 1 cm. above the joint, and the tube is then closed. The reservoir (B) is now charged with a solution of potassium hydrate, prepared by dissolving the solid in an equal weight of water, the stop-cock (*c*) is opened, and the reservoir is raised until the potash solution fills the burette. The stop-cock is then closed, and the reservoir is lowered and is fixed by the clamp near the bottom of the burette.

The side-tube (*b*) is now opened, and the delivery-tube from the combustion apparatus is passed through it into the burette. When only a very minute bubble of nitrogen remains from each bubble after it has been acted on by the solution of alkali in the burette, the carbon dioxide which escapes during the preliminary heating of the magnesite may be considered to be free from air.

The delivery-tube is then removed and its end is immediately immersed in some water to close it from the air; the tube (*b*) is closed, and the air is expelled from the burette (A) through the stop-cock (*c*) by raising the reservoir (B). The stop-cock is then closed, and the reservoir is lowered and clamped near the bottom

of the tube (A). The tube (*b*) is now opened, the delivery-tube is once more inserted into the side-tube (*b*), and the process of combustion is proceeded with, all gas which is evolved during the combustion being collected in the burette (A).

As soon as the evolution of gas ceases, the nitrogen is swept out from the combustion-tube by the carbon dioxide which is expelled by heating the residual magnesite, the delivery-tube is withdrawn from the side-tube (*b*) and the side-tube is again closed.

The gas is then allowed to stand in the burette for about an hour in order that the absorption of the carbon dioxide may be complete. The volume of the nitrogen is now read, after the reservoir has been raised sufficiently to bring the surface of the liquid in it to the same level as that in the burette, and the temperature of the surrounding air and its pressure are also read. This volume will require to be corrected for temperature and pressure by the formula on page 423, the vapour pressure of strong solution of KHO being taken as half that of water at the corresponding temperature.

Estimation of Chlorine, Bromine and Iodine in an Organic Substance.

811. Two methods are here described for estimating halogens in organic bodies, in both of which the halogen is ultimately weighed in combination with silver.

In the first process (812) the substance is burnt with lime, or with soda-lime, and the calcium halogen salt thus produced is dissolved out and precipitated by silver nitrate solution.

In the second process (814) the substance is decomposed by heating it under pressure with strong nitric acid in the presence of silver nitrate: in this case the silver halogen salt is directly produced.

The first method is the more generally applicable, but the second method will as a rule be found the more convenient of the two.

812. Ignition with Lime, or with Soda-lime.—The powdered solid substance is mixed with lime or soda-lime, and the mixture is heated strongly; the halogen is thus obtained in combination with calcium.

The cooled mass is then dissolved in nitric acid, excess of silver nitrate solution is added to this liquid, and the halogen is precipitated and weighed in combination with silver.

The process is rendered somewhat tedious, by the necessity of using a large quantity of nitric acid to neutralise and dissolve the alkaline mass. The operations of filtration and washing the precipitate and filter become therefore somewhat lengthy.

The Lime or Soda-lime which is used for the combustion should be free

from chloride. If it contains chloride, the amount of chlorine present must be estimated and allowed for, and a known quantity of the lime or soda-lime must therefore be used in each determination.

The quicklime may be readily prepared by breaking marble into small pieces of similar size (177), introducing it into a clay crucible, and heating it strongly in a muffle or in a wind-furnace for several hours. The lime thus prepared is removed from the crucible as soon as it is cold, and is preserved in a well-stoppered bottle.

The soda-lime in a granular condition (177) is heated strongly to expel moisture, and is stored in a stoppered bottle.

813. *For Practice in the Estimation* weigh accurately about 0·2 gram of finely powdered chloral hydrate, $CCl_3CH(OH)_2$.

Cleanse a piece of combustion-tube, about 50 cm. in length and about 1 cm. in diameter, close one end by drawing it out in the blow-pipe flame, and fuse the sharp edges of the open end in the flame.

Fill about 5 cm. of the tube with the powdered lime or soda-lime, and add the weighed substance.

Now introduce another 5 cm. of the powdered lime or soda-lime into the combustion-tube, and mix the substance with this portion by pushing down into the tube a long bright piece of wire which is bent like a corkscrew at its end, and turning this wire round in the powder and substance. Almost fill the rest of the tube with granular lime or soda-lime, and then insert a loose plug of asbestos.

A volatile organic liquid would be dropped into the combustion-tube in a small tube or bulb with a capillary opening (800) after the first 5 cm of lime-powder have been introduced, or it might be introduced in the form of vapour as is directed in paragraph 801.

Either leave the end of the combustion-tube open, or draw it out into a narrow tube which is bent obliquely and has its end just immersed beneath the surface of some water contained in a small beaker during the process of combustion (Fig. 74, p. 122).

Now lay the tube in the trough of the combustion-furnace, and heat the front portion containing the granular lime to redness. When the lime is red-hot, gradually extend the heat to the mixture.

As soon as the decomposition is complete, transfer the contents of the tube to a beaker after cutting off the narrow end of the tube if it has been drawn off. Then rinse out the tube with dilute nitric acid into the beaker (*Note*), and add more nitric acid and stir until the lime is completely dissolved. Now filter off any particles of carbon and glass, add an excess of silver nitrate solution to the clear liquid, and filter off, dry, ignite, and weigh the precipitate (149–152); or alternatively neutralise

the nitric acid solution, and then titrate the halogen by standard silver nitrate solution (373).

Note —If iodine is liberated during the combustion, it must be converted into hydriodic acid by means of sulphurous acid before the nitric acid is added. The iodine may be partially converted into iodate during the combustion, and this must be converted into iodide by adding sodium sulphite to the nitric acid solution before the iodide is estimated by silver nitrate.

814. Carius' Method for Estimating the Halogens.—The organic substance is mixed with fuming nitric acid and silver nitrate, and the mixture is then heated for several hours in a sealed glass tube. The halogen is thus obtained in combination with silver, and is weighed in this form.

The Process of Estimation.—Cut off a piece of thick-walled Jena-glass tube or combustion-tube, about 50 cm. in length and 1·5 cm. in diameter. Seal up one end in the blowpipe flame, being careful to make the end strong and round in shape, and to anneal the glass well by allowing it to cool down slowly, finally in the luminous flame. This is the digestion-tube.

For practice in the process weigh out accurately about 0·2 gram of chloral hydrate, $CCl_3.CH(OH)_2$, in a small weighed piece of quill-tubing which is not less than 3 cm. in length and is sealed at one end.

If the substance is a volatile liquid, it is sealed up in a small thin tube (Fig. 127, *a*, p 483) or in a thin bulb-tube. The bulb-tube may be made from a thin-walled ignition-tube, 0 5 cm. broad, by heating its closed end in the flame and blowing it out into a bulb about 1 5 cm. in diameter. When the tube is cold it is weighed, and the substance is introduced. The upper part of the tube is then drawn off and sealed by holding it in a blowpipe flame, and the two parts of the tube with the inclosed substance are weighed The gain in weight of the tube gives the amount of substance taken. The portion of the glass drawn off from the bulb is weighed at once, and the weight is noted down for subsequent use (p. 428).

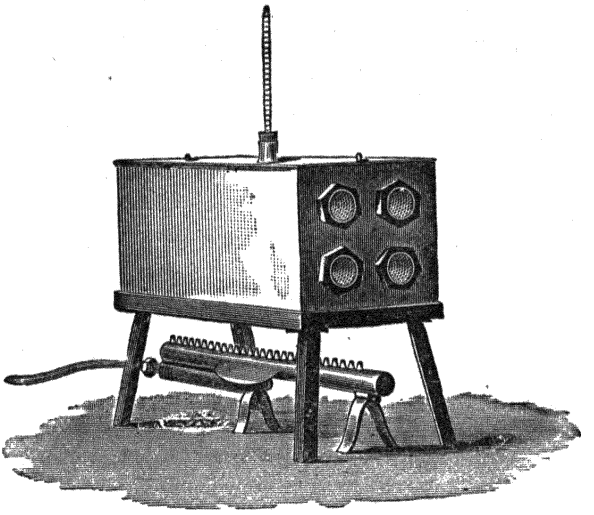
Introduce into the digestion-tube about twice as much solid silver nitrate as is theoretically required to furnish sufficient silver to combine with the halogen. Then pour in 2 c.c. of fuming nitric acid, and push the tube containing the substance down the interior of the digestion-tube until it reaches within about 5 cm. of the acid. The small tube will adhere to the glass surface, owing to its being wet with nitric acid. The greatest care must be taken not to allow the acid or its vapour to reach the substance in the open tube; if the substance is contained in a sealed tube or bulb this danger is avoided.

Now draw out and seal the open end of the digestion-tube. For this purpose hold the tube in a slanting position, so that its contents remain undisturbed in their relative positions, and the acid does not reach the substance. Gradually heat the tube at about 10 cm. from its open end, rotating it continually in the flame, until its sides soften and thicken and begin to fall together.

Then gradually draw off the upper part, leaving a thick-walled sealed capillary end, and carefully anneal this by cooling it first in the luminous flame and finally in the air.

Now place the tube in a loosely fitting wrought-iron tube, and close this with a screw-cap in order to prevent accident if the glass should burst under the pressure to which it is subjected. It is well to wrap the tube in a sheet of filter-paper before placing it in the iron tube, so as to lessen the risk of fracture. Then tilt the tube sufficiently to cause the acid to rinse

FIG. 110.



AIR-BATH FOR HEATING SEALED TUBES.

the small tube down to the bottom, or if the substance has been sealed in a bulb-tube break the bulb by shaking the digestion-tube. The tube is now ready to be heated in the air-bath.

The Air-bath (Fig. 110) is a stout sheet-iron box 60 cm. in length. Four pieces of iron gas-pipe, open at both ends and 5 cm. in internal diameter, pass through holes in the ends of the box. The projecting ends of these pipes have a screw-thread turned on their surface, and a lock-nut is screwed upon each of them in order to keep the tube in position.

A thermometer in a perforated cork is inserted into a hole in the top of the bath, and serves to register the temperature of the interior. A Fletcher burner suitable for heating the bath uniformly is shown in the figure.

When the bath is in use, a sheet-iron cover is placed over it; this rests upon the upper surface of the bath, it is open at the bottom, and the sides and ends are half an inch distant from the bath itself. The cover is kept in position by two studs fixed in the upper surface of the bath, which pass through corresponding

holes in the top of the cover. This cover renders the temperature in the bath more uniform.

It will be seen that four tubes can be heated at the same time in the air-bath.

The bath should be slightly tilted, in order to prevent the liquid in the digestion-tube from entering the sealed capillary while the tube lies in the bath.

When the sealed tube has been inclosed in the wrought-iron tube and the cap has been screwed on, introduce it into the broader tube of the air-bath, place the cover over the air-bath, and light the burner. Watch the thermometer carefully, and allow the temperature to rise until it reaches the desired temperature; then maintain the bath at this temperature for several hours by properly regulating the supply of gas to the burner.

A temperature of 300° C. is sufficient to insure decomposition in all ordinary cases. A lower temperature will frequently suffice, and some simple bodies will be decomposed at a temperature of 150° C.

Then allow the bath and tube to become quite cold, take off the cover, and proceed to remove and open the tube in the following manner:

The tube inclosed in its protecting wrought-iron jacket is taken out of the air-bath in the jacket, the cap is removed, and the capillary end is slid out of the jacket. Care must be taken not to allow the open end of the iron tube to face the person, since there may be very considerable gaseous pressure within the tube, and an explosion which may occur should take place away from the person. The capillary end projecting from the air-bath is drained from any adhering liquid, is then heated in a Bunsen flame until the glass softens and the gas forces an exit and escapes.

When the substance requires to be heated for a long time with the acid to a high temperature, it is best to allow the tube to cool and to permit the gases to escape from the cold tube once or twice during the process of heating, the tube being sealed again each time before the heating is proceeded with. This precaution will often save the tube from bursting.

If there is any doubt about the oxidation of the substance being complete after the capillary has been opened in an ordinary determination, the tube should be sealed up and re-heated.

As soon as the issue of gas ceases, the end of the digestion-tube is cut off with a file, and the contents are rinsed out with water into a beaker. Any large pieces of the small glass tube or bulb are removed and washed, then dried in the steam-oven and weighed, the weight of the end which was drawn off during the sealing, if a glass bulb was used (p. 426), being added. The difference between this weight and that of the original bulb or tube represents the weight of the small pieces of glass which remain in the silver chloride.

The acid liquid is then diluted and boiled for a few minutes, and the silver salt is filtered off (*Note*), washed, dried, and weighed (149). The weight of any small glass fragments, which has been already determined, is then

deducted and the true weight of the silver salt is thus obtained. From this the weight of the halogen and its percentage is calculated.

Note.—If iodine is present in the organic substance, the silver nitrate and silver iodide sometimes fuse together into a yellow mass. The silver nitrate must be removed from this mass, by heating it in the diluted liquid for one or two hours.

Estimation of Sulphur in an Organic Substance.

815. The Sulphur in the Organic Substance is oxidised and converted into Sulphate; it is then precipitated and weighed as Barium Sulphate.—Any of the methods mentioned below may be used.

816. Oxidation by Nitric Acid, as it is effected in Carius' method for determining the halogens (814), is suitable for the estimation of sulphur. The substance is heated with strong nitric acid of 1·5 specific gravity as has been already described (*loc. cit.*), the silver nitrate being omitted, and the sulphur is thus converted into sulphuric acid.

When the tube is cold, its contents are transferred to a porcelain dish. The excess of nitric acid is removed by evaporating the liquid nearly to dryness on the water-bath after adding an excess of hydrochloric acid, some sodium chloride being also added to fix the sulphuric acid. The liquid is then diluted, and the sulphur is estimated as $BaSO_4$ (133).

817. The Methods of estimating Sulphur in Coal (550) and in Zinc-blende (142), are also applicable to its estimation in many organic substances.

Estimation of Phosphorus in an Organic Substance.

818. An Organic Substance containing Phosphorus is subjected to the processes described above (816, 817), and the phosphorus is thus converted into phosphate. The solution obtained by any one of these processes is then rendered alkaline, if necessary, by adding ammonium hydrate, and the phosphate is precipitated with magnesia mixture (167) and estimated as $Mg_2P_2O_7$ (166).

PART V.—SECTION XIV.

THE DETERMINATION OF THE MOLECULAR WEIGHT OF A SUBSTANCE.

819. The first two methods (820, 821) are usually applied to basic or acid organic substances which are not volatile without decomposition. They depend upon the formation of definite bodies of a saline nature, and require a previous knowledge of the basicity of the substance.

The third and fourth methods (822–824) depend upon the lowering of the freezing-point or the raising of the boiling-point of a solvent in which the substance has been dissolved; they are applicable to many organic and to some inorganic substances.

Other methods are subsequently described, which are applicable only to volatile substances and depend upon determining their vapour densities (920–928).

DETERMINATION OF THE MOLECULAR WEIGHT OF AN ORGANIC ACID.

820. The Molecular Weight of an Organic Acid may sometimes be determined by preparing an Insoluble Metallic Salt from the Acid, and then estimating the Weight of the Metal in a known Weight of the Pure Salt.

Since silver is a monovalent metal and forms many insoluble salts, the silver salt is generally selected: but in certain cases the barium or lead salt is converted into the sulphate by evaporation with strong sulphuric acid and subsequent ignition.

Thus the combustion of pure acetic acid gives the empirical formula CH_2O for this acid, and it is evident that either this formula or some multiple of it will represent the molecule of acetic acid.

Only one acetate of the monovalent metals can be obtained, and acetic acid is accordingly inferred to be monobasic.

The molecular weight of acetic acid may therefore be determined by preparing pure dry silver acetate, and then igniting a known weight of this salt and weighing the residual silver. From this result the weight of the silver salt

which contains 107·98 parts of silver may be found by calculation. This will be the molecular weight of the silver salt, and by subtracting from this molecular weight the atomic weight of silver, and adding that of hydrogen, the molecular weight of the acid will be obtained.

Example.—Two grams of pure dry silver acetate gave on ignition 1·2934 grams of silver.

Now the weight of silver thus found will stand in the same ratio to the atomic weight of silver, as the weight of the silver acetate, which was taken, does to the molecular weight of silver acetate.

Therefore the molecular weight of silver acetate $= \frac{107\cdot98 \times 2}{1\cdot2934} = 166\cdot97$.

And the molecular weight of the acid $= 166\cdot97 - 107\cdot98 + 1 = 59\cdot99$. This molecular weight corresponds to the molecular formula $C_2H_4O_2$.

From a polybasic acid more than one corresponding salt of a monovalent metal may usually be prepared. These salts will contain different percentages of the metal, and from a study of the relative proportions of metal present in them, the basicity of the acid may usually be inferred.

For Practice in the Estimation prepare some pure silver succinate, by adding a moderately strong solution of silver nitrate to solution of sodium or ammonium succinate. Filter off the silver succinate, remove dissolved salts from it by washing, and dry the salt at as low a temperature as possible.

Now weigh accurately about 1 gram of the silver succinate into a covered porcelain crucible of known weight, heat it very gently at first, but finally to a red heat for a short time, and weigh it; then repeat the processes of heating and weighing until the weight of the residual silver is constant.

Now calculate the molecular weight in the way already described. Since, however, succinic acid is known to be dibasic, it is evident that $2 \times 107\cdot98$ must be subtracted from the molecular weight of the silver succinate, and 2×1 must be added to the remainder, in order to obtain the molecular weight of the acid.

Determination of the Molecular Weight of an Organic Base.

821. Certain Organic Bases, notably the Alkaloids, combine with Hydrogen Chloride and Platinum Chloride to form Double Salts.—These resemble in constitution the double chloride of ammonium and platinum, $2(NH_3HCl).PtCl_4$, the organic base taking the place of the NH_3.

The molecule of the double salt therefore usually contains two molecules of the organic base, and if R represents a monovalent organic base, the general formula of the double salt will be $2(RHCl).PtCl_4$. When the molecular weight of this organic double salt is known, the value of R can be calculated,

since the weight of the other elements present in the molecule is known and can therefore be subtracted.

The method of procedure is identical in principle with that which has been already described (820). The pure dry double salt is prepared, and a suitable quantity of it is weighed; this is then ignited in the air until it is free from carbon, and the weight of the residual platinum is ascertained.

The molecular weight of the double salt is then obtained from the following proportion statement:

$$\left\{\begin{matrix}\text{The weight of}\\ \text{Pt found}\end{matrix}\right\} : \left\{\begin{matrix}\text{atomic weight}\\ \text{of Pt}\end{matrix}\right\} :: \left\{\begin{matrix}\text{weight of double}\\ \text{salt used}\end{matrix}\right\} : \left\{\begin{matrix}\text{molecular weight}\\ \text{of double salt.}\end{matrix}\right\}$$

The molecular weight of a monovalent base is then found by subtracting from the molecular weight of the double salt the weight represented by H_2PtCl_6, and dividing the remainder by 2.

Example.—2·32 grams of caffeine platino-chloride yielded 0·57 gram of platinum.

$$\text{Hence the molecular weight of the double salt} = \frac{195{\cdot}5 \times 2{\cdot}32}{0{\cdot}57} = 795{\cdot}7.$$

$$\text{Therefore the molecular weight of caffeine} = \frac{795{\cdot}7 - 410{\cdot}2}{2} = 192{\cdot}7.$$

For Practice in the Estimation dissolve some pure caffeine or para-tolnidine in dilute hydrochloric acid, and add to the solution a moderate quantity of platinum chloride solution. Filter off the yellow or orange precipitate of the double salt, wash it about six times with alcohol, and dry it in the steam-oven.

Now weigh out 1·5 gram of this double salt into a weighed porcelain crucible, and heat it gently at first and then strongly. Continue the ignition until all the carbon is burnt away, stirring occasionally so as to promote the combustion of the carbon. Then weigh the residual platinum, and repeat the processes of heating and weighing until the weight of the platinum is constant. From this weight proceed to calculate the molecular weight of the alkaloid as is described above.

Determination of Molecular Weight by the Freezing-point Method (Raoult).

822. The Molecular Weight of a Substance may often be determined by the Lowering of the Freezing-point of a Solvent in which the Substance has been dissolved.—This method is of special value in the case of substances whose molecular weights cannot be determined by the preceding methods (820, 821), or by taking their vapour densities (920-928).

The method depends upon the fact that if quantities of different substances, which are proportional to their molecular weights, are dissolved in equal

amounts of the same solvent, the freezing-point of the solvent is in every case depressed to the same extent. This depression varies directly with the amount of substance used, and inversely with the amount of the solvent.

Hence the depression of the freezing-point of the solvent, which is caused by dissolving the molecular weight in grams of a body of known molecular weight in a known weight of the solvent, is first ascertained. The molecular weight of any other substance can then be readily found, if a known weight of that substance is dissolved in a known weight of the same solvent, and the depression of the freezing-point which is thus caused is noted.

The Formula required for Calculating the Molecular Weight is deduced as follows:

If M = the molecular weight of the substance dissolved;

K = the *Molecular Coefficient of Depression*, or the depression of freezing-point produced by dissolving the molecular weight of the substance in grams in 100 grams of the solvent;

W = the weight in grams taken of the substance, the molecular weight of which is required;

S = the weight of solvent;

D = the observed depression of freezing-point;

Then the depression (D) is proportional to the number of gram-molecules of substance which have been dissolved in 100 grams of solvent, or to $\frac{W}{M} \times \frac{100}{S}$: hence

$$D : K \cdot : \frac{W \times 100}{M \times S} : 1, \text{ or}$$

$$D = K \frac{W \times 100}{M \times S}, \text{ and } M = K \frac{W \times 100}{D \times S}.$$

823. The Process of Determination is conveniently carried out in the apparatus of Beckmann (Fig. 111).

The glass tube *A* contains a stirring-rod made of stout platinum-wire, and a thermometer *D* which can indicate hundredths of a degree.

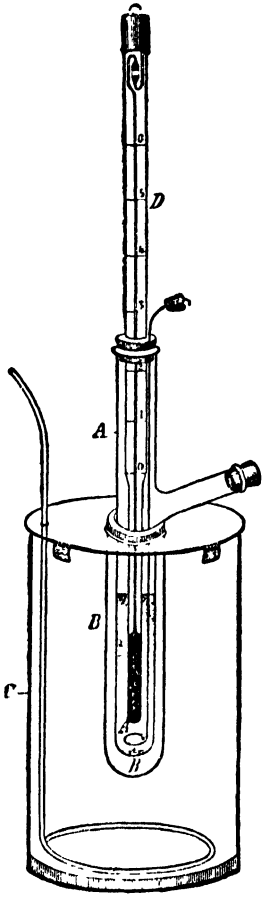
The capillary-tube of the thermometer usually has a bulbous space at the top, which can receive some of the mercury, and thus enable the height of the mercury-thread to be adjusted to suit various freezing-points. The variation in the quantity of mercury present in the stem of the thermometer in different pairs of determinations does not affect the accuracy of the result, because only the difference between the freezing-points of the solvent and of the solution is required and not the actual temperatures of freezing.

A weighed quantity of the solvent is introduced into the tube *A*, which is then placed in a somewhat wider tube *B*, and an air-jacket is thus formed between the tube *A* and the outer vessel *B*. The external vessel *C* contains a stirring-rod, and either water or a freezing-mixture the temperature of which must be from 2° to 5° below the freezing-point of the solvent.

The thermometer is observed while the liquid is constantly stirred. At first the mercury sinks below the true freezing-point, but it rises again as the freezing commences. The highest position of the mercury is read.

When the freezing-point of the solvent has been ascertained as the mean of several determinations, a known weight of the substance the molecular weight of which is required, is introduced through the side-tube into *A*. The liquid is then thoroughly stirred until the substance is dissolved, and the temperature of freezing is again noted. The "ice," which consists only of the solidified solvent, will now form at a lower temperature than before, and the difference between the two temperatures gives the lowering of the freezing-point (*D*).

Fig 111.



Beckmann's Freezing-point Apparatus

The final accurate determination of the freezing-point must be effected in all cases by removing the tube from the jacket, and occasionally dipping it into the freezing-mixture and moving it round until the liquid freezes. When this takes place the tube is immediately removed from the mixture, wiped dry, and placed in the air-jacket once more. The "ice" will probably have melted by this time, if not allow it to do so, then attach the air-jacket *B* and immerse it in the cooling-mixture. Now stir constantly, carefully observing the freezing and noting down the highest temperature as has been described above.

The molecular weight (M) is then calculated from the difference between the two freezing-points which have been noted, by means of the formula given on page 433.

A series of determinations may be obtained if necessary, by adding successive quantities of the substance to the same quantity of solvent.

If the Molecular Coefficient of Depression (K) is unknown it can readily be ascertained by dissolving a definite quantity of a substance of known molecular weight in a weighed quantity of the solvent. The value of K is then calculated from the equation on page 433. The values of K for a few common solvents are for:

Water	19°
Acetic acid	39°
Benzene	49°
Phenol	75°

For Practice in the Method use 6 grams of pure cane-sugar or of glucose; dissolve this in 50 grams of water, for which K = 19, and introduce into the outer vessel a mixture of ice and salt; then proceed as has just been described.

Example—12 616 grams of glucose were dissolved in 92·25 grams of water, the freezing-point of the water was depressed 1 45° C., and K = 19, therefore from the equation on page 433

$$\text{The molecular weight} = \frac{K \times W \times 100}{D \times S} = \frac{19 \times 12{\cdot}616 \times 100}{1\ 45 \times 92\ 25} = 179.$$

Determination of Molecular Weight by the Boiling-point Method.

824. When a Solid Substance is dissolved in a Definite Quantity of a Solvent, the Boiling-point of the Solvent is raised by an Amount proportional to the Number of Gram-molecules of the Dissolved Substance.

A convenient and rapid process for the determination of molecular weights of solids, by the elevation of the boiling-point of the liquid in which they are dissolved, is described below. It is a modification by Walker and Lumsden of the Landsberger method.

When the vapour from a boiling liquid is passed into another portion of the same liquid which contains a substance in solution, the vapour is condensed in the solution, and the heat thus generated raises the temperature of the solution to its boiling-point. The vapour issuing from the solution will then be in equilibrium with the atmospheric pressure, and the temperature of the vapour will therefore be the same as the boiling-point of the solution.

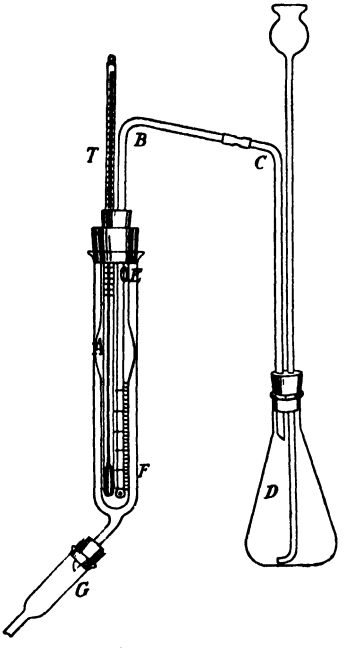
This principle is applied in the process which is described below. The vapour from the boiling liquid is first passed through another portion of the liquid until the boiling-point is constant. The temperature is then observed and a weighed quantity is added of the substance whose molecular weight is to be determined. The vapour of the solvent is then passed again until the substance is dissolved and the boiling-point is constant, and either the weight or the volume of the solution of the substance is finally determined.

In practice it is more convenient to measure the volume of the solution at its boiling-point and to deduce its weight from this volume, but a somewhat more accurate result is obtained by weighing the solution.

From the weight of the solution thus determined and the elevation of boiling-point of the solvent, the molecular weight of the substance can then be calculated. In the arrangement devised by Landsberger the escaping vapour is made to form a jacket round the boiling solution, by this means the errors arising from superheating and radiation are largely reduced.

The **Apparatus** required for the process is shown in Fig. 112.

FIG. 112.



MOLECULAR WEIGHT BY ELEVATION OF BOILING-POINT.

It consists of a bulbed inner vessel (*A*), which contains the solution of the substance. This vessel is connected by a tube (*B C*) with a flask (*D*) containing the solvent to be boiled. The vapour issuing from this flask passes through the solution in the vessel (*A*), and escapes through a hole (*E*) into the jacket (*F*) and thence into the condenser (*G*). The capacity of the inner vessel (*A*) is indicated by cubic centimetre graduations, and the vessel contains a thermometer (*T*) the stem of which is divided into at least tenths of a degree. In order to secure uniform and regular boiling of the liquid in the flask (*D*) a few pieces of unglazed tile are introduced, and a fresh piece of tile is added each time the boiling is started for a determination.

The Method.—Place from 5 to 10 c.c. of the solvent in the vessel (*A*) and about 150 c.c. of the solvent together with a few pieces of unglazed tile in

the flask (*D*). Connect the parts of the apparatus as is shown in the figure, and then boil the liquid in the flask. The vapour will pass into the vessel (*A*) and will quickly raise the temperature of the solvent to the boiling-point. When the temperature becomes constant, read the thermometer to the hundredth of a degree by means of a lens. This temperature is the boiling-point of the solvent.

Now disconnect the tubes (*B C*) and pour out most of the condensed solvent from the vessel (*A*), leaving about 10 c.c. Introduce from 0·5 to 1 gram of the substance into the vessel, place a fresh piece of tile in the liquid in the flask (*D*), connect the tubes (*B C*) as before, and start boiling the liquid again. The thermometer will rise rapidly, and will remain approximately constant at a temperature a little higher than the boiling-point of the solvent. The boiling-point of the solution will then slowly but continuously decrease as the quantity of liquid in the vessel (*A*) increases by condensation of the vapour.

As soon as the highest temperature has been attained, read the thermometer accurately, stop the boiling in the flask, disconnect the tubes *B C*), remove the cork with the tube and thermometer, and quickly read the volume of the solution. The boiling-point of the solution is thus determined, and the difference between this boiling-point and that of the solvent gives the rise of boiling-point which is due to the presence of the substance.

Further determinations should be made by using the solution already present in the vessel (*A*). For this purpose a fresh piece of tile is placed in the flask (*D*) and the boiling is started again. After two or three minutes' boiling, readings of temperature and of volume are taken as before. These operations are repeated, and several determinations of the molecular weight can be obtained in this way with the same quantity of the substance in the course of half an hour.

When the molecular weight of the substance is high or its solubility is small, greater accuracy is desirable. To secure this the solution of the substance in the vessel (*A*) is weighed, after the removal of the thermometer and tube, at the end of the first determination, and the experiment is repeated after an additional quantity of the substance has been introduced.

The Methods of Calculating the Molecular Weight from the volume and from the weight of the solution are shown below. If

w = the weight of substance dissolved;
V = the volume of the solution in c.c.;
D = the elevation of boiling-point observed;
K′ = the elevation for 1 gram-molecule of substance dissolved in 1 c.c. of solvent;
M = the molecular weight of the dissolved substance;

Then since there are $\frac{w}{M}$ gram-molecules in V c.c. of solution, there will be $\frac{w}{MV}$ gram-molecules in 1 c.c. of solution.

If the elevation for 1 gram-molecule in 1 c.c. of solvent = K′, then the elevation for $\frac{w}{MV}$ gram-molecules $= \left(\frac{w}{MV}\right) \times K' = D$, whence

$$M = \frac{K'w}{VD} \quad (1).$$

If on the other hand the solution is weighed each time, the following formula is arrived at by a similar process of reasoning:

$$M = \frac{Kw}{WD} \quad (2),$$

where K = the elevation for 1 gram-molecule in 1 gram of solvent, and W = the weight of the solvent.

Note.—If S = the specific gravity of the solvent at its boiling-point, then $V = \frac{W}{S}$ and $K' = \frac{K}{S}$.

The values of K′ and K for different solvents are as follows:

Solvent.	K′.	K.
Alcohol . . .	1560	1150
Ether . . .	3030	2110
Water . . .	540	540
Acetone . . .	2220	1670
Chloroform . . .	2600	3660
Benzene . . .	3280	2670

For Practice in the Process, about 0·5 to 1 gram of the substance, according to its solubility, should be used. The following substances and solvents will be found suitable: Urea in water; benzoic acid in absolute alcohol; naphthalene in chloroform; and camphor in acetone.

Example.—The following are the results obtained in an actual determination of molecular weight by the above method:

0 829 gram of camphor was dissolved in acetone The series of four successive observations, made by passing the vapour of boiling acetone into this solution, were as follows:

Number of Experiment.	1	2	3	4
Elevation of boiling-point in degrees Centigrade .	1 47	1 09	0 71	0 64
Volume of solution in c c .	8 1	10 7	16 7	19 0

From the first experiment the molecular weight

$$= \frac{2220 \times 0\,829}{1\,47 \times 8\,1} = 154,$$

and from the subsequent experiments the values would be 159, 155, and 151 respectively. The average of these four values is 154 7, a number pretty closely approximating to the value 152 calculated from the molecular formula.

PART VI.

VOLUMETRIC ESTIMATION OF GASES AND VAPOURS.

Introductory Remarks.

634. The measurement of gases and vapours, and the quantitative analysis of gaseous mixtures, usually involve special methods. They are therefore treated of in a separate Section of the book.

Methods have been already described for estimating dissolved gases by gravimetric processes, by titration with standard solutions, and by absorption in a suitable standard solution upon which they can produce a definite chemical effect. But the determination of the quantity of a gas frequently involves the measurement of its volume, either directly, or indirectly by noting the loss of volume which results from its absorption from a gaseous mixture.

When the volume of a gas is dealt with, not only is special apparatus required, but special corrections and calculations must usually be applied to the results obtained in different estimations in order to make them comparable one with another. These corrections are rendered necessary by the appreciable effect which changes of temperature and pressure, and the presence of varying amounts of moisture exert upon the volume of a gas.

Since these particular characters also apply to vapours, it is convenient to describe vapour-density determinations in connection with the estimation of gases

The processes of measuring and analysing gases, which are described in detail in this Section, involve the use of comparatively cheap and simple apparatus. They also either dispense with the use of mercury, or require it only in small quantity.

The volume of a gas is frequently measured over water. This introduces a certain amount of error, since gases are soluble in water in varying degree. The results obtained by these processes are therefore somewhat inferior in accuracy to those yielded when the gases are measured over mercury. But the simpler method of measurement over water is now very generally adopted for certain gases, and is found to furnish results of a very satisfactory nature

when a sufficient volume of gas is employed and proper precautions are taken.

The error caused by the absorption of gas by water in the measuring apparatus may often be eliminated by previously saturating the water with the gas which is to be estimated.

For the description of the larger and more costly forms of gas apparatus, and for directions regarding their use, reference may be made to *Sutton's Volumetric Analysis*. Other books on general gas analysis are mentioned in paragraph **1021**.

PART VI.–SECTION XV.

CALCULATION OF NORMAL VOLUME. CALIBRATION OF MEASURING-VESSELS.

Calculation of Volume under Normal Conditions.

835. The molecules of a gas or vapour recede from one another under increased temperature or decreased pressure, and approach one another under decreased temperature or increased pressure to a far greater extent than do the molecules of an ordinary liquid or a solid.

The volume of a definite weight of any gas therefore varies appreciably with comparatively small changes of temperature and pressure, and the volume of a dry gas is also increased by the introduction of aqueous vapour when the gas is brought into contact with water.

The volume of a gas is usually measured at the temperature of the laboratory, and at the atmospheric pressure. Since however the temperature and atmospheric pressure within the laboratory are subject to variation, the conditions under which different measurements of gas are made may be dissimilar.

The gas may also sometimes be measured while it is standing over water, and at other times while it is exposed to some non-volatile liquids; the gas may accordingly either be saturated with water-vapour, or may be in the dry condition, and these differences will affect its volume.

In order to render different measurements of the volumes of gases comparable with one another, and to be able to calculate the weight of a gas, it is therefore usually necessary to ascertain by calculation the volume which the gas would occupy in the dry state and at 0° C. and 760 mm. pressure. This is usually termed "the volume under normal conditions."

836. Calculation of the Volume of a Gas under Normal Pressure.—The volume of a gas varies inversely as the pressure which is exerted upon it. Hence, if

v = the observed volume of the gas;
p = the observed barometric pressure;
V_n = its volume at 760 mm. pressure (normal);

$$\text{Then } V_n = \frac{p \times v}{760}.$$

This formula supplies the "Correction for Pressure."

Note.—In very accurate determinations, the height of the barometer should be reduced to its equivalent at 0° C. If H represents the height of the barometer in mm. at 0°, and h the height which has been read at the temperature (t) of the laboratory, then $H = h(1 - 0{\cdot}00017t°)$.

837. Calculation of the Volume of a Gas at Normal Temperature.—A gas expands or contracts by one two-hundred and seventy-third (= 0·003665) of its volume at 0° C., for each degree Centigrade rise or fall in its temperature. Hence, if

v = the observed volume of the gas;
t = the observed temperature;
V_o = its volume when reduced to 0° C. (normal);

$$\text{Then } V_o = \frac{273 \times v}{273 + t} = \frac{v}{1 + 0{\cdot}003665t}.$$

These formulæ supply the "Correction for Temperature."

838. Calculation of the Volume of a Gas in the Dry Condition.—When equal volumes of gas are saturated with aqueous vapour at the same temperature, they always contain the same quantity of vapour. The quantity of vapour present increases as the temperature rises, and decreases as the temperature falls.

The water-vapour which is mingled with the gas exerts a certain pressure, which is commonly termed the *Tension of Aqueous Vapour.*

The pressure of the vapour varies with the temperature in the same proportion as its amount varies. This pressure is usually expressed in mm. of mercury, and has been very accurately determined for each degree of temperature (983).

The tension of aqueous vapour acts in opposition to the barometric pressure, and tends to increase the volume of a gas. Hence correction is made for its effect upon the volume of the gas, by subtracting its amount in mm. from the barometric pressure. Thus if w is the tension of aqueous vapour in a volume of moist gas under pressure p, the true pressure on the gas $= p - w$.

839. General Formula for the Calculation of the Volume of a Gas under Normal Conditions.—The preceding corrections are combined into one expression in the following formulæ, in which V represents

the volume of the dry gas at normal pressure and temperature, after correction for saturation with moisture if necessary:

(1) For a dry gas, $V = \frac{p \times 273 \times v}{760(273 + t)} = \frac{p \times v}{760(1 + 0.003665t)}$.

(2) For a moist gas,

$$V = \frac{(p - w) \times 273 \times v}{760(273 + t)} = \frac{(p - w) \times v}{760(1 + 0.003665t)}.$$

These formulæ serve to correct the volume of a gas for temperature, pressure, and aqueous vapour.

The factors which are given in the Table (984) will be found useful for quickly calculating the normal volume of a gas.

The Alteration of Volume which a gas suffers by change of absolute temperature and pressure may be calculated from the following expression: $\frac{PV}{T} = \frac{P_1V_1}{T_1}$: where P, V and T represent the original pressure and volume, and at the absolute temperature $(273 + t)$, and P_1, V_1 and T_1 represent these conditions when altered.

Calibration of Measuring-tubes.

840. The graduations on tubes for measuring gases represent either absolute c.c. and fractions of c.c. capacity (243), or lengths in millimetres on the tube.

If the marks represent millimetre spaces on the tube, the value of each graduation in terms of c.c. must be ascertained. Since a glass tube frequently varies in diameter in different parts, and equal lengths on different parts of a graduated tube do not therefore necessarily correspond to equal capacities, it is usually necessary to calibrate the tube throughout its length.

Mercury and water are the two liquids in common use for calibrating measuring-tubes.

841. **Calibration of the Measuring-tube by means of Mercury.**—The tube is supported vertically with its open end upwards, and successive equal weights of mercury are poured into it from a little tube about 4 c.c. in capacity. The space in the tube which is occupied by each portion of mercury is noted by means of the graduations, and the true volume of the mercury is then calculated from its weight. The capacity of the tube at every graduation can then be determined by calculation (842).

842. *Calibration of the Measuring-tube used in Meyer's Vapour-density Apparatus* (921).—Fix the clean tube in a wooden clamp and make it truly

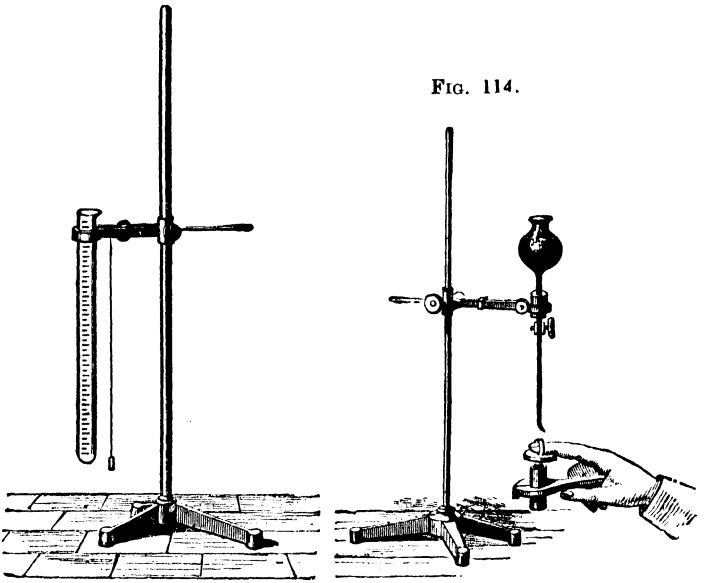
vertical by hanging a plummet beside it and setting the side of the tube parallel with the line of the plummet (Fig. 113).

Now prepare a small vessel, about 4 c.c. in capacity, by drawing out a piece of glass tube at one end in the blowpipe-flame, and grind the edge of the open end perfectly level and smooth. Hold this vessel in a little wooden clamp, and fill it with mercury from a bulbed tube which can be closed by means of a stop-cock (Fig. 114).

As soon as the vessel is quite filled, slide a glass plate along the ground edge of the tube; this will remove the excess of mercury, and will leave the

FIG. 113.

FIG. 114.



MERCURY CALIBRATION OF MEASURING-TUBE.

surface of the metal exactly level. Now pour the mercury from the vessel into the graduated tube. Remove the air-bubbles, which adhere to the inside of the tube, by means of a thin piece of lance-wood or whale-bone; and then read the level of the highest point of the meniscus of the mercury by means of the graduations.

Fill the vessel in a similar way repeatedly, emptying it each time into the graduated tube and carefully reading the level of the mercury after each addition.

These readings are most accurately taken by means of a cathetometer (843) placed at some distance from the tube.

If the cathetometer is not employed, great care must be taken that the eye is placed on the same level as the mercury surface. This may be secured by holding a small vertical mirror behind the tube, in which the reflection of the eye is seen behind that of the meniscus. The reflection in the mirror of the highest point of the meniscus must be seen at the centre of the pupil of the eye during the reading. A piece of cardboard may be slipped down behind the tube until its shade sharply defines the mercury surface.

The weight of mercury which fills the small vessel is now accurately determined, and the temperature of the air is noted. The capacity of the tube between the successive readings may then be found in c.c. from the following expression:

$$V = \frac{g \times (1 + 0{\cdot}000143\,t)}{13{\cdot}596},$$

in which (g) represents the weight of the mercury in grams, and (t) the temperature at which the calibration is made; while 0·000143 is the coefficient of expansion of mercury and 13·596 is its specific gravity.

The method of calculating the capacity of the tube at each graduation will be understood by reference to paragraph 258; but the "error of meniscus" (844) must be added to each volume thus obtained, if the tube is used for measuring gas over mercury.

The capacities do not however require a meniscus correction if the gas is measured over water, for a reason which is explained on the next page.

843. **The Cathetometer** consists of a horizontal telescope sliding on a vertical stem. The telescope is focussed on the tube and is set in a horizontal position by means of a spirit-level; it is then moved vertically on the stem, by turning a screw adjustment, until the point of intersection of the cross-wires exactly corresponds with the highest point of the mercury meniscus, and the graduation is read off. Since the telescope is always horizontal, errors of parallax are thus avoided.

844 **Error of Meniscus**.—During the process of calibration, the convexity of the mercury is turned towards the open end of the tube (Fig 115), but in the measurement of a gas the convexity will be in the opposite direction (Fig. 116) Hence it is obvious that the volume of mercury, which is measured during the calibration in the inverted tube (Fig. 115), is less than the volume of the gas which is measured when the mercury stands at the same division in the erect tube (Fig 116).

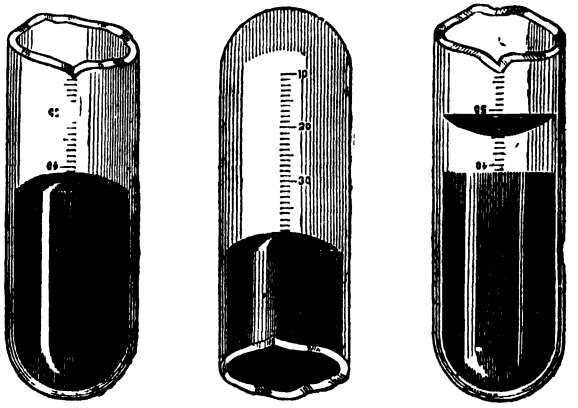
The correction, which is thus rendered necessary, is determined by reading the position of the meniscus in the inverted tube (Fig. 115), and then introducing a few drops of mercuric chloride solution and again reading the level of the mercury surface. The solution overcomes the repulsive action of the glass upon the mercury, and immediately causes the mercury surface to become flat (Fig. 117).

Thus in Fig. 115 the top of the meniscus just touches division 39, whereas in Fig. 117 the mercury stands at 38·7, showing a depression of 0·3.

If gas were measured in the tube, and the mercury stood at division 39 (Fig. 116), and if it were possible to overcome the repulsive action of the glass as before, the horizontal surface would stand at 39·3. Therefore the volume between 38·7 and 39·3, that is 0·6, would escape measurement. Hence 0·6 is the *Error of Meniscus* in this tube.

In practice this error is accordingly equal to double the difference between the reading of the convex surface of mercury, and the reading when the surface is levelled by means of mercuric chloride solution. This number must be added to the calculated capacity of the tube when the volume of the gas is read over mercury.

FIG. 115. FIG. 116. FIG. 117.



ERROR DUE TO MENISCUS.

The allowance for meniscus-error is usually made when the calibration value of the tube is being calculated.

If the tube is to be used for the measurement of gas over water instead of over mercury, the capacity actually observed in the calibration with mercury should be taken without making any correction for meniscus. The convex surface of the mercury during calibration will almost coincide with the concave water-surface when the tube is used in an inverted position, and the error of meniscus will therefore be absent when volumes of gas are read over water.

845. *Calibration of the Measuring-tube in the Lunge Nitrometer* (890).—The measuring-tube of the Lunge nitrometer may be readily calibrated by detaching it from the apparatus, stopping the bottom, and then filling the tube up to the commencement of the graduations with mercury. The tube is clamped vertically (Fig 113, p. 445). Successive equal volumes of mercury are then added from the small tube (Fig. 114, p. 445), and the readings are taken as has been described in paragraph 842. The capacity of the tube between successive readings is obtained from the formula given on page 446. No correction for meniscus is necessary in this case.

Care must be taken that very small measures of mercury are used from 2 c.c. to zero, if small volumes of gas are to be measured.

846. Calibration of Measuring-tubes by means of Water.—This method depends upon ascertaining the capacity of successive portions of the tube by introducing successive known weights of water at a known temperature into the tube, or by allowing them to flow from it. The volume of the water is calculated from its weight, and from this volume the capacity of the tube to each graduation may be ascertained (258).

Calibration of the Hempel Burette (Fig. 118, p. 450).—Since the measurement of gas in this burette is made over water, the calibration of the measuring-tube should be made by means of that liquid in the following manner:

Disconnect the clean measuring-tube (255, *Note*) and attach to its lower end, by a rubber joint, a glass tube about 10 cm. in length with a stop-cock in its middle. The end of this tube must be drawn out into a fine jet, and the stop-cock must be rigidly attached to the measuring-tube by means of thick rubber tube bound with thin copper wire, the ends of the glass tubes touching one another within the joint. The jet should be bent downwards, so as to allow the water to flow from it into a vessel held beneath.

Now completely fill the measuring-tube and stop-cock tube with distilled water which has been recently boiled and then cooled to the temperature of the room, and take care that all air-bubbles are removed from the tube. Then draw off into a stoppered weighing-bottle successive portions of water, which measure 5 c.c. each in the burette, reading off the lowest point of the surface-meniscus of the water (Fig. 80, p. 142) in measuring the volume.

When the top of the tube is being calibrated, smaller volumes of water must be drawn off, if the tube is to be used for measuring small volumes of gas.

Weigh each of these portions of water, noting down the weight and the temperature of the water with the corresponding reading on the tube, and carefully drying the bottle after each weighing.

From the weights of water thus obtained, the corresponding absolute volumes are calculated by applying the correction for the expansion of water from the Table (982). Thus if the first 5 c c. weighed 4·86 grams at 20° C., its absolute volume would be $4·86 \times 1·00157 = 4·868$ c.c.

It will be seen that this calibration is similar to that employed for the calibration of the burette (257), and the calculation of the capacity is made as is directed for that process (258).

Caution.—It should be remembered that in all measurements, in which water or any other liquid which wets glass is used, it is necessary that a certain time should be allowed for the liquid to drain down the sides of the measuring-tube. The time will vary from half a minute to 5 minutes, according to the

nature of the liquid. For ordinary operations with water an interval of tw minutes will suffice for this purpose.

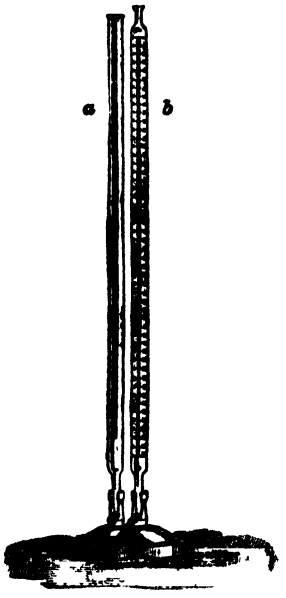
847. **A Convenient Method of Recording the Results of Calibratio** is in the form of a curve plotted upon squared paper. The divisions on th tube should be plotted horizontally, and the correct capacities verticall The curve thus constructed will give the true capacity at any division b direct inspection.

PART VI.–SECTION XVI.

THE HEMPEL GAS-APPARATUS.

THIS apparatus consists of two parts, the Burette, which includes a measuring-tube and a pressure-tube, and the Pipette. The gas is usually measured over water or some aqueous solution.

FIG. 118.



THE HEMPEL BURETTE.

A special form of Burette must be used when the gas cannot be measured over water on account of its solubility in that liquid (861).

857. **The Hempel Gas-burette** (Fig. 118) consists of two connected glass tubes. One of these (*a*) is not graduated, and is called the *Pressure-tube*. The other (*b*), known as the *Measuring-tube*, is usually graduated into 100 c c. with 0·2 c.c. divisions.

The *Pressure-tube* is expanded at its upper edge. The *Measuring-tube* is contracted at the top, and terminates in about 2 cm. of thick-walled capillary-tube; it is calibrated as is directed in paragraph 846.

The lower ends of these tubes are contracted in diameter, and are bent at right angles. They are fitted into slots in semicircular weighted wooden feet, and are connected with one another by a few feet of narrow rubber tubing. This rubber tube may be divided in the middle, and then joined by a short piece of glass tube: the cleaning of the burette is thus facilitated.

858. **The Hempel Gas-pipette.**—The Hempel pipette is used in connection with the burette as an absorbing-vessel. It is shown in its simplest form in Fig. 119. By submitting a gaseous mixture to the successive action of suitable absorbent reagents (862-869) in a series of these pipettes, the

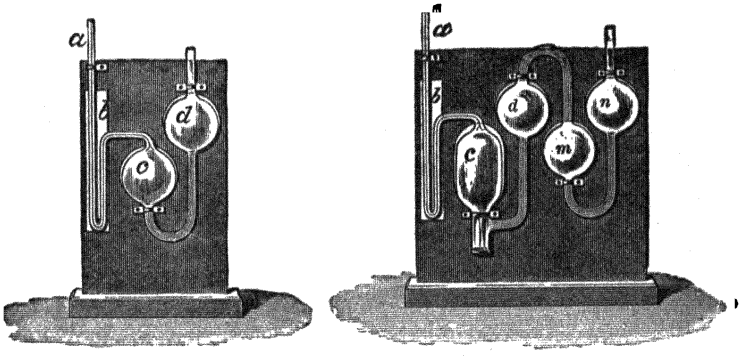
proportions in which the constituent gases are present in the mixture may be ascertained.

The simple pipette (Fig. 119) consists of two connected bulbs, (*c*) and (*d*), which contain the absorbent liquid. The bulb (*c*) terminates in a U-shaped capillary tube (*a*). Behind this tube is a white porcelain scale (*b*), which renders the thread of liquid in the capillary visible when the pipette is in use.

A more complex form of absorption-pipette is shown in Fig. 120. The bulb (*c*) is cylindrical in form, and is tubulated below so as to render the introduction of a solid absorbent possible.

Both these forms of the pipette may be fitted with two extra bulbs (*m*, *n*), as is shown in Fig. 120. These bulbs are partially filled with water; they

FIG. 119. FIG. 120.



THE HEMPEL GAS-PIPETTE.

prevent the external air from coming into contact with the absorbent, and retard the escape of vapour from a volatile absorbent.

859. Fitting together the Hempel Apparatus.—The burette is connected with the pipette in the manner shown in Fig. 121. Two short thick pieces of rubber tube, each carrying a spring clip, are slipped upon the capillary top of the measuring-tube, and upon the capillary-tube (*a*) of the pipette. These rubber joints are tightly bound upon the glass with wire, so as to make them gas-tight. A single clip upon the measuring-tube (*b*) will usually be found sufficient, the other clip being dispensed with.

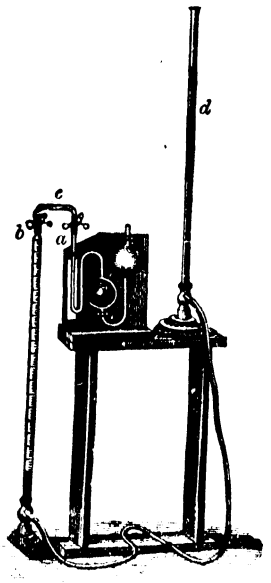
A piece of thick-walled glass tube, 1 millimetre in internal diameter and about 20 cm. in length, is then bent twice at right angles (*c*, Fig. 121). Each end of this tube is pushed into one of the pieces of rubber tube. Connection can now be opened between the absorption-pipette and the measuring-tube by simply releasing the clip. The measuring-tube and the absorption-pipette

can also be disconnected one from the other, without allowing their contents to come into contact with the atmosphere.

860. Manipulation of the Hempel Apparatus.—The following is a general description of the method of using the Hempel apparatus for gas-analysis.

Taking the Sample for Analysis.—Disconnect the pipette (*a*), leaving the tube (*c*) and the rubber tubes and clips attached to the measuring-tube (*b*). Raise the pressure-tube (*d*), which has been filled with water, preferably saturated with the gas to be analysed; then open the clip and pour water into the pressure-tube, until the measuring-tube is full of water and the water begins to flow over from the bent tube (*c*).

FIG. 121.



THE HEMPEL GAS-APPARATUS.

Now close the rubber tube (*a*) by the clip and squeeze the end of the tube between the finger and thumb, so as to exclude air while it is being connected with the vessel containing the gas which is to be examined. Then place the pressure-tube (*d*) at a lower level than the measuring-tube (*b*), and open the clip again. The gas will thus be drawn over into the measuring-tube. 50 c.c. will be found to be a convenient volume for working purposes.

In order to avoid calculation 100 c.c. of the gaseous mixture may be used, since the volumes of the constituent gases which are obtained in the analysis then represent at once percentage proportions of the mixture.

In order to obtain exactly the required volume in the burette, proceed as follows: As soon as rather more than the required volume of gas has entered the measuring-tube, close the rubber tube by the clip. Now close the long rubber tube, which connects the measuring-tube with the pressure-tube, by pinching it with the fingers. Raise the pressure-tube, and by relaxing the fingers allow water to flow into the measuring-tube until it precisely reaches the required graduation. Then at once arrest the inflow of water by pressure of the fingers on the rubber tube. Now open the top of the measuring-tube, by relaxing the pressure of the clip for a moment, so as to allow the excess of gas to escape into the air and to leave the remainder at atmospheric pressure. Next proceed to verify the volume of the gas in the measuring-tube, when the water is brought to precisely the same level in both tubes.

The temperature of the room and the barometric pressure need not usually be read in an ordinary analysis, since these conditions do not appreciably vary during the series of estimations, which are of *relative* volumes only. But if for any reason the *absolute* volume of the gas is to be found under normal conditions, or its weight is to be calculated, the thermometer and barometer must be read, since it then becomes necessary to calculate the volume of the gas under normal conditions (839).

Charging the Pipettes.—Now charge each pipette with its special absorption-reagent (862–869), filling the bulb (*c*, Fig. 119, p. 451) completely, but allowing only a small quantity of the liquid to remain in (*d*). The liquid is introduced by pouring it through a funnel into the wide tube above (*d*), and should then be drawn nearly to the top of the porcelain scale by applying suction to the capillary-tube (*a*), and before a measurement of gas is taken the liquid should always be brought again to the same level in this capillary tube.

When the pipette is not in use, the reagent should be protected from contact with the air by closing the wide tube with a cork, and the capillary tube with a short rubber tube which is stopped with a piece of glass rod.

Process of Absorption.—After the volume of the gaseous mixture has been noted down, proceed to absorb its constituent gases successively. For the purpose connect the measuring-tube with the absorption-pipette by means of the bent capillary-tube, squeezing the end of the rubber tube meanwhile with the fingers so as to exclude air. Then raise the pressure-tube and relax the clip, so as to drive the gas over from the measuring-tube to the absorption-pipette. As soon as the gas has passed completely into the bulb, close the clip, gently shake the contents of the bulb, and allow the gas to stand in contact with the absorbent for five minutes.

Then transfer the gas back to the measuring-tube again by lowering the pressure-tube and relaxing the clip, and as soon as the gas has passed over close the clip again.

Now raise the pressure-tube until the water in both tubes is at the same level after allowing an interval of two minutes for the water to drain from the side of the tube, and read off the volume of the gas.

Transfer the gas again to the pipette, and shake it gently with the reagent for a minute; then measure its volume once more in the burette. If the volume is the same as before, the absorption is complete; the volume of the gas is therefore noted down, and the next absorption is proceeded with.

If a further decrease of volume occurs when the gas is exposed a second time to the same absorbent, the absorption must be repeated; but it is rarely necessary to resort to a third absorption in order to remove a gaseous constituent completely.

Subsequent absorptions are effected by a procedure precisely similar to that

which has been just described, each gas being absorbed by a special and suitable reagent (862–869). A separate pipette should be kept for each reagent.

861. **The Winkler Burette.**—Another form of burette, known as the Winkler burette, must be employed for the analysis of gaseous mixtures which contain a constituent soluble in water.

It is of the same shape as the Hempel burette, but the top of the measuring-tube is supplied with a stop-cock, and the bottom with a three-way cock similar to that shown in Fig 123 (p. 465) By this arrangement the measuring-tube can be cut off from the water in the pressure-tube, and a stream of gas can be passed through the stop-cock into the measuring-tube, and thence out into the air by means of the three-way cock.

The measuring-tube is 100 c c. in capacity, and is graduated in fifths of a c c.

Before the measuring-tube is used, it must be dried. This is most rapidly effected by rinsing it out with alcohol, then with ether, and finally blowing air through it from bellows.

The measuring-tube is filled with the gas to be examined, either by passing a continuous current of the gas through it until all the air has been displaced, or by filling the tube with mercury and letting the gas displace the mercury. The stop-cocks are now closed, and 100 c c of the gas under atmospheric temperature and pressure are obtained for analysis

Water may then be allowed to flow into the measuring-tube from the pressure-tube in order to absorb the soluble gas, or the measuring-tube may be connected with a Hempel pipette, and the further manipulation of the burette may be conducted as with the Hempel burette.

Reagents used for the Absorption of Gases in the Hempel Pipette.

The following directions serve for the preparation of absorption-reagents of suitable strength for gas-analysis:

862. **Potassium Hydrate Solution.**—Dissolve 160 grams of ordinary potassium hydrate in 130 c.c. of water: this will furnish about 200 c.c. of solution.

The solution is used for absorbing carbon dioxide, and acid gases generally.

863. **Alkaline Pyrogallate Solution.**—Dissolve 10 grams of pyrogallic acid in 200 c.c. of the above potassium hydrate solution (862). The solution should be kept in a pipette of the simple form (Fig. 119, p. 451), the openings of which are carefully closed from the air when the pipette is not in use; or the pipette may be provided with the two guard-bulbs (*m*, *n*) shown in Fig. 120.

This solution is used for absorbing oxygen.

Note.—If this reagent is prepared according to the preceding directions, no carbon monoxide is evolved during the absorption of oxygen; but departure from the above proportions may involve serious error in the estimation from this cause.

864. Cuprous Chloride Solution.—Pass sulphur dioxide into a solution of 1 part of sodium chloride and 2 parts of crystallised copper sulphate, and wash the precipitate of cuprous chloride by decantation, first with solution of sulphurous acid, and then with glacial acetic acid. Then press it between filter-paper and dry it in a vacuum desiccator (63).

During its preparation, storage and use, both this substance and its solution must be excluded from free contact with the air.

The salt is employed either in ammoniacal solution (a) or in acid solution (b). The acid solution is generally used, unless the combustion of hydrogen by palladinised asbestos (881) is to follow the absorption by cuprous chloride.

The solution is used for absorbing carbon monoxide.

(a) *The Ammoniacal Solution* is prepared by suspending 15 grams of cuprous chloride in about 100 c.c. of water, contained in a flask of about 250 c c. capacity, and passing ammonia gas into the liquid until all the cuprous chloride is dissolved and the solution assumes a pale blue colour. The liquid is then diluted to 200 c.c. One c c of the solution thus prepared can absorb about 6 c c. of carbon monoxide, before it becomes saturated with the gas and useless for further absorption.

(b) *The Acid Solution* is prepared by dissolving 27 grams of cuprous chloride in 200 c.c. of hydrochloric acid of 1·124 specific gravity. One c.c. of this solution can absorb about 10 c.c. of carbon monoxide.

865. Alcohol.—Rectified spirit is used for absorbing the vapours of hydrocarbons generally.

866. Iodine Solution.—Solution of iodine in potassium iodide solution of about decinormal strength is used for absorbing sulphur dioxide. *Potassium Dichromate* in saturated solution may be used for the same purpose.

867. Ferrous Sulphate, in cold saturated solution, is used for absorbing nitric oxide. *Potassium Permanganate* solution acidified with sulphuric acid may be used for the same purpose

868. Bromine-water, made by shaking bromine with water until some bromine remains undissolved, is used for absorbing the olefine hydrocarbons. *Fuming Sulphuric Acid* serves the same purpose.

869. Fuming Nitric Acid may be used for absorbing the vapour of benzene and the olefine hydrocarbons.

Collection of Gas for Analysis.

870. The Method selected for Collecting a Sample of Gas will vary according to the conditions under which the gas has to be taken, conveyed, and stored. When the gas is collected in the laboratory, it is generally passed direct into the Hempel burette (860) or the Winkler burette (861); and if a larger quantity has to be stored, it is collected in a glass gas-holder. If the gas must not come into contact with water, it may be passed up either into a tube filled with mercury which is closed by inverting its open end in a vessel of mercury, or into a small bell-jar closed with a stop-cock and filled with mercury.

A sample of gas which has to be collected away from the laboratory may occasionally be taken and safely stored as is directed above; or it may be collected by the displacement of air, water, or mercury from a bottle or flask, which is then closed by a tightly fitting cork, both the upper part of the cork and the neck of the vessel being finally uniformly coated with melted paraffin-wax or sealing-wax.

The sample is however usually sealed in a glass tube, which is made by drawing off a piece of broad glass tubing near each end to capillary bore, leaving the intermediate tube with a capacity of from 50 to 100 c.c. The air is displaced from the tube by passing through it a stream of the gas, either by its own pressure or by suction applied by an aspirator (80, 176). After a free current of the gas has passed through the tube for at least fifteen minutes, the two capillaries are sealed by being drawn off in the blowpipe flame.

If the supply of gas which is available is small, the tube is prepared as is directed above and the air is removed from it by a good air-pump. The tube is then sealed, and one end is opened in the gas to be collected; the tube is then sealed again after it has become filled with the gas.

When the sample is to be withdrawn into the Hempel burette, a file-mark is made near each end of the sample-tube. One end is then attached by the rubber joint (*a*, Fig. 121, p. 452) to the Hempel burette, while the other end is immersed in a vessel of water or other suitable liquid. Both the ends are then broken off, and the gas is drawn over into the burette in the usual way by lowering the pressure-tube (*d*).

Estimation of Gases by Absorption in the Hempel Apparatus.

871. The method of estimating the constituents of several ordinary gaseous mixtures, by means of the Hempel apparatus, is given below. It will be understood that the volume of each constituent gas is ascertained by

the difference in the volume of the mixture before and after the absorption of that constituent.

The general procedure and manipulation have been already described in paragraph 860, particulars of the absorbent-reagents are given in paragraphs 862–869, and methods of collection will be found in paragraph 870.

The analysis is rendered more accurate by previously saturating the water in the burette with the gaseous mixture which is to be analysed.

This also applies to the solutions contained in the absorption-pipettes, but since similar gaseous mixtures are generally analysed by using the same pipettes, the liquid in each pipette will gradually become saturated with the gas. When however a fresh solution is employed, the second and third determinations made with the solution will, for the above reason, be more accurate than the first, unless a preliminary saturation of the solution with the necessary gas has been effected.

Since the atmospheric temperature and pressure do not vary appreciably during any one gas analysis, it will not usually be necessary to correct the gaseous volumes for pressure and temperature (839) before calculating the percentage volumes of the constituents.

872. Estimation of Carbon Dioxide in Furnace Gases.—Employ a simple absorption-pipette (858) containing the solution of potassium hydrate (862). A more exact method of estimating a small proportion of carbon dioxide in air is described in paragraphs 912–914.

873. Estimation of Oxygen in Atmospheric Air.—Charge the absorption-pipette with a strong solution of alkaline pyrogallate (863).

The average percentage of oxygen by volume is 20·96.

874. Estimation of Carbon Dioxide, Oxygen, and Nitrogen in a Mixture.—Absorb the gases in the following order by the reagents specified:

(1) Carbon dioxide, by potassium hydrate solution (862).
(2) Oxygen, by alkaline pyrogallate solution (863).
(3) Measure the residual nitrogen.

875. Estimation of Carbon Dioxide, Oxygen, Carbon Monoxide, and Nitrogen in a Furnace Gas.—Absorb the gases in the following order, by the reagents specified:

(1) Carbon dioxide, by potassium hydrate solution (862).
(2) Oxygen, by alkaline pyrogallate solution (863).
(3) Carbon monoxide, by freshly prepared cuprous chloride in acid solution (864, b).
(4) Measure the residual nitrogen.

876. Estimation of Carbon Dioxide, Olefines, Benzene, Oxygen, and Carbon Monoxide, Hydrogen and Methane in Coal-gas, Generator-gas, and Similar Mixtures.—Absorb the gases in the following order, by the reagents specified, using a Hempel burette containing water saturated with the original gas which is to be analysed:

(1) Carbon dioxide, by potassium hydrate solution (862).

(2) Olefines, by saturated bromine-water (868), subsequently removing the bromine-vapour by means of potassium hydrate solution in a separate pipette (*Note*)

(3) Benzene, by fuming nitric acid, subsequently removing the nitrogen oxides by means of the potassium hydrate pipette (*Note*).

(4) Oxygen, by alkaline pyrogallate solution (863).

(5) Carbon monoxide, by freshly made ammonical cuprous chloride solution (864, a).

(6) The residual gas is transferred to a Hempel pipette charged with water, and hydrogen and methane are estimated as is directed in paragraph 882.

(7) Nitrogen will then remain as a residue.

Note.—In the above process, the separate absorption of the olefine hydrocarbons and benzene by bromine-water and by nitric acid respectively is not very satisfactory. An alternative method consists in absorbing these substances simultaneously by fuming sulphuric acid, followed by caustic potash solution.

877. By employing the Winkler Burette (861) or the Lunge Nitrometer (894) the following gases, which are more or less soluble in water, can be estimated by means of the absorbents specified in each case:

Ammonia, by dilute sulphuric acid.

Nitrogen peroxide, by concentrated sulphuric acid, or by a solution of potassium permanganate acidified with sulphuric acid.

Nitric oxide, by a concentrated solution of ferrous sulphate, or by potassium permanganate acidified with sulphuric acid.

Nitrous oxide, by alcohol.

Chlorine, by solution of potassium hydrate (862).

Hydrochloric acid, by the same.

Hydrogen sulphide, by the same.

Sulphur dioxide, by the same, by iodine solution (866), or by saturated solution of potassium dichromate.

Estimation of Gases by Combustion in the Hempel Apparatus.

878. Estimation of Hydrogen by Combustion in Air aided by Palladinised Asbestos.—The hydrogen is mixed with air, and is passed through a glass or fused silica tube of 1 millimetre bore which contains a fibre of asbestos covered with finely divided palladium (*Note*).

The asbestos is gently heated while the mixture of hydrogen and air is being passed over it. The hydrogen combines with the oxygen of the air to form water, which occupies no appreciable space. The contraction in volume which occurs as a result of the combination is therefore noted, and the volume of hydrogen which was originally present will be equal to two-thirds of this contraction.

Hydrogen gas is readily burnt in this way, carbon monoxide is burnt more slowly, and methane is not burnt at all.

Note.—A narrow palladium tube, or a glass or fused silica tube packed with small pieces of palladium, may replace the tube containing palladinised asbestos.

879. **Preparation of the Palladinised Asbestos.** — Dissolve 1 gram of palladium in aqua regia, and evaporate the solution to dryness on the water-bath in order to remove free acid. Dissolve the residue in a small quantity of water, add about 5 c.c. of a saturated solution of sodium formate, and then add sodium carbonate solution until the reaction of the liquid is strongly alkaline.

Introduce into this liquid about 1 gram of soft long-fibred asbestos, which should absorb the whole of the solution. Remove the asbestos and heat it on the water-bath until it is perfectly dry; then soak the fibres in a little water, place them in a funnel, and wash out the soluble salts.

The palladinised asbestos prepared in this way is of a grey colour, and contains about 50 per cent. of palladium. It will cause a mixture of hydrogen and oxygen to combine at the ordinary temperature of the air, but the combination proceeds more rapidly when the fibre is heated.

880 **Preparation of the Capillary Combustion-tube.**—Procure a piece of fused silica or thick-walled hard glass tube one millimetre in bore and 20 cm. in length Then lay a few loose palladinised asbestos fibres (879), about 4 cm. in length, side by side on smooth filter-paper, moisten them with a drop or two of water, and twist them into a thread about as thick as stout sewing-cotton. Take up this thread with the forceps and push it down the tube, which is meanwhile held vertically. Now fill the tube with water, and bring the asbestos thread into the middle part by shaking the tube. Then drain off the water, dry the tube, and bend down its ends at right angles. The tube is now ready to take the place of the ordinary capillary-tube (c, Fig. 121, p. 452).

881. *The Process of Estimation of Hydrogen.*—It is well to obtain some experience, by performing several estimations with known volumes of hydrogen and air, before an estimation of an unknown volume of hydrogen is made by the following process:

The volume of hydrogen which is taken for the estimation should not exceed 25 c.c. Read off the volume precisely, then lower the pressure-tube of the burette and allow about 75 c.c. of air to enter the measuring-tube. This will supply more than sufficient oxygen to burn all the hydrogen. Now read the total volume of the gaseous mixture accurately, after levelling the water, and interpose the capillary combustion-tube between the burette and a simple absorption-pipette (858) which is charged with water only.

Next heat the middle of the tube (880) much short of redness over a small flat gas-flame or the flame of a spirit-lamp, and cause the gaseous mixture to pass through the tube from the measuring-tube into the pipette by raising the pressure-tube. The end of the asbestos thread will usually glow when the gas reaches it, but the flame must not be removed if the tube is of glass, else water may condense and cause it to crack; a silica tube does not crack under these conditions.

As soon as the gas has passed over completely, draw it back again through the heated tube into the measuring-tube. Then cause the gas to pass again forwards and backwards over the heated asbestos. In the case of a readily combustible gas like hydrogen, the combustion should now be complete. Read off the volume of the gas again accurately, and note if it becomes further reduced after the gas has been once more passed over the hot asbestos. These processes must be repeated until no decrease of volume is noticed after the last passage of the gas over the heated asbestos.

By subtracting the volume of the residual gas from the original volume of the mixture, the contraction of volume which has been caused by the combustion of the hydrogen is found. The volume of hydrogen which has been burnt is equal to two-thirds of this contraction.

Example.—In a particular estimation, the following numbers were obtained:

The volume of hydrogen employed = 22 8 c.c.

The total volume of hydrogen + air = 98 0 c.c.

Hence the volume of air added = 98 0 − 22 8 = 75 2 c c.

[Assuming the percentage volume of oxygen in air to be 21, the volume of oxygen introduced = 15 8. Now 22 8 c.c. of hydrogen require 11 4 c c of oxygen for their complete combustion; hence, even if the gas under analysis were all hydrogen, there would be 4 4 c c more oxygen than is required for the combustion of the gas, and therefore an excess of oxygen must have been present.]

The volume of residual gas after the combustion = 64 0 c.c.

Therefore the volume of gas which has disappeared during the combustion = 98·0 − 64 0 = 34 c c.

Hence the volume of hydrogen originally present = $\frac{34 \times 2}{3}$ = 22 66.

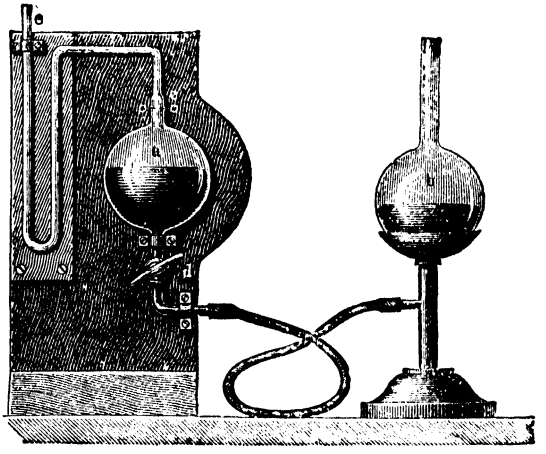
882. Estimation of Hydrogen, Methane, and Nitrogen.

In the analysis of coal-gas and similar mixtures, the gases mentioned in paragraph 876 are first removed by absorption.

One of two methods may then be adopted. Either (1) the hydrogen may be first estimated by being burnt (881), and the methane may then be mixed with oxygen and fired; or (2) the hydrogen and methane may be mixed with oxygen and burnt simultaneously. In either case the nitrogen will be measured by difference.

(1) *First Method.*—The Hempel apparatus is charged with water as usual, and the gas, or an aliquot portion of it, is then mixed with air, and the hydrogen is estimated as is described in paragraph 881. The gaseous mixture with now only contain the methane and nitrogen, together with a known volume of nitrogen and oxygen from the added air. The methane and nitrogen in this mixture are estimated in the following way:

FIG. 122.



THE HEMPEL EXPLOSION-PIPETTE.

About 20 c.c. of the gas are mixed with more than the volume of oxygen required for their complete combustion, the total volume is then carefully measured and the mixture is fired.

Note.—Bunsen states that the proportion of combustible gas in the mixture must be not less than 26 or more than 64 per cent., else nitrogen oxides may be formed. If the percentage is less than 26, the mixture refuses to burn unless a suitable volume of pure electrolytic hydrogen is added. No general rule can be given as to the exact proportions to be used; but the explosion should be observed, and it must be so rapid that the flame cannot be followed by the eye in its progress down the bulb.

The mixture is fired by the spark from an induction-coil in a special form of Hempel Explosion-pipette (Fig. 122) which contains mercury instead of water.

In order to prevent loss of gas during the firing, the rubber joint should be bound by wire on the pipette at (*e*), and should not only be clamped but also closed by the insertion of a tightly fitting piece of glass rod.

The decrease of volume caused by the firing is then noted, and the further diminution of volume resulting from the absorption of the carbon dioxide produced is also found (872). The volume of methane originally present in the mixture will be equal to the volume of carbon dioxide absorbed, as is seen from the equation: $CH_4 + 2O_2 = CO_2 + 2H_2O$.

The volume of nitrogen in the original mixture is found by subtracting the sum of the volumes of hydrogen and of methane from the volume of the original mixture.

(2) *Second Method.*—About 30 c.c. of the mixture of hydrogen, methane, and nitrogen is made up to 75 c.c. by mixture with oxygen (see *Note* above).

The mixture is fired as is directed in the first method, the contraction of volume which is caused by the combustion is noted, and the further contraction which results from the absorption of the carbon dioxide by potassium hydrate solution is also observed. The volumes of hydrogen and of methane are then calculated as follows:

If x = the contraction of volume caused by firing, and
y = the contraction of volume caused by the subsequent absorption with potash,

$$\text{Then the volume of hydrogen} = \frac{2}{3}(x - 2y)$$

$$\text{and the volume of methane} = y.$$

The above equations are founded upon the facts (1) that the contraction of volume caused by firing is due to the combination of free and combined hydrogen with part of the oxygen present, to form water, and (2) that the CH_4 forms its own volume of carbon dioxide.

883. Example of Coal-gas Analysis.—The sample of coal-gas was collected in a Hempel burette, which had been filled with water previously saturated with coal-gas by passing the gas through it. The original volume of gas was 99 c.c., and this was treated successively with the following reagents with the results stated below:

(1) Potassium hydrate gave no absorption, hence carbon dioxide was absent.

(2) Alkaline pyrogallate solution gave:

Before absorption = 99·0 c.c.
After absorption = 98·8 c.c.
∴ The Volume of oxygen = 0·2 c.c., and

$$\text{The Percentage of oxygen} = 0{\cdot}2 \times \frac{100}{99} = 0{\cdot}2$$

(3) Fuming sulphuric acid, followed by potassium hydrate solution gave:

Before absorption = 98 8 c c.
After absorption = 93 5 c c.
∴ The Volume of olefines and benzene = 5·3 c.c, and

$$\text{The Percentage of olefines and benzene} = \frac{5\,3}{99} \times 100 = \underline{5{\cdot}3}$$

(4) Cuprous chloride solution gave:

Before absorption = 93·5 c.c.
After absorption = 87 0 c.c.
∴ The Volume of carbon monoxide = 6 5 c.c., and

$$\text{The Percentage of carbon monoxide} = 6{\cdot}5 \times \frac{100}{99} = \underline{6\,6}$$

(5) The residual 87 c.c. of gas, containing methane, hydrogen and nitrogen, were returned to the pipette, and the water in the burette was exchanged for water saturated with air.

30 8 c c. of the gas were then mixed with sufficient oxygen in the explosion-pipette, and the total volume was now 75 2 c.c. This mixture was fired with the spark of the induction-coil, the volume was read off, and the residual gas was then exposed to absorption by potassium hydrate solution. The volumes read were as follows:

Before firing = 75 2 c c.
After firing = 25 9 c c.
∴ The Total contraction = 49 3 c c.

Before absorption = 25 9 c c.
After absorption = 13 9 c c.
∴ The Carbon dioxide from the methane = 12 0 c c, and

Hence the Volume of methane = 12 0 c c, and

$$\text{The Percentage of methane} = 12 \times \frac{87}{30\,8} \times \frac{100}{99} = \underline{34\,2}\ (\textit{Note}).$$

$$\text{Also the Volume of hydrogen} = \frac{2(49{\cdot}3 - 2 \times 12)}{3} = \frac{2 \times 25\,3}{3} = 16\,9, \text{ and}$$

$$\text{The Percentage of hydrogen} = 16\,9 \times \frac{87}{30\,8} \times \frac{100}{99} = \underline{48{\cdot}2}.$$

The Percentage of nitrogen (by difference) = 100 − 94·5 = 5 5.

Note.—Coal-gas may contain a small amount of ethane and of other paraffin hydrocarbons In the estimation of its constituents as is described above, such paraffins would count as methane, but this would not have any important influence on the result

For Results of Analyses of Coal-gas and of Blast-furnace Gas see paragraphs 969, 970.

884. Estimation of Carbon Monoxide by Combustion.—The processes for estimating hydrogen by combusion (**881, 882**) are also applicable to the estimation of carbon monoxide in a furnace-gas, if the carbon dioxide present in the mixture has been first removed by absorption.

From the equation $\underset{2\text{ vols}}{CO} + \underset{1\text{ vol}}{O} = \underset{2\text{ vols}}{CO_2}$ it will be seen that the original volume of CO is equal to double the contraction caused by its combustion; or to two thirds of the total contraction caused by the combustion, followed by the absorption of the resulting carbon dioxide by potassium hydrate solution.

When carbon monoxide is to be estimated in the presence of hydrogen, it is necessary to note both the contraction caused by firing and the loss of volume which is afterwards caused by the absorption of the carbon dioxide produced, in order to calculate the volume of each of the combustible gases.

885. Estimation of Oxygen by Combustion.—The proportion of oxygen present in the atmosphere may be estimated by the processes of combustion for determining hydrogen (**881, 882**). A known volume of hydrogen in excess is added to the air, and the decrease of volume caused by its combustion is noted. The volume of oxygen originally present is equal to one-third of this decrease.

PART VI.–SECTION XVII.

THE LUNGE NITROMETER. THE RUSSELL-WEST APPARATUS. THE PETTENKOFER PROCESS.

The Lunge Nitrometer.

890. The Lunge Nitrometer (Fig. 123) is so called because it was originally devised for the analysis of "nitrous vitriol." It can be used for many analytical processes which involve the measurement of a gas.

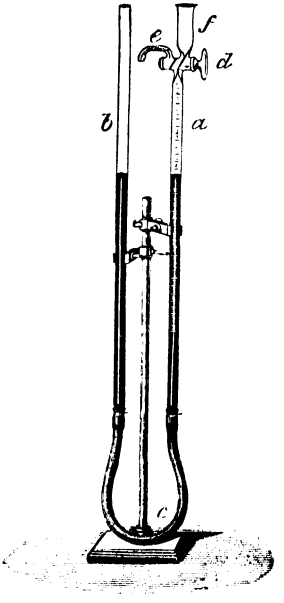
Like the Hempel burette, it consists of two tubes, the measuring-tube and the pressure-tube.

The measuring-tube (*a*) in Fig. 123 has a capacity of 50 c.c., and is graduated into fifths of a c.c.: it is calibrated according to the directions given in paragraph 845. The measuring-tube is connected by means of thick-walled rubber tubing with the pressure-tube (*b*), which is not graduated. The apparatus is usually charged with mercury; but water, glycerine, strong brine, or oil may be used for special purposes instead of mercury.

To the top of the measuring-tube (*a*) is fitted a special stop-cock (*d*), in connection with which is a cup (*f*), and a strong capillary-tube (*e*).

In the figure the stop-cock is shown opening communication between the measuring-tube and the cup. When the stop-cock is turned half round, communication is opened between the capillary-tube and the measuring-tube; but if the stop-cock is turned only one-quarter round, communication between the capillary-tube the measuring-tube and the cup is cut off.

FIG. 123.



THE LUNGE NITROMETER.

It will be seen, therefore, that this stop-cock renders it possible to draw

a gas into the measuring-tube through the capillary-inlet (*e*). The gas can then be exposed to a liquid reagent by pouring the reagent into the cup (*f*), putting the cup into communication with the measuring-tube (*a*), and drawing the liquid into the measuring-tube by lowering the pressure-tube (*b*). The entrance of air into the measuring-tube through the cup is prevented, by turning the stop-cock one-quarter round, as soon as all the liquid has entered.

891. Another Form of the Nitrometer is used for measuring larger quantities of gas. For this purpose a bulb is blown in the measuring-tube (*a*) immediately below the stop-cock. The bulb has a capacity of nearly 100 c.c., and the first graduation on the tube below the bulb is for 100 c.c; the graduations are continued down the tube until 140 c.c. are registered. A bulb is also blown upon the lower part of the pressure-tube (*b*); this bulb must be of sufficient capacity to hold the mercury which is required for the measuring-tube.

According to the volume of gas to be dealt with, either the ordinary form or the more capacious form of the nitrometer is used.

A number of applications of the Lunge nitrometer are described in the following paragraphs.

Estimation of the Amount of Nitrogen Oxides in Nitrous Vitriol.

892. Remove the stop-cock (*d*) from the measuring-tube of the nitrometer (Fig. 123), and cleanse and dry the surfaces of the stop-cock and of the seat into which it fits. Then lightly smear some resin cerate, vaseline, or rubber-grease over the surface of the stop-cock, push the stop-cock into its seat, and turn it until the cup (*f*) is in communication with the measuring-tube (*a*).

Now fill in mercury, until, when the pressure-tube is raised, the mercury fills the measuring-tube (*a*) and just enters the stop-cock, and reaches a level of about 5 cm. in the pressure-tube (*b*). Carefully remove all air-bubbles adhering to the inside of the measuring-tube.

Then close the stop-cock, and lower the pressure-tube until the level of mercury in it is considerably below that in the measuring-tube (*a*). If the apparatus is air-tight and has been freed from air-bubbles, no bubble of air will be visible at the top of the mercury column in the measuring-tube (*a*) after the apparatus has stood for several minutes. Then bring the surfaces of the columns of mercury in both tubes to the same level by raising the pressure-tube (*b*).

Now pour into the cup (*f*) a known quantity of the nitrous vitriol (*Note*) varying from 0·5 to 5 c.c. according to the quantity of nitrogen oxide which it is believed to contain.

Note.—If any SO_2 is present in the nitrous vitriol, it must be oxidised by adding a small quantity of powdered potassium permanganate before the acid is introduced into the nitrometer.

Now cautiously open the stop-cock, and allow the acid, with the exception of a small drop, to run into the measuring-tube (*a*). Then pour into the cup 3 c.c. of strong sulphuric acid, free from nitrous compounds, and allow this to run into the measuring-tube (*a*). Repeat this operation with 3 c.c. more of the acid, taking care that no air enters the tube.

Then grasp the measuring-tube in the hand, unclamp it, and start the evolution of nitric oxide by bringing the acid into contact with the mercury. This is effected by lowering the tube several times almost to the horizontal position, and then suddenly raising it again to an upright position. Finally shake up the mercury with the acid until no more gas is given off.

Then clamp the tubes (*a*, *b*) at such relative heights that the gas in the measuring-tube is approximately under atmospheric pressure. For this purpose it may be assumed that 7·6 mm. of the strong acid in the measuring-tube balance 1 mm. of mercury in the pressure-tube. Allow the apparatus to stand in this position until its contents have gained the temperature of the air.

The levels of the tubes are now once more adjusted as before, if necessary. A little strong acid is then poured into the cup (*f*), and the stop-cock (*d*) is cautiously turned, so as to place the cup and the measuring-tube in communication with one another for a moment. It is easily seen whether the acid in the cup tends to enter the measuring-tube, or to be expelled ; and the level of the pressure-tube can be adjusted accordingly, until the gas is proved by slightly opening the stop-cock to be exactly under atmospheric pressure.

The measuring-tube should always be grasped by the cup (*f*) during the above final adjustments, so as to avoid heating and expanding the gas by touching the graduated part of the tube with the hand

The volume of the gas is then read off, and the atmospheric temperature and pressure are noted down at the same time. It is well to take another reading of the volume after half an hour, and if this agrees with the former one the gas is proved to have attained the atmospheric temperature.

Each c.c. of nitric oxide at 0° and 760 mm. (839, 1) represents 1·343 milligrams of this gas. This is equivalent to 0 627 milligrams of nitrogen, to 1·701 milligrams of nitrogen trioxide, and to 2·830 milligrams of nitric acid.

After the reading of the volume has been taken, lower the measuring-tube and raise the pressure-tube (*b*) ; then open the stop-cock, so as to allow both the gas and the acid to pass from the measuring-tube through the capillary-tube, the acid being collected in a beaker.

Estimation of an Alkaline Nitrate by the Lunge Nitrometer.

893. The above process (**892**) is easily adapted to the estimation of commercial potassium or sodium nitrate. A quantity of the nitrate, which will evolve rather more than 100 c.c. of nitric oxide gas, is weighed, and is introduced into the larger form of the nitrometer (**891**) as is directed below.

For practice in the process, weigh out 0·4 gram of finely powdered sodium nitrate. Place this powder in the cup (*f*) of the nitrometer, and add about half a c.c. of water. As soon as the nitrate is dissolved, draw the solution into the measuring-tube. Then pour half a c.c. of water into the cup, and draw this also into the measuring-tube.

Finally introduce 15 c.c. of strong sulphuric acid, and proceed to make the estimation in the manner described in paragraph **892**. The apparatus should stand for two hours before the reading of the volume is taken, in order that the gas may gain the atmospheric temperature; and another reading, taken half an hour later, should correspond with the first.

After the volume of the gas has been calculated at normal pressure and temperature (**839**, 1), each c.c. represents 3·805 milligrams of sodium nitrate or 4·522 milligrams of potassium nitrate.

Gas Analysis by the Lunge Nitrometer.

894. By employing the Lunge nitrometer (**890**) with the Hempel pipettes (**858**), gases which are soluble in water can be estimated. Instead of the ordinary Hempel pipettes, similar pipettes of smaller size and partially filled with mercury may be used.

All the gases mentioned in paragraph **877**, with the exception of chlorine, may be estimated in this way by means of the nitrometer.

In certain cases the absorption may be effected in the nitrometer itself. For this purpose the absorbent liquid is drawn from the cup into a measured volume of the gas, contained in the measuring-tube. The tube is then shaken, and the volume of the residual gas is read off as has been already described (**892**).

Analysis of Gases Dissolved in Water or in other Liquids.

895. Gases which are dissolved in water may be removed by boiling the water, and may then be received directly in the measuring-tube of the Lunge nitrometer (**896**).

A more accurate method consists in removing the gases in a special apparatus, and then transferring them to a gas-analysis apparatus (897).

A special method for the estimation of dissolved oxygen by titration has been already described (645).

896. *Removal by Boiling into the Lunge Nitrometer.*—Connect a flask, of known capacity, with the capillary-tube (*e*) of the Lunge nitrometer (890) by means of a short piece of narrow rubber tubing, fitting one end of this tubing upon the capillary-tube (*e*) and attaching the other to a short piece of glass tube which passes just through a cork in the neck of the flask.

Now charge the nitrometer with mercury (892), and fill the flask with the liquid containing the gas. Connect the capillary (*e*) with the measuring-tube (*a*), and press down the cork into the neck of the flask. The air from the connecting-tube is thus transferred to the measuring-tube, and the liquid will fill the capillary-tube. Shift the position of the stop-cock, and expel the air from the measuring-tube through the cup (*f*) by raising the mercury level.

Again connect the flask with the measuring-tube (*a*), and heat the liquid in the flask until all the dissolved gas is expelled. Collect the gas in the measuring-tube by lowering the pressure-tube, then allow the gas to cool and measure it. Proceed to analyse the gas by submitting it to the necessary absorbents (862 *et seq.*).

This method is rendered somewhat inaccurate owing to a portion of the unboiled liquid containing the gas being transferred by the boiling to the measuring-tube.

897. *Removal by Heating in Vacuo.*—The more satisfactory method consists in removing the gases from solution by exposing the liquid in a vacuous space, and at the same time heating it if necessary. The gases are then removed from the space by means of a mercury Sprengel pump, and are introduced into the gas-apparatus for analysis.

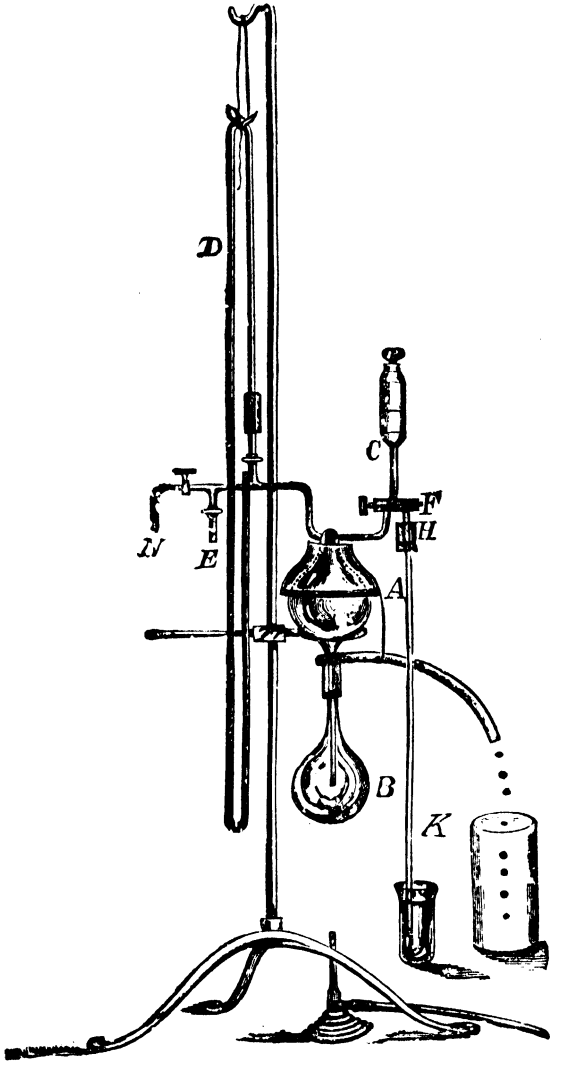
A simple form of apparatus for effecting the removal of the gases from the liquid is shown in Fig. 124.

The glass apparatus, supported by a special stand, has a nearly complete vacuum produced in its interior by connecting the tube *E* with a Geissler water-aspirator (Fig. 48, page 49), the exhaustion being continued until the mercury in the gauge *D* remains stationary. The stop-cock in the tube *E* is then closed, and the tube *N* is connected with a Sprengel mercury pump, by means of which the exhaustion is completed.

The water from which the gas is to be extracted is then poured into the upper vessel *C*, which is graduated to deliver either 25 c.c. or 50 c.c.; the accurately ground stopper is inserted, and the liquid is allowed to descend into the bulb *A* by opening the stop-cock *F*. The water descends into the

flask *B*, the neck of which is connected by a rubber joint with the lower neck of the bulb *A* ; this rubber joint is surrounded by water contained in a glass

FIG. 124.



EXTRACTION OF DISSOLVED GASES.

tube which can be moved up or down on the neck of the flask. A thermometer may be suspended by wire in the flask *B*.

After the liquid has been introduced into the flask *B*, the apparatus is allowed to stand for about an hour in order to permit the dissolved gas to escape into the vacuous space. The evolution of gas may be known to have ceased when the mercury in the gauge *D* ceases to fall. The gas is then removed from the apparatus by setting the Sprengel pump into action, and is collected over mercury and removed to a gas-analysis apparatus.

It is frequently necessary to heat the liquid, in order to remove the carbon dioxide which still remains in solution in the form of bicarbonates in hard waters. The upper bulb *A* is then covered with a porous fabric which is well wetted, the cooled bulb serving to condense any steam which arises from the liquid in the flask *B*. Water may, if necessary, be allowed to drop upon this fabric, the excess flowing off from the water-jacket below by a rubber tube. The water in the flask B is heated by a flame and is kept boiling as long as the mercury in the gauge *D* descends: the gas is then pumped off as before and analysed.

If the liquid has to be drawn from a bottle or other vessel without undergoing exposure to the air, the capillary-tube *H* is filled with distilled water from which the air has been recently removed by boiling, and is attached to the vessel *C*. The tube is immersed in the sample, and the water is drawn up into the vessel *C* by opening the two-way stop-cock *F*.

The Results Obtained by the extraction and analysis of the gases from several samples of water will be found in paragraphs 971–974.

Estimation of Substances which evolve a Definite Amount of Gas when they are Decomposed.

898. For the estimations described in paragraphs 899–905, either the Lunge nitrometer or the apparatus described in paragraph 908 may be used.

The Lunge apparatus is usually filled with mercury, but other liquids may be substituted in special estimations. Thus in testing sweet spirit of nitre, by measuring the amount of nitric oxide gas evolved when the spirit is treated with a solution of potassium iodide and sulphuric acid, a solution of salt is used instead of mercury.

In some cases the decomposition of the substance may be effected in the nitrometer itself, as is described under the estimation of sodium nitrate (893).

But the substance may also be decomposed in a flask connected with the nitrometer, and the amount of air displaced by the gas may be measured; mercury should then be used in the apparatus. An illustration of this method is furnished by the estimation of the amount of carbon dioxide evolved from

a carbonate by treatment with an acid. A bottle or flask, containing a little tube of acid (Fig. 72, p. 110), may be fitted with a cork and plain delivery-tube, and will serve for the decomposition of the carbonate; the acid-tube may be fused in a vertical position upon the bottom of the flask, in order to lessen the risk of breaking it.

If mercury is used in the nitrometer the flask may be connected, by means of a tube passing through the cork and a short piece of rubber tubing, with the capillary-tube (*e*) of the nitrometer.

In calculating the percentage weight from the volume of gas actually read off, it will be necessary to calculate the volume which the gas would have if it were dry and at normal temperature and pressure (839, 2), and then to calculate the weight of this volume from known data (1000).

899. Estimation of Ammonium Salts and of Urea in Urine.—The Lunge apparatus, or that described in paragraph 908, may be used in the estimation of urea and of ammonium salts. Fuller particulars of the reaction, upon which the process depends, are given in paragraphs 906, 910.

About 0·25 gram of the solid substance is accurately weighed out and is introduced into the decomposition-flask (*D*, Fig. 72, p. 110). 10 c.c. of the sodium hypobromite solution (907) are then introduced into the inner tube. A cork with a short delivery-tube is now fitted into the neck of the flask, and the flask is connected by a short piece of rubber tube with the capillary-tube (*e*) of the nitrometer as has been already described, the nitrometer being charged with mercury.

The tap of the nitrometer is then turned so as to bring the flask into communication with the measuring-tube, and the flask is placed on its side and its contents are gently shaken until no more gas is given off. The mercury levels are now roughly adjusted, and the whole apparatus is allowed to stand for fifteen minutes. The levels are then accurately adjusted, and the volume of the gas and the atmospheric temperature and pressure are read. The volume of gas is then corrected for the tension of water-vapour, and for temperature and pressure (839, 2).

Ammonia evolves, under the above conditions, 97·5 per cent. of its nitrogen, and urea 92 per cent. Each c.c. of nitrogen evolved, when corrected for temperature, pressure, and moisture, accordingly corresponds to 0·001562 gram of ammonia, and to 0·002952 gram of urea.

Each c.c. of N may be taken as representing 0·002687 gram of urea, on the assumption that the urea evolves all its nitrogen; this assumption however is only strictly correct when much sugar is present (906).

900. Estimation of Substances which evolve Carbon Dioxide when they are decomposed.—The same apparatus (898, 899) can be

used for estimating the carbon dioxide evolved from carbonates, such as the commercial alkaline carbonates and bicarbonates, limestone and bone-charcoal. The apparatus also serves for the valuation of manganese-ores by means of oxalic acid (416), and for estimating oxalates by means of manganese dioxide (187).

The amount of carbon dioxide evolved falls below that contained in the substance, owing to the solubility of the gas in the acid ; but it is stated that the addition of 7 per cent. to the observed volume corrects this deficiency, if 10 c.c. of hydrochloric acid of 1·12 specific gravity are used for the decomposition of the carbonate :

901 **Estimations by Treatment with Hydrogen Peroxide and Measurement of the Oxygen evolved** —When certain bodies, which contain "active oxygen," are brought into contact with hydrogen peroxide, the active oxygen of both substances is liberated as oxygen gas. The measurement of the volume of oxygen evolved serves to indicate the amount of the substance present The following bodies may be estimated in this way :

902 **Hydrogen Peroxide** may be estimated by mixing its dilute solution with excess of an acid solution of potassium permanganate (330) Two c c of hydrogen peroxide diluted with 10 c c. of water are poured into the inner tube, and a mixture of about 20 c c. of the decinormal permanganate solution with 20 c c. of dilute sulphuric acid is introduced into the decomposition-flask. The following reaction occurs when the liquids are mixed . $2KMnO_4 + 5H_2O_2 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$, from which it is evident that half the measured volume of oxygen which is liberated is yielded by the hydrogen peroxide.

903 **Potassium Permanganate** —The process is the converse of the preceding one (902), excess of H_2O_2 being allowed to act upon a weighed quantity of the permanganate solution acidified with dilute sulphuric acid

904 **Manganese Ores** —Any carbonate present in the ore is first decomposed by means of dilute H_2SO_4, excess of H_2O_2 is then added, and the evolved oxygen is measured :

$$MnO_2 + H_2SO_4 + H_2O_2 = O_2 + MnSO_4 + 2H_2O.$$

905 **Bleaching-powder** —The bleaching-powder solution is treated with H_2O_2 as is described above Half the total volume of the oxygen evolved is liberated by the bleaching-powder, and each c c. of oxygen which is liberated by the bleaching-powder corresponds to 0 006341 gram of "available chlorine."

The Russell-West Apparatus.

This apparatus was originally devised for estimating the percentage of urea in urine, but it may be adapted to many processes of estimation in which gas is evolved by a chemical reaction.

906. The Estimation of the Percentage of Urea in Urine is frequently required for medical purposes.

The chemical reaction of urea solution with an alkaline hypobromite furnishes the most convenient process for its estimation. The result of the reaction is the evolution of 92 per cent. of the nitrogen of the urea in the gaseous form. This nitrogen may be collected and measured in any convenient form of gas-apparatus (899), and the amount of urea which has evolved it may then be readily calculated.

Certain inaccuracies arise when the urea is determined by this process in urine instead of in pure urea solution, and for the following reasons:

Other nitrogenous bodies in the urine besides the urea evolve a minute proportion of nitrogen, but the amount of nitrogen thus evolved is so small that it may be safely disregarded.

The effect of the presence of glucose in diabetic urine is, however, much more considerable. It tends to increase the proportion of nitrogen which is evolved from the urea by the action of the hypobromite; and if the diabetic urine is mixed with a quantity of cane-sugar ten times as great as that of the urea which it contains, the urea will evolve at least 99 per cent. of its nitrogen. The addition of cane-sugar to a diabetic urine is accordingly recommended, since it causes practically the whole of the nitrogen of the urea to be evolved.

The following account of the manipulation is given in connection with the special form of apparatus devised by Russell and West, it can, however, be readily adapted to any other form of apparatus which is suitable for the estimation.

907. *The Sodium Hypobromite Solution* is prepared by dissolving 100 grams of caustic soda in 250 c.c. of water, and mixing 25 c.c. of this cold solution with 2·5 c.c. of bromine immediately before the liquid is required for the estimation. This quantity will suffice for one determination only. The bromine may be kept sealed in separate tubes in the requisite quantity.

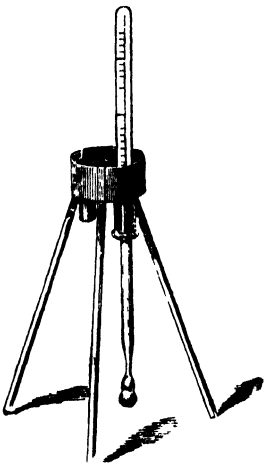
908. The Russell-West Apparatus is shown in Fig. 125. It consists of a little circular metal trough, which is about 5 cm. deep and is supported by three legs. The decomposition-tube in which the reaction occurs is seen beneath the trough, into a tubulure of which it is fitted water-tight by means of a perforated cork. It is a glass tube, about 25 cm. long, and about 1·5 cm. in internal diameter. Its upper end is somewhat narrowed, and projects above the cork, so as to deliver the escaping gas without loss into the measuring-tube. The lower end consists of a tapering bulb, about 5 cm. in length and constricted at its neck to 1 cm. in internal diameter.

The capacity of this bulb should be about 12 c.c. A thin glass rod, about 25 cm. in length, is fitted with a narrow ring of rubber tubing round its lower end, so that when it is dropped into the decomposition-tube it closes the constriction above the bulb.

The Measuring-tube, in which the nitrogen is collected, is about 2 cm. in internal diameter and about 40 c.c. in capacity. This tube may be graduated in c.c.s, but it is usually graduated in such a way that the percentage of urea is read off directly from the graduations. The latter method of graduation is based on the fact that when 5 c.c. of a 2 per cent. solution of urea are treated in the apparatus with hypobromite solution in the usual way, they evolve 37·1 c.c. of nitrogen, measured at ordinary pressure and temperature. This volume of nitrogen is accordingly marked as 2 per cent., and the other graduations, which are derived from this, similarly indicate percentages of urea.

It may be noted that the increase of the normal volume of the nitrogen at ordinary temperature, which is due to temperature and to the pressure of aqueous vapour, almost precisely counterbalances the deficiency of 8 per cent. in the volume of the nitrogen which is evolved from the urea.

FIG. 125.



RUSSELL-WEST APPARATUS

909. The Process of Estimation.—Five c.c. of urine are allowed to flow from a pipette into the decomposition-tube, and the sides of the tube are rinsed down with distilled water, until the bulb is filled as far as the constriction. The glass rod with rubber end is then placed in the tube, so that it closes the constriction. The decomposition-tube is finally filled with the freshly prepared hypobromite solution. Water is then poured into the trough until it is half filled: and the measuring-tube is filled with water, closed with the thumb, inverted in the trough, and placed in the little well seen to the left.

The glass rod is now withdrawn, and the measuring-tube is quickly shifted into the other well of the trough, so as to rest upon the cork and cover the opening of the decomposition-tube.

The reaction commences as soon as the urine and the hypobromite solution mingle, and if the bulb is warmed with a small Bunsen flame the evolution of gas will usually cease in about five minutes. The measuring-tube is then shifted into the well, and the volume of nitrogen is read off as soon

as the gas has had time to attain the temperature of the air. The liquid in the decomposition-tube at the end of the process must smell distinctly of the hypobromite, proving that this reagent is present in excess.

910. **Excessive Urea and Albumen.**—If the urine contains an unusually high percentage of urea, it will be necessary to dilute it with its own volume of water and to use 5 c.c. of this diluted sample. The result obtained must then be multiplied by 2.

If albumen is present in large amount, it must be coagulated by adding a few drops of acetic acid to the urine and heating it: the liquid is then filtered, and the clear filtrate is used for the estimation. If this treatment is omitted, a considerable amount of froth is produced in the measuring-tube, which retards, or renders impossible, the measurement of the nitrogen.

ESTIMATION OF GAS BY ABSORPTION AND TITRATION.

Estimation of Carbon Dioxide in Air by Titration, by the Pettenkofer Method.

912. Since carbon dioxide is a product both of respiration and of combustion, it frequently accumulates in undue proportion in the air of closed rooms. A simple and rapid method of estimating its proportion in the air is therefore of great importance, since the result of the estimation enables a judgment to be formed regarding the efficiency of the system of ventilation which has been adopted. This is especially valuable to engineers and others who are concerned in the heating and ventilation of buildings.

The average percentage volume of carbon dioxide in fresh outside air is from 0·029 to 0·03. This average is calculated from a very large number of the most trustworthy results.

913. **Pettenkofer's Method of determining the Proportion of Carbon Dioxide in Air** depends upon finding the amount of calcium or barium hydrate which is precipitated as carbonate from solution, when lime- or baryta-water in excess is well shaken with a known volume of the air.

This may be effected by using a known volume of lime-water, the strength of which has been determined by titration with a standard acid solution, After the lime-water has been exposed to the measured volume of the air, it is again titrated with the acid. The difference between the two volumes of acid which are required in these titrations gives the volume of the acid solution which is equivalent to the carbon dioxide absorbed from the air. From this result the weight and the volume of carbon dioxide, which was present in the known volume of air, can be calculated.

The following are requisites for this process :

(a) *A strong clear Glass Bottle* is selected, from 8 to 10 litres in capacity, and with an unground neck which can be closed air-tight by means of an accurately fitting rubber cork. The exact capacity of the bottle is ascertained by filling it with water to a scratch on the neck, which marks the bottom of the cork : the water is then poured into a measuring-vessel in order to ascertain its volume. The capacity should be written on the bottle with a diamond pencil, or with the point of a sharp file.

The bottle is thoroughly cleansed, and is rinsed out several times with distilled water. Its interior is then perfectly dried. This is effected either by draining it and leaving it open for some time in an inverted position : or more rapidly, by placing it in a heated oven and occasionally sucking out the air from the interior by means of a clean dry glass tube pushed down to the bottom of the bottle, or blowing out the moist air by bellows. The clean dry rubber cork is then pushed in, until it reaches the mark on the neck.

When experience has been obtained in the estimation, a bottle of only two litres capacity may be used, as this will suffice for one estimation without providing for a repetition

(b) *A Hand Bellows* with rubber tube on the nozzle is required, by means of which the air from any desired locality can be blown into the bottle until the air in the interior has been displaced. A volume of air, at least five or six times as great as the capacity of the bottle, should be blown to the bottom of the bottle by the bellows, which are drawing air from the desired position. Either Fletcher-blowers or ordinary hand-bellows may be used. They should be clean and air-tight.

(c) *Saturated Lime-water* is made by repeatedly shaking up freshly slaked lime with water in a Winchester quart bottle, which is nearly filled with the water. The solution is rendered clear by subsidence or by filtration. The perfectly clear solution is stored in an accurately stoppered Winchester quart bottle. Unless alkalis are known to be absent, a few drops of barium chloride solution should be added to the lime-water.

(d) *The Standard Hydrochloric Acid Solution* is prepared by diluting 50 c.c. of normal hydrochloric acid (290) to a litre with distilled water, which

has been recently boiled for a quarter of an hour to free it from dissolved carbon dioxide, and then cooled. Each c.c. of this twentieth-normal acid corresponds to 0·558 c.c. of carbon dioxide measured at 0° C. and at 760 mm. pressure.

Note —A solution of oxalic acid of one-twentieth normal strength may be prepared more conveniently, if the normal hydrochloric acid is not at hand, by dissolving 3 15 grams of pure crystallised oxalic acid in water and making this solution up to a litre; but the oxalic acid solution is liable to change when it is kept, and must therefore be used as soon as it is prepared. If the acid solution is made by diluting 89 6 c c. of the decinormal acid to a litre, each c c. will correspond exactly to 1 c.c. of carbon dioxide measured under normal conditions.

(e) *Solution of Phenol-phthalein* (269) is the most convenient and suitable indicator. But turmeric-paper (267), which has not lost its full yellow colour, may be used in case of necessity.

914. **The Process of Estimation.**—By means of the bellows (b) a volume of the air which is to be tested, equal to at least six times the capacity of the bottle, is blown down to the bottom of the 8 to 10 litre bottle (a); 100 c.c. of the lime-water (c) are then at once introduced, the rubber cork is inserted, and the atmospheric temperature and barometric pressure are noted down (*Note* 1).

The bottle is now laid on its side and is rolled along on a level surface, so as to wet the interior with the lime-water; this process is repeated several times during half an hour. Twenty c.c. of the liquid are then withdrawn from the bottle, by means of a dry pipette with rubber tube attached to its top, and the bottle is immediately closed (*Note* 2).

The 20 c.c. taken direct from the bottle (a) are at once introduced into a small flask and are titrated by the standard hydrochloric acid (d), the liquid being coloured with solution of phenol-phthalein, and the disappearance of the colour indicating the end of the reaction (269). Or if turmeric-paper must be used, a small drop of the liquid is removed occasionally from the flask and placed upon the paper; the brown alkaline tint on the paper is last seen at the edge of the wet spot, just before it disappears completely on the addition of a little more acid.

At least one repetition of the titration should be made, so as to obtain accurately the volume of acid required. From this result the volume of acid which would be required by 100 c.c. of the original lime-water, after exposure to the air in the bottle, is calculated.

A measured volume of the original lime-water (c) is then titrated with the standard acid, and the volume of acid which would be required to neutralise 100 c.c. of this lime-water is calculated.

The difference between the volumes of the acid solution, which would be

required for 100 c.c. of lime-water before and after its exposure to the sample of air, is thus ascertained. This volume of acid corresponds in neutralising power to the carbon dioxide which was originally present in the sample of air in the bottle.

Note 1 —*The Smaller Bottle* of about 2 litres capacity may be used (*Note*, 913, a) for the air-sample when experience has been obtained in the process. The procedure is similar to that described above for the larger bottle, but only 20 c c. of lime-water are introduced, and the whole of this is subsequently titrated at once by letting the standard acid flow directly into the bottle from the burette.

Note 2 —Throughout the whole of the manipulation in the above process, it is evidently necessary to guard as far as is possible against the further absorption by the lime-water of carbon dioxide from the open air or from the breath This is secured by making the exposure of the lime-water to the open air as brief as possible. Any distilled water which is used for dilution should also have been recently boiled and rapidly cooled, so as to be free from carbon dioxide.

A repetition of the process, with rapid titration, in the presence of air, furnishes a result which is sufficiently accurate for ordinary purposes

The use of the smaller bottle for the air-sample, in which the lime-water is titrated without being removed, is of course preferable.

Example —The results of an actual estimation were as follows :

Capacity of the bottle = 2360 c c ; temperature of the sample of air = 15° C ; atmospheric pressure = 762 mm.

20 c.c. of the original lime-water required 18 0 c c. of $\frac{N}{20}$ HCl, 1 c c. of which corresponds to 0·558 c c. of CO_2 at 0° C. and 760 mm pressure.

20 c c. of the lime-water after being shaken with the sample of air required 15·8 c c. of $\frac{N}{20}$ HCl.

Therefore the CO_2 in the sample is chemically equivalent to 18 0 - 15 8 = 2·2 c c of $\frac{N}{20}$ HCl.

And since each c c. of this acid corresponds to 0 558 c c of CO_2, the volume of CO_2 = 2 2 × 0·558 = 1 2276 c c at 0° and 760 mm. pressure

The volume of air in the bottle at 15° C and 760 mm pressure = $\frac{2360 \times 762}{760(1 + 0\ 003(65 \times 15)} = 2237$ c c at 0° C and 760 mm pressure.

Hence the percentage volume of $CO_2 = \frac{1\ 2276 \times 100}{2237} = 0{\cdot}054$.

915 **The Following Series of Results** will serve to indicate the varying degrees of efficiency attained in the ventilation of different buildings They also indicate the effect on pure country air of polluted colliery air brought in by the wind.

The results are stated as percentages by volume of CO_2 in the air taken from the localities indicated, and are probably accurate to the second place of decimals

Nottingham ·

The top of the Castle Rock; fresh air outside	0 038
University College, the grounds	0 043
„ „ the chemical laboratory, evening, 30 students	0 069
Masonic Hall, lower room, 12 P M.	0·179
„ „ upper room, during dancing	0 312
Circus building, promenade, 10 P M	0 326
Private sitting-room, 1620 cubic feet capacity, open fireplace, closed for 3 hours with two persons and three gas-jets	0 284
Committee-room, closed for 2¼ hours with fifteen persons and twenty-seven gas-jets	0 418
Wesleyan Chapel, near floor, after afternoon service, windows and doors closed	0 218
Pasture fields, Derbyshire, wind from hills, bright morning	0 030
Pasture fields, Derbyshire, morning misty, wind from village and colliery with burning "waste heaps"	0 045

London:

Charing Cross, February; fresh air outside	0 032
Lunatic Asylum ward, outside London	0 054
„ „ fresh air outside	0 025
Air inside Greathead tunnelling shield	0 218
Theatre, gallery	0 175
„ upper circle	0 228
Chelsea, average on fine days	0 040
„ „ foggy days	0 100
Chemical laboratory, 36 students and 40 gas-burners, fine day	0 092
„ „ „ „ foggy day	0 125
Small chemical lecture room, 40 students present for 3 hours	0·151
Chemical lecture theatre, 27 students present for 1 hour	0 053
Gymnasium, 46 men present for 2 hours, ventilated only from the corridor	0 197
Underground railways	0 044 to 0 116
„ „ lifts	0 082 „ 0 152
„ „ carriages (closed)	0 096 „ 0 288

The above results serve as a measure of the adequacy of the ventilating arrangements, which varies inversely as the proportion of carbon dioxide found in the air of the building.

But to enable a correct judgment to be formed, a determination of the percentage of carbonic dioxide present in the air outside the inclosed space should also generally be made, since in many places it cannot be assumed that the external air contains only 0·038 per cent. of carbon dioxide, and manifestly the internal air should be compared with the air outside the inclosure which is being examined The above experimental results show that external air in London in fine weather contains much less carbon dioxide than it does in foggy weather, and this difference naturally affects also the internal air of buildings.

PART VI.–SECTION XVIII.

VAPOUR DENSITY DETERMINATIONS

920. Introductory Remarks.—By the term "vapour density" is usually meant the density or specific gravity of a vapour referred to that of hydrogen as unity.

For chemical purposes hydrogen is invariably selected as the standard instead of air, and mainly for the following reason. It is acknowledged that equal volumes of gases and vapours under similar conditions contain an equal number of molecules, and that the molecule of hydrogen consists of two atoms; accordingly the molecular weight of a gas or vapour may be obtained by multiplying its density by 2. The determination of the vapour density of a substance therefore furnishes a means of ascertaining its molecular weight. This method is supplementary to others which have been already described (820–824).

Among the recent methods for determining vapour density that of Victor Meyer (921) presents the advantage of simplicity as regards the apparatus used, the manipulation, and the calculation of the result; it further requires the use of only a small amount for substance.

The method of Dumas (925) is more complicated in every respect, and requires a larger amount of substance.

The Meyer Vapour Density Method.

921. This method determines the volume of the vapour which is producible from a known weight of a volatile substance, by measuring the volume of air which the vapour displaces.

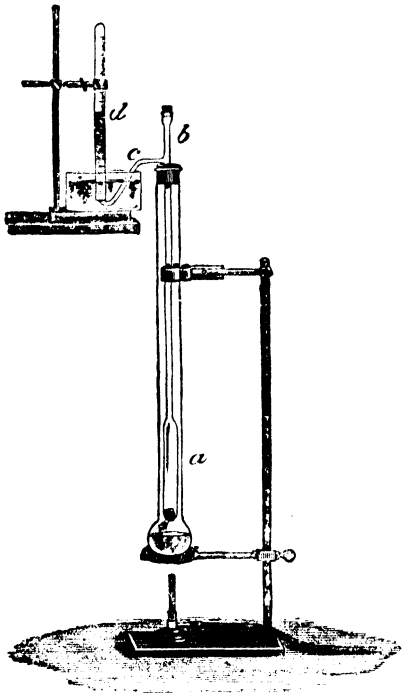
The volume of the displaced air is measured in c.c. at atmospheric temperature and pressure, and while saturated with aqueous vapour; and from this the corrected volume of the air when dry and under normal conditions is calculated (839, 2). This will represent the volume which the vapour of the substance would possess if it could exist under normal conditions. The weight of an equal volume of hydrogen is then found by multiplying the above number

of c.c. by 0·0000899, and the density of the vapour of the substance is obtained by dividing the weight of the substance by this weight of hydrogen.

922. The Apparatus which is employed for the determination is shown in Fig. 126.

The inner vapour-tube (*b*) is long and narrow, and is enlarged into a cylindrical bulb below. The whole tube has a capacity of about 200 c.c., and is somewhat broader at the top so as to admit of being closed by the insertion of a tightly fitting cork. A short distance below the top a bent capillary delivery-tube (*c*) enters at right angles.

FIG. 126.



MEYER'S VAPOUR DENSITY APPARATUS.

A broad outer tube (*a*), which is enlarged into a bulb at the bottom, serves as a heating-jacket for the inner vapour-tube. A liquid, which has a much higher boiling-point than that of the liquid whose vapour density is to be determined, is placed in the bulb of this jacket.

Water is frequently used in the outer jacket; but bodies of higher boiling-point than water, such as amylic alcohol, aniline and sulphur, are sometimes required. A suitable form of air-jacket around the inner tube may replace the vapour; and the inner tube may be made of porcelain and be immersed in melted lead, or in the vapour of boiling zinc, when a higher temperature is required.

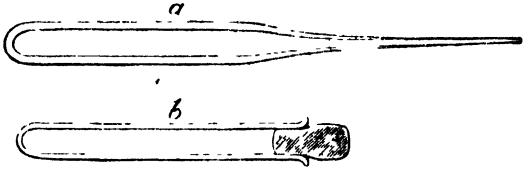
A measuring-tube (*d*), about 100 c.c. in capacity and graduated into fifths of a c.c., is filled with water and is inverted in a vessel of water. This stands at a convenient height for collecting the air escaping through (*c*). A laboratory stool, placed upon the working-bench, is generally of suitable height for supporting the vessel of water.

923. The Process of Estimation.—For practice in the method, the vapour density of pure ether may be determined in the following manner:

The ether used for the estimation must have been purified as follows: It is first freed from alcohol by washing it with salt water, and then dried by being shaken with powdered calcium chloride. The last traces of water are now removed by dropping into the ether some clean slices of sodium, and allowing the liquid to stand for several hours in a loosely corked flask until no more bubbles of hydrogen escape from the surface of the sodium. The ether is then distilled off through a dry condenser into a clean dry bottle, the first portion of the distillate being rejected and only that portion being collected which boils at 34·5° C.

The apparatus is fitted up as is shown in Fig. 126. The interior of the vapour-tubes having been thoroughly cleaned and dried, the bottom is padded inside with dry asbestos or sand, and the top is closed by the cork. The bulb of the jacket-tube is then half-filled with water, and the vapour-tube is fitted centrally into the mouth of the outer tube by pressing in the two halves of a bisected cork, in which small openings are made for the escape of steam. The collecting-trough is now arranged as such a height that the

Fig. 127.



Weighing-tubes.

curved end of the delivery-tube dips beneath the water when the tube is clamped in position over the burner. The water in the outer tube is then heated to boiling, and is kept boiling vigorously by the Bunsen burner, so as to cause steam to escape through the cork in the top of the jacket-tube.

As soon as no more air-bubbles escape from the delivery-tube (*c*) through the water in the trough, the cork is loosened in the top of the vapour-tube, since the air within it has reached steam-heat and the tube is therefore ready for the determination. The measuring-tube (*d*) is filled with water and is clamped in position over the end of the delivery-tube (*c*).

Meanwhile a little glass tube about 3 cm. in length is made out of quill-tubing, one end being closed and the other being drawn out to a capillary. The tube is shown drawn to actual size in Fig. 127*a*. The tube is weighed, and is then heated, and allowed to cool with its capillary point immersed in pure ether until a suitable quantity of the liquid ether has been introduced. The tube is then re-weighed with the capillary end open. Its gain in weight gives the weight of the ether taken for the experiment.

The little glass tube for containing the weighed liquid in the above process may be furnished with an accurately fitting small stopper (Fig. 125, *b*). This is

made by grinding a piece of glass rod into the mouth of the tube with wetted emery-powder or boro-corundum. The necessity of making a fresh tube for each determination is thus obviated.

The tube containing the ether is then at once dropped into the vapour-tube, which is immediately closed by the cork. The ether will begin to boil, and its vapour will displace air from the vapour-tube, which will escape in a stream of bubbles into the measuring-tube. As soon as no more bubbles escape the cork of the vapour-tube is removed.

The measuring-tube (d) is then removed to a tall cylinder of water, which should be at the temperature of the air. The tube is wholly immersed in the water, and as soon as its contents have gained the temperature of the water the tube is raised until the water inside and outside are at the same level. The volume of the air is then carefully read, and the temperature of the water and the barometric pressure are noted at the same time.

924. Calculation of Results.—All the data necessary for the calculation of the vapour density have now been obtained. According to paragraph **839, 2,**

$$\text{The vapour density} = \frac{S \times 760 \times (1 + 0{\cdot}003665t)}{v \times (p - w) \times 0{\cdot}0000899}$$

In which formula:

S = the weight of substance taken.
t = the temperature of the water in the cylinder.
v = the observed volume of the air in c.c.
p = the barometric pressure reduced to 0°.
w = the tension of water-vapour at $t°$.
0·0000899 = the weight of 1 c.c. of hydrogen.

Example.—In a determination of the vapour density of ether, the following numbers were noted down:

Weight of ether taken = 0 073 gram.
Temperature of water = 21 5 C.
Volume of air displaced = 25·3 c.c.
Barometric pressure at 0° = 748 6 mm.
Tension of aqueous vapour = 19 07 mm.

$$\text{Hence the vapour-density} = \frac{0\ 073 \times 760 \times (1 + 0\ 003665 \times 21\ 5)}{25\ 3 \times (748\ 6 - 19\ 07) \times 0\ 0000899} = 36\ 07$$

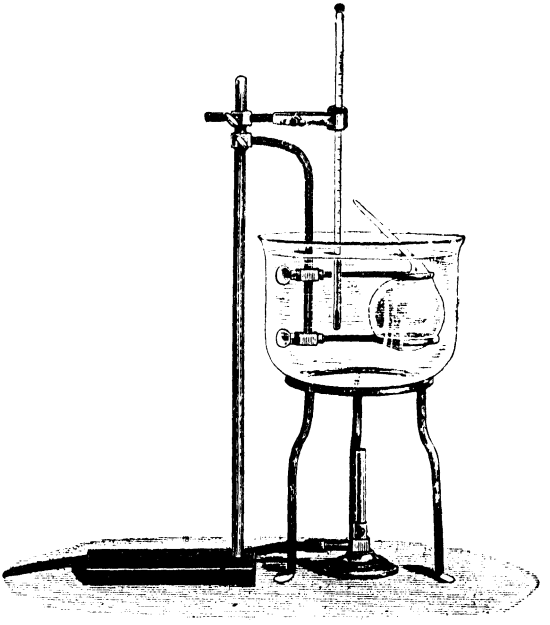
The Dumas Vapour Density Method.

925. This method determines the weight of a definite volume of the vapour of the substance, which has been measured at a known temperature and pressure. From this result the volume which the vapour would possess,

if it could exist under normal conditions of temperature and pressure, is calculated (839, 1). The weight of an equal volume of hydrogen is then obtained by calculation, and the vapour density of the substance is found by dividing the weight of the vapour by that of the hydrogen.

926. **The Apparatus required for the Process** is shown in Fig. 128. A large thin glass bulb, with its neck drawn out, is used for containing

FIG. 128.



DUMAS' VAPOUR DENSITY APPARATUS.

the vapour: it has a capacity of about 200 c.c. Such a bulb may be purchased, or may be made by drawing out the neck of a round flask. After the liquid has been introduced, the bulb is supported in a double clamp, and is immersed in a suitable liquid contained in a large vessel. A copper water-bath, placed on a tripod-stand and heated by a gas-burner, serves the purpose well. The temperature of the liquid in the bath is taken by means of a thermometer, the bulb of which is placed near the middle of the vapour-bulb.

927. **The Process of Estimation.**—For practice in the process, the vapour density of pure benzene may be determined in the following manner:

The empty apparatus having been arranged as is shown in Fig. 128, the bulb is removed together with its clamp. The bath is then nearly filled with water, which is heated to boiling.

Meanwhile the clean dry bulb is weighed, after remaining in the balance-case for some time. About 20 c.c. of the pure benzene are then introduced into the bulb by heating it and allowing it to cool with its open end immersed in the liquid.

The bulb is now fixed in its clamps and is immersed in the gently boiling water in the bath, with the end of the tube projecting about 2 cm. above the surface of the water. The bulb is clamped in this position. The thermometer is also at once fixed, with its bulb level with the middle of the vapour-bulb and close to it.

The benzene will boil vigorously, and the vapour which it evolves will pass out from the neck under pressure expelling the air from the bulb. When the vapour has issued for some time and begins to escape more quietly, it may be kindled at the end of the tube, and the dropping of the flame will then serve to indicate the moment at which the issue of vapour ceases. The end of the tube is then at once sealed by bringing a blowpipe-flame to bear upon it. At this moment the temperature shown by the thermometer immersed in the bath, and the barometric pressure are read.

The bulb is now removed from the bath, and is at once thoroughly dried and allowed to cool. It is then placed in the balance-case for some time in order that it may assume the temperature of the air inside the case. The sealed bulb is then weighed and the temperature within the balance-case is noted.

A file-scratch is now made near the sealed end of the tube of the bulb, and the end is broken off under water which has been freed from air by having been recently boiled for some time and then rapidly cooled. The water will rush into the bulb, and the volume of any air-bubble which remains is then found by transferring it to another vessel and measuring its dimensions (*Note*). The water is then allowed to flow out into a graduated measuring-cylinder, and the volume of the water, together with that of any air-bubble which was in the bulb, when it has been reduced to absolute c.c. will give the capacity of the bulb (243). The water may be weighed instead of being measured, and its volume may then be calculated.

Note.—If the residual bubble of air is of appreciable size it must be allowed for both in the weight of the vapour (G), and in the weight of the hydrogen.

928. Calculation of Results.—All the data for calculating the vapour density from the corrected volumes (839, 1) have now been obtained. The following are the necessary data: let

g = weight of bulb.
G = apparent weight of bulb filled with vapour.
t = temperature of air, second weighing.
T = temperature of bath at the time of sealing the bulb.
p = barometric pressure, height of mercury column reduced to 0°.
c = capacity of bulb in c.c.

The Weight of the Vapour.—Neglecting certain corrections of minor importance, the weight of the vapour which filled the bulb is obtained by subtracting the weight of the bulb from the apparent weight of the bulb and vapour, and adding the weight of the volume of air which was displaced by the bulb at the temperature (t) and pressure (p) of the last weighing. Accordingly:

$$\text{Weight of vapour} = G - g + \frac{c \times p \times 0{\cdot}001293}{760(1 + 0{\cdot}003665t)}.$$

The Weight of the Hydrogen, which would fill the bulb at the temperature of the bath (T) and at the barometric pressure (p), will be found by the following expression:

$$\text{Weight of hydrogen} = \frac{c \times p \times 0{\cdot}0000899}{760(1 + 0{\cdot}003665T)}.$$

The Vapour Density will be found by dividing the weight of the vapour which fills the bulb, by the weight of an equal volume of hydrogen under the same conditions. Accordingly making use of the results of the above calculations:

$$\text{The vapour density} = \frac{\text{weight of vapour}}{\text{weight of hydrogen}}.$$

Example.—In a determination of vapour density,

Weight of the bulb = 23 683 grams.
Apparent weight of the bulb + vapour = 23·957 grams
Temperature of air = 16° C
Temperature of bath = 112° C.
Barometric pressure = 755 mm.
Capacity of bulb = 180 c c

Therefore the weight of vapour filling the bulb at 112° (x)

$$= 23{\cdot}957 - 23{\cdot}683 + \frac{180 \times 755 \times 0\ 001293}{760(1 + 0{\cdot}003665 \times 16)},$$

And the weight of an equal volume of hydrogen (y)

$$= \frac{180 \times 755 \times 0\ 0000899}{760\ (1 + 0{\cdot}003665 \times 112)},$$

And the vapour density $= \frac{x}{y} = 43{\cdot}16.$

PART VII.

TABLES FOR REFERENCE.

RESULTS OF TYPICAL ANALYSES.

ATOMIC WEIGHTS OF ELEMENTS.

FACTORS FOR GRAVIMETRIC ANALYSIS.

EXPANSION OF WATER.

PRESSURE OF AQUEOUS VAPOUR.

FACTORS FOR NORMAL GAS-VOLUME.

ALCOHOL TABLES.

SPECIFIC GRAVITY OF SOLUTIONS OF ACIDS AND ALKALIS.

CONVERSION OF THERMOMETRIC AND TWADDELL DEGREES.

DATA FOR OILS, FATS AND WAXES.

WEIGHTS AND MEASURES.

USEFUL MEMORANDA.

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939 **Introductory Remarks.**—This Section of the book contains tabular matter which will frequently be referred to during the calculation of the results of analysis, as well as for the purposes of comparison when the results have been calculated.

The results obtained from typical analyses of various substances are tabulated in paragraphs 940–974 and will serve as a standard of comparison for the student after he has calculated his results.

During the calculation of the results of gravimetric analyses reference to the table of Atomic Weights (980) will often be necessary, and the use of the Factors for Gravimetric Analysis or their Logarithms (981) will lessen the labour of calculation.

Kopp's Table for the Expansion of Water by heat (982) is added for use in the calculation of results when measuring-vessels are being calibrated (243,

247, 846); and Regnault's tabulated results for the pressure of aqueous vapour (983) are required in calculating the results of gas analyses.

The Table of Factors for converting the Volume of a gas at any temperature and pressure to its Normal Volume at 0° C. and 760 mm. pressure (984), will also be found useful in gas analysis and in vapour density determinations.

The Alcohol Tables (985, 986) furnish the percentage of absolute alcohol or of proof spirit which is present in dilute alcohol, from the result of its specific gravity determination.

Similarly the tables which follow (987-992) give the percentage weights of sulphuric acid, hydrochloric acid, nitric acid, potassium hydrate, sodium hydrate, and ammonia respectively, which are present in aqueous solutions of these substances of known specific gravity.

The next Table (993) furnishes the necessary characteristics for the identification of Fats, Oils, and Waxes.

Then follow the formulæ for calculating specific gravity from degrees Twaddell and *vice versâ* (994), and for the conversion of Thermometric Scales (995).

The tabular matter also includes a scheme showing the relations between the different denominations in the Decimal and English Weights and Measures (996-999), a number of Useful Memoranda of general application, and it concludes with tables of logarithms and anti-logarithms (1001, 1002).

RESULTS OF TYPICAL ANALYSES.

Note.—The numbers given are percentages, unless a statement is made to the contrary.

940. Dolomite, or Magnesian Limestone.

Carbon dioxide, ...	45 64
Silica, ...	1 38
Iron and Aluminium oxides, . . .	1·38
Calcium oxide, ...	30 83
Magnesium oxide, ...	20 99

941. Burnt Lime.

	Chalk lime.	Greystone lime	Lias lime
Calcium oxide, . . .	91 9	78 25	72 20
Calcium carbonate, . .	3 52	0 66	0 71
Iron and Aluminium oxides, .	1 58	3 50	6 00
Insoluble siliceous matter, .	0 39	0 80	0 30
Soluble silica, . . .	—	10 00	15 65
Water, &c (by difference), .	3 32	6 79	5 14

942. Mortar.

Water, ...	10 76	14 7	14 0
Combined water, . . .	2 25	1·6	2 9
Calcium oxide, . . .	6 38	6 4	9 0
Soluble silica, . . .	2 24	1·4	0·7
Iron and Aluminium oxides, .	1·53	1 6	1·1
Fine earthy matter, . .	3 40	8 4	8 6
Coarse insoluble matter, .	73 44	57 1	62 6
Calcium carbonate, .	—	5 9	—
Calcium sulphate, .	—	0·5	—

943. Spathic Iron-ore.

Ferrous oxide,	49·77
Ferric oxide,	0 81
Manganous oxide,	1 03
Calcium oxide,	3·96
Magnesium oxide,	2 83
Carbon dioxide,	37 20
Phosphorus pentoxide	Trace.
Sulphur,	0·04
Water,	0 30
Insoluble residue,	3 12

944. Salt-cake.

Water,	0 05
Insoluble matter,	0·19
Iron and Aluminium oxides,	0 14
Calcium oxide,	0 20
Magnesium oxide,	0 13
Sulphur trioxide,	57 17
Chlorine,	0 02
Sodium oxide,	41 86

945. Portland Cement.

Insoluble residue,	0 36	1·20	0 06	0 32
Soluble silica,	21 52	22 56	23 50	23 12
Aluminium oxide,	7 95	8 55	7 84	7·27
Ferric oxide,	2 69	3 13	2·88	3 65
Calcium oxide,	62·30	59 20	61 80	61·44
Magnesium oxide,	1 24	1·22	1·45	1·10
Sulphur trioxide,	1 11	1 43	0 47	1·29
Carbon dioxide,	1 78	1·54	0 66	0·32
Combined water,	0 27	0 29	0 33	1·19
Alkalis (by difference),	0 78	0 88	1 01	0 30

946. Felspar.

Silica,	65 14
Iron and Aluminium oxides,	18 68
Calcium oxide,	0 47
Magnesium oxide,	0 36
Potassium oxide,	11 82
Sodium oxide,	3·37

947. Glass.

	I	II	III.
Silica,	71 71	70 71	51 40
Potassium oxide,	12 70	—	9 40
Sodium oxide,	2 50	13 25	—
Calcium oxide,	10 30	13 38	—
Lead oxide,	—	—	37 40
Iron and Aluminium oxides,	9 60	1 92	2 00

I. Bohemian glass. II. Window glass. III. Flint glass

948. Zinc-blende.

Insoluble residue,	14 43
Copper,	1 81
Iron,	12 61
Sulphur,	28 40
Zinc,	43 06

Corresponding to ZnS, 64 2; FeS, 19 8.

949. Galena.

Sulphur,	13 90
Lead,	83 58
Iron,	0 83
Manganese,	1 26
Silver,	0 14

950. Copper-pyrites.

Sulphur,	35 16
Copper,	30 00
Iron,	32 20
Insoluble residue,	2 64

951. Brass.

Copper,	70 30
Zinc,	29 30
Tin,	0 17
Lead,	0 28

952. Bronze Coin.

Copper,	94 85
Tin,	3 90
Zinc,	1·14

953. Type-metal.

Lead,	61 30
Antimony,	18·80
Tin,	20 20

954. White, or Antifriction Metal.

Tin,	82 5	79 2
Antimony,	8 6	11 4
Copper,	7 7	5 2
Lead,	—	2 4

955. German-silver.

	I.	II.
Copper,	62 46	62 40
Zinc,	20 85	22·15
Nickel,	15 47	15 05
Iron,	1 05	Trace.

956. Red Hæmatite-ores.

	I.	II.
Ferric oxide,	86 50	93 75
Manganous oxide,	0 21	Trace.
Aluminium oxide,	—	0 73
Calcium oxide,	2 77	0 61
Magnesium oxide,	1·46	0 23
Sulphur,	—	0 03
Sulphur trioxide,	0·11	—
Carbon dioxide,	2 96	—
Phosphorus pentoxide,	Trace.	0·32
Water, and organic matter,	—	1 09
Silica, and insoluble matter,	6 55	3 27

I. Ore from Ulverston, Lancashire. II. Ore from Lake Superior

957. Iron and Steel.

	Bessemer Pig-iron.	Wrought-iron	Bessemer Steel
Iron,	93 301	99·13	99 445
Graphite,	2·930	—	—
Combined carbon,	0 618	0 15	0 234
Silicon,	2 72	0·14	0 033
Sulphur,	0 062	0·04	—
Phosphorus,	0 039	0 47	0 044
Manganese,	0 105	0 14	0·139
Copper,	0·010	—	0·105
Arsenic,	0·075	—	—

958. Coal.

	Anthracite.	Non caking Long Flame	Caking Coal.
Moisture,	—	11 72	4 36
Volatile matter,	6 84	47 34	35 92
Coke,	93 16	50 08	57·94
Ash,	1 68	2 58	1 78
Sulphur,	0 77	0·57	2·11
Calorific power,	8629	7425	7484

959. Superphosphate of Lime.

Moisture,	15·00
Organic matter,	12 00
Soluble phosphate,	18 00
Equal to $Ca_3(PO_4)_2$,	28 28
Insoluble phosphate,	6 00
Calcium sulphate,	41 95
Alkalis, &c.,	0 55
Sand,	6 50

960. Cambridge Coprolites.

Moisture, Combined water, Organic matter,	4 04
Silicious matter,	8 19
Calcium phosphate,	58 09
Calcium carbonate,	21·12
Iron oxide,	2 18
Aluminium oxide,	2 05
Magnesium oxide, alkalis, &c.,	4 33

961. Bone Meal.

	Raw	Steamed
Moisture,	6 91	8 45
*Organic matter,	39 31	17 29
Calcium phosphate,	46 60	63 99
†Calcium carbonate, &c,	5 78	8 97
Sand,	1 40	1 30
*Containing nitrogen,	4 35	1 35
(Equal to ammonia),	5 28	1 6
†Containing calcium oxide,	—	4 57

962. Basic Slag.

Moisture,	0 13
Calcium oxide,	32 42
*Phosphorus pentoxide,	18 44
Ferrous oxide, &c,	39 46
Silica,	9 55
*Equal to $Ca_3(PO_4)_2$,	40 26

963 Peruvian Guano.

Moisture,	9 71
*Organic matter,	40 19
Calcium phosphate, $Ca_3(PO_4)_2$,	19 00
†Alkalis, &c,	13 05
Sand,	18 05
*Containing nitrogen,	8 45
Equal to ammonia,	10 26
†Containing P_2O_5,	0 40
Equal to $Ca_3(PO_4)_2$,	0 87
Total P_2O_5,	9 10
Equal to $Ca_3(PO_4)_2$,	19 87

964. Water.

Parts per 100,000.

	Upland Surface.	Deep Well (Nottingham).	Shallow Well (Belvoir)	Trent River Water (Polluted).
Total solids, . . .	7 8	19 4	69 5	55 4
Ammonia, . . .	Nil	Nil	0 001	0 074
Albuminoid ammonia, .	0 002	0·002	0 008	0 111
Oxygen consumed, . .	0 05	0·037	0 005	0 082
Chlorine, . . .	0 8	1·5	4 8	5 5
Nitrite, ...	Nil	Nil	Nil	Nil.
Nitrogen as nitrate, . .	Nil	0 76	2 83	0 33
Temporary hardness, . .	Nil.	9 7	15 4	18 5
Permanent ,, . .	2 3	3 5	23 4	16 5
Total ,, . .	2 3	13 2	38 8	35 0

965. Milk.

	Poor Quality.	Average Quality. I.	Average Quality. II.	Rich Quality.
Water, . . .	88 58	87·70	87 79	86 48
*Fat, ...	2 30	3 58	3 58	5 08
†Proteins, . . .	3 56	7 98	3 50	3 23
Lactose, &c. (by difference),	4 76		4·32	4 47
Ash, ...	0 8	0 74	0 81	0 74
Specific gravity at 60° F,	1 0326	...	1 0300	1 0275
*Fat by calculation, .	...	...	3 7	5·3
†Containing nitrogen, .	...	...	0 56	0 51

966. Butter and Margarine.

	Irish Butter. I.	Irish Butter. II.	Salt Butter. I.	Salt Butter. II	Margarine I.	Margarine II.
Water,	14·9	14 3	13 5	9·5	7 8	14 6
Fat,	82 5	84 6	84 3	88 1	89 5	83·2
Curd,	1·9	0 8	0 3	1 0	1 7	1·8
Salt,	0 7	0 3	1 9	1 4	1 0	0 4
Reichert-Meissl,	29 5 $\frac{N}{10}$	34 0 $\frac{N}{10}$	31 4 $\frac{N}{10}$	33·3 $\frac{N}{10}$	1 7 $\frac{N}{10}$	2 9 $\frac{N}{10}$
Insoluble acids,	85 6%	85 8%	86 3%	86 1%	94·1%	93 6%
Saponification, KOH,	22 51%	22 39%	22 35%	23 4%	19 29%	19 94%
Specific gravity $\frac{100°}{15·5°}$ C.	0 8652	0 8669	0 8662	0·8667	0 8613	0 8628

967. Pale Resin Soap.

Fatty anhydride,	48 44
Sodium oxide (soda) in combination,	6·85
Resin,	23 97
Sodium silicate,	0 29
Silica,	0 55
Sodium carbonate,	1·53
Sodium hydrate (caustic soda),	Trace.
Water,	18 37

968. Soaps.

	Curd.	Castile.	Tallow.	Soft
Water,	27·5	14 0	20 9	38 4
Fatty anhydride,	67 7	77 0	71 0	48 4
Alkali, combined,	7·6	8·7	8·9	12 0
Alkali, free,	0 1	0·3	0 3	3 2
Silica,	0 5	—	—	0 2
Insoluble in alcohol,	—	1·1	1 6	1·1

969. Coal-gas, "Pure" and "Enriched."

	Pure.					Enriched.	
	I.	II.	III.	IV.	V.	I.	II
Carbon dioxide, .	0·00	0 00	1 43	0 38	0 0	1 44	2 83
Oxygen, . .	0 00	0 00	0 55	0 00	0 2	0 00	0 00
Olefines & Benzenes,	5 60	6 00	2 75	6 17	5 3	5 17	5 66
Carbon monoxide, .	9 60	9 24	7 69	4 86	6 6	16 26	16 98
Methane, . .	38 96	40 48	31 32	40 67	34 2	25 84	23 58
Hydrogen, . .	42·94	40 00	50 22	41 72	48 2	41·82	40 85
Nitrogen (by difference), . .	2 90	4 28	6 04	6 20	5 5	9 47	10·10

970. Blast-furnace Gas.

Carbon dioxide, ...	6 8
Oxygen, ...	0 1
Carbon monoxide, ...	29 8
Ethylene, ...	0 0
Hydrogen, ...	5 4
Methane, ...	2 2
Nitrogen (by difference), ...	55 7

971. Gases Dissolved in Water.

Percentage Composition of Total Gas evolved on boiling.

	Rain-water (972).	Notting-ham Supply (973).	Grand Junction Canal (974).	Deep Chalk Well.
Oxygen, ...	30 7	22·0	9·8	0·4
Nitrogen, ...	61 8	66·2	22·1	25·9
Carbon dioxide, . .	7 5	11·8	68·1	73·7

972. Gases Dissolved in Rain-water.

Volume of Gas in c.c. evolved from 100 c.c. of Rain-water.

	At 50° C	By Boiling	Total.
Oxygen, ...	0 671	0 014	0 685
Nitrogen, ...	1 348	0 033	1·381
Carbon dioxide, . . .	0 045	0·071	0 116
Total volumes, . . .	2·064	0 118	2·182

973. Gases Dissolved in Deep Well-water.

Volume of Gas in c.c. evolved from 100 c.c. of Nottingham Water-supply from deep wells in sandstone.

	At 15 5° C	By Boiling	Total.
Oxygen, ...	0 40	0 76	1 16
Nitrogen, ...	1·24	2 25	3 49
Carbon dioxide, . . .	0 10	0 52	0 62
Total volumes, . .	1 74	3 53	5 27

974. Gases Dissolved in Canal-water.

Volume of Gas in c.c. evolved from 100 c.c. of Grand Junction Canal Water.

	At 50° C.	By Boiling.	Total.
Oxygen, ...	0·609	0·011	0 620
Nitrogen, ...	1·391	0·007	1·398
Carbon dioxide, . . .	0 420	3 877	4·297
Total volumes, . . .	2·420	3·895	6 315

980. ATOMIC WEIGHTS OF THE ELEMENTS.

International Atomic Weights for 1913.

Name	Symbol	Atomic Weight.	Name.	Symbol	Atomic Weight.
Aluminium	Al	27·1	Mercury	Hg	200·6
Antimony	Sb	120·2	Molybdenum	Mo	96·0
Argon	A	39·88	Neodymium	Nd	144 3
Arsenic	As	74·96	Niton (Ra-emanation)	Nt	222·4
Barium	Ba	137·37	Neon	Ne	20·2
Beryllium or Glucinum	Be	9·1	Nickel	Ni	58·68
Bismuth	Bi	208·0	Nitrogen	N	14 01
Boron	B	11·0	Osmium	Os	190·9
Bromine	Br	79·92	**Oxygen**	**O**	**16·00**
Cadmium	Cd	112·40	Palladium	Pd	106·7
Cæsium	Cs	132·81	Phosphorus	P	31·04
Calcium	Ca	40·07	Platinum	Pt	195·2
Carbon	C	12 00	Potassium	K	39·10
Cerium	Ce	140 25	Praseodymium	Pr	140·6
Chlorine	Cl	35·46	Radium	Ra	226·4
Chromium	Cr	52 0	Rhodium	Rh	102·9
Cobalt	Co	58 97	Rubidium	Rb	85·45
Columbium	Cb	93 5	Ruthenium	Ru	101·7
Copper	Cu	63·57	Samarium	Sa	150·4
Dysprosium	Dy	162·5	Scandium	Sc	44·1
Erbium	E	167·7	Selenion	Se	79·2
Europium	Eu	152 0	Silicon	Si	28·3
Fluorine	F	19 0	Silver	Ag	107·88
Gadolinium	Gd	157·3	Sodium	Na	23·00
Gallium	G	69·9	Strontium	Sr	87·63
Germanium	Ge	72·5	Sulphur	S	32·07
Glucinum, *see* Beryllium.			Tantalum	Ta	181·5
			Tellurion	Te	127·5
Gold	Au	197 2	Terbium	Tr	159·2
Helium	He	3·99	Thallium	Tl	204·0
Holmium	Ho	163·5	Thorium	Th	232·0
Hydrogen	H	1·008	Thulium	Tm	168·5
Indium	In	114·8	Tin	Sn	119·0
Iodine	I	126·92	Titanium	Ti	48·1
Iridium	Ir	193·1	Tungsten	W	184·0
Iron	Fe	55·84	Uranium	U	238·5
Krypton	K	82·92	Vanadium	V	51·0
Lanthanum	La	139·0	Xenon	X	130·2
Lead	Pb	207·10	Ytterbium	Yb	172·0
Lithium	Li	6·94	Yttrium	Y	89·0
Lutecium	Lu	174·0	Zinc	Zn	65·37
Magnesium	Mg	24·32	Zirconium	Zr	90·6
Manganese	Mn	54·93			

FACTORS FOR GRAVIMETRIC ANALYSIS.

981. The weight of the substance in the second column, when multiplied by the factor, furnishes the corresponding weight of the substance on the same line in the first column. Thus the weight of Ag in 0·64 gram of AgCl = 0·64 × 0·75276 = 0·48176.

Required.	Weighed as	Factor.	Logarithm.
Ag	AgCl	0 75276	$\bar{1}$ 87665
AgCl	Ag	1·32845	0·12335
AgBr	Ag	1 74085	0·24077
Al	Al_2O_3	0 53033	1 72455
As	As_2S_3	0 60931	$\bar{1}$ 78484
As	$Mg_2As_2O_7$	0 48275	$\bar{1}$ 68372
As_2O_3	As_2S_3	0 80429	$\bar{1}$ 90541
As_2O_3	$Mg_2As_2O_7$	0 63723	$\bar{1}$ 80430
As_2O_5	As_2S_3	0 93428	$\bar{1}$ 97048
As_2O_5	$Mg_2As_2O_7$	0 74021	$\bar{1}$ 86936
AsO_4	As_2S_3	1 12926	0·52809
AsO_4	$Mg_2As_2O_7$	0 89470	$\bar{1}$·95168
Ba	$BaSO_4$	0 58854	$\bar{1}$·76977
BaO	$BaSO_4$	0·65707	$\bar{1}$ 81761
Bi	Bi_2O_3	0 89677	$\bar{1}$ 95268
B_2O_3	AgCl	0 48752	$\bar{1}$ 68799
Br	AgBr	0 42557	$\bar{1}$ 62897
Cd	CdS	0 77807	$\bar{1}$ 89002
CdO	CdS	0 88883	$\bar{1}$·94881
Ca	CaO	0 71429	1 85387
Ca	$CaCO_3$	0 40000	$\bar{1}$·60206
CaO	$CaCO_3$	0 56000	$\bar{1}$ 74819
C	CO_2	0 27273	$\bar{1}$ 43573
CO_3	CO_2	1 36364	0·13470
Cl	AgCl	0 24724	$\bar{1}$ 39311
ClO_3	AgCl	0·58203	$\bar{1}$·76494
CN	Ag	0 24127	$\bar{1}$ 38250
CN	AgCN	0 19437	$\bar{1}$ 28863
Cr	Cr_2O_3	0 68463	$\bar{1}$ 83545
CrO_3	Cr_2O_3	1 31537	0 11905
CrO_4	Cr_2O_3	1 52562	0 18345
CoO	Co	1 27119	0 10421
Cu	CuO	0 79823	$\bar{1}$ 90213
Cu	Cu_2S	0 79869	$\bar{1}$·90238
CuO	Cu_2S	0 99963	$\bar{1}$ 99984
F	CaF_2	0 48718	$\bar{1}$·68769
Fe	Fe_2O_3	0 70000	$\bar{1}$·84510
H	H_2O	0·11111	$\bar{1}$ 04575
HCl	AgCl	0·25422	$\bar{1}$·40521
HCN	AgCN	0 20184	$\bar{1}$ 30500
Hg	HgS	0·86202	$\bar{1}$·93552

Required.	Weighed as	Factor.	Logarithm.
H_2SO	$BaSO_4$	0 42003	$\bar{1}$·62328
I	AgI	0 54031	$\bar{1}$·73264
K	K_2SO	0·44907	$\bar{1}$·65232
K	K_2PtCl_6	0·16118	$\bar{1}$·20730
K_2O	K_2SO_4	0·54084	$\bar{1}$·73306
K_2O	K_2PtCl_6	0·19411	$\bar{1}$·28805
K_2O	KCl	0 63204	$\bar{1}$·80074
KCl	K_2PtCl_6	0 30712	$\bar{1}$·48731
Mg	$Mg_2P_2O_7$	0 21875	$\bar{1}$·33995
MgO	$Mg_2P_2O_7$	0 36243	$\bar{1}$·55922
Mn	Mn_3O_4	0·72052	$\bar{1}$·85765
MnO	Mn_3O_4	0·93013	$\bar{1}$·96854
MnO_4	Mn_3O_4	1·55895	0·19283
Na	Na_2SO_4	0 32428	$\bar{1}$·51092
Na	NaCl	0 39412	$\bar{1}$·59563
Na_2O	Na_2SO_4	0 43683	$\bar{1}$·64031
Na_2O	NaCl	0 53085	$\bar{1}$·72497
Ni	NiO	0·78194	$\bar{1}$·89532
N	Pt	0·14415	$\bar{1}$·15881
N	$(NH_4)_2PtCl_6$	0 06330	$\bar{2}$ 80143
NH_3	Pt	0 17491	$\bar{1}$ 24291
NH_3	$(NH_4)_2PtCl_6$	0·07683	$\bar{2}$ 88553
NH_4	Pt	0·18522	$\bar{1}$ 26768
NH_4	$(NH_4)_2PtCl_6$	0·08133	$\bar{2}$·91029
Pb	PbO	0·92822	$\bar{1}$·96765
Pb	$PbSO_4$	0 68293	$\bar{1}$·83437
PbO	$PbSO_4$	0 73574	$\bar{1}$ 86673
P	$Mg_2P_2O_7$	0 27838	$\bar{1}$ 44463
P_2O_5	Mg_2P_2O	0 63757	$\bar{1}$·80453
PO_4	$Mg_2P_2O_7$	0 85309	$\bar{1}$·93099
Sb	Sb_2S_3	0·71390	$\bar{1}$ 85364
Sb	Sb_2O_4	0 78948	$\bar{1}$ 89734
Sb_2O_3	Sb_2S_3	0 85668	$\bar{1}$·93282
Sb_2O_3	Sb_2O_4	0 94737	$\bar{1}$·97652
Si	SiO_2	0 46703	$\bar{1}$·66934
Sn	SnO_2	0 78738	$\bar{1}$·89618
Sr	$SrSO_4$	0·47697	$\bar{1}$·67849
SrO	$SrSO_4$	0·56409	$\bar{1}$·75135
S	$BaSO_4$	0·13732	$\bar{1}$·13775
SO_2	$BaSO_4$	0·27440	$\bar{1}$·43837
SO_3	$BaSO_4$	0·34293	$\bar{1}$·53520
SO_4	$BaSO_4$	0.41146	$\bar{1}$·61433
S_2O_3	$BaSO_4$	0 24013	$\bar{1}$·38044
Zn	ZnO	0 80344	$\bar{1}$·90495
Zn	ZnS	0 67104	$\bar{1}$·82675
ZnO	ZnS	0·83521	$\bar{1}$·92180

982. Expansion of Water.

(Kopp).

Temperature, Centigrade	Volume (Volume at 0°=1).	Density (Density at 0°=1).	Volume (Volume at 4°=1).	Density (Density at 4°=1).
0	1·00000	1 000000	1 00012	0 999877
1	0·99995	1·000053	1·00007	0 999930
2	0 99991	1·000092	1 00003	0 999969
3	0 99989	1 000115	1 00001	0 999992
4	0 99988	1·000123	1 00000	1·000000
5	0·99988	1 000117	1 00001	0 999994
6	0 99990	1 000097	1 00003	0 999973
7	0 99994	1 000062	1 00006	0 999939
8	0 99999	1 000014	1 00011	0 999890
9	1·00005	0 999952	1 00017	0 999829
10	1 00012	0 999876	1 00025	0 999753
11	1·00021	0 999785	1 00034	0 999664
12	1·00031	0 999686	1 00044	0 999562
13	1·00043	0 999572	1 00055	0 999449
14	1 00056	0 999445	1 00068	0 999322
15	1 00070	0 999306	1 00082	0 999183
16	1 00085	0 999155	1 00097	0 999032
17	1 00101	0 998992	1 00113	0·998869
18	1·00118	0 998817	1 00131	0 998695
19	1·00137	0·998631	1 00149	0 998509
20	1·00157	0·998435	1·00169	0 998312
21	1 00178	0·998228	1 00190	0·998104
22	1 00200	0·998010	1·00212	0·997886
23	1·00223	0 997780	1 00235	0 997657
24	1 00247	0·997541	1·00259	0 997419
25	1·00271	0 997293	1 00284	0 997170
26	1·00295	0 997035	1 00310	0·996912
27	1·00319	0·996767	1·00337	0·996644
28	1·00347	0·996489	1 00365	0·996367
29	1·00376	0·996202	1 00393	0 996082
30	1·00406	0·996008	1·00423	0 995787

983 Pressure of Aqueous Vapour for each Tenth of a Degree Centigrade from 0° to 30° C.

(Regnault).

Temp C	Press^{e}. in mm of Mercury.	Temp. C.	Press^{e}. in mm of Mercury.	Temp C.	Press^{e} in mm of Mercury.	Temp. C.	Press^{e}. in mm. of Mercury.	Temp. C.	Press^{e}. in mm. of Mercury.
0 0	4 6	6 0	7 0	12 0	10 5	18 0	15·4	24 0	22·2
1	4 6	1	7 0	·1	10 5	1	15 5	·1	22 3
2	4 7	·2	7 1	·2	10 6	·2	15 6	·2	22 5
3	4 7	·3	7 1	·3	10 7	·3	15 7	·3	22 6
4	4 7	·4	7 2	·4	10 7	·4	15 7	·4	22 7
·5	4 8	·5	7 2	·5	10 8	·5	15 8	·5	22 9
6	4 8	·6	7 3	·6	10 9	·6	15 9	·6	23 0
7	4 9	·7	7 3	·7	10 9	·7	16 0	·7	23 1
8	4 9	8	7 4	·8	11 0	·8	16 1	·8	23 3
9	4 9	9	7 4	·9	11 1	·9	16 2	9	23 4
1 0	4 9	7 0	7 5	13 0	11 2	19 0	16 3	25 0	23 5
1	5 0	1	7 5	·1	11 2	1	16 4	1	23·7
2	5 0	2	7 6	·2	11 3	·2	16 6	·2	23 8
3	5 0	3	7 6	·3	11 4	3	16 7	·3	24 0
·4	5 1	·4	7 7	·4	11 5	·4	16 8	·4	24 1
5	5 1	·5	7 8	5	11 5	5	16 9	·5	24 3
6	5 2	6	7 8	·6	11 6	6	17 0	6	24 4
·7	5 2	7	7 9	·7	11 7	7	17 1	·7	24 6
·8	5 2	8	7 9	8	11 8	8	17 2	8	24 7
·9	5 3	9	8 0	9	11 8	9	17 3	9	24 8
2 0	5 3	8 0	8 0	14 0	11 9	20 0	17 4	26 0	25 0
1	5 3	1	8 1	1	12 0	1	17 5	1	25 1
2	5 4	·2	8 1	·2	12 1	2	17 6	2	25 3
3	5 4	·3	8 2	·3	12 1	·3	17 7	3	25 4
4	5 5	·4	8 2	·4	12 2	·4	17 8	4	25 6
·5	5 5	·5	8 3	·5	12 3	·5	17 9	5	25 7
·6	5 5	·6	8 3	·6	12 4	·6	18 0	6	25 9
7	5 6	·7	8 4	7	12 5	·7	18 2	7	26 0
·8	5 6	·8	8 5	·8	12 5	·8	18 3	8	26 2
9	5 6	·9	8 5	9	12 6	·9	18 4	·9	26 4
3 0	5 7	9 0	8 6	15 0	12 7	21 0	18 5	27 0	26 5
1	5 7	1	8 6	1	12 8	·1	18 6	·1	26 7
2	5 8	·2	8 7	·2	12 9	·2	18 7	·2	26·8
3	5 8	·3	8 7	·3	12 9	3	18 8	·3	27 0
·4	5 8	4	8 8	·4	13 0	·4	19 0	·4	27 1
·5	5 9	·5	8 9	·5	13 1	.5	19 1	5	27·3
6	5 9	·6	8 9	·6	13 2	·6	19 2	·6	27·5
7	6 0	·7	9 0	·7	13 3	·7	19 3	·7	27·6
·8	6 0	·8	9 0	·8	13 4	·8	19 4	·8	27·8
·9	6 1	9	9 1	·9	13 5	·9	19 5	·9	27 9
4 0	6 1	10 0	9 2	16 0	13 5	22 0	19 7	28 0	28 1
1	6 1	1	9 2	1	13 6	·1	19 8	·1	28·3
·2	6 2	2	9 3	·2	13 7	·2	19 9	·2	28·4
·3	6 2	3	9 3	·3	13 8	3	20 0	·3	28·6
4	6 3	·4	9 4	·4	13 9	·4	20 1	·4	28 8
5	6 3	5	9 5	·5	14 0	·5	20 3	·5	28 9
6	6·4	6	9 5	·6	14 1	·6	20 4	·6	29 1
·7	6 4	7	9 6	·7	14 2	·7	20 5	·7	29 3
·8	6 4	·8	9 7	·8	14 2	·8	20 6	·8	29·4
9	6 5	·9	9·7	·9	14 3	·9	20 8	·9	29 6
5 0	6 5	11 0	9 8	17 0	14·4	23 0	20 9	29 0	29·8
·1	6 6	1	9 9	·1	14 5	·1	21 0	·1	30 0
·2	6 6	·2	9 9	·2	14 6	·2	21 1	·2	30·1
3	6 7	·3	10 0	·3	14 7	·3	21 3	·3	30 3
·4	6 7	·4	10 1	·4	14 8	·4	21 4	·4	30 5
·5	6 8	·5	10 1	·5	14 9	·5	21 5	·5	30 7
·6	6 8	·6	10 2	·6	15 0	·6	21 7	·6	30 8
·7	6 9	·7	10 3	·7	15 1	7	21 8	·7	31 0
·8	6 9	·8	10 3	·8	15 2	8	21 9	·8	31 2
·9	7 0	·9	10 4	·9	15 3	·9	22 1	·9	31·4

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984. FACTORS FOR CALCULATING THE

The volume of a gas, measured at an ordinary temperature and pressure, the observed volume by the factor. The factor is found in the vertical spheric pressure in mm. in the first column of the table. Thus the factor

Pressure.	7°	8°	9°	10°	11°	12°	13°	14°
730	·9365	·9332	·9299	·9266	·9233	9201	·9169	·9137
731	·9378	·9345	·9311	·9278	·9246	9214	·9182	·9150
732	·9391	·9357	·9324	·9291	·9258	·9226	9194	·9162
733	·9404	·9370	·9337	·9304	·9271	·9239	·9207	9175
734	·9416	·9383	·9350	·9317	·9284	·9252	·9220	·9187
735	·9429	·9396	9362	·9329	·9297	·9264	9232	9200
736	·9442	·9408	·9375	·9342	·9309	·9276	·9244	·9212
737	9455	·9421	9388	·9354	·9321	·9288	·9255	·9225
738	·9468	·9434	·9401	·9368	·9335	·9302	9269	·9237
739	·9481	9447	·9413	·9381	·9348	·9315	·9282	·9250
740	·9493	·9459	·9426	·9393	·9360	·9327	.9294	9262
741	·9506	9472	·9439	9406	·9373	·9340	·9307	·9275
742	·9519	·9485	9452	9419	·9386	·9352	·9320	9287
743	·9532	9498	.9464	·9431	·9398	·9365	·9332	·9300
744	·9545	·9511	9477	·9444	·9411	·9378	·9345	·9312
745	·9558	·9523	·9490	·9457	·9424	·9390	·9357	·9325
746	·9570	·9536	9502	9469	·9436	·9403	·9370	·9337
747	·9583	·9549	·9515	·9482	·9449	·9416	·9383	·9350
748	·9596	·9562	9528	·9495	·9462	·9428	9395	·9362
749	·9609	·9575	·9541	·9507	·9474	·9441	·9408	·9375
750	·9622	·9587	·9554	·9520	·9486	·9453	·9421	3387
751	·9635	·9600	·9566	·9533	·9499	·9466	·9434	·9400
752	·9647	·9613	·9579	·9545	·9512	·9478	·9446	·9412
753	9660	·9626	·9592	·9558	·9524	·9491	·9459	·9425
754	·9673	·9638	·9604	·9571	·9536	·9503	·9471	·9437

VOLUME OF A GAS AT 0° C. AND 760 MM.

may be converted into its volume under normal conditions by multiplying column under the observed temperature and on the same level as the atmo- for 16° and 731 mm. is 0 9086.

Pressure.	15°	16°	17°	18°	19°	20°	21°	22°
730	·9105	·9074	·9042	·9011	·8980	·8950	·8919	·8887
731	·9118	·9086	·9055	·9023	·8993	·8962	·8932	8899
732	·9130	·9099	·9067	·9035	·9005	·8974	·8944	·8911
733	·9143	·9111	9079	9048	·9017	8986	·8956	·8923
734	·9155	·9123	·9092	·9060	·9030	·8999	8968	8935
735	·9168	·9136	9104	9072	·9042	·9011	·8980	8948
736	·9180	·9148	·9116	·9085	·9054	·9023	·8993	8960
737	.9193	9161	·9129	·9098	·9067	·9035	·9005	8972
738	·9205	9172	·9141	·9110	9079	·9047	9017	8984
739	·9218	9186	·9153	·9122	·9091	·9059	·9029	·8996
740	9230	·9198	·9166	·9135	·9103	·9071	·9041	9009
741	·9243	·9211	·9178	·9147	·9116	·9084	·9054	·9021
742	·9255	·9223	·9191	·9159	·9128	·9096	·9066	·9033
743	·9268	·9236	·9203	·9172	·9140	·9108	·9078	9045
744	·9280	·9248	·9215	·9184	·9153	·9120	·9090	·9057
745	·9293	9261	·9228	9197	·9165	·9133	9102	9070
746	·9305	9273	·9240	·9209	·9177	·9145	·9115	·9082
747	·9318	·9285	·9252	·9221	·9190	·9157	·9127	·9094
748	·9330	·9297	·9265	9234	·9202	9169	9139	·9106
749	·9343	·9310	·9277	·9246	·9214	·9182	·9151	·9118
750	·9354	·9322	·9290	·9258	·9226	·9194	.9164	·9130
751	·9367	·9335	·9302	·9270	·9239	·9206	·9176	·9143
752	·9379	·9347	·9314	·9283	·9251	·9218	·9188	·9155
753	·9392	·9360	·9327	·9295	·9263	·9231	·9200	·9167
754	·9404	·9372	·9339	·9307	·9276	·9243	·9212	·9179

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984. FACTORS FOR CALCULATING THE VOLUME

Pressure.	7°	8°	9°	10°	11°	12°	13°	14°
755	9686	·9651	·9617	·9583	·9548	·9516	·9484	·9450
756	·9699	·9664	·9630	·9596	·9561	·9528	·9496	·9462
757	·9712	·9677	·9643	·9609	·9574	9541	·9509	·9475
758	·9724	·9690	·9655	·9621	·9587	·9554	·9522	·9487
759	·9737	·9702	·9668	·9633	·9600	·9566	·9535	9500
760	·9750	·9715	·9681	·9646	·9613	·9579	·9547	·9512
761	·9763	·9728	·9693	9659	·9625	·9591	·9560	9525
762	·9776	·9741	·9706	·9672	·9638	·9604	·9572	·9537
763	·9788	·9754	·9719	·9684	·9650	·9617	·9585	·9550
764	·9801	·9766	·9732	·9697	·9663	·9630	·9598	·9562
765	·9814	·9779	·9744	·9710	·9676	·9642	·9610	·9575
766	.9827	·9792	.9757	·9722	·9688	·9655	·9623	·9587
767	·9840	·9805	.9770	·9735	·9701	·9668	·9635	·9600
768	·9853	·9817	·9783	·9748	·9714	·9680	·9648	·9612
769	·9865	·9830	·9795	·9760	·9726	·9693	·9660	9625
770	·9878	·9843	.9808	·9773	·9739	·9705	·9673	·9637
771	·9891	·9856	·9821	·9786	·9752	·9718	·9685	9650
772	·9904	·9868	·9834	·9798	·9764	·9731	·9698	9662
773	·9917	·9881	·9846	9811	·9777	·9743	·9710	·9675
774	·9930	·9894	·9859	·9824	·9790	·9751	·9723	·9687
775	·9942	·9907	·9872	·9836	·9802	·9768	·9735	·9700
776	·9955	·9919	·9884	·9849	·9815	·9781	·9748	9712
777	·9968	·9932	·9897	·9862	·9828	·9794	·9760	·9725
778	·9981	·9945	·9910	·9874	·9840	·9806	·9773	·9737
779	·9994	·9958	·9923	·9887	·9853	·9819	·9785	·9750
780	1·0007	·9971	·9935	·9899	·9866	·9831	·9798	·9762

OF A GAS AT 0° C. AND 760 MM. (*continued*).

Pressure.	15°	16°	17°	18°	19°	20°	21°	22°
755	·9417	·9385	·9351	·9320	·9288	·9255	·9225	·9191
756	·9429	·9397	·9364	·9332	·9300	·9267	·9237	·9204
757	·9442	·9410	·9376	·9344	·9313	9280	·9249	·9216
758	·9454	·9422	·9389	·9357	·9325	·9292	·9261	·9228
759	·9467	·9434	·9401	·9369	·9337	·9304	·9273	·9240
760	·9479	·9446	·9414	·9381	·9349	·9316	·9286	·9252
761	·9492	9459	·9426	·9394	·9362	·9329	·9298	·9264
762	·9504	9471	·9438	·9406	·9374	·9341	·9310	9276
763	·9517	·9484	·9451	·9418	·9387	·9353	·9322	·9289
764	9529	·9496	·9463	·9431	·9399	·9365	·9334	·9301
765	·9542	·9509	·9475	·9443	·9411	·9378	·9347	·9313
766	·9554	·9521	·9488	·9455	·9424	·9390	·9359	·9325
767	·9567	·9533	·9500	·9468	·9436	·9402	·9371	.9337
768	·9579	·9545	·9512	·9480	·9448	·9414	·9383	9349
769	·9592	·9558	·9525	·9492	·9460	·9427	·9395	·9362
770	·9604	·9571	·9538	·9505	·9472	·9439	·9408	·9374
771	·9617	·9583	·9550	·9517	·9485	·9451	·9420	·9386
772	·9629	·9595	·9562	·9529	·9497	·9463	·9432	·9398
773	9642	·9608	·9575	·9542	·9509	.9476	9444	·9410
774	·9654	·9620	·9587	·9554	·9522	·9488	·9456	·9422
775	·9667	·9632	·9600	·9566	·9534	·9500	·9469	·9435
776	·9679	·9644	·0613	·9579	·9546	·9512	·9481	·9447
777	·9692	·9657	·9625	·9591	·9559	·9525	·9493	·9459
778	·9704	·9670	·9638	·9603	·9571	·9537	·9505	·9471
779	·9717	9682	·9650	·9615	·9582	9549	9517	·9483
780	·9729	·9695	·9662	·9628	·9595	·9562	9530	9496

ALCOHOL TABLE I.

985. PERCENTAGE OF ABSOLUTE ALCOHOL, BY WEIGHT AND BY VOLUME, CORRESPONDING TO THE SPECIFIC GRAVITY TAKEN AT 60° F., OR 15·5° C. WATER = 1.

I. Percentage of Alcohol by Volume.				II. Percentage of Alcohol by Weight.			
Per cent.	Specific Gravity.	Per cent.	Specific Gravity.	Per cent	Specific Gravity	Per cent	Specific Gravity
0	1·0000	50	0·9343	0	1·0000	50	0 9183
1	0 9985	51	0·9323	1	0·9981	51	0 9160
2	0 9970	52	0·9303	2	0·9963	52	0 9138
3	0 9956	53	0 9283	3	0·9944	53	0 9116
4	0 9942	54	0 9263	4	0 9928	54	0 9049
5	0 9928	55	0 9242	5	0 9912	55	0 9072
6	0 9915	56	0 9221	6	0 9896	56	0 9049
7	0 9902	57	0 9200	7	0·9880	57	0 9027
8	0 9890	58	0 9178	8	0 9866	58	0 9004
9	0 9878	59	0 9156	9	0 9852	59	0 8981
10	0·9866	60	0·9134	10	0·9839	60	0 8958
11	0 9854	61	0 9112	11	0 9826	61	0·8935
12	0 9843	62	0 9090	12	0 9813	62	0 8911
13	0 9832	63	0 9067	13	0 9800	63	0 8888
14	0 9821	64	0 9044	14	0 9788	64	0 8865
15	0 9811	65	0 9021	15	0·9775	65	0 8842
16	0 9800	66	0·8997	16	0·9763	66	0 8818
17	0·9790	67	0·8973	17	0·9751	67	0 8795
18	0·9780	68	0 8949	18	0 9739	68	0 8772
19	0·9770	69	0·8925	19	0·9727	69	0 8748
20	0·9760	70	0·8900	20	0·9714	70	0 8724
21	0·9750	71	0·8875	21	0 9702	71	0 8700
22	0·9740	72	0 8850	22	0 9690	72	0 8676
23	0 9729	73	0 8825	23	0 9677	73	0 8652
24	0·9719	74	0 8799	24	0 9664	74	0 8629
25	0 9709	75	0 8773	25	0·9651	75	0 8605
26	0·9698	76	0·8747	26	0·9637	76	0 8581
27	0·9688	77	0 8720	27	0·9622	77	0 8557
28	0·9677	78	0·8693	28	0·9607	78	0 8533
29	0 9666	79	0·8666	29	0·9592	79	0 8509
30	0 9655	80	0·8639	30	0·9577	80	0 8484
31	0 9643	81	0 8611	31	0·9560	81	0 8459
32	0 9631	82	0 8583	32	0 9544	82	0 8235
33	0 9618	83	0 8555	33	0·9526	83	0 8409
34	0 9605	84	0 8526	34	0·9508	84	0 8385
35	0·9592	85	0·8496	35	0·9490	85	0 8359
36	0 9579	86	0 8466	36	0·9472	86	0·8333
37	0·9565	87	0·8436	37	0·9453	87	0 8307
38	0·9550	88	0 8405	38	0·9433	88	0 8282
39	0 9535	89	0 8373	39	0·9413	89	0 8256
40	0 9519	90	0 8339	40	0·9394	90	0 8229
41	0·9503	91	0·8306	41	0·9374	91	0 8203
42	0·9487	92	0·8272	42	0·9353	92	0 8176
43	0·9470	93	0 8237	43	0 9332	93	0·8149
44	0·9452	94	0·8201	44	0·9311	94	0·8122
45	0·9435	95	0·8164	45	0·9291	95	0·8094
46	0·9417	96	0·8125	46	0·9269	96	0 8065
47	0·9399	97	0·8084	47	0·9249	97	0·8036
48	0·9381	98	0·8047	48	0·9227	98	0·8006
49	0 9362	99	0·7995	49	0·9204	99	0·7976
50	0·9343	100	0·7946	50	0·9183	100	0·7946

ALCOHOL TABLE II.

986. PERCENTAGE OF ABSOLUTE ALCOHOL BY WEIGHT, AND OF PROOF-SPIRIT BY VOLUME, IN DILUTE ALCOHOL OF KNOWN SPECIFIC GRAVITY. WATER = 1000.

Specific Gravity at 60° F or 15° 5 C.	Absolute Alcohol per cent. by Weight.	Proof-spirit per cent. by Volume	Specific Gravity at 60° F or 15° 5 C.	Absolute Alcohol per cent by Weight.	Proof-spirit per cent by Volume.	Specific Gravity at 60° F. or 15° 5 C.	Absolute Alcohol per cent. by Weight.	Proof-spirit per cent by Volume
995 0	2·74	6 02	992 8	4·02	8 81	990 6	5 39	11·79
994 9	2·79	6 13	992 7	4 08	8 94	990 5	5 45	11·92
994 8	2 85	6 26	992·6	4 14	9 07	990 4	5 51	12 05
994 7	2·91	6·39	992 5	4 20	9 20	990 3	5 58	12 20
994·6	2 97	6 52	992 4	4·27	9 36	990 2	5 64	12 33
994 5	3·02	6 63	992 3	4 33	9 49	990 1	5 70	12 46
994 4	3 08	6 76	992·2	4 39	9·62	990 0	5 77	12 61
994 3	3 14	6·89	992 1	4·45	9·75			
994·2	3 20	7 02	992 0	4 51	9 88	989 9	5 83	12 74
994 1	3 26	7 16				989 8	5 88	12 87
994 0	3 32	7 29	991 9	4·57	10·01	989 7	5 96	13 02
			991·8	4 64	10 16	989 6	6 02	13 15
993 9	3 37	7 40	991 7	4 70	10 29	989 5	6 09	13 30
993·8	3 43	7·53	991 6	4 76	10 42	989 4	6 15	13 43
993·7	3 49	7 66	991 5	4 82	10·55	989 3	6 22	13 59
993 6	3 55	7·79	991 4	4 88	10·68	989 2	6 29	13 74
993 5	3 61	7·92	991·3	4 94	10 81	989 1	6 35	13 87
993 4	3·67	8·05	991 2	5 01	10 96	989 0	6·42	14 02
993 3	3 73	8·18	991·1	5 07	11·09			
993·2	3·78	8·29	991 0	5·13	11 22	988 9	6 49	14·17
993·1	3 84	8 42				988 8	6 55	14 30
993 0	3·90	8·55	990·9	5 20	11 38	988 7	6·62	14·45
			990·8	5·26	11·51	988 6	6·69	14·60
992·9	3 96	8 68	990 7	5·32	11·64	968·5	6·75	14·73

SULPHURIC ACID.

987. Percentage by Weight of H_2SO_4 present in Aqueous Solution of known Specific Gravity at 15·5° C.

(Lunge and Isler.)

Specific Gravity.	Percentage of H_2SO_4.	Specific Gravity.	Percentage of H_2SO_4	Specific Gravity.	Percentage of H_2SO_4.
1·005	0 83	1·190	26·04	1 375	47·47
1·010	1·57	1 195	26 68	1 380	48 00
1 015	2·30	1 200	27·32	1 385	48 53
1·020	3·03	1 205	27 95	1 390	49 06
1 025	3 76	1 210	28 58	1·395	49 59
1 030	4 49	1·215	29 21	1·400	50·11
1·035	5 23	1 220	29 84	1 405	50 63
1·040	5·96	1 225	30 48	1 410	51 15
1 045	6 67	1 230	31·11	1 415	51 66
1·050	7·37	1 235	31 70	1 420	52 15
1 055	8 07	1·240	32·28	1 425	52 63
1 060	8 77	1 245	32 86	1 430	53 11
1·065	9 47	1·250	33 43	1 435	53 59
1·070	10·19	1 255	34·00	1·440	54 07
1 075	10·90	1·260	34·57	1 445	54 55
1 080	11 60	1 265	35 14	1 450	55 03
1 085	12 30	1 270	35·71	1 455	55·50
1 090	12 99	1·275	36 29	1·460	55 97
1 095	13 67	1 280	36 87	1·465	56 43
1 100	14 35	1 285	37 45	1 470	56·90
1 105	15 03	1·290	38 03	1·475	57 37
1·110	15 71	1 295	38 61	1·480	57 83
1 115	16·36	1 300	39 19	1·485	58 28
1·120	17 01	1 305	39 77	1·490	58 74
1 125	17·66	1 310	40 35	1·495	59 22
1·130	18·31	1·315	40 93	1·500	59 70
1·135	18 96	1 320	41·50	1·505	60 18
1 140	19 61	1·325	42·08	1·510	60 65
1·145	20 26	1·330	42 66	1 515	61·12
1·150	20·91	1·335	43 20	1 520	61·59
1·155	21 55	1·340	43·74	1·525	62 06
1·160	22 19	1·345	44·28	1·530	62·53
1·165	22·83	1 350	44 82	1 535	63·00
1·170	23·47	1·355	45·35	1·540	63 43
1·175	24·12	1 360	45·88	1·545	63·85
1·180	24·76	1·365	46 41	1 550	64 26
1·185	25·40	1·370	46·94	1·555	64 67

SULPHURIC ACID (*continued*).

Specific Gravity.	Percentage of H_2SO_4	Specific Gravity.	Percentage of H_2SO_4	Specific Gravity.	Percentage of H_2SO_4
1·560	65 08	1·700	77 17	1 823	90 60
1 565	65 49	1 705	77 60	1 824	90 80
1 570	65 90	1·710	78 04	1 825	91 00
1 575	66 30	1 715	78 48	1 826	91 25
1 580	66 71	1·720	78 92	1 827	91 50
1 585	67·13	1 725	79 36	1 828	91 70
1 590	67 59	1 730	79 80	1 829	91 90
1 595	68 05	1 735	80 24	1 830	92 10
1 600	68 51	1 740	80 68	1 831	92 30
1 605	68 97	1 745	81 12	1 832	92 52
1 610	69 43	1 750	81 56	1 833	92 75
1 615	69 89	1 755	82 00	1 834	93 05
1·620	70 32	1 760	82 44	1 835	93 43
1·625	70 74	1 765	82 88	1 836	93 80
1 630	71 16	1 770	83 32	1 837	94 20
1 635	71 57	1 775	83 90	1 838	94 60
1 640	71·99	1 780	84 50	1 839	95 00
1·645	72 40	1 785	85 10	1 840	95 60
1 650	72 87	1 790	85 70	1 8405	95 95
1 655	73 23	1 795	86 30	1 8410	97 00
1·660	73 64	1 800	86 90	1 8415	97 70
1 665	74 07	1 805	87 60	1 8410	98·20
1 670	74 51	1 810	88 30	1 8405	98 70
1 675	74 97	1 815	89 05	1 8400	99 20
1 680	75 42	1 820	90 05	1 8395	99 45
1·685	75 86	1 821	90 20	1 8390	99 70
1·690	76 30	1 822	90 40	1 8385	99 95
1·695	76 73				

HYDROCHLORIC ACID.

988. PERCENTAGE BY WEIGHT OF HCl PRESENT IN AQUEOUS SOLUTION OF KNOWN SPECIFIC GRAVITY AT 15·5° C., COMPARED WITH WATER AT 4° C. AND REDUCED TO VACUUM AS UNITY.

(Lunge and Marchlewski.)

Specific Gravity.	Percentage of Hydrochloric Acid	Specific Gravity	Percentage of Hydrochloric Acid.
1·000	0·16	1 105	20 97
1 005	1·15	1 110	21 92
1·010	2 14	1 115	22 86
1·015	3 12	1 120	23 82
1·020	4 13	1·125	24 78
1·025	5 15	1·130	25 75
1·030	6 15	1·135	26·70
1·035	7 15	1 140	27·66
1·040	8·16	1·145	28 61
1 045	9 16	1 150	29 57
1·050	10 17	1·155	30 55
1·055	11·18	1·160	31·52
1·060	12 19	1·165	32 49
1·065	13 19	1·170	33 46
1 070	14 17	1 175	34 42
1 075	15 16	1 180	35 39
1·080	16·15	1 185	36 31
1 085	17 13	1·190	37 23
1·090	18 11	1·195	38 16
1 095	19 06	1 200	39 11
1·100	20 01		

NITRIC ACID.

989. PERCENTAGE BY WEIGHT OF HNO_3 PRESENT IN AQUEOUS SOLUTION OF KNOWN SPECIFIC GRAVITY AT 15·5° C., COMPARED WITH WATER AT 4° C. AND REDUCED TO VACUUM AS UNITY.

(Lunge and Rey.)

Specific Gravity	Percentage of HNO_3	Specific Gravity	Percentage of HNO_3	Specific Gravity	Percentage of HNO_3
1 000	0 10	1·175	28 63	1 350	55 79
1·005	1 00	1 180	29 38	1 355	56 66
1 010	1 90	1 185	30 13	1 360	57 57
1·015	2 80	1·190	30 88	1 365	58 48
1 020	3 70	1 195	31 62	1 370	59 39
1·025	4 60	1 200	32·36	1 375	60 30
1·030	5 50	1 205	33 09	1·380	61·27
1·035	6 38	1 210	33 82	1·385	62 24
1 040	7 26	1 215	34 55	1 390	63 23
1 045	8 13	1 220	35 28	1·395	64 25
1 050	8 99	1·225	36 03	1·400	65 30
1·055	9 84	1 230	36 78	1 405	66 40
1 060	10 68	1 235	37·53	1 410	67·50
1 065	11·51	1 240	38 29	1 415	68 63
1 070	12 33	1 245	39 05	1·420	69 80
1 075	13 15	1 250	39 82	1 425	70 98
1 080	13 95	1 255	40 58	1 430	72 17
1 085	14·74	1 260	41·34	1 435	73 39
1 090	15·33	1·265	42 10	1 440	74 68
1 095	16·32	1·270	42 87	1 445	75·98
1·100	17 11	1 275	43 64	1 450	77·28
1 105	17 89	1 280	44 41	1 455	78 60
1 110	18 67	1 285	45 18	1 460	79 98
1·115	19 45	1·290	45 95	1 465	81·42
1·120	20 23	1 295	46 72	1 470	82·90
1·125	21 00	1·300	47 49	1 475	84 45
1 130	21·77	1 305	48 26	1 480	86 05
1·135	22·54	1 310	49 07	1 485	87·70
1 140	23 31	1 315	49 89	1 490	89 60
1·145	24 08	1 320	50 71	1 495	91·60
1·150	24 84	1·325	51 53	1·500	94·09
1 155	25 60	1 330	52 37	1 505	96 39
1·160	26 36	1 335	53 22	1 510	98·10
1·165	27 12	1·340	54 07	1 515	99 07
1·170	27 88	1 345	54 93	1·520	99·67

POTASSIUM HYDRATE.

990. Percentage by Weight of KOH in Aqueous Solution of known Specific Gravity at 15·5° C.

(Lunge.)

Specific Gravity.	Percentage of KOH	Specific Gravity.	Percentage of KOH.	Specific Gravity.	Percentage of KOH
1 007	0 9	1·162	18 6	1·370	36 9
1 014	1·7	1 171	19·5	1 383	37 8
1 022	2 6	1 180	20 5	1·397	38 9
1 029	3 5	1 190	21 4	1 410	39 9
1·037	4 5	1 200	22 4	1 424	40 9
1 045	5 6	1 210	23 3	1 438	42·1
1 052	6 4	1 220	24 2	1 453	43 4
1·060	7 4	1 231	25 1	1 468	44 6
1 067	8 2	1 241	26 1	1 483	45 8
1 075	9 2	1 252	27 0	1 498	47 1
1 083	10 1	1 263	28 0	1 514	48 3
1·091	10 9	1 274	28 9	1 530	49 4
1·100	12·0	1·285	29 8	1 546	50 6
1·108	12·9	1·297	30 7	1 563	51·9
1·116	13 8	1 308	41 8	1·580	53 2
1·125	14 8	1 320	32 7	1 597	54·5
1·134	15 7	1 332	33 7	1 615	55 9
1·142	16 5	1 345	34 9	1 634	57·5
1·152	17·6	1 357	35·9		

SODIUM HYDRATE.

991. PERCENTAGE BY WEIGHT OF NaOH IN AQUEOUS SOLUTION OF KNOWN SPECIFIC GRAVITY AT 15·5° C.

(Lunge.)

Specific Gravity.	Percentage of NaOH.	Specific Gravity.	Percentage of NaOH.	Specific Gravity	Percentage of NaOH.
1 007	0 61	1 142	12 64	1·320	28 83
1 014	1 20	1·152	13 55	1·332	29 93
1 022	2·00	1·162	14 37	1 345	31·22
1·029	2·71	1·171	15 13	1 357	32 47
1 036	3 35	1·180	15 91	1·370	33 69
1·045	4 00	1·190	16 77	1·383	34·96
1·052	4 64	1·200	17 67	1 397	36 25
1 060	5 29	1 210	18·58	1 410	37·47
1 067	5·87	1 220	19·58	1·424	38 80
1·075	6 55	1 231	20 59	1 438	39 99
1·083	7 31	1 241	21 42	1 453	41 41
1 091	8 00	1 252	22·64	1·468	42 83
1·100	8 68	1 263	23 37	1·483	44 38
1·108	9 42	1 274	24 81	1 498	46·15
1·116	10 06	1 285	25 80	1 514	47·60
1 125	10 97	1 297	26 83	1 530	49 02
1·134	11 84	1 308	27 80		

AMMONIA.

992. PERCENTAGE BY WEIGHT OF NH_3 IN AQUEOUS SOLUTION OF KNOWN SPECIFIC GRAVITY AT 15·5° C.

(Lunge and Wiernik)

Specific Gravity.	Percentage of NH_3.	Specific Gravity.	Percentage of NH_3	Specific Gravity.	Percentage of NH_3
1 000	0 00	0·960	9 91	0 920	21 75
0 998	0 45	0 958	10 47	0 918	22 39
0 996	0 91	0 956	11 03	0 916	23 03
0 994	1 37	0·954	11·60	0 914	23 68
0 992	1 84	0 952	12·17	0 912	24 33
0 990	2 31	0 950	12 74	0 910	24 99
0·988	2 80	0 048	13 31	0 908	25 60
0 986	3 30	0·946	13 88	0 906	26 31
0 984	3 80	0 944	14 46	0 904	26 98
0 982	4 30	0 942	15 04	0 902	27·65
0 980	4 80	0 940	15 63	0 900	28·33
0 978	5 30	0 938	16·22	0·898	29 01
0 976	5 80	0·936	16·82	0 896	29 69
0·974	6 30	0·934	17·42	0 894	30 37
0·972	6 80	0·932	18 03	0·892	31·05
0·970	7·31	0·930	18 64	0·890	31·75
0 968	7·82	0·928	19·25	0·888	32 50
0·966	8·33	0·926	19 87	0 886	33·25
0·964	8·84	0·924	20 49	0 884	34·10
0·962	9·35	0 922	21 12	0·882	34·95

Oils and Fats.							
Name. Mainly in order of Iodine values.	Specific gravity.		Melting-point.	Insoluble fatty acids + unsaponifiable (Hehner value)	Reichert value (R) or Reichert-Meissl value (RM)	Saponification value. (Koettstorfer value)	Iodine value.
	C°.		C°.	Per cent	C c of $\frac{N}{10}$ KOH	Milligrams of KOH	Per Cent
Drying Oils.							
Linseed	15	0 9315-0 9345	-20	95 5	—	192-195	171-201
Hemp-seed	15	0 9255-0 9280	—	—	—	192 5	148
Walnut, or nut-oil	15	0 9250-0 9260	—	95 4	—	195	145
Poppy-seed	15	0 9240-0 9270	—	95 2	0 0 (R M)	195	133-143
Semi-Drying Oils.							
Cotton-seed	15	0 9220-0 9250	3-4	95-96	—	193-195	108-110
Sesame	15	0 9230-0 9237	—	95 7	1 2 (R M)	189-193	103-108
Rape (Colza)	15 5	0 9132-0 9168	—	95 1	0 3	170-179	94-102
Croton	15	0 9500	—	89 0	12-13 6 (R M)	210-215	102-104
Castor	15 5	0 9600-0 9679	—	—	1 4	183-186	83-86
Non-Drying Oils.							
Almond	15	0 9175-0 9195	—	96 2	—	191	93-97
Arachis	15	0 9170-0 9209	0	95 8	—	190-196	83-100
Olive	15	0 916	—	95	0 3	185-196	79-88
Marine Animal Oils							
Cod-liver	15	0 9210-0 9270	—	95 3	—	171-189	167
Seal	15	0 9155-0 9263	—	95 45	0 07-022	189-196	127-141
Whale	15 5	0 9250	—	93 5	0 7-2 04	188 0	121-136

Oils and Fats.				Mixed Fatty Acids.					
Maumené Thermal Test.	Acetyl value	Acid value.	Unsaponifiable matter	Specific gravity		Melting-point.	Neutralisation number, or Mean molecular weight.	Iodine value	
C°		Milligrams of KOH	Per Cent	C°.		C°.	Milligrams of KOH	Mixed Acids	Liquid Acids
110–12	3 98	0 8–8 4	0 42–1 1	15 5	0 9233	17–21	197	179–209 8	190–201
97	—	—	1 08	—	—	18–19	—	141	—
103	—	—	—	—	—	16–18	—	150	167
88	—	0 7–11 0	0 43	100	0 8886	20 5	199	139	150
75–90	7 6–18	0 0	0 73–1 64	15 5	0 920–6 0 9219	35–38	202–208	111–115	147–151
65 5	—	0 23–66	0 95–1 32	—	—	26–32	200·4	110 45	129–136
55–64	14 7	1 4–13 2	0 58–1 0	100	0 8758	16–19	185 0	99–103	121–125
—	19–32	—	0 55	—	—	—	201	111·5	—
46–47	-	0 14	—	15 5	0 9509	13	192·1	87–93	106 9
52 5	—	1 5	—	—	—	13–14	204	93–96 5	101·7
45–51	—	1 2–32	0 54–0 94	100	0 8790	27 7–32	201 6	96–103	105–128
41 5–45	10 64	1 9–50	0 46–1 0	100	0 8749	24–27	193	86–90	95·5–103 5
102–113	4–8	1–25	0 54–7 83	—	—	21–25	204–207	130 5–170	—
92	16 5	1 9–40	0 38–1 4	—	—	22–33	193 2	—	—
92	—	0 5–37	0·92–3 72	100	0 8922	27 0	—	131·2	144·7

Oils and Fats

Name. Mainly in order of Iodine values	Specific gravity.		Melting-point	Insoluble fatty acids + unsaponifiable (Hehner value)	Reichert value (R) or Reichert-Meissl value (RM)	Saponification value (Koettstorfer value)	Iodine value
	C°.		C°	Per cent	Cc of $\frac{N}{10}$ KOH	Milligrams of KOH	Per cent
Terrestrial Animal Oils							
Sheep's foot	15	0 9175	—	—	—	194 7	74 2
Horse's foot	15	0 913–0 927	—	—	—	195 9	73 8–90
Neat's foot	15	0 914–0 916	—	95·2	1 0	194 3	69 3–70 4
Other Oils.							
Rosin oil (distilled from crude rosin)	15	0 966–0 990	—	—	—	10–35	40–80
Mineral oil (burning and lubricating oil from petroleum)						0	0–15
Vegetable Fats							
Cotton-seed stearine	15	0 9188–0 9230	29–32	95 9	—	195	90–103
Palm oil	15	0 921	27–42·5	94 97	0 5	196–202	51 5
Cacao butter (cocoa butter)	15	0 9500–0 976	28–33	94 59	0 2–0 8 (R M)	193 55	32–41
Palm-nut oil	15	0 9520	23–28	87 6–91 1	5–6 (R M)	242–250	13–14
Cocoa-nut oil	40	0 9115	21–24	88 6–90	7–8 4 (R M.)	246–260	8–9 5
Japan wax	15	0 9700–0 9800	50–54	90 6	—	217–237 5	4 9–8 5
Animal Fats							
Lard	15	0 934–0·938	36–40 5	93–96	—	195 4	50–70
Bone	15	0 914–0 916	21–22	—	—	199	55·4
Beef tallow	15	0 943–0·952	45–50	95 6	0 25	190 9–200	41–47 5
Mutton tallow	15	0 937–0 953	44–45	95 5	—	193 2–200	38–46
Butter	15	0 926–0 940	28–33	86 5–89 8	12·5–15 2	227	26–38

Oils and Fats				Mixed Fatty Acids					
Maumené thermal test	Acetyl value	Acid value	Unsaponifiable matter	Specific gravity		Melting-point	Neutralisation number, or Mean molecular weight.	Iodine value.	
C°		Milligrams of KOH	Per cent	C°		C°	Milligrams of KOH	Mixed Acids.	Liquid Acids
49·5	—	—	—	—	—	—	—	—	—
38	13	—	—	—	—	—	—	—	—
47–48·5	22·0	—	—	100	0·8713–0·8749	29·8–30·8	202·9–206·3	61·9–63·3	—
7·2	—	—	—	—	—	—	—	—	—
0·38	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	27–30	—	94	—
—	18	24–200	—	100	0·8701	47–50	205·6	53·3	94·6
—	2·8	1·1–1·88	—	—	—	48–50	190	33–39	—
—	1·9–8·4	8·36	—	—	—	25–28·5	258–264	12·0	—
—	0·9–12·3	5–50	—	98–99	0·8354	25–27	258–266	8·4–9·3	51
—	27–31·2	7–33	1·1–1·63	98–99	0·8480	56–62	213·7	—	—
24–27·5	2·6	0·54–1·28	0·23	99	0·8445	43–44	201·8	64	92·1
—	4·2	1·6	—	15	0·9300	44–46	204·5	55·5	—
—	11·3	29·6	0·5–1·8	—	—	30	200	55·7–57·4	—
—	2·7–8·6	3·5–50·0	—	100	0·8698	43–44	197·2	41·3	92·4
—	1·9–8·6	0·45–35·38	—	37·75	0·9075	38–40	210–220	28–31	—

Waxes.							
Name. Mainly in order of Iodine values.	Specific gravity.		Melting-point.	Acid value.	Saponification value (Koettstorfer value)	Reichert value (R) or Reichert-Meissl value (RM).	Iodine value
	C°.		C°	Milligrams of KOH	Milligrams of KOH	Cc of $\frac{N}{10}$ KOH	Per cent
Liquid Waxes.							
Sperm oil . .	15	0 8799-0 8835	—	—	125 2-132 6	1 3	81 90
Arctic sperm oil	15	0 8764	—	—	.123-135 9	1 4	67-82 1
Solid Waxes.							
Carnauba wax	15	0 990-0 999	85-86	4-7	79-95	—	13 5
Wool wax, wool grease	17	0 9413-0 9449	31-35	—	102 4	—	17 1-28 9
Beeswax .	15	0 964-0 970	61 5	19-21	90-98	0 34-0 54	7 9-11
Spermaceti (Cetin)	15	0 905-0 960	42-49	—	123-135	—	—
Insect wax . .	15	0 926-0 970	80 5-83	—	80 5-93	—	—

Waxes		Mixed Fatty Acids						Alcohols + Unsaponifiable		
Maumene Thermal Test	Acetyl value.	Fatty acids	Specific gravity		Melting-point.	Neutralisation number, or Mean molecular weight	Iodine value		Melting-point	Iodine value.
		Per cent	C°.		C°.		Per cent	Per cent	C°	Per cent
51	4 5–6 4	60–64	15 5	0 899	13 3	281–294	83 2–85 6	37–41	25·5–25 7	65
41–47	4 1–6 4	61–65	—	—	10 3–10 8	—	82 7	31 7–42·6	23 5–26 5	65
—	55 24	—	—	—	—	—	—	55	—	—
—	23 3	59 8	—	—	41 8	327 5	17	43 1–51 8	33 5	26 4–36
—	15 24	—	—	—	—	—	—	52–55	—	—
—	2 63	—	—	—	—	—	—	51 5	—	—
—	—	—	—	—	—	—	—	—	—	—

RELATION OF DEGREES TWADDELL TO SPECIFIC GRAVITY.

994. The relation of degrees Twaddell to the specific gravity of a liquid is most readily stated by assuming the specific gravity of water to be 1000 instead of unity. On this assumption—

$$\text{Degrees Twaddell} = \frac{\text{Specific gravity} - 1000}{5}$$

$$\text{Specific gravity} = (\text{Degrees Twaddell} \times 5) + 1000.$$

THERMOMETRIC SCALES.

995. There are two different thermometric scales in use in this country, the Centigrade and Fahrenheit; the former of these is now always used for scientific purposes. The two scales are mutually convertible by the following formulæ, in which F° represents a temperature on the Fahrenheit scale, and C° a temperature on the Centigrade scale:

$$F° = \frac{9\ C°}{5} + 32$$

$$C° = \frac{5(F° - 32)}{9}$$

The temperatures referred to in this treatise are given on the Centigrade scale.

WEIGHTS AND MEASURES.

996. The corresponding values of the Metric and English weights and measures are given below. The use of the Metric or decimal system is strongly recommended on account of its extreme simplicity. The smaller denominations are a tenth, hundredth, thousandth, &c., of the unit chosen; they are designated by the Latin prefixes deci-, centi-, milli-, &c. The higher denominations are 10 times, 100 times, 1000, &c., times the unit, and are named by the Greek prefixes deca-, hecto-, kilo-, &c. Examples of the use of these prefixes will be found in the Tables which follow.

The "unit of length" in the Metric system is the "metre," which is equal to 39·37 inches. The "unit of volume" is the "litre," or cubic decimetre. The "unit of weight" is the gram, which is the weight of one cubic centimetre of distilled water at 4° C.

The chief conveniences arising from the use of this system are:

(1) That all the different denominations can be written as one; since they are either multiples by ten, or are decimal fractions, of the unit. Thus 5 decagrams, 3 grams, 4 decigrams, 8 milligrams would be written 53 408 grams

(2) That since one cubic centimetre of water at 4° C. weighs a gram, the *weight* of water in grams may be obtained from its *measure*, by simply converting the volume into cubic centimetres. The number thus obtained will represent at once the corresponding weight of water in grams This weight is only strictly accurate when the water is measured at 4° C. But for ordinary purposes the error introduced, when the water is at the temperature of the air, is too small to be of any importance in the preparation of solutions. The correction for water at temperatures different from 4° C. may be obtained from paragraph 982.

The Weights and Measures which are most frequently used for chemical purposes are the gram, the millimetre (mm.), the litre, and the cubic centimetre (c.c.) which is one-thousandth of a litre.

997. ENGLISH WEIGHTS AND MEASURES.

APOTHECARIES WEIGHT

lb		oz		drms.		scruples		grains
1	=	12	=	96	=	288	=	5760
		1	=	8	=	24	=	480
				1	=	3	=	60
						1	=	20

AVOIRDUPOIS WEIGHT.

lb		oz		drms		grains
1	=	16	=	256	=	7000
		1	=	16	=	437·5
				1	=	27·343

IMPERIAL MEASURE.

gallon.		pints.		fluid oz		fluid drms
1	=	8	=	160	=	1280
		1	=	20	=	160
				1	=	8

1 gallon = 70,000 grains of water at 16° 7 C.
1 fluid ounce = $\frac{1}{20}$ pint = 437·5 " " "
1 gallon = 277·280 cubic inches. " "
1 fluid ounce = 1·733 "

998. METRIC WEIGHTS AND MEASURES.

MEASURES OF LENGTH.

	metre		inches		ENGLISH. mile	furlong	yards	feet	inches.
Millimetre =	0·001	=	0·03937	=	.	.	.	.	0·03937
Centimetre =	0·01	=	0·39371	=	.	.		.	0·39371
Decimetre =	0·1	=	3·93708	=	.	.	.	.	3·9371
Metre =	1·0	=	39·37079	=	.	.	.	3	3·371
Decametre =	10·0	=	393·70790	=	.	.	10	2	9·7
Hectometre =	100·0	=	3937·07900	=	.	.	109	1	1
Kilometre =	1000·0	=	39370·79000	=	.	4	213	4	10·2
Myriometre =	10000·0	=	393707·90000	=	6	1	156	0	6

1 inch = 0·0254 metre = 2·5399 centimetres
1 foot = 0·3048
1 sq. inch = 6·4514 sq. centimetres.

MEASURES OF CAPACITY.

1 litre = 1 cubic decimetre.

	litre	cubic inches	pints
Millilitre, or Cubic centimetre (c c)	= 0 001	= 0 06103	= 0 00176
Centilitre	= 0 01	= 0 61027	= 0 01761
Decilitre	= 0 1	= 6 1027	= 0 17608
Litre	= 1 0	= 61 027	= 1 76077
Decalitre	= 10 0	= 610 27	= 17 60773
Hectolitre	= 100 0	= 6102 7	= 176 07734
Kilolitre	= 1000 0	= 61027 0	= 1760 77341
Myrialitre	= 10000 0	= 610270 0	= 17607 73414

1 cubic inch = 0 01639 litre.
1 cubic foot = 28 31531 litres.
1 gallon = 4 54336 „

MEASURES OF WEIGHT.

1 gram = the weight of 1 cubic centimetre (c c) of water at 4° C.

	grams	grains	Avoirdupois.
Milligram	= 0 001	= 0 01543	
Centigram	= 0 01	= 0 15432	
Decigram	= 0 1	= 1 54323	
Gram	= 1 0	= 15 43235	lbs oz drms
Decagram	= 10 0	= 154 32349	= 0 0 5 65
Hectogram	= 100 0	= 1543 23488	= 0 3 8 5
Kilogram	= 1000 0	= 15432 34880	= 2 3 5
Myriogram	= 10000 0	= 154323 48800	= 22 1 2

1 grain = 0 0649 gram.
1 oz (Troy) = 31 1035 grams.
1 lb. (Avoirdupois) = 453 593 „

999. DATA FOR CONVERSION OF WEIGHTS AND MEASURES.

Cubic feet × 6 2355 = gallons.
Cubic inches × 0·003607 = gallons.
Ounces × 28 349 = grams.
Grains × 0·0648 = grams.
Grams × 15 432 = grains
Pints × 567 936 = cubic centimetres.
Gallons × 4 548 = litres.
Litres × 0 22 = gallons.

Centimetres × 0 3937 = inches.
Inches × 2·54 = centimetres.

$$\frac{\text{Grains per gallon}}{0\,7} = \text{parts per 100.000.}$$

Parts per 100,000 × 0 7 = grains per gallon.

Note.—In paragraph 116 there will be found the tabulated equivalents for capacity in liquid ounces and in c.c., and for lengths in inches and in cm.

1000. USEFUL MEMORANDA.

Weight of 1 c.c of dry hydrogen at 0° C and 760 mm. = 0 0000899 gram.
Weight of 1 c.c. of dry nitrogen at 0° C and 760 mm. = 0 001257 gram
Weight of 1 c.c of dry air at 0° C and 760 mm. = 0 001293 gram.
1 gram of hydrogen at 0° C and 760 mm. measures 11 12 litres.
1 gram of air at 0° C and 760 mm. measures 0 773 litre.
Specific gravity of hydrogen, air as unit = 0 0695
Specific gravity of air, hydrogen as unit = 14 38
Weight of 1 c.c. of mercury at 0° C = 13·596 grams
Coefficient of expansion for gases = $\frac{1}{273}$ = 0·003665
Average percentage of oxygen in air, by volume = 20·96.

1001. Logarithms.

	0	1	2	3	4	5	6	7	8	9	Proportional Parts								
											1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4	8	12	17	21	25	29	33	37
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	11	15	19	23	26	30	34
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3	7	10	14	17	21	24	28	31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	6	10	13	16	19	23	26	29
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3	6	9	12	15	18	21	24	27
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	6	8	11	14	17	20	22	25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	13	16	18	21	24
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	2	5	7	10	12	15	17	20	22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16	19	21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	7	9	11	13	16	18	20
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7

Logarithms—*continued.*

	0	1	2	3	4	5	6	7	8	9	Proportional Parts.								
											1	2	3	4	5	6	7	8	9
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	3	4

1002. Anti-logarithms.

	0	1	2	3	4	5	6	7	8	9	Proportional Parts.								
											1	2	3	4	5	6	7	8	9
·00	1000	1002	1005	1007	1009	1012	1014	1016	1019	1021	0	0	1	1	1	1	2	2	2
·01	1023	1026	1028	1030	1033	1035	1038	1040	1042	1045	0	0	1	1	1	1	2	2	2
·02	1047	1050	1052	1054	1057	1059	1062	1064	1067	1069	0	0	1	1	1	1	2	2	2
·03	1072	1074	1076	1079	1081	1084	1086	1089	1091	1094	0	0	1	1	1	1	2	2	2
·04	1096	1099	1102	1104	1107	1109	1112	1114	1117	1119	0	1	1	1	1	2	2	2	2
05	1122	1125	1127	1130	1132	1135	1138	1140	1143	1146	0	1	1	1	1	2	2	2	2
·06	1148	1151	1153	1156	1159	1161	1164	1167	1169	1172	0	1	1	1	1	2	2	2	2
07	1175	1178	1180	1183	1186	1189	1191	1194	1197	1199	0	1	1	1	1	2	2	2	2
08	1202	1205	1208	1211	1213	1216	1219	1222	1225	1227	0	1	1	1	1	2	2	2	3
09	1230	1233	1236	1239	1242	1245	1247	1250	1253	1256	0	1	1	1	1	2	2	2	3
10	1259	1262	1265	1268	1271	1274	1276	1279	1282	1285	0	1	1	1	1	2	2	2	3
11	1288	1291	1294	1297	1300	1303	1306	1309	1312	1315	0	1	1	1	2	2	2	2	3
12	1318	1321	1324	1327	1330	1334	1337	1340	1343	1346	0	1	1	1	2	2	2	2	3
13	1349	1352	1355	1358	1361	1365	1368	1371	1374	1 77	0	1	1	1	2	2	2	3	3
·14	1380	1384	1387	1390	1393	1396	1400	1403	1406	1409	0	1	1	1	2	2	2	3	3
15	1413	1416	1419	1422	1426	1429	1432	1435	1439	1442	0	1	1	1	2	2	2	3	3
16	1445	1449	1452	1455	1459	1462	1466	1469	1472	1476	0	1	1	1	2	2	2	3	3
17	1479	1483	1486	1489	1493	1496	1500	1503	1507	1510	0	1	1	1	2	2	2	3	3
18	1514	1517	1521	1524	1528	1531	1535	1538	1542	1545	0	1	1	1	2	2	2	3	3
·19	1549	1552	1556	1560	1563	1567	1570	1574	1578	1581	0	1	1	1	2	2	3	3	3
·20	1585	1589	1592	1596	1600	1603	1607	1611	1614	1618	0	1	1	1	2	2	3	3	3
·21	1622	1626	1629	1633	1637	1641	1644	1648	165 2	1656	0	1	1	2	2	2	3	3	3
22	1660	1663	1667	1671	1675	1679	1683	1687	1690	1694	0	1	1	2	2	2	3	3	3
·23	1698	1702	1706	1710	1714	1718	1722	1726	1730	1734	0	1	1	2	2	2	3	3	4
24	1738	1742	1746	1750	1754	1758	1762	1766	1770	1774	0	1	1	2	2	2	3	3	4
·25	1778	1782	1786	1791	1795	1799	1803	1807	1811	1816	0	1	1	2	2	2	3	3	4
·26	1820	1824	1828	1832	1837	1841	1845	1849	1854	1858	0	1	1	2	2	3	3	3	4
·27	1862	1866	1871	1875	1879	1884	1888	1892	1897	1901	0	1	1	2	2	3	3	3	4
28	1905	1910	1914	1919	1923	1928	1932	1936	1941	1945	0	1	1	2	2	3	3	4	4
·29	1950	1954	1959	1963	1968	1972	1977	1982	1986	1991	0	1	1	2	2	3	3	4	4
·30	1995	2000	2004	2009	2014	2018	2023	2028	2032	2037	0	1	1	2	2	3	3	4	4
·31	2042	2046	2051	2056	2061	2065	2070	2075	2080	2084	0	1	1	2	2	3	3	4	4
·32	2089	2094	2099	2104	2109	2113	2118	2123	2128	2133	0	1	1	2	2	3	3	4	4
33	2138	2143	2148	2153	2158	2163	2168	2173	2178	2183	0	1	1	2	2	3	3	4	4
·34	2188	2193	2198	2203	2208	2213	2218	2223	2228	2234	1	1	2	2	3	3	4	4	5
35	2239	2244	2249	2254	2259	2265	2270	2275	2280	2286	1	1	2	2	3	3	4	4	5
·36	2291	2296	2301	2307	2312	2317	2323	2328	2333	2339	1	1	2	2	3	3	4	4	5
37	2344	2350	2355	2360	2366	2371	2377	2382	2388	2393	1	1	2	2	3	3	4	4	5
·38	2399	2404	2410	2415	2421	2427	2432	2438	2443	2449	1	1	2	2	3	3	4	4	5
·39	2455	2460	2466	2472	2477	2483	2489	2495	2500	2506	1	1	2	2	3	3	4	5	5
·40	2512	2518	2523	2529	2535	2541	2547	2553	2559	2564	1	1	2	2	3	4	4	5	5
·41	2570	2576	2582	2588	2594	2600	2606	2612	2618	2624	1	1	2	2	3	4	4	5	5
·42	2630	2636	2642	2649	2655	2661	2667	2673	2679	2685	1	1	2	2	3	4	4	5	6
·43	2692	2698	2704	2710	2716	2723	2729	2735	2742	2748	1	1	2	3	3	4	4	5	6
·44	2754	2761	2767	2773	2780	2786	2793	2799	2805	2812	1	1	2	3	3	4	4	5	6
·45	2818	2825	2831	2838	2844	2851	2858	2864	2871	2877	1	1	2	3	3	4	5	5	6
·46	2884	2891	2897	2904	2911	2917	2924	2931	2938	2944	1	1	2	3	3	4	5	5	6
·47	2951	2958	2965	2972	2979	2985	2992	2999	3006	3013	1	1	2	3	3	4	5	5	6
·48	3020	3027	3034	3041	3048	3055	3062	3069	3076	3083	1	1	2	3	4	4	5	6	6
·49	3090	3097	3105	3112	3119	3126	3133	3141	3148	3155	1	1	2	3	4	4	5	6	6

Anti-logarithms—*continued.*

	0	1	2	3	4	5	6	7	8	9	Proportional Parts.								
											1	2	3	4	5	6	7	8	9
50	3162	3170	3177	3184	3192	3199	3206	3214	3221	3228	1	1	2	3	4	4	5	6	7
·51	3236	3243	3251	3258	3266	3273	3281	3289	3296	3304	1	2	2	3	4	5	5	6	7
52	3311	3319	3327	3334	3342	3350	3357	3365	3373	3381	1	2	2	3	4	5	5	6	7
53	3388	3396	3404	3412	3420	3428	3436	3443	3451	3459	1	2	2	3	4	5	6	6	7
·54	3467	3475	3483	3491	3499	3508	3516	3524	3532	3540	1	2	2	3	4	5	6	6	7
55	3548	3556	3565	3573	3581	3589	3597	3606	3614	3622	1	2	2	3	4	5	6	7	7
56	3631	3639	3648	3656	3664	3673	3681	3690	3698	3707	1	2	3	3	4	5	6	7	8
57	3715	3724	3733	3741	3750	3758	3767	3776	3784	3793	1	2	3	3	4	5	6	7	8
58	3802	3811	3819	3828	3837	3846	3855	3864	3873	3882	1	2	3	4	4	5	6	7	8
59	3890	3899	3908	3917	3926	3936	3945	3954	3963	3972	1	2	3	4	5	5	6	7	8
60	3981	3990	3999	4009	4018	4027	4036	4046	4055	4064	1	2	3	4	5	6	6	7	8
·61	4074	4083	4093	4102	4111	4121	4130	4140	4150	4159	1	2	3	4	5	6	7	8	9
62	4169	4178	4188	4198	4207	4217	4227	4236	4246	4256	1	2	3	4	5	6	7	8	9
63	4266	4276	4285	4295	4305	4315	4325	4335	4345	4355	1	2	3	4	5	6	7	8	9
64	4365	4375	4385	4395	4406	4416	4426	4436	4446	4457	1	2	3	4	5	6	7	8	9
·65	4467	4477	4487	4498	4508	4519	4529	4539	4550	4560	1	2	3	4	5	6	7	8	9
·66	4571	4581	4592	4603	4613	4624	4634	4645	4656	4667	1	2	3	4	5	6	7	9	10
·67	4677	4688	4699	4710	4721	4732	4742	4753	4764	4775	1	2	3	4	5	7	8	9	10
68	4786	4797	4808	4819	4831	4842	4853	4864	4875	4887	1	2	3	4	6	7	8	9	10
·69	4898	4909	4920	4932	4943	4955	4966	4977	4989	5000	1	2	3	5	6	7	8	9	10
·70	5012	5023	5035	5047	5058	5070	5082	5093	5105	5117	1	2	4	5	6	7	8	9	11
·71	5129	5140	5152	5164	5176	5188	5200	5212	5224	5236	1	2	4	5	6	7	8	10	11
·72	5248	5260	5272	5284	5297	5309	5321	5333	5346	5358	1	2	4	5	6	7	9	10	11
·73	5370	5383	5395	5408	5420	5433	5445	5458	5470	5483	1	3	4	5	6	8	9	10	11
74	5495	5508	5521	5534	5546	5559	5572	5585	5598	5610	1	3	4	5	6	8	9	10	12
·75	5623	5636	5649	5662	5675	5689	5702	5715	5728	5741	1	3	4	5	7	8	9	10	12
·76	5754	5768	5781	5794	5808	5821	5834	5848	5861	5875	1	3	4	5	7	8	9	11	12
77	5888	5902	5916	5929	5943	5957	5970	5984	5998	6012	1	3	4	5	7	8	10	11	12
·78	6026	6039	6053	6067	6081	6095	6109	6124	6138	6152	1	3	4	6	7	8	10	11	13
·79	6166	6180	6194	6209	6223	6237	6252	6266	6281	6295	1	3	4	6	7	9	10	11	13
80	6310	6324	6339	6353	6368	6383	6397	6412	6427	6442	1	3	4	6	7	9	10	12	13
81	6457	6471	6486	6501	6516	6531	6546	6561	6577	6592	2	3	5	6	8	9	11	12	14
82	6607	6622	6637	6653	6668	6683	6699	6714	6730	6745	2	3	5	6	8	9	11	12	14
·83	6761	6776	6792	6808	6823	6839	6855	6871	6887	6902	2	3	5	6	8	9	11	13	14
84	6918	6934	6950	6966	6982	6998	7015	7031	7047	7063	2	3	5	6	8	10	11	13	15
·85	7079	7096	7112	7129	7145	7161	7178	7194	7211	7228	2	3	5	7	8	10	12	13	15
·86	7244	7261	7278	7295	7311	7328	7345	7362	7379	7396	2	3	5	7	8	10	12	13	15
·87	7413	7430	7447	7464	7482	7499	7516	7534	7551	7568	2	3	5	7	9	10	12	14	16
·88	7586	7603	7621	7638	7656	7674	7691	7709	7727	7745	2	4	5	7	9	11	12	14	16
·89	7762	7780	7798	7816	7834	7852	7870	7889	7907	7925	2	4	5	7	9	11	13	14	16
90	7943	7962	7980	7998	8017	8035	8054	8072	8091	8110	2	4	6	7	9	11	13	15	17
·91	8128	8147	8166	8185	8204	8222	8241	8260	8279	8299	2	4	6	8	9	11	13	15	17
·92	8318	8337	8356	8375	8395	8414	8433	8453	8472	8492	2	4	6	8	10	12	14	15	17
·93	8511	8531	8551	8570	8590	8610	8630	8650	8670	8690	2	4	6	8	10	12	14	16	18
·94	8710	8730	8750	8770	8790	8810	8831	8851	8872	8892	2	4	6	8	10	12	14	16	18
·95	8913	8933	8954	8974	8995	9016	9036	9057	9078	9099	2	4	6	8	10	12	15	17	19
·96	9120	9141	9162	9183	9204	9226	9247	9268	9290	9311	2	4	6	8	11	13	15	17	19
·97	9333	9354	9376	9397	9419	9441	9462	9484	9506	9528	2	4	7	9	11	13	15	17	20
·98	9550	9572	9594	9616	9638	9661	9683	9705	9727	9750	2	4	7	9	11	13	16	18	20
·99	9772	9795	9817	9840	9863	9886	9908	9931	9954	9977	2	5	7	9	11	14	16	18	20

PART VIII.

PREPARATION OF GASES.
USE OF COMPRESSED GASES.
DISTILLATION OF WATER.
LISTS OF APPARATUS AND CHEMICALS.
BOOKS FOR REFERENCE.

Introductory Remarks.—Full descriptions will be found in *Clowes' Practical Chemistry*, Section VII., of the fitting and furnishing of the Chemical Laboratory, of the preparation of reagents and of reagent-bottles, and of methods of storage. There are also descriptive lists of the chemicals and apparatus required for general laboratory purposes and for qualitative analysis, as well as lists of chemical names with symbols and formulæ.

Some of these descriptions are reproduced in Part VIII. of this book, and are followed by lists of the additional apparatus and chemicals which are required for quantitative analysis.

The Preparation of Gases.

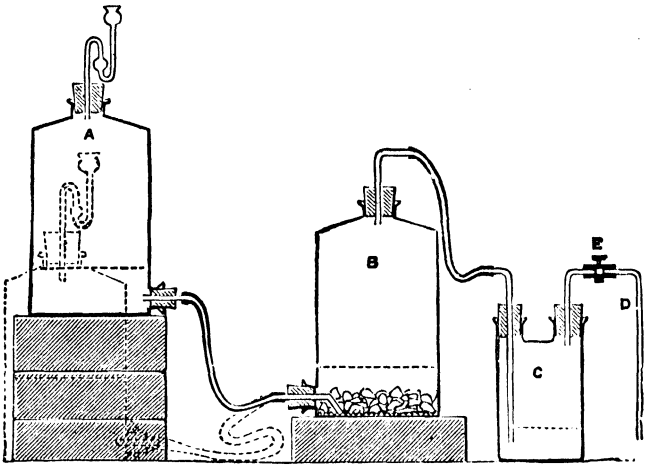
1010. A Convenient Form of Apparatus for furnishing a continuous stream of certain gases in a dry condition is shown in Fig. 129. It is suitable for the preparation of gas by the action of a liquid upon a solid substance at ordinary temperature.

Two bottles (A, B), with tubulures near the bottom, are connected below by means of rubber tubing as is shown in section in the figure. The acid-bottle (A) contains the liquid, and is raised so as to deliver its contents into the generating-bottle (B) which contains the solid. The gas which is evolved in the generating-bottle (B) is forced out by the pressure of the liquid in the acid-bottle (A), and escapes through strong sulphuric acid, or other purifying liquid, which is contained in the washing-bottle (C).

The escape of the gas can be regulated by adjusting a screw-clamp (E). When the clamp is closed, the pressure produced by the gas collecting in the generating-bottle (B) forces back the liquid into the acid-bottle (A), and thus stops the further generation of the gas. The production of gas recommences

as soon as the clamp is opened, since the liquid from the acid-bottle flows once more into the generating-bottle as soon as the pressure of the gas is reduced.

Fig. 129.

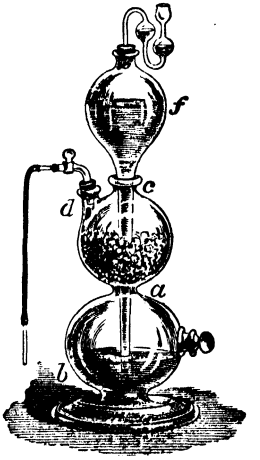


The Hydrogen Sulphide Generator.

When the apparatus is not in use, the acid-bottle is lowered in order to remove unnecessary pressure: the bottle is shown in this position in dotted outline in the figure.

A layer of roughly broken glass, about 3 cm. in depth, should be placed upon the bottom of the generating-bottle (B), so as to prevent the solid from remaining in contact with acid at the bottom of the bottle when the apparatus is not in use. The bottles are fitted with rubber corks, and these are fastened down by wire to the necks and tubulures of the bottles in order to prevent them from being loosened or displaced.

Fig. 130.



The Kipp Generator.

1011. The Kipp Apparatus (Fig. 130) may also be used for generating gases. It is similar in its action to the apparatus already described (**1010**), but the acid vessel is placed above the generating vessel, and the two are connected together rigidly when they are fitted up for use.

1012. In preparing the following Gases, the materials specified **below should be used in the apparatus (1010, 1011):**

Hydrogen : zinc and dilute sulphuric or hydrochloric acid.

Carbon dioxide : marble and dilute hydrochloric acid.

Hydrogen sulphide : ferrous sulphide and either dilute hydrochloric or sulphuric acid.

Hydrogen chloride : lumps of rock salt and strong sulphuric acid.

Use of Compressed Gases.

1013. Most of the gases which are frequently required for use in the laboratory can now be purchased and stored in the compressed or liquefied condition. They are sent out in steel cylinders provided with a screw-valve, and a suitably regulated stream of gas may be obtained by the careful adjustment of this valve. A regulator may be interposed in order to prevent the possibility of the gas issuing under too great a pressure.

Oxygen, hydrogen, carbon dioxide, hydrogen sulphide, chlorine, coal-gas, air and other gases may now be kept in stock in the compressed state in the laboratory, and they are then ready for use at any moment.

By a special fitting applied to the cylinder of liquid carbon dioxide, the liquid may be allowed to issue into the air and furnish the solid carbon dioxide: this substance may be used either alone, or made into a paste with ether, as a powerful cooling agent Liquid air, which can now be produced in a laboratory apparatus, serves as a still more powerful refrigerator.

Sulphur dioxide is usually supplied in the liquid state in strong glass bottles furnished with metal screw-valves. When the valve is opened a constant stream of the gas is obtained by the evaporation of the liquid.

The Distillation of Water.

1014. The Process of Distillation of Water may be carried on in the constant still which has been already described in paragraph 60.

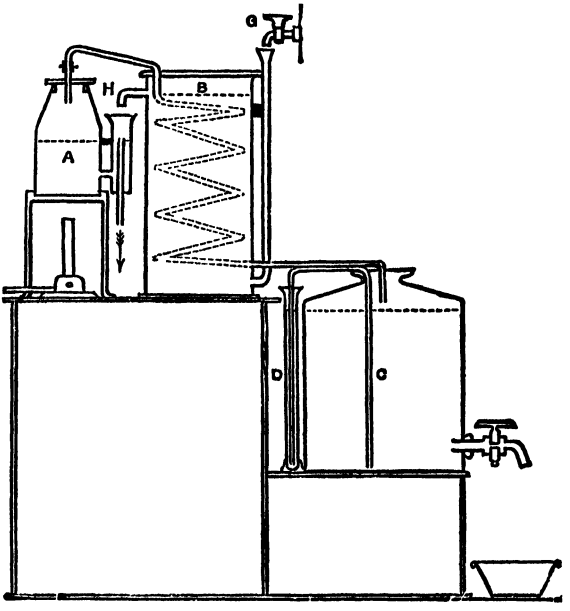
Another form of constant still is shown in Fig. 131 (p. 535), but the Brown condenser (Fig. 28, p. 32) is more efficient than the form shown here. The apparatus is represented in section about one-twentieth its working size, with the exception of the side-feed to the boiler, which is about one-tenth its real diameter.

The water in a copper still (A) is heated by the flame of a Fletcher burner or of a large-sized Bunsen burner. The steam thus generated passes from the

top of the still through a spiral block-tin tube, which is immersed in water in the copper condensing-vessel (B). From this condenser the distilled water flows into a large stoneware vessel (C), which is furnished with a tap below from which the water is drawn when required. A long syphon-tube (CD) serves as a gauge to indicate the level of the water inside the jar.

The lower part of the condensing-vessel (B) is constantly supplied with cold water from a tap (G) through the long funnel-tube. The hot water over-

FIG. 131.



A CONSTANT WATER-STILL.

flowing from the condenser passes from the tube (H) at the top of the condenser into a side-feed for supplying the boiler. From the side-feed the excess of water flows down a central tube through a waste-pipe to the sink, as is shown by the arrow.

The spiral block-tin pipe in the condenser must be of sufficient diameter to prevent it from offering any obstruction to the free escape of the steam from the boiler. Every part of this tube must have a downward slope in order to prevent water from collecting in it, and the coils must be supported by a suitable framework of wood or metal in order to prevent them from sinking from their original position.

The copper still should be furnished with a broad lid screwing upon its mouth, for convenience in removing the deposit which collects within. If

this lid should be fastened a brass tube carrying a screw-union, by which the tin condensing-pipe may be connected steam-tight with the still.

When the still is working the boiler is constantly supplied with the hottest water from the condenser through the side-feed, and the water in the boiler is thus always maintained at the level shown by the dotted line.

As soon as the apparatus has been properly fitted up and the supply of water has been duly adjusted, it is only necessary to light gas under the still when the distillation is started and to extinguish it when it is to be stopped, and no attention is required during the process of distillation. The incrustation must be occasionally removed from the interior of the still, and from the supply-tube for hot water from the condensing-vessel; this is effected either mechanically or by dissolving it in dilute hydrochloric acid.

The wooden stand, which supports the still and the storage-jar, may be fitted with shelves and doors so as to serve as a store-closet.

This copper still, which is 60 cm. in circumference below and 20 cm. in height, and is kept filled with water to a height of 10 cm., yields about 2 litres of distilled water per hour when it is heated by a large Bunsen burner.

In laboratories which require a larger supply of distilled water than can be furnished by the above apparatus, a copper still of several gallons capacity may be set in masonry and heated either by a large gas-burner or by a small furnace fed with coal or coke. The hot water from the upper part of the condenser should pass into a small cistern, the overflow-pipe of which is so arranged as to maintain its water-surface level with that required in the still The still is supplied with hot water by connecting it with this cistern by means of a tube bent downwards in its middle, so as to hinder the circulation of water between the still and the cistern

1015. Pure Distilled Water free from Organic Matter.—If the distilled water which is used in the Permanganate Process (618) is not known to be free from organic matter, it should be treated in the following way:

About 1 gram of potassium hydrate and 0·2 gram of potassium permanganate are added to about 5 litres of distilled water in the distillation-flask (612), or in a large tin can (Fig. 107, p. 418), which is fitted with a reflux condenser. The liquid is gently boiled for twenty-four hours, and is then distilled into Nessler cylinders (611) as long as the distillate gives any colour with Nessler solution (610). As soon as the distillate is proved to be free from ammonia and organic matter, it is received in a clean Winchester quart bottle.

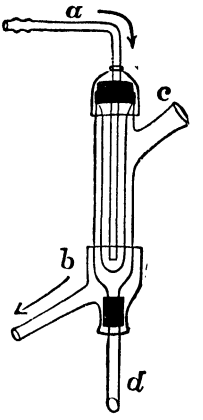
Condensers.

1016. The Liebig Condenser (Fig. 96, p. 334) is now often replaced by other forms of condenser.

One of these is shown in Fig. 99, p. 350, in which the inner tube is spiral in form, and therefore affords a large condensing surface in a comparatively small space.

The Cribb Condenser (Fig. 132) is another form which is both compact and efficient. The condenser proper consists of two concentric tubes which are fused together at the top. An interior chamber is thus formed in which the condensation is effected.

Fig. 132.



The Cribb Condenser.

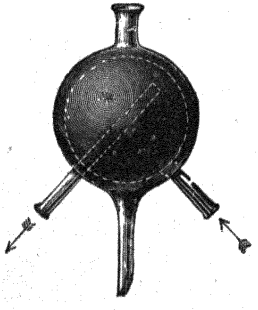
Cold water is conveyed by the tube (*a*) into the interior of the inner tube, it then overflows and passes round the exterior of the outer tube and finally flows away by the side-tube (*b*).

The vapour passes into the condenser at the inlet (*c*), and the condensed liquid is collected by means of a receiver placed under the tube (*d*).

In this apparatus the condensing-chamber is small but offers a very large cooling surface; the water is also caused to flow over the outer tube of the condenser, where it is freely exposed to the air and abstracts additional heat while it is being vaporised.

Care must be taken that the condensing water does not overflow down the tube (*d*) into the receiver. A modification of the apparatus is now made in which the outer cooling water layer is inclosed by a jacket, and is thus prevented from entering the receiver.

Fig. 133.



The Soxhlet Condenser.

The Soxhlet Condenser (Fig. 133) is another very convenient form of condenser. It consists of two concentric glass or metal spheres, the inner sphere being supplied with a current of cold water which flows as is shown by the arrows, and the vapour to be condensed passing between the inner and the outer spheres. By this means very thorough condensation is effected. The apparatus is specially useful as a reflux condenser.

If very volatile liquids are used, an upright tube about 1 cm. in diameter and 60 cm. long may be inserted in the upper orifice of the condenser by means of a perforated cork. This precaution effectively prevents any escape of vapour.

List of Apparatus Required.

The following apparatus will be required for Quantitative Analysis in addition to that usually provided for Qualitative Analysis. See *Clowes' Qualitative Analysis*, eighth edition (1108–1132). The numbers in brackets refer to paragraphs in the preceding text.

1017. Apparatus for Each Student.

Parts I. and II.—Gravimetric.

Weighing-bottle (16).
Pair of watch-glasses 5 cm in diameter, with clip (16).
Desiccators (62, 63).
Beakers, two 250 c c., and two 500 c c
Quantitative filter-papers; 9 cm. and 11 cm in diameter. Schleicher and Schull's are recommended (76, 81, 88).
Three funnels, with ground edges
Two porcelain crucibles, 4 cm and 4 5 cm in diameter.
Two porcelain dishes, 10 cm in diameter.
Two clock-glasses, 10 cm in diameter.
Mounted piece of platinum wire, 15 cm in length.

1018. Apparatus for General Use.

Apparatus marked with an asterisk will only serve for about six students. Numbers in brackets refer to paragraphs in which the apparatus is figured, mentioned, or described.

Parts I. and II.—Gravimetric.

*A balance (1), preferably with a short beam.
*A box of accurate weights, the larger weights of brass and the smaller ones of platinum or aluminium (4), with several riders (6).
Specific gravity bottle, 50 grams capacity (32, 34, 35).
Sprengel tube (36, 37).
Hydrometers (38).
*Two Centigrade thermometers, graduated on the stem; one from 10° to 100°, the other from 0° to 300°.
Fractionating-flasks of 200 cc., 300 cc., and 2 litres capacity (42, 612). The largest size must be fitted with a ground glass stopper.
Steel percussion mortar (56).
Porous tiles or plates (107).
Iron mortar, 20 cm. in diameter.
Water-oven (59).
Air-oven (61).
Air-bath (73, *d*).
Beakers, 1 litre in capacity.
Beaker-flasks (69).

Sieves of brass wire (56, 177).
Porcelain dishes, 20 cm in diameter.
Round flask, 300 c c (305)
Funnels, 15 cm. in diameter.
Filter flask (79)
Separating-funnel (79).
Rose crucible, or substitute (92).
Gooch crucibles and cones (82).
Iron plate on feet (73).
*Platinum crucible, 3 cm. high and across, about 20 grams in weight (90)
Platinum capsule, 5 cm in diameter, 2 cm. deep (90).
Fused silica capsules, about same size (90).
Nickel crucibles, 5 cm. in diameter.
Platinum dish, 9 cm in diameter.
Silver dish. 9 cm. in diameter
Nickel dish, 10 cm in diameter.
*Geissler pump (80).
Hot-water funnel jacket (107)
Filters, cut, 25 cm in diameter.
*U-tubes of various shapes (177, 178, 352)
Calcium chloride tubes, straight, 10 cm
*Liebig's or Geissler's potash-bulbs (175, 790).
50 c c pipettes, ungraduated (254).
Two 300 c c. conical flasks.
Schrotter's carbonic acid apparatus (183, 184)
Straight bulb-tube (191).
Combustion tubing, 1·5 cm. and 2 5 cm in internal diameter
Porcelain boats, small and large (196, 528, 786).

Parts III., IV., V.—Volumetric and General.

*Measuring-flasks; 1000, 500, 250, 200, 100 c c. capacity (248)
*Pipettes; 50, 25, 20, 10, and 5 c c. capacity (254).
Pipette, 10 c c. graduated into tenths of a c c (254).
*Mohr's burettes, 50 c.c. capacity graduated into tenths of c.c ; one with glass stop-cock below (256).
*Measuring-cylinders, graduated throughout and 1000, 500, 250, and 100 c c. capacity (259).
Erdmann's float (256).
Weight burette (292).
Eggertz's carbon tubes (530).
Calorimeters (554, 555, 556).
Six Nessler cylinders, 15 cm. in height, 4 cm. in diameter, about 100 c.c. capacity (611).
Microscope, with one-sixth objective.
Schmidt's milk-tube (667).
Soxhlet extractor (671).
Condensers (1016)
Butter-flask (683).
Alcohol still for beer (693).

Erlenmeyer's combustion-furnace, 75–80 cm. in length (783).
Copper-gauze (788).
Silver-gauze (788).
Calcium chloride U-tubes (789).
Nitrogen bulbs, Will and Varrentrap's (805).
Nitrogen-measuring tube (810)
Digester for sealed tubes (814).
Raoult's apparatus (822).
Thermometer, which can be read to the hundredth of a degree (822).
Boiling-point molecular weight apparatus (824).

Assaying.

Cupels and cupel mould (576).
Conical mould (579).
Assay-tongs (577).
Gas muffle-furnace (577).
Wind-furnace.
Crucibles, wrought-iron and clay (572, 579).

Part VI.—Gas Analysis.

The Hempel apparatus and pipettes (857)
The Winkler burette (861).
Explosion pipette (882)
The Lunge nitrometer (890).
Truman's apparatus (897).
The Russell-West apparatus (906).
Graduated gas-tubes, 50, 100, 200 c.c.
Bottle for air-sample (913)
The Meyer apparatus (921).
The Dumas apparatus (926).

1019. List of Chemical Reagents Required.

This list is supplementary to the lists already given for Qualitative Analysis (1159–1172) in *Clowes' Practical Chemistry*, eighth edition. The numbers in brackets refer to paragraphs in which the reagents are described or referred to.

Fuming nitric acid, 1·5 sp. gr. (142).
Sodium peroxide (141).
Bromine (140).
Magnesia-mixture (167).
Soda-lime (177).
Pumice (177).
Hydrofluoric acid solution, pure (210).
Litmus (264).
Cochineal (266).
Turmeric (267).
Methyl-orange (268).
Phenol-phthalein (269).
Sodium (289).
Steel pianoforte wire (305).
Ferrous ammonium sulphate (307, 108, *c*).
Ammonium bisulphite (313).
Potassium permanganate, crystals (317).
Iodine (331, 110).
Potassium iodate (*Note*, p. 178).
Starch solution (333).
Sodium sulphide (379).
Glacial acetic acid (380).
Uranium nitrate (380)
Tricalcium phosphate (382).
Neutral potassium oxalate.
Succinic acid (509).
Ammonium acetate (435).

Ammonium molybdate solution (520).
Chromic anhydride (527).
Copper ammonium chloride (528, 108).
Bone-ash (576)
Sheet-lead, free from silver (578).
Pure silver (581).
Argol, or crude tartar (572).
Red lead (579).
Flour (579).
Nessler solution (608).
Metaphenylene-diamine (620, *a*).
Silver nitrite (620, *c*).
Phenol (624)
Emplastrum plumbi *B.P.*, (626, *b*).
Oleic acid (626, *c*).
Sheet-lead strips (638).
Ether (666).
Fehling solution (699).
Chloroform (707).
Hide-powder (709).
Gallotannic acid (714).
Indigo-carmine, pure (712, *b*).
Gelatin, Nelson's (712, *c*).
Kaolin (712, *d*).
Absolute alcohol (724).
Petroleum ether (729).
Copper oxide, by oxidation (787).
Asbestos
Pyrogallic acid (863).
Cuprous chloride solution (864).
Fuming sulphuric acid (876).
Palladium (879).
Hydrogen peroxide, 10 per cent. solution (901).
Resin cerate, vaseline, rubber grease, (892)
Mercury, free from foreign metals.

1020. List of Substances for Experiments and Analysis.

Note.—Substances which are marked with an asterisk (*) must be purified by recrystallisation (**106**).

Iceland spar.
Sugar-candy.
Petroleum.
*Potassium chlorate.
*Copper sulphate.
*Alum.
*Nickel ammonium sulphate.
*Ferrous ammonium sulphate.
*Chrome alum.
*Potassium dichromate
*Barium chloride.
Strontium carbonate (109).
Zinc-blende
*Sodium sulphite.
Sodium thiosulphate.
Calcium carbonate (109).
*Ammonium oxalate.
*Sodium chloride (109).
*Sodium bromide.
*Potassium iodide.
*Lead acetate.
Bismuth oxide (162).
*Zinc sulphate.
*Magnesium sulphate
*Sodium hydrogen phosphate.
*Sodium arsenate
*Potassium chloride.
*Oxalic acid.
*Cadmium sulphate.
*Tartar emetic (109).
Arsenious oxide (110).
*Stannous chloride.
*Cobalt sulphate
*Potassium nitrate.
*Borax.
*Boric acid.
Vinegar.
Bleaching-powder.
Hæmatite.
Silver Alloy.
Calamine.
Malachite.
Soda-ash.
Magnesian limestone.

Spathic iron-ore.
Manganese-spar.
Salt-cake.
Furnace-slag.
Felspar.
Galena.
Glass.
Copper-pyrites.
Brass borings or turnings
Bronze ,, ,,
German-silver ,, ,,
Type-metal ,, ,,
Clay-ironstone.
Cast-iron borings or drillings
Steel borings or drillings.
Superphosphate.
Guano
Basic slag.
Milk.
Butter.
Beer.
Moist-sugar.
Tea.
Sumach.
Soap.
Cane-sugar crystals.
Urea.
Acetanilide.
Chloral hydrate.
Ammonium succinate.
Paratoluidine.
Caffeine
Sodium nitrate.
Ether, pure.
Benzene, pure.
Argentiferous galena.
Gold-quartz.
Various fats, oils and waxes (745–771).

1021. List of Books for Reference.

For General Analysis.

Fresenius' Quantitative Analysis.
Treadwell's Analytical Chemistry.

For Volumetric Analysis.

Sutton's Volumetric Analysis.

For Gas Analysis.

Sutton's Volumetric Analysis.
Bunsen's Gasometrische Methode (or English edition).
Hempel's Gas Analysis.
Winkler's Gas Analysis.
Travers' Experimental Study of Gases.

For Special Analyses.

Crookes' Select Methods of Chemical Analysis.
Allen's Commercial Organic Analysis.
Frankland's Water Analysis.
Blyth's Text-book of Food Analysis.
Addyman's Agricultural Analysis.
Procter's Text-book on Tanning.

Beringer's Text-book of Assaying.
Van Furman's Manual of Practical Assaying.
Aaron's Assaying (3 Parts).
Parry's Assay of Antimony and Tin.
Hiorn's Practical Metallurgy and Assaying.
Classen's Application of Electrolysis to Chemical Analysis.
Smith's Electrochemical Analysis.
Low's Technical Methods in Ore Analysis.
Washington's Chemical Analysis of Rocks.
Dittrich's Anleitung zur Gesteinsanalyse.
Analysis of Silicate and Carbonate Rocks (Bulletin 305, U.S.A. Geological Survey).
Blair's Chemistry of Iron.
Ibbotson and Brearley's Analysis of Steel Works Materials.
Arnold's Steel-Works Analysis.
Lewkowitsch's Chemical Analysis of Oils, Fats, and Waxes.
Stillman's Engineering Chemistry.
Phillips' Engineering Chemistry.
Butterfield's Gas Manufacture.
Lunge's Sulphuric Acid and Alkali.
Lunge and Hurter's Alkali-maker's Handbook.
Lunge-Keane, Technical Methods of Chemical Analysis.
Groves and Thorp's Chemical Technology.
Gattermann's Practical Methods of Organic Chemistry.
Lassar-Cohn's Practical Organic Chemistry.
Watts' Dictionary of Chemistry.
Thorpe's Dictionary of Applied Chemistry.
Methodes de Calorimetrie, 1908, by Louginine and Shukerew (pp. 45-63).

The Analyst.
The Chemical News.
The Journal of the Chemical Society.
The Journal of the Society of Chemical Industry.

Comey's Dictionary of Chemical Solubilities (Inorganic).
Landolt-Bornstein Physikalisch-Chemische Tabellen.
Bayley's Chemists' Pocket-book.
Castell Evans' Physico-chemical Tables.
Ostwald's Physico-chemical Measurements.
Physical and Chemical Constants by Kaye and Laby.

APPENDIX

1022. Oven for Drying at Constant Temperature.—The drying-ovens described in pars 59 and 61 may often be advantageously replaced by the one described below. In this oven the substance to be dried may be exposed with certainty to the desired temperature while a current of air or other gas, either in the ordinary or dried condition, and maintained at the desired temperature, is passing over it. The temperature is attained by surrounding the drying-vessel with the vapour of a boiling liquid, or with the liquid itself, which boils at the desired point.

FIG. 134.

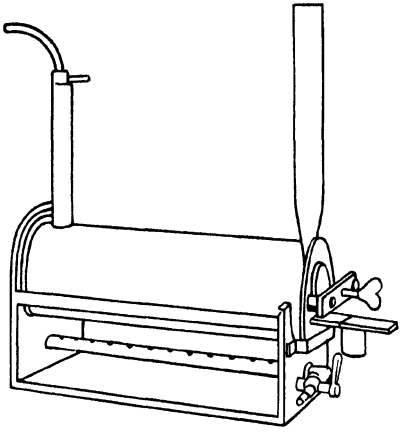
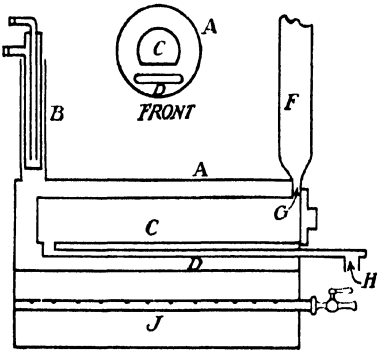


FIG 135.



OVEN FOR DRYING AT CONSTANT TEMPERATURE.

A muffle-shaped copper drying-chamber (C), for containing the substances to be dried, is supported horizontally in a round copper-jacket (A), the space between the chamber and the jacket being partly or completely filled with the liquid of the desired boiling-point, and the liquid is maintained at its boiling-point by a series of gas-jets from an air-burner beneath the jacket. The vapour of the boiling liquid is constantly condensed by the arrangement shown at (B) and returned as liquid to the jacket.

The admission of air to the interior of the drying chamber takes place through a flat copper tube (D) which passes through the boiling liquid or its vapour, without touching the jacket, and opens into the further end of the drying-chamber; the exit of the air is through a copper chimney (F) let into

the front end of the drying-chamber above the door by which the substances are introduced. If the ordinary air is to be admitted by this tube its inlet is left open to the atmosphere; but by suitably connecting the inlet end, dried air or other gases can be allowed to pass over the substance to be dried. This form of oven secures a considerable reduction of space around the substance, and insures the maintenance of a uniform temperature throughout the drying-chamber.

Convenient dimensions for the apparatus are as follows: outside measurement of round jacket 14 in. long and $4\frac{1}{4}$ in. in diameter; the drying-chamber is $2\frac{3}{8}$ in. across at the bottom and $1\frac{5}{8}$ in. high, with a greatest diameter of $2\frac{1}{2}$ in.: the chimney is 11 in. high.

The substances to be dried are conveniently ranged along a copper tray, which is too short to stop the air-inlet, and the tray is then pushed into the drying-chamber. Six watch-glasses or flat weighing-bottles can be placed on such a tray at one time.

1023. Analysis of Commercial Aluminium.—The examination of the commercial metal is now a matter of much importance. The method described below serves also for aluminium alloys.

The commercial metal may contain the following impurities:—carbon, silicon, manganese, sulphur, phosphorus, iron, copper, nitrogen and sodium; and of these the sodium is most deleterious.

The impurities are estimated as is described below. The sample for analysis is required in the condition of filings, turnings, or borings.

Carbon. The total carbon is estimated in 2 grams of *coarse* borings of the metal by dissolving away the aluminium and iron in a solution of cupric ammonium chloride, and then burning the residual carbon and weighing the CO_2 produced (528).

Silicon may be present both in the free graphitic state and as combined silicon. The total silicon present in both these forms may be estimated by fusing 3 grams of the metal with sodium carbonate, treating the cool mass with excess of HCl or H_2SO_4, evaporating to dryness and then heating the residue to render the silica insoluble (210). After the residue has been treated with dilute HCl, the silica may be filtered off, washed, ignited and weighed, and the weight of silicon calculated. The filtrate and washings are reserved.

Manganese is estimated by treating 5 grams of the metal as is directed for the estimation of manganese in steel by the bismuthate method (1028).

Sulphur is determined by dissolving 5 grams of the metal in aqua regia, precipitating the resulting H_2SO_4 as $BaSO_4$, and weighing the sulphur in this form (535).

Phosphorus is estimated by treating 5 grams of the metal as is directed for pig-iron, and weighing the resulting lead molybdate (537, 538, 1026).

Iron is determined in the filtrate from the above estimation of silicon. The filtrate and washings are made up to a definite volume, and two thirds of the liquid are used for the estimation, the remainder being reserved for the determination of aluminium which follows.

Sodium hydrate solution is added to the liquid in quantity sufficient to redissolve the precipitated $Al(OH)_3$, and the liquid is diluted to 300 c.c. and allowed to stand; the precipitate of $Fe(OH)_3$ is then filtered off, washed, and dissolved in dilute acid, and the iron in this solution is reduced to the ferrous condition and titrated with standard dichromate or permanganate solution (310, 323). The Fe thus found was contained in 2 grams of the commercial aluminium.

Aluminium. The remaining third part of the filtrate from the silicon estimation, corresponding to 1 gram of the commercial aluminium, is shaken with 2 grams of powdered sodium phosphate until the salt is dissolved, and ammonia solution is added until a permanent precipitate is formed: the precipitate is then just redissolved by the gradual addition of HCl and boiling, and the liquid is made up to 300 c.c. with hot water. An excess of 10 grams of sodium thiosulphate, above the amount required to reduce any ferric iron present, and 20 c.c. of acetic acid are now added, the whole is boiled for fifteen minutes, and the precipitate is filtered off, washed, dried and ignited. The ignited substance is then heated with HCl, any insoluble matter is removed by filtration, and the aluminium is again precipitated as $AlPO_4$, as is directed above, and the precipitate is filtered off, washed, dried, ignited and weighed. From the weight found the weight of Al is calculated.

Copper is determined in 5 grams of the commercial aluminium. Dissolve this in HCl and filter, reserving the filtrate. Wash the insoluble residue, dry and ignite it, and heat it with HF, HNO_3 and H_2SO_4, continuing the heating until the two former acids have been removed by evaporation; then dilute the residual liquid and add it to the above filtrate.

Now precipitate the copper from the whole liquid by passing H_2S or by adding a few grams of $Na_2S_2O_3$, filter off the precipitated sulphide, and either weigh it as Cu_2S (474) or dissolve it in HNO_3, add an excess of NaOH, then $H\bar{A}$ in excess, and estimate the copper volumetrically by KI and standard thiosulphate (357).

Sodium. The following method of estimation depends upon the fact that aluminium nitrate is decomposed and yields a residue of Al_2O_3 at a much lower temperature than is necessary to decompose sodium nitrate.

Five grams of the aluminium are dissolved in strong HNO_3 diluted with an equal quantity of water, and the solution is evaporated to dryness in a

platinum dish. The solid residue is then reduced to powder in an agate mortar, and heated below the fusing-point of sodium nitrate until no more nitrous fumes are evolved. The mass is then digested with boiling water, the liquid is decanted off, and the undissolved alumina is washed three or four times by decantation.

The filtrate and washings are mixed, a few drops of nitric acid are added, and the liquid is evaporated to dryness. The residue is then dissolved in boiling water, any undissolved alumina being removed by filtration, and the clear solution is mixed with HCl, and again evaporated to dryness and heated to 300° C.

The sodium chloride which remains is then precipitated by silver nitrate, and the resulting silver chloride is weighed. From the weight of AgCl obtained the corresponding weight of Na is calculated.

1024. Estimation of Titanium in Iron-ores.—This method is alternative to that described in par. 523.

The aluminium and titanium must be present dissolved in acetic acid, in order to keep the alkaline earth phosphates in solution. This solution of the ore is precipitated by the addition of sodium phosphate and thiosulphate; and the precipitated $AlPO_4$ and TiO_2 are separated, after the removal of the silica, by fusion with Na_2CO_3 and extraction with water containing NaOH. The undissolved sodium titanate is dissolved in HCl, and precipitated as TiO_2 by means of $Na_2S_2O_3$ solution.

Heat from 3 to 5 grams of the finely-powdered ore with HCl until it is decomposed, evaporate the whole to dryness, heat the residue to render silica insoluble, extract the residue with HCl, and filter, reserving the filtrate. Wash, ignite and weigh the silica; then pour upon it some HF and a few drops of H_2SO_4, evaporate, ignite the residue, dissolve it in HCl and add the solution to the above filtrate.

Introduce into this liquid from 2 to 3 grams of powdered sodium phosphate and dissolve the salt by stirring; then add ammonia solution gradually until a slight permanent precipitate is produced and just redissolve this by the cautious addition of HCl; finally add an excess of one or two c.c. of the acid.

Now dilute the acid liquid to about 300 c.c. with hot water, add an excess of 10 grams of powdered sodium thiosulphate over the amount required to reduce any ferric iron present to the ferrous state, then add 20 c.c. of dilute acetic acid and boil the liquid for 15 minutes.

The precipitate of TiO_2 and $AlPO_4$ thus obtained is filtered off, washed by decantation with hot dilute $H\bar{A}$ and finally with boiling water, and then filtered, dried and ignited. The precipitate, which may contain SiO_2, F_2O_3 and Al_2O_3, is redissolved in HCl, the liquid is filtered if necessary, nearly

neutralised with AmOH, and reprecipitated as before by means of $Na_2S_2O_3$ and Na_2HPO_4 in acetic acid solution, but using only 1 gram of the sodium phosphate.

The phosphate precipitate is now treated with HCl, which only partly dissolves the titanium. The undissolved residue is filtered off, and is heated with HF and H_2SO_4 in a platinum vessel until the HF has been removed by evaporation and the silica volatilised: the residue is then dissolved in HCl, and the solution is added to the above solution in HCl.

The whole liquid is now reprecipitated by Na_2HPO_4 and $Na_2S_2O_3$ in acetic acid solution as before, and the precipitate containing the $AlPO_4$ and TiO_2 is washed, dried, and ignited; it is then powdered, mixed with about six times its mass of Na_2CO_3, and fused at a gentle heat for ten minutes in a platinum dish. The cool mass is now treated with warm water containing a little NaOH, free from dissolved alumina and silica, and the liquid is filtered.

The whole of the titanium is now present as sodium titanate in the undissolved residue. This residue is ignited and then dissolved in the least possible quantity of HCl: the acid solution is boiled, and $Na_2S_2O_3$ is added and the boiling is continued for fifteen minutes. The precipitate is then washed by decantation first with water and then with very dilute $H\bar{A}$, it is then filtered off, dried, ignited and weighed as TiO_2.

Note.—The aluminium may, if necessary, be estimated in the above water and NaOH filtrate, by acidifying with $H\bar{A}$ and adding Na_2HPO_4, and filtering, washing, igniting and weighing the $AlPO_4$.

1025. Analysis of Bauxite.—About 1 gram of the powdered sample is accurately weighed into a crucible and dried at 105° C. to determine the hygroscopic moisture; it is then ignited to ascertain by the loss the amount of combined water.

About 0·5 gram of the very finely powdered sample is then weighed accurately and fused with $KHSO_4$. The cool mass is heated with dilute HCl, and then evaporated to dryness, the residue being heated to render the silica insoluble (**210**). The mass is then treated with dilute HCl, and the diluted liquid is filtered to remove the undissolved matter, reserving this *original filtrate.*

The undissolved matter is boiled for fifteen minutes with sodium carbonate solution, and the residue is filtered off, washed, dried, ignited and weighed as insoluble matter. The alkaline solution is reserved.

The alkaline solution and washings from above are acidified with HCl, and then evaporated to dryness; the residue, after being heated to render the silica insoluble, is extracted with dilute HCl and the silica is removed by filtration and retained: the acid filtrate may be once more evaporated

and the residue treated as above for the separation of the last trace of silica, which is filtered off and retained on the filter.

The *original filtrate* is evaporated to dryness (210), the residue is heated with dilute HCl, and the silica is filtered off and retained, this *main filtrate* being also retained.

All three portions of silica from the above procedure are thoroughly washed from alkali-salts, then dried, ignited and weighed. The ignited silica is evaporated with HF and a few drops of H_2SO_4 in a platinum vessel, and the residue is ignited and weighed: the loss of weight caused by this treatment is the weight of silica present. Any residue is dissolved and added to the above *main filtrate*.

The *main filtrate* from above is mixed with a slight excess of bromine-water, and the Al_2O_3, Fe_2O_3 and TiO_2 are precipitated together by adding a slight excess of ammonia solution and then warming the liquid for about half an hour, or until the excess of ammonia has been removed. The precipitate is now filtered off, washed, and reserved for further examination: the filtrate is mixed with excess of ammonia and Ca and Mg are estimated in it (426, 427).

The precipitate of Al_2O_3, Fe_2O_3 and TiO_2 is dissolved in HCl, the solution is evaporated if necessary to a small volume, and is poured into strong pure solution of NaOH. The liquid is heated for some time, and is then diluted and filtered, and Al is determined in the filtrate by acidifying and adding excess of ammonia (130). The precipitate, which contains Fe_2O_3 and TiO_2, is filtered off, well washed, ignited and weighed.

The ignited precipitate of Fe_2O_3 and TiO_2 is then fused with $KHSO_4$, the cool mass is dissolved in water, and the liquid is saturated with SO_2. From 10 to 20 grams of sodium acetate are now dissolved in a small quantity of water and the solution is mixed with the above liquid, to which about a quarter of its total volume of acetic acid is then added. The whole is now boiled for about two hours and the TiO_2 is filtered off at once through a double filter. The TiO_2 must be well washed with boiling water, adding SO_2 to the first washings if much Fe is present, and the precipitate is ignited and weighed as TiO_2. The weight of the Fe_2O_3 is found by difference.

An alternative method consists in igniting and weighing the dried and ignited precipitate of Al_2O_3, Fe_2O_3 and TiO_2, then finely powdering it and mixing it with ten times its weight of pure Na_2CO_3 obtained from $NaHCO_3$, fusing the mixture, and extracting the cool mass with boiling water. The residue of Fe_2O_3 and TiO_2 is then filtered off, thoroughly washed, ignited and weighed, and the weight of the Al_2O_3 is found by difference. The ignited mixture of Fe_2O_3 and TiO_2 is treated as is directed in the preceding paragraph.

1026. Estimation of Phosphorus in Iron by Weighing the Lead Molybdate ($PbMoO_4$).—After the phospho-molybdate precipitate has been obtained, as is directed in par. 538, dissolve it in 1 c.c. of strong ammonium hydrate solution, wash out the filter and beaker well with water, and acidify the solution and washings with 10 c.c. of dilute HCl, then add 10 c c. of a solution of lead acetate containing 40 grams in the litre. Prepare solutions of NH_4Cl and of ammonium acetate, each containing 200 grams of the salt in the litre, mix 50 c.c. of each of these solutions and warm the mixture. Then mix it with the above liquid, heat, filter, wash the precipitate with warm water, and ignite, and weigh it as $PbMoO_4$. This weight must be multiplied by 0 007 to obtain the weight of phosphorus corresponding to the molybdate.

1027. The Bismuthate Method for Estimating Manganese in Iron and Steel.—This method is more expeditious than the method described in par. 540, since it does not involve the previous separation of the iron from the solution. This advantage is also possessed by the colorimetric method which follows (1028).

The bismuthate method depends on the oxidation of the manganese in solution to permanganic acid by means of sodium bismuthate in the presence of nitric acid ; the permanganic acid thus produced is then mixed with an excess of standard ferrous ammonium sulphate solution and the excess of ferrous salt is titrated with standard permanganate solution (318, 319)

The process is carried out as follows. If the sample consists of steel, 1·1 grams are dissolved by heating the steel with 35 c.c. of HNO_3 of 1·2 specific gravity: if iron is to be dealt with three times the weight must be used, and the amount of acid must be increased.

After the action of the acid is completed, oxidise the organic matter present in the solution by adding sodium bismuthate (see *Note* below) gradually until the pink colour of the permanganic acid either persists or becomes changed to brown manganic oxide when the liquid is boiled : this will generally require about 2 grams of the bismuthate. Then add either sulphurous acid or hydrogen peroxide gradually until the liquid is clear, and cool it.

When the liquid is cold, shake it well after adding about 1 gram of sodium bismuthate : then filter the liquid, which is coloured by $HMnO_4$, through an asbestos filter into a flask, and wash the filter with water containing 3 per cent. of HNO_3 until the washings are colourless.

Now add to the filtrate and washings a known volume of decinormal ferrous ammonium sulphate solution, sufficient being used to be in excess of that required to completely reduce the $HMnO_4$, and titrate the excess of ferrous salt in the liquid by means of decinormal permanganate solution (318, 319).

Each c.c. of the standard ferrous solution which is oxidised by the $HMnO_4$ corresponds to 0·1 per cent. of Mn for each 1·1 gram of the metal taken.

Note —Sodium bismuthate may be purchased; or it may be prepared by heating 20 parts of NaOH nearly to redness in an iron crucible, and adding gradually 10 parts of basic bismuth nitrate which has been dried at 100° C.: 2 parts of sodium peroxide are then added, and the brownish-yellow fused mass is poured out upon an iron plate to cool. It is then broken up, extracted with water, washed by decantation, collected on an asbestos filter, dried at 100° C. and finely powdered.

1028. Colorimetric Estimation of Manganese in Iron and Steel.— When the solution of iron or steel in nitric acid is heated with ammonium persulphate in the presence of a small amount of silver nitrate, the manganese present in the solution is converted by oxidation into permanganic acid, and this may be estimated colorimetrically by comparison with the colour similarly produced by steel with a known percentage of manganese, as in the method for estimating carbon in iron and steel (530).

The process is carried out as follows. Dissolve 0·2 gram of the sample of steel, and the same weight of the "standard" steel (see *Note* below), in two test-tubes in separate 10 c.c. portions of nitric acid of 1·2 specific gravity, by heating the tubes in the water-bath until nitrous fumes cease to be evolved.

Then add to each liquid 15 c.c. of a solution of silver nitrate containing 1·33 grams of the salt in the litre, the 15 c.c. corresponding therefore to 0·2 gram of $AgNO_3$; and, after adding about 1 gram of ammonium persulphate, continue to heat the tubes in the water-bath for about half a minute after the production of colour by formation of $HMnO_4$ has commenced.

Now place the tubes in cold water, transfer the cold liquids to graduated tubes (530), and equalise the intensities of the colorations by diluting the one with stronger colour with the necessary amount of water. The procedure and method of calculation are described in par. 530.

Note.—If the steel contains more than 0·75 per cent of manganese, only 0·1 gram of the sample should be used for the estimation.

For pig-iron 1 gram may be used: this is dissolved in 30 c.c. of the nitric acid, the liquid is filtered into a measuring flask and its volume is made up to 100 c.c. 20 c.c. of this solution are introduced into a test-tube, and just sufficient ammonium persulphate is added to render the solution clear; then 15 c.c. of the silver nitrate solution and the ammonium persulphate are added, and the procedure described above is followed.

As in the colorimetric estimation of carbon in steel (530) the "standard" must be similar in character to the steel which is under examination.

1029. Estimation of Moisture in Coal.—As has been stated in par. 546, the estimation of moisture in coal by drying it at 100° C. can never be relied upon as being exact. It is generally considered, however, that more constant

and relatively accurate results may be obtained by drying the coal at 110° C. and making sure that it is maintained at that temperature during the drying process.

This temperature may be conveniently attained by drying the coal in the apparatus described in par. 1022, and using either toluene as the liquid in the jacket, or a mixture of glycerine and water containing 73 per cent. of glycerine and having a specific gravity of 1·19.

If the glycerine mixture is used it must entirely fill the jacket, since the liquid gives a constant boiling temperature although its vapour does not do so. The use of this mixture obviates any risks which might arise from the inflammability of the toluene vapour.

1030. **Analysis of Air-dried Coal.**—Since coal usually contains some adhering water, it is necessary as is stated in par. 545 to powder the whole sample very quickly, inclose it in a stoppered bottle, and to deal with the separate portions to be weighed as quickly as possible, else water may be lost to varying extents during manipulation of different parts of the general sample. A better plan, when possible, is to powder the general sample and to spread it out in a thin layer and leave it exposed to the air until it has lost its adherent water. This air-dried coal can be bottled and used for weighing off the separate portions required for the estimations. It will be necessary to determine the moisture in the original coal, and then to redetermine moisture in the air-dried coal in order to correct the results obtained from air-dried coal to those on the dry coal. The air-dried coal is better suited for the calorific power determination, since after the coal has been heated it has lost some of its volatile combustible constituents.

1031. **Blichfeldt's Method of Estimating Foreign Fats in Butter.**—Blichfeldt has described a process for the estimation of butter-fat and cocoa-nut fat in margarine and similar mixtures, which may contain both of these fats as well as ordinary oleo-margarine. It is based, like the Reichert-Wollney process, on the determination of the amounts and properties of the volatile acids which are obtainable from the mixture under certain standard conditions.

Reichert determined the butter-fat in the mixture by estimating the alkali-neutralising value of the volatile acids soluble in water (685), and the process was modified and standardised by Wollney (760): Polenske then attempted to introduce a correction by determining the alkali-neutralising value of the insoluble acids under somewhat different conditions from those adopted by Reichert and Wollney, and by making an allowance for the soluble acids which are probably associated with these in cocoa-nut fat.

Blichfeldt attempts to solve the difficult problem of estimating the relative and actual proportions of the soluble and insoluble volatile acids, which

are members of the same homologous series, by taking advantage of the differing solubility of their silver salts in an aqueous solution of sodium nitrate.

For the process a solution of caustic potash is prepared, of which 100 grams contain 50 grams of KOH. 20 grams of the filtered fat are weighed accurately in a 300 c.c. Jena flask, and 8 c.c. of the potash solution and 25 c.c. of glycerol are introduced. This mixture is cautiously heated over a naked flame, with constant shaking, until saponification sets in, great care being taken to avoid overheating.

The product, which should be straw-yellow in colour, is cooled and is then made up to 200 c.c. with hot distilled water which has been boiled for some time to free it from carbon dioxide.

50 c.c. of this soap-solution, corresponding to 5 grams of the original fat, are measured into a 300 c.c. Jena flask, and 50 c.c. of the hot boiled distilled water are added, followed by 50 c.c. of dilute sulphuric acid containing 25 c.c. of the strong acid in a litre, and 1 gram of coarsely powdered pumice.

The flask is now connected by means of a perforated rubber stopper with the condensing apparatus shown in Fig. 136 taken from the *Journal* of the Society of Chemical Industry.

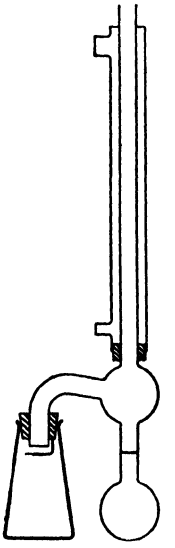


FIG. 136.—THE BLICHFELDT APPARATUS.

In this apparatus the top outlet-tube for the condenser water should be larger than the inlet-tube, and a small glass plate should be attached below the rubber stopper to prevent the mixture in the flask from being carried over by splashing. The receiver has a mark which represents a capacity for 100 grams of water at 65° C.

The distillation is started and is carried on at such a rate that the distillate fills the receiver to the mark in about 20 minutes. As soon as the distillation is finished, the flask and condenser-jacket are removed, and the side-tube is closed by a cork. A few drops of phenol-phthalein solution, and a known excess of from 5 to 10 c.c of decinormal caustic soda solution are now introduced through the condenser-tube, which is then also closed with a cork. The volatile acids are then completely dissolved in the alkali-solution by warming the apparatus on the water-bath with frequent shaking.

The resulting solution of the sodium salts of the volatile acids is transferred to a 200 c.c. measuring-flask, and the condenser-tube is rinsed out several times with warm water into the flask. The volatile acids are then determined in the cooled liquid by difference by titrating the excess of alkali with decinormal sulphuric acid.

The insoluble silver salts are now precipitated from this neutral liquid by adding decinormal silver nitrate solution about equal in amount to the decinormal alkali solution which was used, and 20 grams of pure sodium nitrate are added and dissolved by shaking the flask The liquid is then made up to 200 c c., is repeatedly shaken for about five minutes, and is filtered into a 175 c c. measuring-flask.

The excess of silver nitrate is now determined in the clear liquid volumetrically by adding a volume of decinormal sodium chloride solution, equivalent to seven-eighths of the volume of silver nitrate previously added, and determining the excess of NaCl present by means of decinormal $AgNO_3$ solution, using five drops of saturated K_2CrO_4 solution as indicator; and the difference between eight-sevenths of the number of c.c. of the sodium chloride solution required for the 175 c.c. and the volume of decinormal silver nitrate solution originally used, represents the number of c.c. equivalent to those fatty acids which have yielded insoluble silver salts.

By subtracting this number from the number of c.c. of the decinormal alkali solution corresponding to the total volatile acids, the corresponding number of c.c. equivalent to the acids which would yield soluble silver salts is obtained.

The calculation of the amounts of butter and of cocoa-nut or palm-kernel oil in a mixture is based by the author on the following values :

	Total volatile acids	Silver salts	
		Soluble	Insoluble
Butter	32	29	3
Cocoa-nut oil	20	4	16
Palm-kernel oil	15	3	12

Example of Results obtained from a margarine mixture made from a known butter and containing 50 per cent. of the butter.

N/10 alkali added to the volatile acids. . . .	24·7 c.c.
N/10 H_2SO_4 required to neutralise excess of alkali .	5 4 „
	19 3 „
Deduction for blank experiment	0·3 „
N/10 alkali required by total volatile acids . . .	19·0 „ (A)

N/10 silver nitrate added to salts of volatile acids . .	20·0 c.c
N/10 sodium chloride added to 175 c.c. of filtrate . .	17·5 „
Excess of NaCl found in solution	6·8 „
N/10 sodium chloride required for excess of silver nitrate:	
10·7 × $\frac{4}{7}$	12 3 „
Equivalent of silver salt precipitated	7·7 „ (B)

Equivalent of volatile acids (A) . . .	19·0 c c.	Numbers found for the mixture
„ „ insoluble volatile acids (B) .	7·7 „	
„ „ soluble volatile acids . .	11·3 „	

And the butter used in the margarine mixture yielded by the same process:

Equivalent of volatile acids	26 7 c.c.
„ „ insoluble volatile acids . . .	4·1 „
„ „ soluble volatile acids	22 6 „

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Note.—In the separations enumerated below, the name of the substance separated is only entered once; thus in the separation of silver and lead, the separation is only found under the heading silver, and not under lead.

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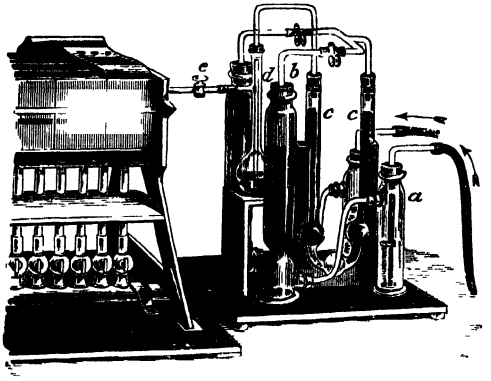
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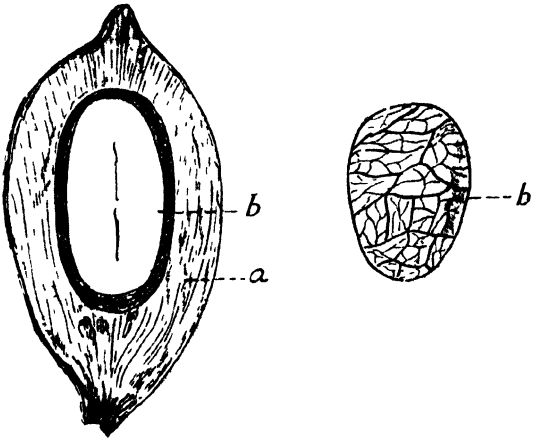
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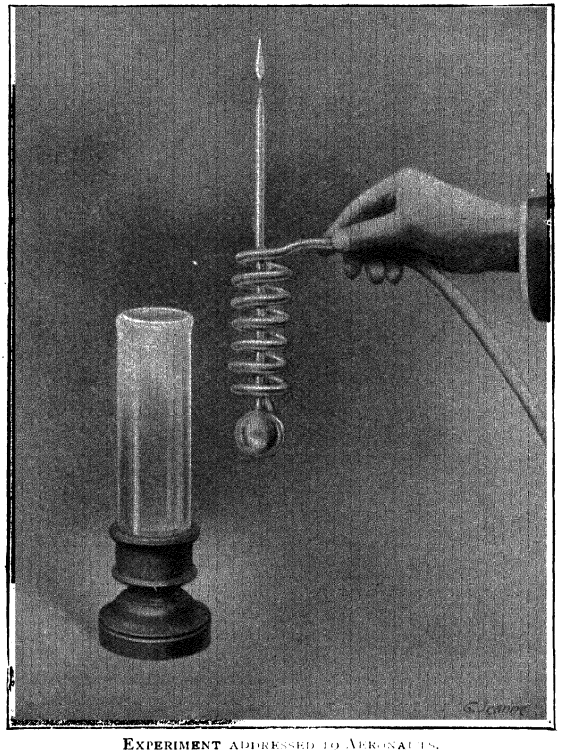
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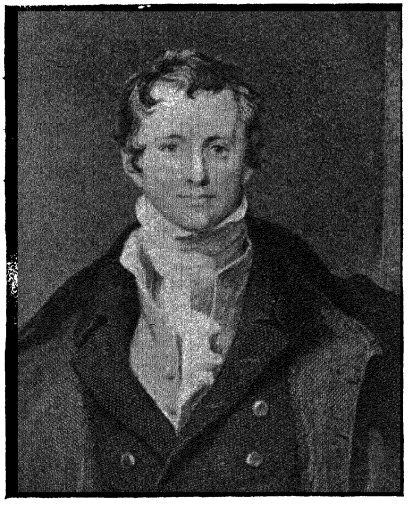
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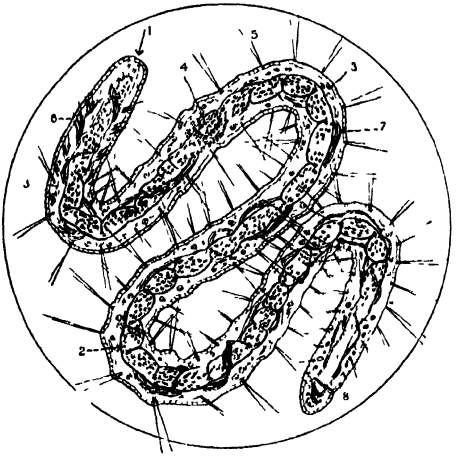
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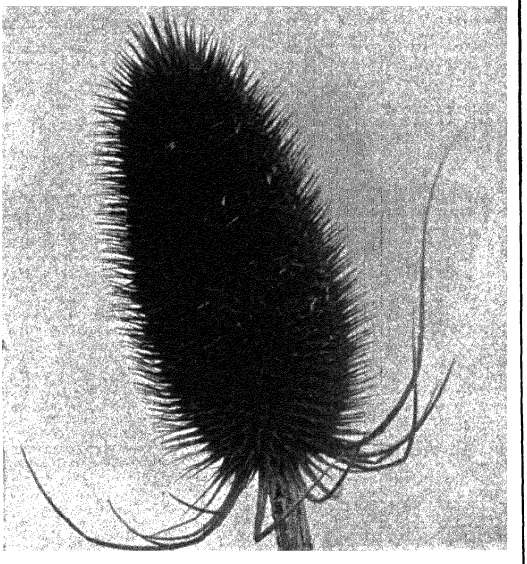
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