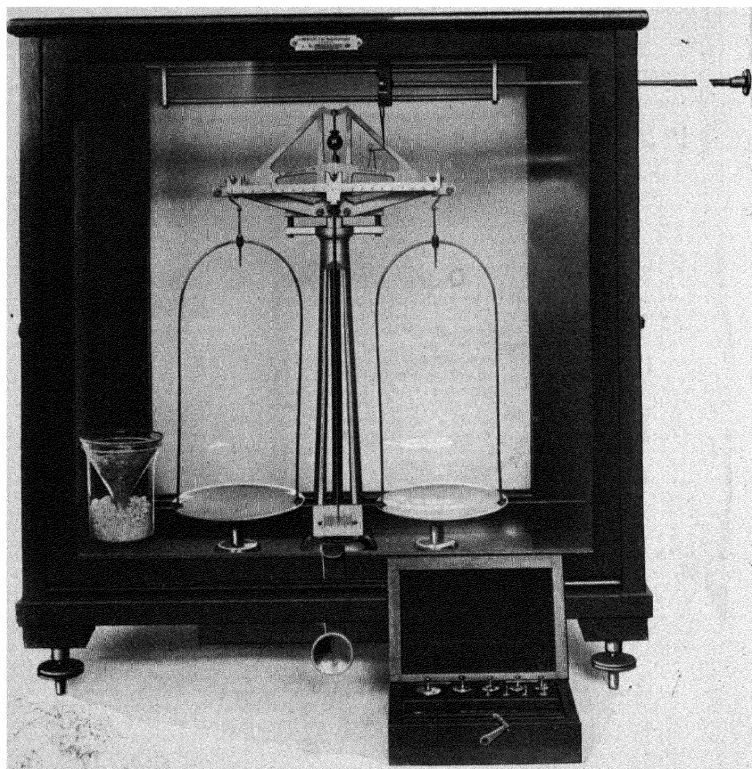


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QUANTITATIVE CHEMICAL ANALYSIS

AND
INORGANIC PREPARATIONS

BY

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In Two Parts

PART I

PREPARATION OF INORGANIC SALTS
AND SIMPLE EXERCISES IN GRAVIMETRIC AND
VOLUMETRIC ANALYSIS

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A Short System of Qualitative Analysis. FOR
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**Quantitative Chemical Analysis and Inorganic Pre-
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The Foundations of Chemical Theory. THE ELEMENTS
OF PHYSICAL AND GENERAL CHEMISTRY

Atoms and Molecules. Being Part I and Chapter XII
of *The Foundations of Chemical Theory*.

By R. M. Caven, D.Sc., and G. D. Lander, D.Sc.

Systematic Inorganic Chemistry, FROM THE STAND-
POINT OF THE PERIODIC LAW.

First edition, 1923

Reprinted, 1925

Reprinted, with a few alterations, 1927

Reprinted, with additions, 1928

Reprinted, with appendix, 1929

Reprinted, 1931, 1934, 1936, 1938

Reprinted, with additions, 1940

Reprinted, 1941

Preface

This textbook of quantitative analysis is intended to provide instruction for the student of chemistry, after he has passed the most elementary stage, until he is ready to take an honours degree, or a diploma, such as that of the Institute of Chemistry.

Excepting qualitative analysis, which is otherwise provided for, the aim has been to include within one volume, published in two parts, all, and not more than all, the practical exercises in inorganic chemistry which the full-time student can be expected to carry out. On this account, inorganic preparations find a place in the volume; in Part I a few typical salts are prepared for subsequent analysis; in Part II a more extensive selection of preparations appears.

The work begins in Part I with simple preparations and gravimetric exercises, because these require little chemical knowledge, but provide just that training in manipulative skill and neatness which the student must have, and should receive before he begins qualitative analysis. This simple gravimetric work is followed by volumetric analysis. Much attention is here devoted to the preparation of solutions for acidimetry and alkalimetry, and the use of indicators under various conditions. Notice may be directed to a method of standardizing sulphuric acid by reference to decinormal oxalic acid solution through the medium of a convenient solution of alkali which the author has used successfully for many years.

The use of standard permanganate, dichromate, iodine and thiosulphate, and silver nitrate solutions follows the exercises on acids and alkalis; but the treatment in Part I is not intended to be exhaustive, and is resumed in Part II.

In practice, a break may be made conveniently before these latter exercises, so that time can be devoted to qualitative analysis, because the chemistry of the later volumetric reactions will be understood better with the experience thus gained.

Besides inorganic preparations and a more extensive course in volumetric analysis, Part II contains exercises in the gravimetric separation of the metals of salts mixed in solution, and instructions for the complete analysis of some typical minerals, commercial products, and alloys.

The author is indebted to several well-known textbooks of quantitative analysis; and he wishes to acknowledge that to a large extent he has built upon the foundation laid by his predecessors in the Royal Technical College. He ventures to hope, therefore, that this circumstance, combined with the fact that he has brought to his task a teaching experience of more than a quarter of a century, will serve to justify this addition to the books which have been written on quantitative analysis.

R. M. C.

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QUANTITATIVE CHEMICAL ANALYSIS

PART I

INTRODUCTION

The work of the analyst is to discover and determine the qualitative and quantitative composition of the manifold substances and mixtures of substances, whether solid, liquid, or gaseous, which come within the scope of human interest and inquiry.

The student will gain confidence that he may be able eventually to analyse substances of unknown composition, if he first prepares and analyses some well-known substances which can be easily obtained in a state of purity. Consequently the first section of this book contains instructions for the preparation and partial quantitative analysis of some representative salts.

A chemical substance or mixture of substances may be analysed *gravimetrically* or *volumetrically*, i.e. the operations which provide the data by which the quantitative composition is estimated may be those of weighing or of measurement. In the former case a sensitive balance and accurate weights are required; in the latter accurately graduated glass vessels. The volumetric analysis of liquid solutions depends primarily,

however, on the use of the balance as well, for solutions of standard strength are required, i.e. solutions containing in unit volumes weighed quantities of pure chemical substances, whereby the unknown may be compared with the known through some chemical reaction carried to completion. There is often a choice between gravimetric and volumetric methods. For example, it may be necessary to determine the amount of iron present in combination in a certain volume of a given solution. This may be done gravimetrically or volumetrically.

Gravimetrically the iron in a convenient volume of the solution may be converted into and precipitated as an insoluble compound, which can be filtered off and weighed in the same or a modified form after suitable treatment. All that is necessary is for the iron to be obtained finally in the form of a single, definite, chemical compound. In this case the metal in the ferric condition is precipitated as hydroxide, and weighed after drying and ignition in the form of ferric oxide, Fe_2O_3 .

Volumetrically the amount of iron in another measured amount of the same solution may be estimated by the quantity of oxidizing agent required to convert it completely from the ferrous to the ferric state. For this purpose the iron is first obtained entirely in the ferrous state, by reduction if necessary, and is then oxidized by an observed volume of a standard solution of potassium permanganate or dichromate.

In all cases of volumetric analysis it is necessary to know when the reactions taking place have been completed; this is shown, as a rule, by some visible change brought about by another reaction which occurs only when the main reaction is at an end. The reagent which undergoes this visible change is called an *indicator*. An indicator may be internal or external, i.e. it may be present in the solution during the *titration**—as the operation of adding the required volume of one solution to a measured volume of the other is called—because it changes

* French, *titre*, standard.

permanently only when the reaction is completed; or it may be used outside the solution which is being titrated, a drop of which is removed from time to time and mixed with the indicator until the required change in the appearance of the latter is at length observed. In this latter case the volume of the solution is being diminished by the removal of successive drops, but generally the error is negligible, and is reduced to a minimum by a second titration, when an amount of the reagent very little short of that known to be required can be added before any of the solution is removed.

Examples of internal indicators are litmus and other colouring matters used in titrating acids and alkalis, as well as starch solution used to show the presence of free iodine; whilst external indicators are represented by potassium ferricyanide, which shows a blue colour only while ferrous iron is present in the drop of liquid added to it, and also starch potassium iodide paper, which turns bluish-black so long as free chlorine or hypochlorite is present in the solution brought into contact with it.

Gas analysis, i.e. the analysis of a gaseous mixture, such as coal gas, is likewise volumetric analysis, but it differs from the volumetric analysis of substances in solution, because it depends on chemical transformation or combination only so far as these are necessary to cause gases to be absorbed by liquids; and since a diminution in volume is the only quantitative observation required, there need be no reference to the balance in gas analysis.

USE OF INSTRUMENTS

The Balance and Weights.

The balance employed in quantitative chemical analysis exceeds in delicacy that used for rougher purposes, not only because of the care bestowed on the construction of its various parts, but because friction is reduced to a minimum by the use of agate planes and knife edges to support the beam upon the central pillar and the pan suspensions upon the ends of the beam. A maximum load up to 100 gm. or even 200 gm. in each pan is provided for, though this load is seldom carried. The weights usually range from 50 to 0.01 gm., those from 1 gm. and upwards being of brass, and preferably gilded, whilst the fractions of a gram are of platinum, aluminium, or bronze. Weights of less value than 0.01 gm. may be supplied, but are not used, for a reason to be explained shortly. The following are the denominations in grams of the individual weights.

50	20	10	10	
5	2	1	1	1
0.5	0.2	0.1	0.1	
0.05	0.02	0.01	0.01	

It will be seen that a similar order of sequence is observed throughout, and that the sum of the weights down to 1 gm. is 100 gm., whilst the total weight of the fractions of a gram

is 0.99 gm. The remaining 0.01 gm. required to make the sum of the fractions equal to 1.0 gm. is supplied by the weight of the rider (q.v.).

The student should observe that by proper use any total weight between 100 gm. and 0.01 gm. can be placed upon the balance pan. The weights, however, must be taken in sequence of descending value. If the weights are taken at random there may not be enough; for example, if a 1.0 gm. weight ought to have been employed, and an attempt is made to supply its lack by means of smaller weights, it is plain that all the latter will be used, and none left for any fractional values of a gram. Hence the need to keep and use the weights in proper order.

It will be noticed that the beam of the balance, or a flat metal bar attached to it, is graduated in ten equal parts on each side of the centre, and that these parts are subdivided into fifths. This device is to enable values lower than 0.01 gm. to be computed without the use of separate small weights. For this purpose a *rider*, consisting of a suitably shaped piece of wire of gold or aluminium, and weighing 0.01 gm., is employed. When the rider lies upon the scale pan its full weight is exercised, and the same is true when it hangs upon the tenth graduation mark, which is vertically above the point of suspension of the pan. The effective weight in milligrams depends, however, upon the position of the rider on the beam; if, for example, it is placed upon the fifth graduation mark, the weight is 5 mgm. or 0.005 gm., and so on. Thus weights down to a single milligram or fractions of a milligram can be ascertained by means of the rider.

The Operation of Weighing.

If the student possesses his own weights and rider he should see that the former always occupy their proper places in the box when not in use. There are only two proper places for

the weights to occupy; one place is the box, the other is the balance pan; and the weights should be transferred from one place to the other always by means of forceps, and not with the fingers. Moreover, the smaller weights just fit the rectangular places made for them in the framework in the box. There they should lie with their upturned corners at the right hand; if they are carelessly placed, or carelessly removed from the box, they may be bent or broken. In case the weights are shared by several students, it is well to keep them permanently within the balance case upon a piece of card so ruled that each weight may have a place like that shown in the scheme on p. 4.

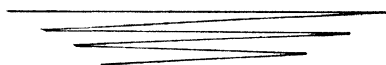
Balance Regulations.

The following regulations with regard to the use of the chemical balance should be carefully read and carried out by the student.

1. Weigh only on the balance allotted to you.
2. Liquid acids, caustic alkalis, and other corrosive substances must not be brought into the balance-room, but must be weighed on a rough balance outside.
3. If it is necessary to weigh such substances as iodine or bleaching powder these must be contained in weighing bottles which must not be opened inside the balance case.
4. All powders and crystals must be weighed in suitable vessels and not on paper or on the bare pan.
5. Great care must be taken not to spill anything on the pans or on the floor of the balance case. If anything is spilled it must be removed at once, and every part of the balance left clean.
6. Be careful to remove all your weights and the rider when you have finished weighing; then close the balance case.
7. If you find the balance out of order or not adjusted, or have any accident with it whilst weighing, you must at once inform a demonstrator.

Before weighing anything the student may examine the

balance in the following way. Let him seat himself at a convenient height immediately in front of the balance case, and, having observed that the balance is clean and the pans are empty, turn to the left, with his left hand, the milled head that projects beneath the centre of the case. This motion withdraws the supports from the beam, which can now swing freely. Probably the beam will begin to oscillate, but if not the door in front of the balance case may be raised for a moment to allow a current of air to be wafted against the right pan by a quick, downward motion of the right hand. The pointer, which projects downwards from the centre of the beam, will now swing to and fro across the scale fixed at the base of the central column. The pointer should be made to swing about six divisions to the right and left of the zero mark on the scale, and if it covers an equal space on either side of this mark the balance is properly adjusted and ready for use. Strictly speaking, this statement is not true, for, like a swinging pendulum, the beam with its attached pointer tends to come to rest. Therefore the track of the pointer over the scale is more correctly represented thus:



For general purposes of chemical analysis, however, when the weighing is carried to the nearest half-milligram, it is sufficient to observe equality of swing on either side. The pans should be brought to rest gently, so as not to jerk the balance.

For practice in weighing, choose a clean and dry beaker, dish, or watch-glass. Place the object to be weighed on the left-hand pan and the weights on the right. This is done because, unlike the process of weighing sugar by the grocer, it is the weights that have to be adjusted and not the amount of substance weighed; and the weights are better moved by

the right hand than by the left. Have the box of weights in front of the balance on the right-hand side, and lift them to the balance pan by means of forceps. A chemist never fingers the weights. Begin with a weight which you judge will be too heavy, turn the milled head slowly, and the more heavily weighted pan will remain stationary while the pointer swings to the left; if the weight is too much use the next smaller weight, and so on, trying each denomination in turn until the accumulated weights on the right-hand pan are less than 0.01 gm. short of the weight of the object. Then place the rider on the beam, close the balance case, and finish the weighing. To do this move the rider to its required position on the beam by lifting it by means of the hook attached to the sliding lever, and start the beam swinging. Bring the beam to rest before altering the position of the rider. When the pointer swings equally on both sides of the centre of the scale, the weighing is finished. Read off the weight to the nearest centigram from the empty spaces in the box, and add the milligrams from the figure on the scale over which the rider hangs. Then return the weights in order to the box, recounting the total weight in so doing as a check. Finally, close the balance case, and lift the rider from the beam. If it is remembered that the values of the weights decrease by series which are successive submultiples of ten, there will be no difficulty in writing down the total weight directly, without first recording the individual weights, as the following illustration shows:

Weight of dish:

Grams, $10 + 5 + 1$	=	16.
Decigrams, $0.5 + 0.2 + 0.1$	=	.8
Centigrams, $0.02 + 0.01 + 0.01$	=	.04
Milligrams (by rider), 3.5	=	.0035
		<u>16.8435</u>

Graduated Vessels.

Graduated vessels are of four kinds: flasks, cylinders, pipettes,* burettes.†

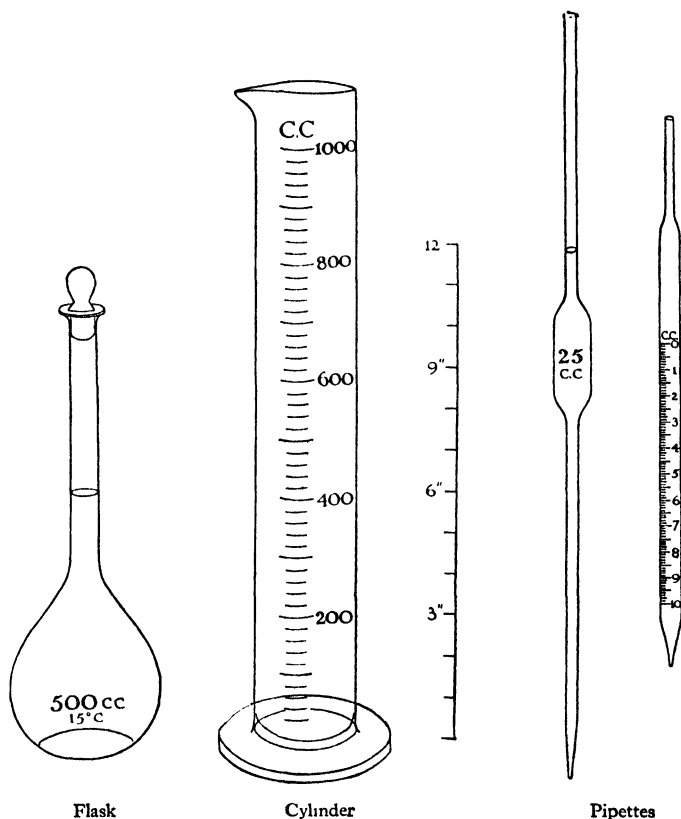


Fig. 1.—Graduated Vessels

Graduated flasks may range in size from 10 c. c. to 2 litres or more. Their necks are long, and as narrow as is consistent with their capacity. They may be closed by ground-in

* Diminutive of *pipe*.

† Diminutive of French *buire*, flagon.

stoppers or by rubber stoppers or corks. They may be graduated either to contain or to deliver a stated volume of liquid at a certain temperature, e.g. 15° C.* The former kind of graduation is the more useful for volumetric analysis, since a flask is generally employed to dilute a solution to a required volume. Sometimes there are two graduation marks on the neck, the lower one for the volume to be contained in the flask, the upper for the same volume to be delivered from it, the difference between the two marks indicating the volume of liquid adhering to the sides of the flask when emptied.

Graduated cylinders, ranging from 10 to 1000 c. c., are convenient for measuring required volumes of liquid when great accuracy is not necessary. A litre cylinder, for example, will measure approximately 1 litre of water; but even if the cylinder is accurately graduated, the error of measurement is likely to be greater than with a flask of corresponding capacity, because of the wider surface of the liquid in the cylinder. Therefore graduated flasks are preferred to cylinders for making up given volumes of standard solutions.

Pipettes are glass cylinders terminating in narrow tubes at the ends. The upper tube is made flat at the top so that it may be closed air-tight by the finger, and a ring is etched upon it to mark the place to which the pipette must be filled so as to contain the prescribed volume of liquid. The lower tube is drawn out to a fine point, so that the contained liquid, flowing freely, may not leave the pipette too fast.

Use of a pipette.—A beginner generally handles a pipette as if it were a dagger, leaving his thumb to close the top of the instrument. This is a clumsy way, and is to be avoided. The pipette should be held lightly between the thumb and second, third, and fourth fingers of the right hand, leaving the first finger free. Then the tip of the pipette should be

* The volumes of a liquid delivered at different temperatures depend only on the change of volume of the containing vessel. It is generally only necessary in volumetric analysis for different vessels to agree among themselves at atmospheric temperature. See Part II, p. 8.

placed below the surface of the liquid to be measured, whilst suction is applied by the mouth at the upper end, and the first finger is held in readiness to close the top of the tube directly the latter is removed from the mouth. When a standard solution is to be measured, a little of it is first drawn into the pipette and made to wet the whole of the inner surface by rotating the instrument in a horizontal position. This liquid is then rejected; and so dilution of the measured solution by the water which may have been in the pipette originally is avoided.

The standard solution is then drawn up into the pipette beyond the graduation mark, the first finger is quickly pressed against the top of the tube (see fig. 2), and then the pressure is carefully relaxed so that the liquid flows slowly down the tube until it reaches the graduation mark. The surface of

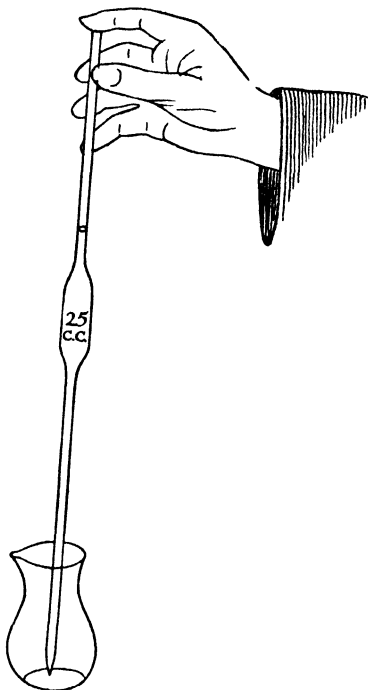


Fig. 2.—How to hold a Pipette

the water is curved, that is, it forms a meniscus.* The flow is arrested by increasing the pressure when the convex lower surface of the meniscus just touches the mark, and the liquid is at once delivered into the chosen vessel by removing the finger. The finger-tip and the top of the pipette should both be dry.

* Greek, *μηνίσκος*, the crescent moon.

There is some risk of the liquid being drawn up into the mouth. This risk, which is reduced to a minimum by practice, is partly avoided by taking care that the tip of the pipette is always well below the level of the liquid with which the instrument is being filled, so that no air can be drawn up and cause splashing. The student is advised to practise the use of the pipette by measuring water in it. Concentrated acids, potassium cyanide solution, and other poisonous substances must never be measured in a pipette.

How to deliver the exact amount of liquid requires consideration. If a 20-c. c. pipette, say, was made to contain only 20 c. c. of liquid, it would be necessary to wash it out with water so as to obtain the required amount of substance in solution. This is not the case, however, and the pipette must not be washed out for that purpose. The liquid left on the sides of the pipette when the main volume of it has run out will take some time to drain, and the quicker the pipette is emptied the more will be the amount of this liquid. A good pipette of 20 or 25 c. c. capacity should empty itself in about 30 sec., and then should be allowed to drain for another 15 sec., the last drop of liquid being removed from its tip by bringing this into contact with the surface of the liquid or side of the containing vessel. The pipette should not be blown out.

Graduated pipettes are tubes graduated to deliver any required volume of liquid up to, say, 10 c. c. They are of uniform bore throughout, except that they are drawn out to a narrow aperture at the lower end and may be narrowed also at the upper end above the graduations (see fig. 1). It is easy to permit or arrest the flow of liquid, and so to deliver any required volume, by varying the pressure of the first finger on the upper end.

The *burette* is the instrument by which a small accurately known amount of liquid is delivered in the process of titration. It is a cylinder of uniform bore, terminated after a constriction

by a glass tap, or a piece of rubber tubing provided with a burette clip, and a glass jet through which the liquid is delivered.

The burette is generally made to hold 50 c. c., and is graduated in tenths of a cubic centimetre. If the student has a 50-c. c. burette with a tap he should prepare it for use in the following way. The tap should first be removed and put aside in a safe place; then the burette may be thoroughly cleaned with soap and warm water with the help of a burette brush. This is desirable so as to remove any grease adhering to the interior, but care must be taken to leave no soap in the burette, for this would give an alkaline reaction. If the burette is stained on account of permanganate the stain may be removed with sulphurous acid. Silver nitrate leaves a black stain of silver which can be dissolved by dilute nitric acid. A careful student, however, always cleans his burette with water before he puts it away.

The greasing of the tap requires care; as a rule the student applies a great deal too much grease, and consequently gets it into the hole in the barrel, and thence into the tip of the burette. If this has happened the grease should be removed by ether, aided with a piece of platinum wire. The tap and the cavity into which it fits should first be dried, and then a very little grease, which may be vaseline either alone or thickened with resin, should be rubbed upon the barrel of the tap. There should be just enough vaseline to cause the ground glass to appear transparent after the tap has been placed in position

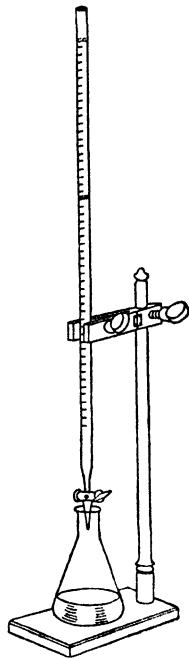


Fig. 3.—Burette in Stand

and rotated. The tap may be secured in position by a twisted rubber band.

Use of the burette.—When the burette is clean and the tap in order, the student may learn its use. The burette should be clamped in a burette stand so as to be vertical, and then be filled with distilled water. It is best to use a small funnel in filling the burette; it is not wise to fill it from a tap or the tube of a wash-bottle or pipette, as it is easy to fracture the top by careless handling. If a funnel is used it should be removed before a measured volume of liquid is withdrawn from the burette, otherwise a drop might fall from the end of the funnel and vitiate the reading. It is convenient, however, to make the upper end of the burette itself funnel-shaped by softening it in a flame, and pressing it out with a conical piece of charcoal.

When the burette has been filled above the zero graduation mark, and the funnel withdrawn, the tap is turned so as to allow the falling liquid to drive out all air from the narrow delivery tube below the tap. This is important, since if a bubble of air remained and was displaced during a titration, it would count as solution, the volume of which actually used would be less than that indicated by the volume of the air-bubble. Adjustment of the liquid to the zero mark may then be made. The student will notice that the surface of the water in the burette is curved, that is it forms a meniscus (cf. *pipette*). This is well seen by holding a piece of white paper or card behind the burette, sloped upwards at an angle of 45° so as to reflect down-coming light horizontally through the liquid. Various devices have been proposed for accurate burette reading but this simple procedure is sufficient. The meniscus presents a rather complicated phenomenon. A fine horizontal line marks the circular edge of the liquid against the burette wall; below this is seen a dark curve with a sharp lower outline, and farther down another curve is faintly seen (see fig. 4). The liquid is adjusted to the zero mark by

turning the tap so that drops fall slowly until the dark curve meets this mark tangentially. In reading the burette, however, care must always be taken to avoid parallax, i.e. an apparent difference in position due to different positions of the observer's eye. Thus the observer must always look horizontally, i.e. his eye must be level with the top of the liquid in the burette. The rate at which liquid leaves the burette can be carefully adjusted if the tap has been well greased; and it is often convenient to allow the liquid to fall continuously for a time in separate drops during the progress of a titration. It will be understood that some liquid remains on the wet inner surface of the burette when liquid has been withdrawn, and if this has been done quickly a deficiency amounting to $\frac{1}{10}$ or $\frac{2}{10}$ c. c. will occur if the lower reading is taken at once. In such case two or three minutes should elapse before the reading is taken to secure an accurate result. The student may show this by rapidly emptying his burette down to the 50-c. c. mark, and then reading it after two minutes, when the volume indicated will be found to be about 49.9 c. c. This error will not occur if about two minutes are occupied in emptying the burette; and when a titration is done slowly, as is usually the case, the question concerning it does not arise.

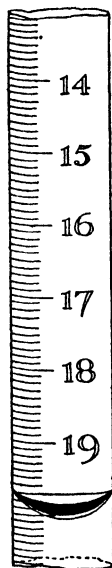


Fig. 4. — Part of Burette, full size, showing meniscus. The bottom of the dark curve is in line with 20-c. c. mark, but the number is omitted for the sake of clearness.

The burette is not graduated throughout its entire length. It is convenient if there are 3 or 4 in. above the zero mark to allow a funnel to be inserted without its stem reaching the graduations. The extent of the space below the lowest graduations is immaterial, since the volume of liquid delivered is

shown by the difference between the two readings. It is well to start every titration at the zero mark.

It is usual for beginners to assume that the pipettes and burettes they use are correctly graduated. For accurate work, however, these instruments should be standardized. Instructions for standardization will be found in Part II of this book.

PRINCIPLES AND PRACTICE OF GRAVIMETRIC ANALYSIS

Almost certainly the student will have carried out already some simple operations of gravimetric analysis. If he has separated salt from sand by means of water, collected the sand on a filter, washed it free from salt, dried and weighed it, and so estimated the proportion of sand in the mixture, he has performed a simple gravimetric analysis. Other simple examples of such analysis are: the determination of the water of crystallization in hydrated barium chloride by estimating the loss the salt undergoes on ignition, and the discovery of the equivalent of tin by finding the increase in weight the metal undergoes when it is acted on by nitric acid, and the product ignited.

Thus the process of gravimetric analysis consists essentially in obtaining, from a weighed quantity of a substance or mixture, a single substance which is either one of those originally present, or a derivative of it, the operation being carried out without loss so that from the weight of substance obtained the proportion of related substance originally present can be calculated.

In the first example cited above, the sand is easily collected because it is insoluble in water. An equally valid but more lengthy operation would be to evaporate the solution of salt obtained by the action of water on the mixture, and weigh the residue. If the two operations were combined and properly carried out the sum of the two percentages would equal 100, unless the mixture contained volatile matter, e.g. moisture,

which would escape detection. In such case it would be easy to determine "loss on ignition", that is, the loss of weight a weighed quantity of the mixture underwent when heated, and so to complete the quantitative analysis of the mixture. Evidently, however, such analysis would be complete only if water extracted or left a single constituent of the mixture.

Since a substance to be analysed is generally for this purpose dissolved in water with or without the help of acid, a common method of obtaining a solid derivative suitable to be weighed is by *precipitation*. Thus from a solution containing barium the sulphate may be precipitated by dilute sulphuric acid; or conversely, a soluble sulphate in solution may be converted into barium sulphate by the addition of barium chloride. For reliable results to be obtained, however, the solubility in water of the precipitate must be so small that the quantity of the salt remaining unprecipitated will be too minute to affect the accuracy of the analysis. For example, whilst barium, or sulphate, can be estimated by precipitation as barium sulphate, calcium cannot be estimated as calcium sulphate, because this salt is too soluble in water for precipitation to approach completeness.

The principle of *solubility product* applies here, and may be illustrated with reference to barium sulphate. Barium and sulphate can exist together in solution only when the product of the concentration of these ions falls below a certain value, which in this case is extremely small. The larger the concentration of sulphate, therefore, the less is the concentration of barium that can exist in solution with it, and vice versa. Hence it follows that the most complete precipitation of barium is secured by the presence of excess of sulphate, and vice versa. This principle is, of course, departed from when complex ions are formed in solution.

The method of collecting and treating a precipitate previous

to weighing it depends upon its physical and chemical properties. These are various, as the student of qualitative analysis discovers. Barium sulphate, for example, which, when precipitated from cold dilute solution, is very fine and difficult to filter, may be obtained granular by suitable treatment. It may then be collected on a filter paper, from which it need not be detached when the paper is incinerated; for, although a little barium sulphate is reduced to sulphide during this process, reoxidation to sulphate is easily effected by roasting the residue in the air for a short time.

Silver chloride has very different properties. It is generally precipitated from dilute nitric acid solution of silver, and obtained in a coagulated form when the precipitant has been added in excess. Hence it can be filtered readily; but since it is easily reducible to metal, which needs to be dissolved in nitric acid, forming nitrate before it can be reconverted to chloride, it must be removed from the filter paper as much as possible before the latter is incinerated, so that very little silver chloride suffers reduction; or better, it may be filtered through asbestos instead of paper, when reduction to metal on subsequent ignition can be avoided.

Precipitates may be colloidal, e.g. metallic sulphides; or gelatinous, e.g. hydrated alumina and silica; or distinctly crystalline, as hydrated magnesium ammonium phosphate. These different properties affect the ease of filtration, but do not necessitate essential differences of procedure.

The complete quantitative analysis of a natural or artificial mixture of compounds involves analytical separations, which are lengthy and require much care for their proper completion. Often the methods of qualitative analysis are available for the quantitative separation of metals in solution, but the frequent need for reprecipitation to obtain complete separation, as well as the necessity for evaporating filtrates to reduce them to manageable bulk, and, in the case of the alkali metals, the

need for evaporation to dryness and ignition, involve a high degree of skill and patience.

Sometimes a particular constituent, e.g. iron, can be estimated by an independent volumetric process; sometimes it can be separated electrolytically with convenience, e.g. copper; and sometimes it can be precipitated by the use of a specific reagent which leaves all other constituents unaffected. Nickel, for example, under suitable conditions, can be precipitated

from solution, without separation of other metals, by means of dimethyl glyoxime. If such specific methods of separation were available for all metals, quantitative analysis would be much simplified and shortened.

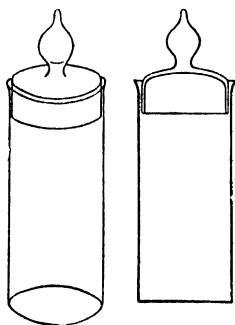


Fig. 5.—View and section of weighing bottle (one-fourth actual size).

Apparatus and Procedure.—The beginner will require a weighing bottle, several glass beakers, preferably of the broad form and lipped, and varying in size from 200 to 500 c. c.; some stirring rods rounded at the ends, long enough to protrude about 2 in. above the edges

of the beakers, and provided with tightly fitting rubber caps, which may be pieces of thin rubber tubing about 1 in. long; also clock glasses to cover the beakers. A square of iron-wire gauze with a circular covering of asbestos is the best support for a beaker that is being heated on a tripod. The outfit should also include several well-shaped plain-glass funnels, with long narrow stems cut off obliquely, together with circular filter papers, 11 cm. in diameter, which are of suitable texture to retain finely divided precipitates such as those of barium sulphate and calcium oxalate, and which leave when burnt a negligible weight of ash. A camel-hair brush for transferring precipitates to crucibles, and sheets of red or black glazed paper will also be required. Crucibles of porcelain and

transparent or opalescent silica will suffice for many purposes, but a crucible of platinum is much to be preferred for containing those precipitates which do not act upon this metal. Probably, however, the student will have to postpone the use of this luxury till later in his course. Silica triangles for supporting crucibles have now largely replaced those of pipeclay, and are much to be preferred because they do not crack when quickly heated. A clean duster and glass cloth should be provided; an old large pocket handkerchief answers well the latter purpose.

These are the chief items of outfit, beyond the ordinary laboratory apparatus, which the beginner in quantitative analysis will require. Other and more special apparatus will be mentioned as it is needed.

Particular attention must be paid by the student to the necessity for scrupulous cleanliness, neatness, and delicacy in every operation he performs. Quantitative analysis is a fine art which cannot be learned by the clumsy and untidy student till he mends his ways. Qualitative analysis, if indulged in early by the untrained student, may give excuse for sloppiness and inaccuracy, habits which should never be allowed to grow upon the chemist. That is one of the reasons why some quantitative work should take precedence over qualitative analysis in the student's course.

All apparatus should be chemically clean, and the bench well dusted before quantitative work is begun. Dirty beakers on the bench are as offensive as dirty cups and plates set out upon a table. It is not too much to ask that the chemical student should emulate the cleanliness of the good housewife.

No water should remain on the bench when quantitative filtration is proceeding. If a student starts with a clean and dry bench and filter stand, and finishes with the same, he is assured that he has spilled nothing during filtration.

SIMPLE INORGANIC PREPARATIONS AND GRAVIMETRIC ANALYSIS

I. Barium Chloride, $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$.

Barium chloride is easily prepared by decomposing barium carbonate with dilute hydrochloric acid thus:



The salt is much more soluble in hot than cold water, and crystallizes readily on cooling its hot concentrated solution. Since other chlorides with which it might be contaminated are more soluble in water than barium chloride, this salt will be obtained pure with a single crystallization, and when dried in the air will be found to contain its proper amount of combined water, since it is neither deliquescent nor efflorescent. Moreover, when the hydrated salt is heated gently in a crucible till it ceases to lose weight, all the combined water is expelled, leaving the pure anhydrous salt. In this respect barium chloride, being the salt of a powerful metal, differs from hydrated magnesium chloride, which on similar ignition suffers hydrolysis, losing hydrogen chloride and leaving a basic salt.

Preparation.

Weigh 10 gm. of precipitated barium carbonate on the rough balance, transfer it to a small conical flask, together with a little water, place a funnel in the neck of the flask, and carefully pour dilute hydrochloric acid through the funnel upon the salt, a little at a time, so as to keep under control the effervescence due to escape of carbon dioxide gas. Enough acid

should be used to dissolve all the salt, but large excess should be avoided. Raise the solution to the boiling-point to expel dissolved carbon dioxide and filter, receiving the filtrate in a suitable beaker. Then evaporate the clear solution till a little of it, removed on a glass rod, crystallizes there. At this stage allow the solution to cool, stirring well, or cool it by placing the beaker in cold water in order to obtain the salt in the form

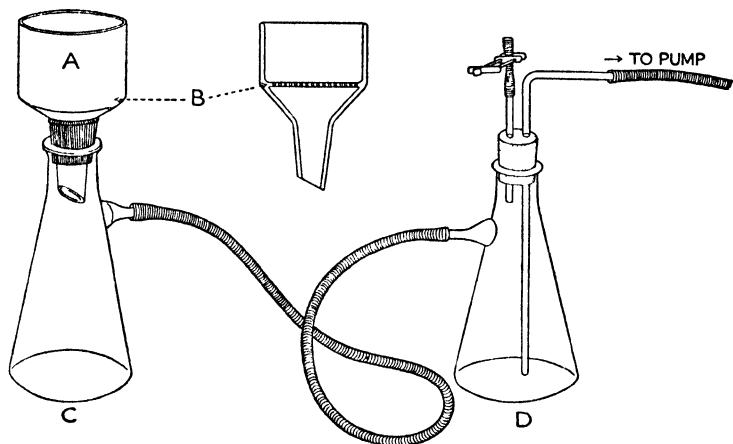


Fig. 6.—Apparatus for Filtration of Crystallized Salts

A, Porcelain funnel, also given in section to show perforated horizontal plate B.
C, Filtering flask. D, Second flask.

of a fine, crystalline meal. In such form a salt is likely to be purer than when obtained in larger crystals, since the latter may occlude some of the mother liquor during their growth.

Filter and drain the salt by means of a Büchner funnel and filtering flask attached to the water-pump on the bench. This apparatus takes the form shown in fig. 6. The funnel A is of porcelain, and at the bottom of the shallow cylinder is a horizontal plate B which is perforated with a number of small holes communicating with the stem below. This stem fits tightly into a rubber stopper which closes the

mouth of the filtering flask c; the latter is made of thick glass to bear atmospheric pressure when evacuated. To the side tube of this flask is attached rubber tubing leading through the second flask D to the pump. This tubing must also be thick-walled, or it would collapse when air was drawn from within it, and the action of the pump would consequently cease. The second flask serves as a trap to catch water driven backwards by air entering through the pump when the action of the latter is stopped; otherwise this water would traverse the rubber tube and enter the filtering flask. Air can be let into the flask D by opening the screw clip attached to rubber tubing on a glass tube passing through a second hole in the stopper of this flask. There are several forms of water-pump, but each depends on air being trapped and drawn down through a narrow neck by a swiftly moving jet of water. A good pressure of water is necessary to produce this effect; and the presence of fine bubbles of air in the water is seen by the whiteness of the latter as it passes through the pump.

To use this apparatus place in the Büchner funnel a circular piece of filter paper of suitable size to fit over the holes, wet it and apply gentle suction, which causes the paper to cling tightly to the base of the funnel. Then pour into the funnel the thick suspension of barium chloride crystals, and spread it over the paper by means of a spatula. It is interesting to notice how quickly the crystals are pumped free from mother liquor; to dry them, however, it is necessary to spread them on either filter paper or a piece of porous plate; the latter is to be preferred. These porous plates are of unglazed white pottery, and should be supplied wrapped in tissue paper to keep them clean. It is not necessary to use a whole plate to dry a small quantity of crystals; a plate may be broken into several pieces by a sharp blow from a hammer or the base of a Bunsen burner.

Remove the mass of crystals from the funnel and spread

them out upon a piece of porous plate. The remaining water will quickly drain away into the plate, and after a few hours the crystals will be found to be quite dry, since the mass of them will be crisp, and easily separated into the coarse-grained powder of which the crystals consist.

Two mistakes with regard to the drying of crystals containing water of crystallization must be avoided. They must never be heated or placed in a desiccator over sulphuric acid or other drying agent. A hydrated salt is stable within certain limits of water-vapour pressure in the air about it. By heating the salt or by removing atmospheric water vapour these limits may be exceeded.

The dry specimen of barium chloride may be preserved in a specimen tube or a clean, corked test tube. From the mother liquor a further crop of crystals can be obtained after evaporation. These, however, may not be as pure as the first crop, and should not be mixed with them. The student should weigh each crop and estimate the percentage yield, since it is easy to calculate what weight of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ 10 gm. of BaCO_3 should yield.

A further interesting exercise will be to employ as much of the salt as is not otherwise required to grow a crop of larger crystals. To do this dissolve the salt in a little warm water in a beaker to produce a solution which is about saturated when cooled to atmospheric temperature. The depth of the solution in the beaker need not exceed $\frac{1}{4}$ in. Cover the beaker loosely with a piece of filter paper, and set it aside. After an hour or two, perceptible crystals will be found, and these will grow as water gradually evaporates from the solution. The student should draw the crystals and try to decide to what crystallographic system they belong.

Analysis.

A complete quantitative analysis of the salt $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ involves:

- (i) Estimation of water of crystallization by determining loss on ignition.
- (ii) Estimation of barium by precipitating and weighing as barium sulphate.
- (iii) Estimation of chloride by precipitating and weighing as silver chloride.

(i) Estimation of Water of Crystallization.

To contain the salt employ a porcelain or silica crucible of about 1 in. upper diameter. The crucible should be provided with a lid, though this need not be weighed. Before being weighed, a crucible, after being thoroughly cleansed, should always be ignited, i.e. heated in a flame, and then cooled in a desiccator to remove any extraneous moisture. It will thus be weighed originally and finally in the same condition. A *desiccator*, which may be obtained on loan from the stores, generally takes the form shown in fig. 7. It is a glass vessel consisting of two parts B and C, and a lid A, which fits the vessel by means of ground-glass surfaces made air-tight by grease. C contains the desiccating agent, which is either granulated anhydrous calcium chloride or sulphuric acid poured upon broken pumice-stone. A perforated zinc disc, or a piece of wire gauze, separates C from B, and upon this rest the down-turned legs of a triangle which serves to support the crucible. The crucible should never rest directly on the zinc or gauze, partly because it may pick up material therefrom, but also because without support it is liable to be upset as the desiccator is carried to the balance. The crucible should be placed in the desiccator whilst warm, though not hot. Consequently the air within expands, and often lifts the lid that some may escape. Therefore when all has cooled to

atmospheric temperature the air inside will be somewhat rarefied, and when the desiccator is opened the gust of entering air may blow out of the crucible any fine particles which it contains. To prevent this accident, the lid should be placed upon the crucible; and to open the desiccator it is best to slide the lid sideways till a minute space only is opened. The lid may afterwards be withdrawn easily.

Weigh the empty crucible, and place in it 1.0 gm. of your barium chloride. If exactly 1 gm. is taken, the subsequent calculation of percentage loss is simplified. Support the crucible over a flame by means of a triangle. The flame should be turned low, so as not quite to touch the bottom of the crucible. As the salt loses its water it becomes whiter and more opaque. Finally the crucible may be raised to a dull red heat by the application of the flame. The reason for applying the heat gradually is that if the crystals are heated suddenly the internal combined water being liberated and converted into steam, may burst the crystals and fling parts of them out of the crucible. Let the crucible cool sufficiently, transfer it by means of the tongs to the desiccator, place the lid upon it, close the desiccator, and after about fifteen minutes weigh the crucible. Then repeat the heating and weigh again.

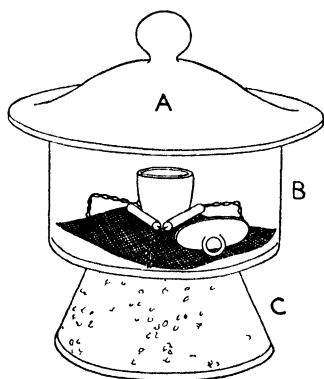


Fig 7 —Desiccator

Here is an important matter to remember. Whenever a vessel and its contents have to be weighed after being heated, the process must be repeated until the weight has become constant, i.e. until two successive weighings do not differ

by more than $\frac{1}{2}$ mgm. This is plainly necessary in order to have evidence that the chemical change taking place has been completed.

From the loss of weight calculate the percentage of water of crystallization in the barium chloride, and the number of molecules of water of crystallization to which this corresponds.

Method of entering Notes.—The student should obtain a stiff-covered quarto notebook, and should enter on each right-hand page, in impersonal form, concise descriptions of the experiments he carries out, reserving the left-hand page for any desirable drawings or diagrams and all analytical figures and results. On this page also may be affixed, neatly, any graphs by which his experimental results are expressed. The general appearance of neatness depends partly on a student's handwriting, but a bad writer may produce a respectable notebook with care and the avoidance of mistakes that need correction.

The question of a rough notebook arises. The ideal is to work so neatly that a rough notebook is unnecessary, the results obtained being immediately entered in ink by means of a fountain pen. This is the method of the research chemist. The beginner may be permitted a rough notebook, however, in which to record analytical figures in pencil, provided he enters them in his fair notebook in the laboratory, library, or other convenient place, and submits his record to a demonstrator before proceeding to the next experiment. Analytical results must never be taken down on scraps of paper, which may be lost; and rough notes must never be allowed to accumulate, but must be entered up whilst the impressions of the experiment are fresh in the memory.

The following is the form in which the results of the above experiment should be entered:

	I	II
Weight of crucible + hydrated salt	=	gm.
Weight of crucible	=	gm.
Weight of hydrated salt taken	=	gm.

Weight of crucible + hydrated salt	=	I	II	gm.
Weight of crucible + salt after heating				
= (i)	}	=		gm.
(ii)				
(iii)				
Loss of weight = water expelled	=	—	—	gm.

$$\text{Percentage of water in hydrated salt} = \frac{\text{loss of weight} \times 100}{\text{weight of hydrated salt}} =$$

The experiment should be done in duplicate, and the two results entered up side by side. They should not differ by more than 0.5 per cent from each other or from the calculated value, since the salt used should be pure.

Note on Percentage Error.—By percentage error is meant the percentage error on the percentage of the constituent being estimated, not on 100 per cent. For example, if a hydrated salt should contain 20.0 per cent of water, a 0.5 per cent error would mean an error of ± 0.1 per cent and not ± 0.5 per cent in the estimated amount of water, since 0.1 is 0.5 per cent of 20.0.

This standard of accuracy should be maintained in all ordinary cases of simple gravimetric analysis.

(ii) Estimation of Barium. First perform the following qualitative experiments:

Dilute a few drops of the bench barium chloride solution with half a test-tubeful of water, and divide the diluted solution into two parts. Do the same with some sulphuric acid. Then (a) mix the cold dilute solutions of barium chloride and sulphuric acid and observe the character of the precipitate; (b) heat both solutions to boiling before mixing, and compare the precipitate with that obtained from the cold solutions. It will be noticed that in (b) the precipitate will settle more quickly than in (a), and if an attempt is made to filter both precipitates, that formed from the hot solutions will filter readily, whilst that formed cold will be difficult to filter, and will probably run through the filter paper.

Evidently, then, in the quantitative experiment to follow, both solutions should be boiling when precipitation takes place, so that the barium sulphate may be obtained in the more granular and easily filtered form. The finely divided form may, however, be gradually converted into the granular form by keeping it in contact with the heated solution for a length of time. Barium sulphate is soluble in water to the extent of from 2 to 3 mgm. per litre, and the granular rather than the finely divided form separates from the hot solution because the former is slightly less easily dissolved in hot water than the latter, though it is the more soluble form which is first precipitated from cold solution.

The Process.—It is desirable to have 0.5 to 0.7 gm. of precipitated barium sulphate to weigh; therefore take a corresponding amount of your barium chloride for the estimation, weighing it on a tared watch-glass. Dissolve the salt in about 100 c. c. of distilled water in a 500-c. c. beaker, and add a few cubic centimetres of dilute hydrochloric acid. Place in the beaker a glass rod with rounded ends, cover the beaker with a clock-glass, and heat the solution to boiling. Meanwhile pour into a boiling tube rather more than sufficient dilute sulphuric acid to precipitate the barium. This volume can be calculated if the concentration of the dilute sulphuric acid (e.g. 2N) is known. Heat the acid to boiling, remove the clock-glass from the beaker, and mix the two boiling solutions by stirring. Again cover with the clock-glass, leaving the glass rod protruding through the lip of the beaker, and adjust the flame so that the liquid is kept for one hour just short of boiling, and quiescent. The precipitate will gradually settle, leaving the supernatant liquid clear. A few drops more sulphuric acid may now be added to make sure that all the barium is precipitated. Meanwhile prepare the filter.

Preparation of a Filter.—Much care should be bestowed on the preparation of a filter in gravimetric work.

An 11-cm. filter of suitable texture, the ash of which is of negligible weight,* should be folded into four in the usual way and tested by being fitted into the funnel dry. It should fit the funnel tightly; if it does not, the second fold should be opened to give a little more paper. As a rule, slightly more than a quadrant is needed to make a satisfactory filter. The filter must not fill the funnel to the rim; it should leave not less than $\frac{1}{4}$ in. of glass free at the top. The filter is then wetted, and with the first finger carefully pressed to the glass and made to fit it closely all over. The purpose of this procedure is to prevent air passages forming between the paper and the glass; then when liquid begins to run through the filter it will displace all the air from the stem of the funnel provided this is narrow; and the column of liquid with which the stem becomes filled will on account of its weight have an accelerating effect upon the filtration. This effect may be enhanced by fixing on to the end of the funnel a tube bent as shown in fig. 8. Only in cases of difficult filtration, however, is this device necessary; and it must be remembered that by causing too great a pull upon the filter paper, the paper may be ruptured and the filtration spoilt.

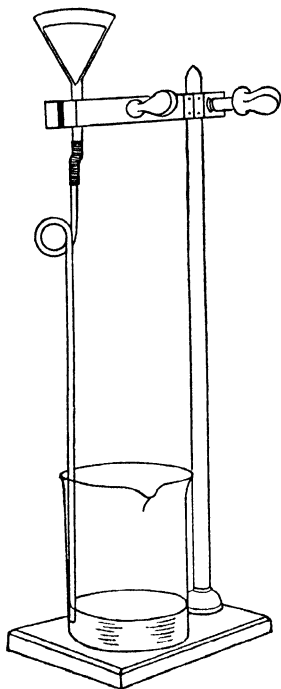


Fig. 8.—Accelerated Filtration

* If an "ashless" filter cannot be obtained the weight of ash must be known, and subtracted finally from that of the crucible contents. Good quality filter paper which can retain fine particles must be used.

Filtration.—Filtration may now be proceeded with. The precipitate is to be washed several times by decantation and finally on the filter. Since the solution contains excess of sulphuric acid which is to be eliminated by washing, the process may be observed by testing successive portions of wash-water for sulphate.

Place the prepared filter in the filter stand and provide a beaker to receive the filtrate. Cause the stem of the funnel just to touch the side of the beaker, so that the liquid will flow down without splashing. Never allow the liquid to drop freely from the funnel, as it is quite possible for drops to be thrown out of the beaker by splashing. Take hold of the beaker near the rim with the first finger and thumb of the right hand—it will probably not be too hot to hold, and the chemist must learn to handle hot things—and lift out the glass rod with the left hand. Direct the glass rod into the filter so that its end nearly touches the apex, and bring the tip of the beaker against the side of the rod just above the funnel. Then by carefully inclining the beaker pour the supernatant liquid through the filter without disturbing the precipitate. The liquid will run through so quickly that it should be possible to pour the whole of it into the funnel at a single operation, leaving the precipitate undisturbed at the bottom of the beaker.

That is the first decantation. Pour off a little of the filtrate into a test tube to test for sulphate, and reject the rest. Now add to the precipitate in the beaker a volume of boiling water from the wash-bottle about equal to the volume of the original solution; stir well, allow to settle, and again decant. Test the filtrate for sulphate as before. Whilst the original filtrate contained much sulphate, the second filtrate consisting of the first wash-water will contain little; the more thorough the decantation the less will be the sulphate remaining.* Repeat

* **Theory of Washing.**—If the amount of substance in x c. c. of solution wetting the precipitate is y gm., and ax c. c. of wash-water are used, the amount of substance remaining when the wash-water has run through, leaving the same volume of solution wetting the pre-

the washing and filtration; the second wash-water will probably show scarcely a trace of sulphate.

The precipitate is now to be transferred to the filter; this is a delicate operation which requires much care. First, attention must be paid to the *wash-bottle*. The jet must be moderately fine and be firmly fixed to the delivery tube by a good piece of rubber tubing. It is disastrous to have the jet fall off into the beaker at a critical point in the operation. String or rag should have been bound round the neck of the wash-bottle so that the latter may be held with comfort when containing boiling water. If the wash-bottle is held in the right hand, the beaker and the rod must be held in the left unless the latter is discarded. The rod may be held across the middle of the beaker so as to point from the lip into the funnel, and thus serve to lead into the filter the precipitate which is being washed from the beaker. This is difficult, however, and care must be taken that the rod does not slip away sideways. The student may prefer to lay aside the rod, taking care to lose none of the precipitate adhering to it, and to wash the precipitate from the beaker into the filter by a well-directed jet of water alone. In this case, however, loss by splashing must be carefully guarded against. When transferring the precipitate the student must avoid filling the filter too full; and, if necessary, he must wait till the filter empties before finishing the operation. When all the precipitate has been transferred safely to the filter the sides of the beaker are rubbed with the stirring rod tipped with rubber, or with a camel-hair brush to loosen any adhering particles of precipitate,

precipitate as before, will be $\frac{y}{a+1}$ gm. If the process is repeated the amount will be $\frac{y}{(a+1)^2}$ gm., and after n times $\frac{y}{(a+1)^n}$ gm. In order that this quantity may be as small as possible the relative value of a must be large. If the volume of wash-water used is constant, the most satisfactory result will be secured by allowing the precipitate to drain as thoroughly as possible after each washing. It is therefore of little use to add more water until all the liquid has run through the filter. The actual amount of washing required will probably be greater than this theory indicates owing to adsorption, i.e. the retention of dissolved substance at the surface of the precipitate.

which are then washed into the filter. Finally, the precipitate is washed on the filter till the wash-water is quite free from sulphate, and the precipitate lies flat in the apex of the filter. If a little of the precipitate has crept up the sides of the funnel above the filter paper this can be dealt with subsequently.

Drying and Ignition of the Precipitate.—It is frequently recommended to dry completely in the steam oven the filter containing the barium sulphate, and then to remove the precipitate from the filter paper, the latter being ignited separately from the precipitate. There is no sacrifice of accuracy, however, and much gain of time by adopting the following method.

Partially dry the filter in the oven or in the air until it can be removed from the funnel damp, but not dripping wet. In this condition it can be lifted out by the fingers after being loosened, if necessary, by means of a knife blade inserted between the paper and the glass. Place the filter directly in the crucible, folding it over so that the paper occupies as small a space as possible. If a little barium sulphate is discovered on the glass funnel, this may be secured by rubbing the glass with the damp filter before it is removed, or by using a small moistened piece of another filter, and adding this to the contents of the crucible.

Now place the crucible on the triangle supported on a tripod and heat it with a small non-luminous flame. The filter will soon be quite dry, and will then catch fire in contact with the flame. Whilst the paper is burning the tip of the flame should touch the bottom of the crucible; if it surrounds the latter free combustion is hindered. Do not use the crucible lid during this operation, for this retards combustion and receives a deposit of carbonaceous matter from the destructive distillation of the paper, which would otherwise have been completely burnt. When the flame from the burning paper ceases the black residue will glow as the carbon burns away. After

the residue has become white allow it to cool, then add to it a drop of dilute sulphuric acid,* cautiously evaporate till sulphuric acid fumes cease to be evolved, then roast the residue for a few minutes by causing the tip of the Bunsen flame, with maximum air supply, to heat the bottom of the crucible red hot. Allow the crucible to cool sufficiently, transfer it to the desiccator by the use of the tongs, put the lid upon it, and weigh it when cold. Repeat the heating, cooling, and weighing, and when the weight is constant calculate from the amount of barium sulphate obtained the percentage of barium in the salt.

(iii) Estimation of Chloride.

Chloride is estimated gravimetrically by converting it into silver chloride, which is collected and weighed.

The student may learn the properties of silver chloride by the following experiment. Add to some dilute hydrochloric acid in a test tube one drop of dilute silver nitrate solution, and shake. The precipitated silver chloride appears as a turbidity, but there is no coagulation. Continue to add the silver nitrate with shaking. When the two reagents have been mixed in about equivalent quantities, shaking produces coagulation of the precipitate into flocks so that the liquid becomes nearly clear. The addition of a little dilute nitric acid and warming promotes coagulation. Thus the precipitated silver chloride can be obtained in a condition fit for easy filtration. Now allow the precipitate in the test tube to stand for some minutes in sunlight, or for an hour or two in the brightest daylight available. Notice that it turns violet. This is an example of the well-known action of light on silver salts; it is a change

* The following is the reason for this procedure. When barium chloride is being precipitated by sulphuric acid a little of the former is carried down with the precipitate, and so fails to be converted into sulphate. Now since the molecular weight of BaCl_2 is less than that of BaSO_4 , the precipitate will weigh less than if it were all BaSO_4 , and the estimation will give a low result. Any BaCl_2 in the precipitate, however, is easily converted into sulphate by means of sulphuric acid.

accompanied by the loss of chlorine, involving, therefore, a diminution in weight which the analyst must avoid. Consequently when the estimation is being performed in bright weather the precipitate must be protected from the light as much as possible by a piece of brown or black paper held round the beaker by a rubber band.

The Process.

Precipitation.—Weigh 0.3 to 0.4 gm. of your barium chloride; dissolve it in about 100 c. c. of cold water in a suitable beaker, add about 5 c. c. dilute nitric acid and silver nitrate solution with constant stirring until the latter is just in excess. To add the requisite amount of silver nitrate without unnecessary excess it is well to calculate and weigh the required quantity of the solid salt, or to use a measured volume of a solution of known strength. It does not suffice to use the solution prepared for qualitative analysis; this is far too dilute. The liquid containing the precipitate is now to be warmed, but not boiled, to complete the coagulation. Stand the beaker, therefore, on the water bath or hot plate, protect its contents from the light if necessary, and stir at intervals until the coagulated precipitate collects at the bottom of the beaker and the liquid above it is quite clear. Add a few drops more silver nitrate to make sure that precipitation is complete. If this is so, filtration may be proceeded with.

Filtration.—The precipitated silver chloride may be filtered through filter paper or asbestos. The latter is preferable, but both methods should be practised for the sake of the manipulation required.

(a) *Filtration through Paper.*

Prepare the filter in the usual way, decant the hot supernatant liquid through it, and wash the precipitate several times by decantation, using hot water mixed with a little dilute nitric acid; then transfer the precipitate to the filter,

wash it again on the filter with the same mixture until the wash-water shows with hydrochloric acid no turbidity due to silver; finally wash it with a little hot water to remove the nitric acid, and dry in the steam oven. Before placing the funnel with its contents in the oven, it is well to cover it with a piece of filter paper pressed downwards round the rim, having first marked the paper for the purpose of identification. Funnels are kept upright in the oven by means of a shelf provided with holes for their stems to pass through. About an hour will be required to dry the precipitate thoroughly.

The precipitate is to be ignited in a porcelain or silica crucible, which should be weighed together with its lid. The following is the procedure:

Have ready two pieces of black glazed paper, one about 4 in. and the other about 8 in. square; also a clean pocket-knife and a camel-hair brush. Lift out the dry filter from the funnel, and gently rub its sides together to detach as far as possible adhering pieces of silver chloride. Empty the loosened precipitate on to the smaller square of black paper and cover it with the funnel. Then, with the tip of the knife-blade, remove all you can of the precipitate from the filter, taking care, however, not to remove any fluff from the paper. It is necessary to be very careful at this stage, as when the paper is opened out it is springy, and there is danger on this account of particles of the precipitate being thrown out. The larger square of black paper may be placed on the bench and the filter held over it so that stray particles may not be lost. All the precipitate, except what cannot be removed from the paper, is now placed under the funnel on the small black square, the camel-hair brush being used to sweep it together.

The filter paper is now to be incinerated. Fold it into as small a compass as possible with the apex inside, and place it in the crucible; also add at this stage any trace of silver

chloride that may be left on the funnel, removing it therefrom by a moistened scrap of filter paper. Burn the filter, keeping the lid off the crucible. After complete combustion of the paper, a small quantity of metallic silver will remain, owing to reduction of the chloride during incineration. This must be converted first into nitrate and then into chloride in the following way. By means of a pointed glass rod add about two drops of concentrated nitric acid to the silver, and warm very gently. The action of the acid on the silver is shown by brown fumes. Then add similarly two drops of concentrated hydrochloric acid. A curd of silver chloride will immediately appear. Now very gently evaporate all the acid by placing the crucible 2 in. away from the tip of a tiny Bunsen flame. Allow the crucible to cool, place it on the larger piece of black paper, and carefully brush into it the main quantity of the precipitate. Although the silver chloride has been dried at a temperature approaching 100°C. , it will still contain a little water, and needs gentle ignition to make it anhydrous. Heat it for a few minutes with a very small flame, and if it shows signs of fusion round the edges, at once remove the flame. Silver chloride fuses at 460°C. , and may be volatilized at a higher temperature. Cool the crucible in the desiccator and weigh it; then repeat the heating till a constant weight is obtained.

(b) *Filtration through Asbestos.*

From the description of the asbestos filter which follows, the student will understand that it is to be preferred to the paper filter for silver chloride, because there is no transference of the precipitate nor reduction of any of it to metallic silver.

Preparation of the Filter.—The filtering vessel consists of a porcelain crucible having a broad flat base pierced with a number of fine holes; this is known as a *Gooch crucible*. The filter is made by covering these holes with a compact

layer of asbestos, through which the solution can pass whilst the precipitate is retained. The asbestos must be *fibrous*; the fluffy kind, which clings to the fingers and the clothes is useless, for even pure water runs only slowly through a filter made of it. If a suitably prepared specimen is not available, the fibrous mineral itself may be employed. The fibres are separated and cut up with scissors into $\frac{1}{4}$ -in. lengths. They should then be boiled with concentrated hydrochloric acid to remove iron, afterwards washed free from acid, and suspended in water to make a thin mixture easily poured. To prepare the filter, fix the crucible by means of a broad piece of rubber tubing into the adapter which passes through the rubber stopper of a filtering flask. The rubber may pass within the adapter or be stretched over it, but it must make an air-tight joint between the crucible and the adapter. Then pour a little of the asbestos mix-

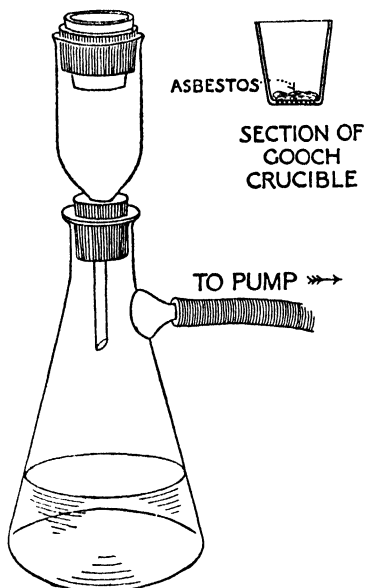


Fig. 9.—Asbestos Filter

ture into the crucible, and allow the asbestos gradually to settle down as the water trickles through. Next put on the pump and so draw the asbestos down into a compact mat. If the holes are all covered, and the mat is continuous, there is probably sufficient asbestos. Test the filter by pouring water through it while the pump is working. If the filter is properly made, the water will pass through very fast, so that a filtration can be carried out in a minute or two. The filter

should be dried at the same temperature as that at which the precipitate is subsequently dried. Silver chloride needs to be heated to not less than 130° C. to be rendered anhydrous. The Gooch filter may therefore be dried at this temperature in an air oven, after being heated for some time in the steam oven to remove most of the water. It may be more conveniently dried, however, by being suspended a short distance above a small flame. When the weight of the filter is constant, fit it into the adapter connected with the filtering flask, fill the crucible with water, and gradually apply suction. Then filter the silver chloride, washing by decantation and on the filter as before. It should be possible to pour the liquid continuously in a thin stream from the beaker into the crucible, and then readily to transfer the precipitate by means of a jet of water from the wash-bottle. Care must be taken during this latter operation not to cause the funnel to overflow. The final washing is more easily carried out than when filter paper is employed. Lastly, the Gooch crucible containing the precipitate on its asbestos mat is dried, first in the steam oven and then at 130° C., or directly over a small flame. In the latter case, however, the crucible must be placed within another crucible with a solid base, and may be conveniently embedded in fluffy asbestos. This procedure is necessary, since reducing gases from the flame would otherwise penetrate the holes and the asbestos mat, and so affect the silver chloride.

The percentage of chloride in barium chloride found by this method should agree closely with that found by the older method of filtration. The student can now make up his mind which method he would prefer to use in future. Provided the Gooch filter is successfully made, there can be no doubt which method is the more expeditious.

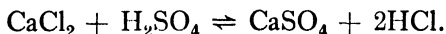
The analysis of barium chloride is now completed, and the results should be entered in the following way:

Quantitative Analysis of Barium Chloride, $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$

	Found.	Calculated.	
Ba ^{..}			per cent.
Cl'			"
H ₂ O			"
		100 · 00	"

II. Calcium Sulphate, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.

Calcium sulphate differs from barium sulphate in being more soluble in water and by crystallizing with two molecules of water. The student should consider the significance of these properties with reference to the natural occurrence and uses of the two sulphates. Calcium sulphate is obtained from the chloride by the following reaction:



Notice that the reaction is reversible, and prove it to be so by the following experiment.

Mix together dilute solutions of calcium chloride and sulphuric acid. If the solutions are sufficiently dilute the precipitation of calcium sulphate will be not immediate but gradual; in fact the salt will gradually crystallize from the solution in which it is sparingly soluble. When the precipitate has formed add concentrated hydrochloric acid and heat. Solution will take place, the reaction being thus reversed by excess of hydrochloric acid. Allow the solution to cool; needle-shaped crystals of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ will separate. This illustrates the way in which the hydrated salt may be obtained pure for analysis.

Preparation.

Weigh 5 gm. of crystallized calcium chloride, $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, dissolve it in about 50 c. c. of water, and filter the solution if any suspended matter remains. Calculate how much sulphuric

acid is necessary to convert this quantity of chloride into sulphate; measure the sulphuric acid,* and add it to the calcium chloride solution contained in a suitable beaker. Stir well, and when the precipitate has formed filter it by suction, using a Büchner funnel, and discard the filtrate. Then dissolve the moist precipitate in a sufficiency of hot concentrated hydrochloric acid diluted with an equal volume of water; allow the solution to cool until no more crystals separate; filter as before and wash the crystals on the funnel with water until the wash-water is only faintly acid. Then dry the salt on a piece of porous plate in the air, but protected from dust, and keep it in a clean and dry corked test tube.

Analysis.

Analysis will consist in the estimate of (i) water of crystallization, (ii) calcium, and (iii) sulphate.

(i) Estimation of Water of Crystallization.

The student will remember that when gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, is heated to 120° to 130° C. it is converted into plaster of Paris, $2\text{CaSO}_4 \cdot \text{H}_2\text{O}$, but that if heated above the latter temperature it becomes anhydrous or "dead burnt". Therefore the water of crystallization in the prepared specimen of calcium sulphate can be estimated by the loss on gentle ignition.

Weigh about 1 gm. of your salt in a silica crucible, and ignite it till its weight is constant. From the loss of weight incurred calculate the percentage of water which was present.

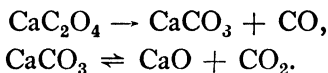
(ii) Estimation of Calcium.

The oxalate is one of the most insoluble salts of calcium; this metal is therefore precipitated from solution by ammonium oxalate in presence of ammonia with a completeness sufficient for quantitative estimation. Moreover, precipitation is not interfered with by the presence of ammonium salts such as

* 2N sulphuric acid contains 98 gm. per litre.

the chloride which, for example, dissolves calcium carbonate. Like barium sulphate, however, calcium oxalate, $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$, separates from cold solution in a finely divided form difficult to filter. Both solutions should therefore be at or near the boiling-point when precipitation is carried out. Perform the following qualitative experiments: (i) precipitate a very little calcium carbonate by adding 1 drop of ammonium carbonate to 1 drop of calcium chloride solution, and dissolve this precipitate in a sufficiency of ammonium chloride; then add to this solution a few drops of ammonium oxalate; calcium oxalate is precipitated. (ii) Precipitate calcium oxalate (*a*) from cold, (*b*) from boiling solution, and notice that the powder settles more quickly in the latter case.

Calcium oxalate is not generally weighed, but is converted into carbonate or oxide, thus



Gentle ignition suffices for the first change, but prolonged heating at a bright red heat is necessary for the second. It is convenient, moreover, finally to convert the lime, whether completely calcined or not, into calcium sulphate.

The Process.—Weigh about 0.5 gm. of your calcium sulphate, suspend it in about 100 c. c. of water in a beaker, heat nearly to boiling, then with stirring add sufficient concentrated hydrochloric acid to dissolve the salt. Add ammonia till the liquid is alkaline; keep nearly boiling and then add excess of boiling ammonium oxalate solution; stir and allow the precipitate to settle, keeping the liquid hot meanwhile. It is well if the precipitate can be kept in contact with the hot liquid for several hours, so that it may become as granular as possible.

Modified Procedure.—It is sometimes recommended* to employ

* Clowes and Coleman's *Quantitative Analysis*.

as the precipitant pure solid ammonium oxalate in preference to the solution, since the precipitate is likely to be more granular when formed from the concentrated solution at the surface of the dissolving crystals. The student may therefore employ this method, taking rather more than the theoretical quantity of the salt $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ for the purpose.

When the precipitate has settled decant the supernatant liquid through a paper filter; wash the precipitate two or three times by decantation with hot water containing a little ammonium oxalate, in which it is less soluble than in pure water; decant the washings through the filter, then transfer the precipitate to the filter and wash it there until it is free from chloride.

The precipitate need not be dried completely, since it is not necessary to separate it from the filter paper. When sufficiently dry to be removed from the funnel, transfer the filter and contents bodily to the weighed crucible; a platinum crucible is to be preferred, but one of silica or porcelain will suffice. Dry the filter carefully, and allow the paper to burn away completely. Some of the calcium oxalate will have already been converted into carbonate and the precipitate may appear grey. It may be weighed successively as carbonate, oxide, and sulphate by the following procedure.

To Weigh as Carbonate.—Nearly cover the crucible with the lid and heat the former until the bottom is just visibly red, maintaining this temperature for about fifteen minutes. This will convert the oxalate to carbonate, but a little oxide may have been produced during the combustion of the filter paper. Consequently it is necessary to recarbonate any oxide present. To do this make a concentrated solution of ammonium carbonate, which has been proved to be free from non-volatile matter, and add a few drops to the contents of the crucible. Carefully evaporate the water, either by the use of a tiny flame, or more safely by employing the steam oven, and then gently ignite the residue until visible fumes and smell of ammonia

cease to be perceived. Cool in the desiccator and weigh; then repeat the process until the weight is constant.

To Weigh as Oxide.—To convert $\frac{1}{2}$ gm. of calcium carbonate to oxide it is necessary to heat it to a bright red heat for about twenty minutes. It is more difficult to do this in porcelain or silica than in platinum; and unless a powerful Méker burner, or compressed air to maintain a continuous blow-pipe, is available, it will be found difficult to complete the process, except in platinum. A greater heat is secured by covering the crucible with the lid, but it must be remembered that the reaction is reversible, so that the evolved carbon dioxide must be allowed to escape freely. Therefore the crucible should not be quite covered. If the student is unable by repeated ignitions to decompose the carbonate completely, he may omit the estimation as oxide and adopt the sulphate method instead.

To Weigh as Sulphate.—Carefully slake the oxide obtained in the last experiment by adding to the cold solid a few drops of water; then add two or three drops of dilute sulphuric acid, and carefully evaporate off the water; afterwards very gently raise the temperature until fumes of sulphuric acid appear, and continue heating till these fumes cease to be evolved. Carry out this operation in the fume chamber. Take care that none of the acid has distilled on to the upper parts of the crucible. Then ignite the residue gently, cool, and weigh it. Repeat the operation till the weight is constant.

Collect together the weights of calcium carbonate, oxide, and sulphate obtained in these three operations, and show that the percentages of calcium indicated as present in the original salt are the same.

Estimation of Sulphate.

Estimation of sulphate is reciprocal to that of barium, since the sulphate is precipitated by adding barium chloride, and the resulting barium sulphate is weighed. Weigh not more than

0.5 gm. of your calcium sulphate, dissolve it in dilute hydrochloric acid, dilute to 250 c. c., heat to boiling, and add excess of barium chloride * solution dropwise, with stirring. Keep the mixture hot for one hour on the steam bath, or over a small flame, then proceed as in the estimation of barium.

Tabulation of Results.

Tabulate the percentages of Ca^{++} , SO_4^{--} , and H_2O found in the analysis of your prepared specimen of calcium sulphate, and place side by side with your results the percentages calculated from the formula $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, thus:

	Found.			Theory.
Ca^{++}	23.32	..	..	23.26
SO_4^{--}	55.75	..	..	55.81
$2\text{H}_2\text{O}$	20.89	..	..	20.93
	<u>99.96</u>	..	..	<u>100.00</u>

III. Copper Sulphate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.

The student is familiar with the preparation of sulphur dioxide by heating together copper and concentrated sulphuric acid, in which copper sulphate is produced. This reaction is sometimes employed for preparing copper sulphate; it is undesirable, however, for two reasons: first, because some of the copper is invariably converted into cuprous sulphide, Cu_2S , which appears as a black residue when the product is poured into water; second, because a large excess of sulphuric acid is present at the end of the reaction, which makes difficult the purification of the copper sulphate. It is therefore better to employ cupric oxide or carbonate as the source of

* It was observed in connection with the precipitation of barium from barium chloride by means of sulphuric acid that some barium chloride is likely to be carried down from solution with the sulphate. The same thing may occur here if the barium chloride is added too quickly so as to be present in excess during the precipitation. To avoid this condition it is best to add the boiling barium chloride drop by drop to the boiling sulphate solution, adding excess of the former after the precipitation is finished.

The addition of sulphuric acid during ignition of the precipitate should be avoided here, since this increases the error due to occluded barium chloride.

the copper, since both these compounds readily dissolve in dilute sulphuric acid, forming the sulphate.

Preparation.

Weigh 5 gm. of copper oxide in the form of black powder, and dissolve it, with the aid of heat, in the minimum quantity of dilute sulphuric acid. It is very desirable to avoid excess of acid, and it is therefore best to place in a beaker or flask less than sufficient dilute acid to dissolve the copper oxide, and after heating it to boiling to add most of the oxide, and then a little more acid, finishing if possible with a little powder remaining undissolved. Some of this powder may be metallic copper, either present originally in the oxide or more probably separated from cuprous oxide by the reaction: $\text{Cu}_2\text{O} + \text{H}_2\text{SO}_4 = \text{CuSO}_4 + \text{Cu} + \text{H}_2\text{O}$.

Filter the solution, which should be deep blue, and evaporate it until a little cooled in a test tube quickly crystallizes. Then cool the main portion of the solution with stirring, until the salt separates as a fine meal of crystals; filter these with suction, pumping them as free from liquor as possible, and spread them on a porous plate to dry in the usual way. A further crop of crystals can be obtained from the mother liquor by immersing in crushed ice the vessel containing it.

That a large proportion of the copper sulphate formed can be obtained by efficiently cooling its saturated solution is shown by the following solubility figures:

Deg. C.	Grams $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ per 100 gm. water.	Deg. C.	Grams $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ per 100 gm. water.
10°	37.0	70°	94.6
30°	48.8	90°	156.4
50°	65.8	100°	203.3

Keep your salt in a clean corked test tube. The crystals retain their right complement of water in ordinary moist air.

Large crystals of the salt can be obtained by slow formation.

Dissolve 2 or 3 gm. of your preparation in a little distilled water so as to obtain a cold saturated solution, or use some of the mother liquor from the original crystals, provided this has not been cooled below atmospheric temperature, and set aside the solution to crystallize slowly.

Analysis.

The complete analysis of crystallized copper sulphate involves the estimation of (i) water of crystallization, (ii) copper, (iii) sulphate.

(i) Estimation of Water of Crystallization.

Copper sulphate loses all its water of crystallization at about 220° C. Dehydration may be effected either (a) by heating the salt to this temperature in an air oven, or (b) by gently igniting it in a current of dry air and collecting the evolved water in a weighed calcium chloride tube.

(a) Procure a pair of watch-glasses with well-fitting ground edges and held together by a clamp. Weigh the watch-glasses and clamp, and take for the estimation about 1 gm. of your copper sulphate, weighing it accurately in one of the watch-glasses. Adjust the temperature of an air oven to about 220° C. by the use of a thermometer suspended within it; then place the watch-glass containing the salt in the oven on a little three-legged platform made by turning down the radial limbs of a pipe-clay triangle. Heat the salt for an hour, then remove it from the oven, clamp the other watch-glass in position, and, after cooling in a desiccator, weigh the dehydrated salt. Heat again for half an hour, and weigh after cooling. Repeat the heating, cooling, and weighing until no further loss occurs, then calculate from the loss the percentage of water of crystallization in the salt. An alternative use of the observed loss is to calculate by means of it the value of x in the formula $\text{CuSO}_4 \cdot x\text{H}_2\text{O}$.

(b) Obtain a piece of combustion tubing about 8 in. long,

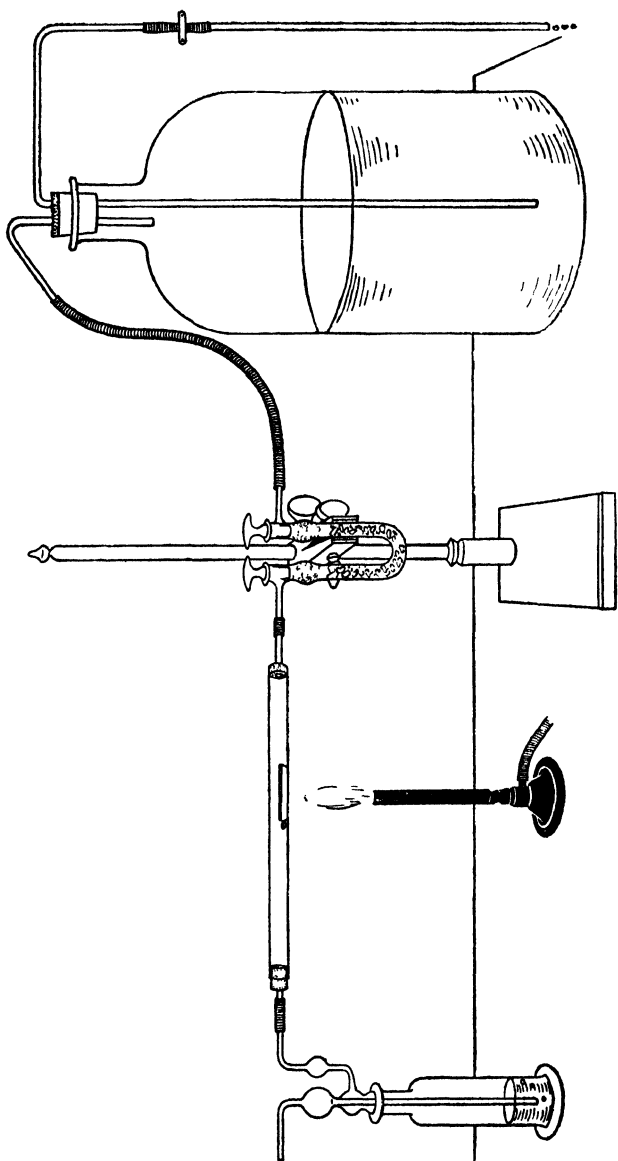


Fig. 10.—Apparatus for estimating water of crystallization in copper sulphate

and make its ends smooth by fusing them in a blowpipe flame; also choose a porcelain boat, from 2 to 3 in. long, which will slide easily into the tube. Clean and dry a plain U tube, fill it to just below the level of the side tubes with granular anhydrous calcium chloride, and keep this in place with a little cotton-wool. Then close the tube with corks and cover them with paraffin wax, preferably by inverting the tube and submerging each cork in the molten wax contained in a dish.* Provide caps, each consisting of 1 in. of small rubber tubing and a short piece of glass rod, to close the side tubes of the calcium chloride tube while it is being weighed. Choose one-hole rubber stoppers to fit the ends of the combustion tube, and pass through them short, tightly fitting pieces of glass tubing. Provide a wash-bottle to contain concentrated sulphuric acid, and an aspirator by means of which air can be drawn through the apparatus.

To carry out the experiment, ignite, cool, and weigh the porcelain boat, place in it as much finely divided copper sulphate as it will conveniently hold, but preferably not less than 1 gm., and again weigh; then push the boat into the middle of the tube, and clamp the latter so that it may be heated with a Bunsen flame. Weigh the calcium chloride tube, remove its caps, and fit together the apparatus in the way shown in fig. 10, using suitable pieces of india-rubber tubing to make the connections. Start the aspirator, arranging that air bubbles pass in quick succession through the sulphuric acid. Then gently heat the tube, moving the Bunsen flame to and fro beneath the boat. As the water is evolved it will collect in small drops in the cooler end of the tube next the calcium chloride tube, and, by extending the heating in this direction, the water may be evaporated and drawn over into the calcium chloride. When it is judged that all the water has been evolved and the salt appears almost white, allow the tube to cool whilst continuing

* If a stoppered U-tube is available this is to be preferred.

the passage of air. Heat again gently to see if any more water is evolved, and if any appears draw this over into the absorption tube. When the salt seems to be quite dehydrated, detach the U tube, fit on the caps, and weigh it when cold. From the increase in weight calculate the percentage of water in the hydrated salt.

Note.—No attempt is made in this experiment to regulate the temperature to which the copper sulphate is heated, and it has already been shown that too strong heating decomposes the anhydrous salt. This will not take place, however, if care is taken, and the flame is moved about during the heating. It will be noticed that a gentle heat, far short of low redness, is sufficient to drive off all the water.

(ii) Estimation of Copper.

Copper can be estimated gravimetrically by weighing it in the form of metallic copper, cupric oxide CuO , cuprous sulphide Cu_2S , or cuprous thiocyanate CuCNS . To weigh as CuO is the simplest method of estimation, and this is chosen here.

Preliminary Experiment.—Study the action of sodium hydroxide solution on copper sulphate in the following way. Add a few drops of sodium hydroxide to some copper sulphate solution in a test tube. Observe that with the first drop a greenish-blue precipitate appears, which becomes deep blue when more alkali is added. The first precipitate is a basic cupric sulphate, which is converted into cupric hydroxide, $\text{Cu}(\text{OH})_2$, by further alkali. Next heat the liquid containing the deep blue precipitate, and notice that this becomes discoloured, and eventually turns very dark brown, and then easily settles to the bottom of the tube, leaving the supernatant liquid clear and colourless.

The hydroxide has been losing water, and the dark brown precipitate has the composition $3\text{CuO} \cdot \text{H}_2\text{O}$. Now add sodium

hydroxide drop by drop to some boiling copper sulphate solution, and notice that the precipitate obtained quickly becomes dark brown, and that owing to the settling of the precipitate it is possible to see when sufficient alkali has been added, and so to avoid adding a large excess. There is reason for avoiding excess of alkali, as the following experiment shows. Add to a small quantity of concentrated sodium hydroxide solution one drop of copper sulphate solution; observe that on shaking the precipitate gradually dissolves, forming a deep blue solution. Whether chemical combination between cupric and sodium hydroxides takes place, or whether the effect is due to the former hydroxide becoming colloidal, it is evident that excess of alkali tends to hold copper in solution, and should therefore be carefully avoided.

The Process.—Weigh carefully from 0.7 to 1.0 gm. of your copper sulphate; dissolve it in about 100 c. c. of water in a large porcelain dish or glass beaker, preferably the former, and heat the solution to boiling. Now add to the boiling liquid a solution of pure sodium hydroxide drop by drop, whilst constantly stirring with your rubber-tipped glass rod, until the supernatant liquid becomes colourless. Filter through paper, decanting and washing the precipitate several times with hot water until the decanted liquid, after passing through the filter, ceases to show an alkaline reaction. Then transfer the precipitate to the filter and again wash, making sure that all alkali has been removed.

If any precipitate adheres to the dish or beaker too firmly to be removed by rubbing, dissolve this precipitate in a few drops of dilute nitric acid, heat the solution to boiling, and precipitate as before by adding sodium hydroxide just in excess. Filter through a fresh filter and wash thoroughly. Dry the filter or filters in the steam oven.

Meanwhile prepare a porcelain or silica crucible, and have ready your glazed paper and camel-hair brush. Remove as

much copper oxide as possible from the thoroughly dried filter paper, receiving it on the small square of glazed paper and covering it with the funnel. Burn the filter or filters in the open crucible with a small hot Bunsen flame touching the bottom. When all the carbon has burnt away, continue roasting the residue in the crucible for a short time to secure oxidation of metallic copper resulting from reduction of the oxide. It is sometimes recommended to add a drop of nitric acid at this stage to effect oxidation, but this is unnecessary provided the residue is heated in an oxidizing atmosphere. Allow the crucible to cool and add the main quantity of the dried precipitate. Again heat, cool in the desiccator, and weigh. Repeat the heating till the weight is constant. From the weight of CuO obtained calculate the percentage of copper in the salt.

(iii) Estimation of Sulphate.

Weigh about 0.7 gm. of your copper sulphate, dissolve the salt in about 100 c. c. of water in a 500-c. c. beaker, add a little dilute hydrochloric acid, and proceed as in the previous estimation of sulphate, washing the precipitate by decantation and on the filter till the wash-water is colourless and free from chloride.

It may here be noted that barium sulphate possesses the power of adsorbing, i.e. of retaining at the surface of its particles, minute quantities of substances dissolved in the liquid with which it is in contact. Consequently, however thoroughly the precipitate has been washed, it may appear a little discoloured after ignition owing to the presence of a trace of copper oxide. The trace of impurity will not be sufficient, however, in this case appreciably to affect the quantitative result.

Tabulate your results as before, placing the theoretical figures alongside your own.

IV. Ferrous Sulphate, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$: Ferrous Ammonium Sulphate, $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$.

Ferrous sulphate, or green vitriol, is easily prepared by dissolving iron in dilute sulphuric acid, and crystallizing the salt from the resulting solution.

Place 10 gm. or more of iron filings in a large beaker or flask, cover them with dilute sulphuric acid, and apply heat till hydrogen begins to be evolved briskly. Allow most of the iron to dissolve, adding more acid if necessary; then filter the solution hot, and rapidly cool the pale green filtrate so as to obtain the salt in the form of a fine crystalline meal. Filter off and drain the crystals by means of the Büchner funnel and vacuum flask, and dry them on filter paper or a piece of porous plate. When they are crisp preserve them in a small stoppered bottle or a well-corked test tube.

Ferrous ammonium sulphate, commonly known as *Mohr's salt*, is a typical example of a double salt, which can be readily crystallized from a mixed solution of its constituent salts. It may be prepared conveniently by dissolving a weighed quantity, say 10 gm., of iron filings in the minimum amount of dilute sulphuric acid contained in a suitable flask and heated on the water bath, as in the preparation of ferrous sulphate, and then adding to the solution the required quantity of ammonium sulphate calculated from the ratio $\text{Fe} : (\text{NH}_4)_2\text{SO}_4$. Enough water should be present to dissolve all the latter salt whilst the flask is immersed in boiling water. The solution is then to be filtered quickly from the finely divided carbon which has separated from the iron, and the filtrate cooled by holding the flask containing it in running water. The double salt soon crystallizes in granular form, and should be separated from the mother liquor and dried in the usual way. It is well, however, to wash the drained crystals with a little alcohol to

displace the adhering solution which contains some sulphuric acid. The salt will be found to be rather paler in colour than ferrous sulphate.

Analysis of Ferrous Ammonium Sulphate.*

The complete analysis of this salt would involve the estimation of iron, sulphate, ammonium as ammonia, and water of crystallization. Iron and sulphate are to be estimated gravimetrically by the processes now to be described; the iron can also be determined volumetrically by a method to be described later. Ammonia is also to be estimated volumetrically (p. 102); but the water of crystallization in this salt cannot be determined conveniently, for when the compound is heated in air not only is the iron oxidized, but the ammonium sulphate is volatilized.

(i) Estimation of Iron.

To understand the procedure to be adopted the student may perform the following qualitative experiments:

(a) Add to a solution of ferrous sulphate ammonia in excess. Observe that the precipitate is at first dingy white, becomes dull green, and then nearly black, and finally by atmospheric oxidation turns to rust colour. It is plainly undesirable to have to deal with a precipitate of this kind in quantitative analysis.

(b) Add much ammonium chloride to ferrous sulphate solution, followed by ammonia in excess. The precipitate is less in quantity than might be expected, and indeed from a purely ferrous solution ferrous hydroxide is not precipitated at all by ammonia in presence of much ammonium chloride. Now since ammonium chloride is frequently present in solutions from which iron is to be precipitated, the iron must not

* The instructions which follow may be applied equally to the analysis of crystallized ferrous sulphate.

be present in the ferrous state or precipitation will be incomplete.

(c) Study the oxidation of iron thus. To some ferrous solution add a few drops of concentrated nitric acid; observe that the solution turns nearly black; this is due to the reduction of some of the nitric acid to nitric oxide, NO, by means of ferrous sulphate, and the combination of this gas with some of the unchanged ferrous salt to form a dark coloured compound, the same indeed as is formed in the "brown ring" test for nitrate. Now heat the solution; brown fumes are evolved and the solution turns yellow; the iron has thus been oxidized to the ferric state. Add ammonia in excess to a few drops of this solution; a rich brown precipitate is formed which on heating is seen to float freely in a colourless liquid. This is ferric hydroxide, $\text{Fe}(\text{OH})_3$, which can be readily filtered, and when ignited yields pure ferric oxide, Fe_2O_3 . Iron is estimated gravimetrically by being weighed in this condition.

The Process.—Weigh from 0.7 to 1.0 gm. of your ferrous ammonium sulphate; place it in a Jena glass beaker of 500 c. c. capacity, or preferably in a 6-in. porcelain dish. Dissolve the salt in water together with a few drops of dilute sulphuric acid. Provide a rubber-tipped stirring rod and a clock-glass to cover the beaker or dish. Add to the solution a few cubic centimetres of concentrated nitric acid and gradually heat. Observe the process of oxidation, and when it is judged to be complete (test by adding more nitric acid), dilute the solution to 200 c. c. and heat to boiling. To the fully oxidized solution add some ammonium chloride and then ammonia, carefully with stirring, until the precipitate is permanent. A distinct though not a large excess of ammonia must be present, or the precipitate may contain some basic sulphate instead of hydroxide. Filter the precipitate through paper, washing by decantation and on the filter till the washings

are free from chloride. Do not dry the filter completely, but ignite the damp filter and contents together in an open porcelain or silica or, better, a platinum crucible. Take care that all the carbon from the filter paper burns away, and then thoroughly roast the residue. The pure Fe_2O_3 finally obtained will consist of nearly black, brittle fragments, together with some particles of a dull red colour derived from that part of the precipitate which adhered to the filter paper. When a constant weight of Fe_2O_3 has been obtained, calculate from it the percentage of iron in the salt.

(ii) Estimation of Sulphate.

The precipitation of sulphate as barium sulphate cannot be carried out accurately if the solution contains ferric iron. To overcome this difficulty either of the following methods may be adopted.

(a) The iron may be precipitated by ammonia, the ferric hydroxide filtered off, and washed free from sulphate, all the sulphate being precipitated from the filtrate after acidifying it with hydrochloric acid. The filtrate from the estimation of the iron in the previous experiment can be employed, provided no sulphuric acid was added to the liquid.

(b) The sulphate may be precipitated by barium chloride from ammoniacal solution in presence of suspended ferric hydroxide, the latter being then dissolved by adding hydrochloric acid in excess. Since iron was not in solution during the precipitation of barium sulphate, its presence afterwards will not contaminate the precipitate.

Employ not more than 0.7 gm. of ferrous ammonium sulphate for the estimation of sulphate, and from the weight of barium sulphate obtained calculate the percentage of sulphate in the salt.

The analysis of ferrous ammonium sulphate will be completed later by the estimation of ammonia volumetrically.

V. Lead Nitrate, $\text{Pb}(\text{NO}_3)_2$.

This salt, which crystallizes anhydrous and pure from a slightly acid aqueous solution, may be conveniently prepared by dissolving metallic lead, or the monoxide or carbonate of this metal, in warm dilute nitric acid and evaporating the solution until it will crystallize on cooling.

Preparation.

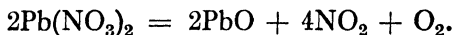
Place 5 gm. of lead foil in a porcelain dish or beaker, cover it with a little water, and then add concentrated nitric acid whilst stirring and warming the mixture until the metal dissolves readily. When solution is effected, evaporate the solution until, from a few drops of it placed upon a watch-glass, crystals separate on cooling; then quickly filter the solution and cool it with shaking, so that a crystalline meal separates. Filter off the crystals, wash them with a very little water to remove adhering nitric acid, drain, and dry them. The crystals will be pure, provided they have been separated from an acid solution. If the salt is crystallized from water alone, it is liable to be slightly basic, owing to hydrolysis.

Large crystals of the salt can be obtained by arranging for their slow growth. These consist of regular octahedra, and are colourless and transparent when pure; if they are formed in absence of acid, so as to be slightly basic, they are opaque and porcelain-like.

Analysis.

Place a little lead nitrate in a dry test tube and heat it strongly. If the crystals are large the salt decrepitates, but this does not occur so much with the powder. The salt evolves brown fumes which are a mixture of nitrogen peroxide and oxygen, and, after passing through two forms of basic

nitrate, leaves a residue of monoxide, produced according to the reaction:



Thus, since $\text{Pb}(\text{NO}_3)_2$ decomposes into PbO and the elements of N_2O_5 , nitrate expressed as N_2O_5 is estimated by determining loss on ignition.

Lead is estimated by being precipitated and weighed as sulphate.

(i) Estimation of Nitrate.

Weigh accurately about 1 gm. of dry and finely powdered lead nitrate in a porcelain or silica crucible which has been weighed with its lid. Suspend the crucible on a triangle above a small flame, and gently ignite the salt, at first almost covering the crucible with the lid to prevent possible loss by fragments of the salt being ejected from the crucible. Eventually heat the crucible strongly with the lid off, taking care, however, that no reducing gases from the flame enter it. If any fragments of the salt are found adhering to the lid, take care that they too are decomposed before the crucible and its contents are weighed. Cool the crucible and contents in a desiccator and weigh them; then repeat the operation till the weight is constant.

Finally, calculate the loss of weight, representing N_2O_5 , as percentage of nitrate, NO_3' .

(ii) Estimation of Lead.

Lead sulphate is soluble in about 22,000 parts of water at atmospheric temperature; it is less soluble in dilute sulphuric acid, although in the concentrated acid with which it combines chemically it is much more soluble than in water. In alcohol, lead sulphate is practically insoluble. Since lead nitrate is the salt to be analysed, and dilute nitric acid exerts solvent action on lead sulphate, it is desirable to volatilize the nitric acid liberated in the precipitation of the sulphate by sulphuric acid.

These considerations will explain the following procedure.

Method.—Weigh about 0.5 gm. of your lead nitrate, place it in a 4-in. porcelain dish provided with a clock-glass and suitable stirring rod, and dissolve it in a little water. Add to the solution with stirring 5 c. c. of concentrated sulphuric acid; place the dish, covered with the clock-glass, on asbestos-covered gauze supported on a tripod stand, and heat with a small flame so as to secure slow and continuous evaporation. When evaporation has proceeded so far that fumes of sulphuric acid begin to appear, remove the flame and allow the contents of the dish to become quite cold. Then add with stirring 20 c. c. of water, remembering that caution is necessary in adding water to concentrated sulphuric acid. If convenient, allow the precipitate to remain in the liquid for a few hours; it will then filter better. Filter through an asbestos filter in a Gooch crucible; transfer the precipitate to the filter by the use of dilute sulphuric acid in a wash-bottle, and wash it free from acid by alcohol. Evaporate the alcohol remaining on the precipitate in the steam oven; afterwards ignite the precipitate in the crucible by placing the latter inside a larger crucible of porcelain or nickel, which is then heated with a gas flame. The covering crucible is necessary, since the flame gases would otherwise reach the lead sulphate through the holes in the base of the Gooch crucible and reduce it. Weigh the crucible and contents after cooling, and repeat the ignition till the weight is constant.

From the weight of lead sulphate obtained, calculate the percentage of lead in lead nitrate.

VI. Sodium Phosphate, $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$.

Of the three phosphates of sodium, NaH_2PO_4 , Na_2HPO_4 , and Na_3PO_4 , the first is acid, the third strongly and the second faintly alkaline to litmus.* The second is the easiest salt to

* The student should seek for an explanation of these facts in a textbook of descriptive or theoretical chemistry. See also p. 155.

prepare, and is formed by adding the requisite quantity of sodium hydroxide or carbonate to an aqueous solution of phosphoric acid.

Preparation.

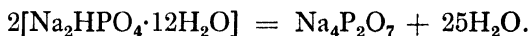
Measure 5 c. c. of syrupy phosphoric acid, and dilute it to about 50 c. c. with water. Warm the solution, and add to it anhydrous sodium carbonate little by little until effervescence ceases. Heat the solution to boiling, and filter it if necessary. This will be the case if the phosphoric acid was prepared from bone-ash containing iron, calcium, or magnesium, for the phosphates of these metals will then be precipitated when the acid is neutralized. Receive the hot filtered solution in a flask, and quickly cool it so as to separate the sodium phosphate in small crystals. Crystallization may be retarded owing to supersaturation; if so, the eventual separation of crystals after agitation or scratching will be accompanied by a perceptible rise in temperature. Filter off the crystals and dry them in the air in the usual way.

Analysis.

Two estimations can be made: (i) loss on ignition; (ii) phosphate.

(i) Loss on Ignition.

Ignition of hydrated disodium hydrogen phosphate not only drives off water of crystallization, but converts the salt into pyrophosphate thus:



Perform this experiment qualitatively by placing a small amount of the salt in a test tube, and heating it at first gently and then strongly in a Bunsen flame. The salt melts in its water of crystallization, then dries up as the water is evolved, and pyrophosphate is formed. Allow the test tube to cool,

and dissolve its contents in cold water. Show that the solution gives a white precipitate with silver nitrate ($\text{Ag}_4\text{P}_2\text{O}_7$), whilst sodium phosphate gives a yellow precipitate (Ag_3PO_4).

For the estimation take about 1 gm. of your crystallized salt, placing it in a porcelain or silica crucible weighed with its lid. Place the crucible on a triangle supported about an inch above a tiny Bunsen flame, put the lid nearly on, and apply heat very cautiously, since the evaporation of water from the fused salt is liable to cause spurting with consequent loss. When the salt has become dry again increase the temperature until the crucible is red hot; then after a few minutes cool and weigh it. Repeat heating and weighing until the weight is constant. From the loss of weight calculate the percentage of water in the salt.*

(ii) Phosphate.

Phosphate is estimated by precipitation as magnesium ammonium phosphate, $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$, and weighed as the pyrophosphate, $\text{Mg}_2\text{P}_2\text{O}_7$, into which the former salt is converted by strong ignition.

Take about 0.7 gm. of your sodium phosphate, and in order to secure the precipitation of all the phosphate in the form of $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$, adopt the following procedure. Dissolve the salt in about 100 c. c. of water in a suitable beaker, add to the solution a little dilute hydrochloric acid, 25 c. c. of "magnesia mixture",† and 5 gm. of ammonium chloride dissolved in a little hot water. No precipitate will yet appear, because the solution is acid. Heat the liquid almost to boiling, add two drops of methyl-red indicator solution, and then add with stirring dilute ammonia solution drop by drop until

* Twenty-four twenty-fifths of this is water of crystallization. Crystallized hydrated sodium phosphate is efflorescent. If a low result is obtained here, this may be because the salt did not contain its full complement of water. In such case recrystallization is necessary.

† "Magnesia mixture" is made as follows: 5.5 gm. $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and 10.5 gm. of NH_4Cl are dissolved in water, together with a little hydrochloric acid, and the solution is diluted to 100 c. c.

a turbidity just appears: almost simultaneously the indicator will turn yellow. Stir until this precipitate becomes crystalline (avoid touching the sides of the beaker), then continue adding ammonia dropwise until precipitation is complete. The indicator will now be permanently yellow and the solution will smell slightly of ammonia. Cool the mixture, then slowly add, with stirring, strong ammonia solution equal in volume to one-fifth that of the solution. This quantity of ammonia is added because the precipitate is distinctly soluble in water, but much less soluble in ammonia solution. Any precipitate adhering to the glass rod should now be washed into the ammoniacal liquid by means of a few drops of dilute hydrochloric acid. After four hours filter the precipitate through an asbestos filter, and wash it with dilute ammonia till it is free from chloride. Ignite the precipitate, at first gently, then at the full temperature of a Méker burner, having the Gooch crucible inside an iron or nickel crucible. When the weight is constant, calculate from the amount of $\text{Mg}_2\text{P}_2\text{O}_7$ obtained the percentage of P_2O_5 in the sodium phosphate.

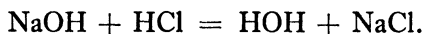
Express your results thus:*

<i>Percentage Composition of $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$</i>			
	Found.		Calculated.
H_2O	..	..	
P_2O_5	..	..	
Na_2O (by diff.)	..	..	
	100.00		100.00

* This method of expressing the results of an analysis is convenient when a compound can be represented as composed of various oxides, and it is always adopted in stating the composition of such minerals as silicates. It cannot of course be used to express the composition of compounds containing no oxygen, such as chlorides.

PRINCIPLES OF VOLUMETRIC ANALYSIS

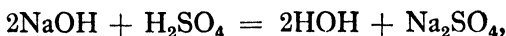
Consider the simple reaction of neutralization represented by the equation:



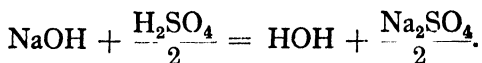
Expressed in molecular weights this states that 40 parts by weight of sodium hydroxide and 36.5 parts of hydrogen chloride in solution just neutralize one another. Suppose, therefore, that 40 gm. of sodium hydroxide (i.e. 1 gram-molecule) are dissolved in water, and the solution is diluted with thorough mixing till it measures a litre, and similarly 36.5 gm (1 gram-molecule) of hydrogen chloride are made to occupy a litre of solution; then not only would these two solutions, each occupying a litre, produce a neutral solution of sodium chloride when mixed together, but smaller equal volumes of each would similarly neutralize one another. These two solutions of alkali and acid respectively are therefore *equivalent*.

Further, the hydrogen chloride solution contains 1 gm. of acidic hydrogen, or if completely ionized, 1 gm. of hydrogen ions per litre; and similarly the sodium hydroxide solution contains 17 gm. of hydroxide ions per litre. Such solutions are said to be of *normal* $\left(N \text{ or } \frac{N}{1}\right)$ strength; solutions of one-tenth this strength are *decinormal* $\left(\frac{N}{10}\right)$, and so on.

Now consider the reaction:

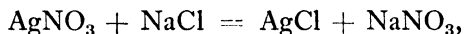


or say,



Thus to be equivalent to normal sodium hydroxide solution, or, otherwise, to contain 1 gm. of hydrogen ions, a litre of sulphuric acid solution must contain half a gram-molecule ($\text{H}_2\text{SO}_4 = \frac{98}{2} = 49$ gm.) of hydrogen sulphate per litre. Similarly normal sodium carbonate solution contains $\text{Na}_2\text{CO}_3 = \frac{106}{2} = 53$ gm. of the pure salt per litre.

Sodium chloride and silver nitrate solutions are used in volumetric analysis on account of the reaction:



in which silver chloride is precipitated. By the same principle normal solutions of these salts would contain each a gram-molecule of the salt, i.e. 170 gm. of silver nitrate and 58.5 gm. of sodium chloride. As a matter of fact, however, these solutions are not employed in a concentration exceeding decinormal.

Solutions of potassium permanganate, KMnO_4 , and potassium dichromate, $\text{K}_2\text{Cr}_2\text{O}_7$, are also employed, on account of their oxidizing power. Therefore the available oxygen they contain is the criterion in determining normal or decinormal strength.

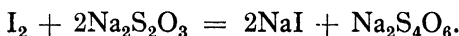
Now 2KMnO_4 (M.W. 316) contains 5 available oxygen atoms, which are equivalent to 10 hydrogen atoms. Therefore a decinormal solution of this reagent contains:

$$\frac{1}{10} \left(\frac{2\text{KMnO}_4}{10} \right) = 3.16 \text{ gm. per litre.}$$

Similarly $\text{K}_2\text{Cr}_2\text{O}_7$ (M.W. 294) contains 3 available oxygen atoms, equivalent to 6 hydrogen atoms; therefore a decinormal solution contains:

$$\frac{\text{K}_2\text{Cr}_2\text{O}_7}{60} = 4.9 \text{ gm. per litre.}$$

On the other hand, consider sodium thiosulphate, $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ (M.W. 248), which is employed in the reaction:



Since 1 molecule of thiosulphate is equivalent to 1 atom of iodine, it follows that decinormal sodium thiosulphate solution, equivalent to decinormal iodine containing 12.69 gm. per litre, is decimolecular and contains 24.8 gm. per litre.

Calculations in Volumetric Analysis.

Suppose that a solution of sodium hydroxide is to be titrated with $\frac{N}{10}$ acid, and that either $\frac{N}{10}\text{HCl}$ or $\frac{N}{10}\text{H}_2\text{SO}_4$ is available. It is immaterial which acid is used, since both will show the same end reaction with the usual indicators. Therefore it is not necessary to know which acid has actually been provided, and the molecular weight of the acid is not brought into the calculation of the strength of the alkali solution titrated.

Thus suppose that the sodium hydroxide in 20 c. c. of the solution required 15 c. c. of $\frac{N}{10}$ acid to neutralize it; then since $\frac{N}{10}$ sodium hydroxide contains 4.0 gm. per litre, this particular solution contained:

$$\frac{4.0 \times 15.0}{20} = 3.0 \text{ gm. NaOH per litre.}$$

The statement might be extended thus, supposing $\frac{N}{10}\text{HCl}$ solution has been employed:

$$\begin{aligned} &\text{Weight of acid used to neutralize the sodium hydroxide in} \\ &\quad 20 \text{ c. c. of solution} \\ &\quad = 15.0 \times 0.00365 \text{ gm. HCl.} \end{aligned}$$

$$\begin{aligned} &\text{Weight of sodium hydroxide equivalent to this acid} \\ &\quad = \frac{15.0 \times 0.00365 \times 40}{36.5}. \end{aligned}$$

Weight of sodium hydroxide in one litre

$$= \frac{15.0 \times 0.00365 \times 40 \times 1000}{36.5 \times 20} = 3.0 \text{ gm.}$$

But why employ all these figures? The same principle may be applied to standard solutions of potassium permanganate or dichromate, the sole question of importance concerning them being: how much available oxygen do they contain per unit volume?

For practical purposes decinormal solutions of acids are decinormal solutions of hydrogen ions, and decinormal solutions of oxidizing agents are decinormal solutions of available oxygen. Therefore once the solutions are made of standard strength the molecular weights of the compounds actually present in them can be ignored, since all but the active participants in them can be regarded as adventitious.

All that it is necessary to know for purposes of calculation about $\frac{N}{10}$ KMnO_4 solution, for example, is that 1 c. c. of it contains 0.0008 gm. of available oxygen, which oxidizes 0.0056 gm. of iron from the ferrous to the ferric state, or liberates 0.01269 gm. of iodine from hydriodic acid, &c.

Calculation and Use of a Factor.

If the solution to be employed should not be exactly normal or decinormal a slight complication arises. Suppose, for example, an attempt has been made to prepare $\frac{N}{10}$ H_2SO_4 , and it is found by titrating it against $\frac{N}{10}$ sodium carbonate solution that 19.8 c. c. of the acid neutralize 20.0 c. c. of the alkali. The acid is evidently slightly stronger than decinormal; and to convert to decinormal strength any volume employed, this volume must be multiplied by $\frac{20.0}{19.8} = 1.01$, for $19.8 \times 1.01 = 20.0$.

The figure 1.01 is called the *factor* for the solution; and it should be noted that when the given solution is stronger than decinormal the factor is greater than unity, and when weaker it is less.

When the factor of a solution is to be employed, every volume of the solution used must be multiplied by this factor before any calculation depending on the volume is made.

Definition.

A normal $\left(\frac{N}{1}\right)$ solution is a solution containing one gram-equivalent of the reacting substance per litre. Seminormal $\left(\frac{N}{2}\right)$, fifth-normal $\left(\frac{N}{5}\right)$, decinormal $\left(\frac{N}{10}\right)$, &c., solutions are of strengths corresponding with these denominations.

Examples.

A normal solution of an acid contains 1 gm. of acidic hydrogen in a litre; a normal solution of an alkali is a solution which, volume for volume, neutralizes a corresponding solution of an acid.

Note.—A normal alkali solution is not conveniently defined as containing 17 gm. of hydroxyl (OH) per litre, because substances which in solution do not immediately contain this radicle in equivalent amount function as alkalis by reason of neutralizing acids. Such are NH_3 , Na_2CO_3 , $\text{Na}_2\text{B}_4\text{O}_7$, &c.

For practice the student may calculate the amount of substance contained in 1 litre of a decinormal solution of each of the following compounds, first considering, however, for what purpose the compound is employed:

$\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$; $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$; NH_3 ; HNO_3 ; NaOCl ;
 $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$; K_2CrO_4 ; KClO_3 ; H_2O_2 .

ACIDIMETRY AND ALKALIMETRY

The estimation of acids and alkalis in solution by the processes of volumetric analysis, i.e. acidimetry and alkalimetry respectively, requires for its performance the use of *indicators*, because the point of neutralization of an acid by an alkali, or vice versa, does not otherwise become apparent.

The student is already familiar with the use of litmus paper in testing for acids and alkalis; the same substance is used in aqueous solution as an indicator in volumetric analysis; besides *litmus*, however, there are other indicators, the chief of which are *methyl orange* and *phenolphthalein*.

Nature and Preparation of Indicators

There are three indicators in common use; these are:

Litmus,
Methyl orange,
Phenolphthalein.

Litmus is a vegetable colouring matter produced from certain lichens by oxidation. As a manufactured product it is mixed with chalk, gypsum, and sometimes alkali carbonate, and its aqueous solution consists of the calcium or alkali salts of the litmus acid. The solution for use in volumetric analysis is generally prepared by extracting the commercial product with boiling water, filtering or decanting the solution from the insoluble matter, acidifying the clear liquid with acetic acid, and then boiling it to expel excess of acid. A few drops of chloroform added to the solution preserve it from bacterial decomposition; air should have access to the stock-bottle or the colour may fade. The solution should be kept in a white-glass narrow-necked bottle, provided with a cork grooved for the entrance of air, and carrying a tube of convenient length,

drawn out slightly at the bottom, to serve as a pipette, so that a suitable volume of indicator may be delivered.

The solution should be of such a strength that three or four drops in 50 c. c. of water will give a depth of colour sufficient for observing the change from blue to red, or vice versa.

Note.—Litmus contains several colouring matters, the chief of which is *azolitmin*. This substance can be obtained from litmus by a lengthy process, and is more sensitive than the crude material. It is employed for specially delicate work in which grades of colour are taken to show slight differences of acidity near the neutral point.

Methyl orange and phenolphthalein differ from litmus in being synthetic products, and therefore definite organic compounds with specific properties.

Methyl Orange is the sodium salt of a complex organic acid.* A concentrated aqueous solution of this salt is deep orange, but on dilution this colour changes to yellow. Acid changes the yellow colour to red; a slight change from pure yellow towards red is taken to indicate the end of a titration of alkali with acid. As little of the indicator as possible should be used; in good daylight the tint in alkaline solution need not be deeper than straw colour. The colour change is not so easy to see as that with litmus or phenolphthalein, and this is specially the case in artificial light.† It is a good plan, in case there is doubt about the point at which the change takes place, to match the colour of the solution being titrated with similarly tinted water; a difference of tint will then be readily observed.

There is no common practice as to the strength of methyl orange solution employed; but 0.02 gm. in 100 c. c. of water will be found a convenient strength. The weaker the solution the less the likelihood of too much being taken for a titration.

* Dimethyl-amino-azo-benzene sulphonic acid, $(\text{CH}_3)_2\text{NC}_6\text{H}_4\cdot\text{N}:\text{N}\cdot\text{C}_6\text{H}_4\text{SO}_3\text{H}$.

† "Screened" methyl orange should be used in artificial light (see p. 159).

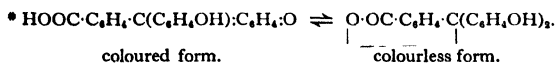
It is convenient to keep the solution in a bottle provided with a pipette passing through a grooved cork.

Phenolphthalein is a complex "aromatic" compound formed, as its name indicates, by combination between phenol and phthalic acid. It is a very feeble acid, and, on neutralization, undergoes an intramolecular transformation* which is the cause of the remarkable change from colourless to crimson colour. This compound is not soluble in water, but is used in alcoholic solution; 1 gm. dissolved in 100 c. c. of ordinary duty-free alcohol forms a solution of convenient strength. It may be stored for use in a similar way to methyl orange.

Study of Indicators

Since indicators are required to show when the point of neutrality is reached as an acid is added to an alkali or vice versa, it is necessary for them to undergo a sharp colour change at this point, or more correctly when the minimum excess of acid or alkali is present. The sharpness of the change produced when, say, a single drop of acid has been added in excess of that required for neutralization depends upon the concentration of the acid and upon its intrinsic strength.

For example, 0.1 c. c. of $\frac{N}{1} \text{H}_2\text{SO}_4$ would be expected to produce a more marked colour change in an indicator than the same volume of $\frac{N}{10} \text{H}_2\text{SO}_4$, unless, indeed, the latter volume of acid were sufficient in itself fully to change the colour. Also a given small volume of a "strong" acid, i.e. one whose acidic hydrogen is largely ionized † in solution would be expected to produce a more decided effect upon



† The student should familiarize himself with the theory of electrolytic dissociation, or ionization. An elementary account of the subject will be found in the author's *Foundations of Chemical Theory*.

an indicator than the same volume of a "weak" acid containing but a small proportion of its acidic hydrogen in the ionized state. Indicators themselves, however, differ in sensitiveness, and consequently a choice of indicator needs to be made according to the kind of acid or alkali to be titrated.

The three common acids—hydrochloric, nitric, and sulphuric—resemble one another in their action on indicators; various organic acids, of which oxalic acid is most commonly employed, are distinctly weaker than the mineral acids, whilst boric and carbonic acids are so weak as scarcely to affect some indicators at all. Alkalis also differ among themselves in their behaviour towards indicators. Sodium and potassium hydroxide, for example, being "strong" bases, i.e. yielding each a high concentration of hydroxide ions in aqueous solution, behave similarly towards indicators; but ammonia solution, which contains only a small proportion of ammonium and hydroxide ions, behaves as a "weak" base, and needs a suitably chosen indicator for its accurate estimation. A few experiments will illustrate these points.

(i) Effect of Different Acids on Methyl Orange.—

Procure some decinormal ($\frac{N}{10}$) sulphuric acid, and also some $\frac{N}{10}$ oxalic acid. Add two or three drops of methyl orange solution to about 500 c. c. of tap water, or distilled water made very slightly alkaline, and pour 100 c. c. of the faintly yellow solution into each of two similar flasks. Then titrate one of the solutions with the $\frac{N}{10}$ sulphuric acid until a distinctly pink tint is produced, and note the volume of acid employed. Now add an equal volume of $\frac{N}{10}$ oxalic acid to the liquid in the other flask. Notice that the same colour change does not take place, and that on adding more oxalic

acid there is a gradual transition from yellow to pink, so that it cannot be decided at what point precisely the titration is finished.

Now it appears that since a certain volume of oxalic acid does not affect methyl orange so decidedly as an equal volume of sulphuric acid of equivalent normality, oxalic acid is a weaker acid than sulphuric acid; and further, since the colour change which $\frac{N}{10}$ oxalic acid produces upon methyl orange is gradual, it is concluded that this indicator is unsuitable for use with oxalic acid.

(ii) Effect of Acids on Phenolphthalein.—Repeat the experiment, using phenolphthalein as indicator, and adding sufficient alkali to turn the indicator pink before measuring off the solution into the two flasks. No difference will be observed between the effect of the two acids in this case, a sufficiently sharp colour change being brought about with either acid. From this it appears not only that phenolphthalein is a more sensitive indicator than methyl orange, but that its sensitiveness is such that the superior “strength” of sulphuric over oxalic acid is superfluous, so far as affecting this indicator is concerned. Therefore it is concluded that phenolphthalein can be used in titrating with oxalic acid, or in comparing the normality of oxalic and sulphuric acids.

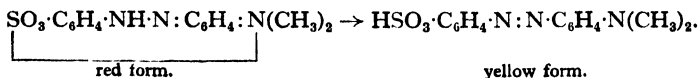
(iii) Effect of Carbonic Acid on Different Indicators.—Examine the effect of carbonic acid (H_2CO_3) upon the three indicators in the following way. Place water to the depth of an inch in each of three test tubes, and add the indicators methyl orange, litmus, and phenolphthalein respectively, followed by sufficient exceedingly dilute alkali in each case to enable the indicator to show an alkaline reaction. Then add carbonic acid from the breath by blowing down a glass tube through each solution, and observe that methyl orange is unaffected, blue litmus is turned bluish red, and crimson

phenolphthalein is made colourless. This result shows that the indicators increase in sensitiveness in the order named.

Now boil the solutions containing the indicators that have been affected, and notice that the original colours are restored. This is because carbonic acid is destroyed by boiling, and the carbon dioxide which produced it driven from the solution.

(iv) **Effect of Dilution on an Indicator.**— Since phenolphthalein and, to a less degree, litmus are affected by carbonic acid, the addition of distilled water containing dissolved carbon dioxide to a solution containing either of these indicators must necessarily diminish to a slight extent the effective alkalinity of the solution, and this fact needs to be borne in mind in doing careful work with these indicators. Dilution of a solution containing methyl orange influences the indicator, however, in another way, which is illustrated thus:

To 25 c. c. of a slightly alkaline solution containing methyl orange add enough $\frac{N}{10}$ sulphuric acid to change the colour somewhat towards pink. Then measure 100 c. c. of distilled water, and gradually add it to the solution containing the indicator. Notice that the colour gradually reverts to the original yellow, which will probably be completely restored when all the distilled water has been added. This effect must be due to dilution alone, since methyl orange is unaffected by any carbonic acid the water added may contain. Again it appears that too much dilution with neutral water should be avoided when a solution containing methyl orange is being titrated. The explanation of this phenomenon is that water by reducing the concentration of the hydrogen ions of the acid causes the indicator to change according to the reaction:



(v) Effect of Ammonia on Different Indicators.—

Dissolve about 1 gm. of ammonium sulphate in 500 c. c. of water, and add, say, 10 c. c. of $\frac{N}{10}$ sulphuric acid to the solution.

Place 100 c. c. of this solution in each of your two flasks; then add methyl orange to one solution and phenolphthalein to the other. Titrate with decinormal sodium hydroxide, first the solution containing methyl orange, and then that containing phenolphthalein, observing the volume of alkali used in each case. It will be noticed that a volume of alkali equal to that necessary to turn the methyl orange in the one flask yellow leaves the phenolphthalein in the other colourless; and that considerable excess of alkali is necessary before even a pale pink colour becomes permanent in the latter case. This experiment shows the uselessness of phenolphthalein as an indicator in titrating solutions containing ammonia.

(vi) Effect of Temperature on Indicators.—Prepare some very dilute sodium hydroxide solution by adding a few drops of the bench reagent to 500 c. c. of water. Add methyl orange to this solution, and take two quantities of 100 c. c. as in former experiments. Titrate one quantity of this solution with sufficient decinormal sulphuric acid to produce a pink tint, and then add the same volume of acid to the other solution, so that both appear precisely the same. Next, heat one solution and observe that pink gives place to yellow as if alkali had been added to the liquid; then cool the solution and notice that the pink colour returns. This experiment shows the necessity of titrating solutions containing methyl orange at atmospheric temperature.

Such necessity does not obtain with litmus or phenolphthalein. Litmus is frequently employed as an indicator in boiling solution, though phenolphthalein is generally used cold.

The Use of Indicators.

From the foregoing experiments the following conclusions regarding the use of indicators are reached.

Litmus may be used in titrating alkali hydroxides and ammonia both with mineral acids and oxalic acid; and carbonates may be titrated as hydroxides if the liquid is boiled to destroy carbonic acid, which affects litmus.

Methyl Orange may be used in titrating alkali hydroxides and carbonates as well as ammonia with mineral acids, but not with oxalic acid. In the case of alkali carbonates it is unnecessary to dissipate the liberated carbonic acid by boiling, since this feeble acid is practically without effect on methyl orange; titrations in presence of methyl orange must not, however, be performed at elevated temperature because the point of neutrality is thereby displaced.

Phenolphthalein can be used in titrating alkali hydroxides with mineral acids or oxalic acid, or carbonates if the liquid is boiled to expel carbon dioxide. Ammonia, which does not give a sharp end-point with phenolphthalein, cannot be titrated with the use of this indicator.

The Theory of Indicators.

The following brief explanation of these facts may be given here.

The three indicators are weak organic acids whose alkali salts, which ionize in solution, show colours different from those of their free non-ionized acids; this is owing to intramolecular rearrangement of the constituent atoms of their complex molecules. Of these acids that of methyl orange is the strongest, and that of phenolphthalein the weakest. Consequently the acid of *methyl orange* is too strong to be displaced from combination at all by carbonic acid, or completely by oxalic acid, with which it is comparable in strength; and it is

strong enough to form an ionizable salt with ammonia, and so to give a sharp colour change therewith. The acid of *phenolphthalein*, on the other hand, is weak enough to be displaced sharply from combination by oxalic acid, which is relatively so much stronger, and even by carbonic acid; but for the same reason it is not strong enough to form a stable ionizable salt with ammonia. The acid of *litmus*, lying in strength between the acids of methyl orange and phenolphthalein, is sharply displaced from combination with alkalis by oxalic acid, and forms a stable salt with ammonia; whilst it responds partially to the influence of carbonic acid, which on this account should be eliminated.

Preparation of Standard Solutions of Acids and Alkalis.

Standard solutions of acids and alkalis may be of normal $\left(\frac{N}{1}\right)$, semi-normal $\left(\frac{N}{2}\right)$, or decinormal $\left(\frac{N}{10}\right)$ strength; the more usual practice is to work with $\frac{N}{10}$ solutions.

Sulphuric acid and sodium hydroxide are the acid and alkali most commonly employed. These, however, cannot be weighed in a pure, anhydrous condition. Sodium carbonate, Na_2CO_3 (ignited), and oxalic acid, $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (recrystallized), are suitable substances for standardizing purposes, because $\frac{N}{10}$ solutions of them can be prepared by weighing the exact amount of solid required, dissolving it in water, and diluting the solution to the proper volume.

The present purpose is to prepare a sufficiency of approximately $\frac{N}{10}$ and accurately standardized solutions of sulphuric acid and sodium hydroxide; and the following is the order of procedure.

(i) Preparation of 500 c. c. of $\frac{N}{10}$ Sodium Carbonate Solution.

Either sodium hydrogen carbonate or nominally anhydrous sodium carbonate may be the material employed. Sodium hydrogen carbonate is easily converted into the anhydrous normal carbonate by gently igniting it in a porcelain dish over a small flame. Probably, however, the anhydrous normal carbonate will be available. Nevertheless it must not be assumed to be quite free from water, and must be gently heated for a few minutes in a dish with stirring, and be transferred while still hot to a weighing bottle or dry test tube fitted with a cork.

Calculate the quantity of Na_2CO_3 necessary to make 500 c. c. of a $\frac{N}{10}$ solution, and weigh this quantity on a tared watch-glass. Particular attention should be given to the best way of dissolving the salt in water. When cold water is poured upon anhydrous sodium carbonate a hard cake is formed which dissolves only slowly. This is due to the formation of the crystalline monohydrate $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$. If hot water is used this compound is not formed and the salt dissolves readily. The common practice of beginners is to place a funnel in the neck of the 500-c. c. flask, drop the salt into the funnel, and then add cold water. In this case such procedure is most unwise, since it results in the formation of a hard mass, probably in the neck of the funnel. The salt should be dissolved in a little boiling water, preferably in a small beaker. This is easily done, and a lipped beaker should be chosen a little wider than the watch-glass. The salt may then be dropped into the beaker, portions adhering to the surface of the watch-glass being washed down with a jet of hot water; the whole will then be quickly dissolved. The solution should be diluted with cold water and poured into the 500-c. c. flask, the beaker

being washed out with a little more water to avoid loss. The solution in the flask must be cooled to atmospheric temperature, and then diluted to 500 c. c.

(ii) Preparation of 1 litre of approximately N 10 Sulphuric Acid.

It is well to prepare the sulphuric acid somewhat stronger than decinormal; then, after finding its strength by titrating it into decinormal sodium carbonate solution, to dilute it so as to make it as nearly as possible decinormal, and finally to determine a factor for the solution by a second titration.

To make a litre of solution of convenient strength, take approximately 6 gm. of concentrated sulphuric acid of about 97 per cent strength. It is better to measure than to weigh the acid. The density of concentrated sulphuric acid is 1.84; therefore calculate what volume of a liquid of such a density will weigh 6 gm.; measure the acid in a small graduated cylinder; pour the measured volume into water in a beaker—distilled water need not be used—and after rinsing out the cylinder with a little water and adding the washings to the liquid in the beaker, pour the solution into a litre flask, and dilute with water to a litre. Store the solution in a suitable bottle.

(iii) Preparation of 1 litre of approximately N 10 Sodium Hydroxide.

Sodium hydroxide may be supplied in the form of sticks or coarse crystalline fragments; the latter form is the more convenient. Owing to its corrosive nature, this substance must never be weighed on the fine chemical balance nor brought into contact with the pan of any balance.

Counterpoise a watch- or clock-glass on the rough chemical balance, and then weigh approximately not less than 5 gm. of sodium hydroxide; dissolve the alkali in water in a small beaker; pour the solution into a litre flask, and dilute it with thorough mixing till it measures 1 litre. It is preferable to use distilled

water in making this solution, or a precipitate may separate. If this happens, the solution can be strained through a plug of glass wool pressed into the stem of a funnel. The solution should be exposed as little as possible to air, from which it continuously absorbs carbon dioxide. Transfer the solution to a stock bottle.

(iv) Preparation of 250 c. c. of Decinormal Oxalic Acid.

Oxalic acid, $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, recrystallized and dried in the air, is pure enough to serve as a standard acid substance in volumetric analysis. Calculate the quantity of acid necessary to make 250 c. c. of a decinormal solution, remembering that the water of crystallization accompanies the acid in the crystals, and that the acid is dibasic. Weigh accurately the required quantity of acid, and dissolve it in distilled water in a small beaker; transfer the solution to a 250-c. c. flask, rinse out the beaker, and dilute the solution in the flask to 250 c. c. with distilled water at atmospheric temperature.

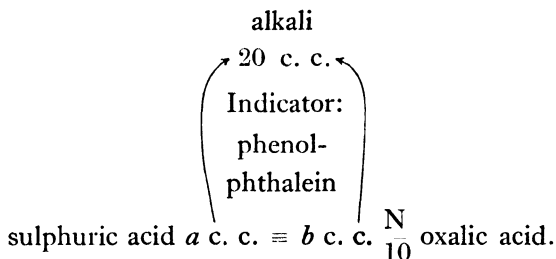
Standardization of Sulphuric Acid Solution.

Sulphuric acid solution can be standardized directly by means of decinormal sodium carbonate solution, and indirectly by reference to decinormal oxalic acid solution through the medium of an approximately decinormal solution of alkali, in the following way.

The approximately decinormal sulphuric acid is first titrated into a measured volume of solution of alkali of convenient strength, an indicator being used which serves for both sulphuric and oxalic acids, i.e. phenolphthalein. The accurately decinormal oxalic acid is next titrated into an equal volume of the same alkali solution, using the same indicator. Let a c. c. of sulphuric acid be employed and b c. c. of decinormal oxalic acid. Then these two quantities of acid are equivalent, since they have

produced the same effect with alkali. So the sulphuric acid is $\frac{b}{a}$ times decinormal; this ratio is the factor for the acid. This is the case although the composition of the alkali may remain unknown; thus the latter might be sodium or potassium hydroxide indifferently, or might contain an unknown proportion of carbonate.

The principle may be expressed diagrammatically thus:



By this procedure the sulphuric acid is standardized with reference to decinormal oxalic acid without incurring the difficulty which arises from the presence of carbonate in the alkali.

The Process of Standardization.

(i) **By means of Decinormal Sodium Carbonate**
Solution:—The indicator for this titration may be either methyl orange or litmus. When methyl orange is used the liquid must be cold, but when litmus is employed the solution must be boiled to decompose the liberated carbonic acid and expel carbon dioxide from the solution (see p. 74).

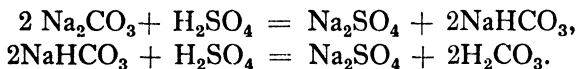
Rinse out your burette with a little of the acid, fill it, and adjust the level of the acid to the zero mark. Clamp the burette in a stand, and provide a piece of white paper, e.g. a round of 11-cm. filter paper, on which to place the flask when titrating.

(a) *Use of Methyl Orange.*—Measure 20 c. c. of decinormal

sodium carbonate solution by means of a pipette, using this instrument according to the instructions given on p. 11. Place this solution in a titrating flask, such as a 200 c. c. conical flask. Add a few drops of methyl orange, and titrate the alkali with the sulphuric acid (see p. 15) until the indicator just turns orange. Repeat the operation several times, until you are able to perform two successive titrations which do not differ by more than 0.1, or if possible 0.05 c. c.

(b) *Use of Litmus*.—Now carry out the titrations using litmus and boiling the solution. Since evaporation by boiling will reduce the volume of the liquid, a little water may be added to the 20 c. c. of sodium carbonate solution before the titration is commenced, and it may be necessary to add more water during the process. Arrange to support the flask on a tripod with gauze so as to boil the liquid by means of a Bunsen flame, and have a strip of folded paper ready to place round the neck of the flask so as to lift it whilst hot. Do not support the burette above the flask on the tripod, but bring the flask to the burette in its stand when acid is to be added.

Begin the titration cold, and observe that the litmus changes to bluish red when about half* the amount of acid which will be necessary for complete neutralization has been added. This is because free carbonic acid affects litmus, and this acid is present directly after the stage of half-neutralization, as the following equations show:



The completion of the first reaction marks the stage of half-neutralization, since half the sodium carbonate has been converted into sulphate. Immediately the second reaction begins, free carbonic acid is present; and this affects litmus. Now heat the solution to boiling, observe the escaping bubbles

* The observed change in the litmus will correspond exactly with the half-neutralization point only when by cooling the solution in ice the escape of carbon dioxide is prevented.

of carbon dioxide as the liquid becomes hot, and notice that the blue colour of the litmus gradually returns as the liquid boils. When the solution is blue, add more acid till it becomes red again, and continue boiling and adding acid until after a final drop of acid no blue colour returns, but a red colour remains which is brighter than that produced by carbonic acid. This permanent change is due to a minute excess of sulphuric acid which remains when neutralization is completed.

The volume of sulphuric acid used should be identical with that employed when methyl orange was the indicator. Repeat the titration till agreeing results are obtained. The process is more tedious than the methyl orange titration, but the result may be more accurate because the colour change with litmus is more sudden.

(ii) By Means of Decinormal Oxalic Acid through Sodium Hydroxide Solution.—First fill the burette with your approximately decinormal sulphuric acid, and titrate the latter into 20 c. c. of your prepared solution of sodium hydroxide, using phenolphthalein as indicator at atmospheric temperature. After agreeing results have been obtained, empty the burette, and fill it with the decinormal oxalic solution you have made. Titrate this acid similarly into 20 c. c. of the same sodium hydroxide solution; and then compare the volumes of the two acids used for the same volume of alkali. The volumes of sulphuric and oxalic acids in this experiment should bear the same ratio to one another as the volume of the same sulphuric acid bears to that of decinormal sodium carbonate solution in experiment (i).

Dilution of Sulphuric Acid to Decinormal Strength.

Suppose that 15 c. c. of a solution of sulphuric acid are needed to neutralize 20 c. c. of decinormal sodium carbonate solution in experiment (i), and this ratio has been confirmed by the result of experiment (ii). Then the sulphuric acid is

$\frac{20}{15}$ times decinormal, and 15 c. c. of it diluted with water to 20 c. c. will thereby be made decinormal. For practical purposes the addition of 5 c. c. of water to 15 c. c. of the acid may be regarded as producing the same result as diluting 15 c. c. to 20 c. c.; but this is on the assumption that dilution is not accompanied by shrinkage of volume. It is better to avoid the question of such shrinkage by measuring the acid available, calculating the volume to which it needs to be diluted, and then adding water till this volume is reached.

Therefore measure the remaining volume of your approximately decinormal sulphuric acid in a litre graduated cylinder, and, using your titration figure, calculate by simple proportion the volume to which the solution must be diluted, or otherwise calculate how much of your acid when diluted with water will yield a litre of $\frac{N}{10}$ acid; then measure and dilute the acid accordingly.

It will be possible to do this only if the acid has turned out to be stronger than decinormal. Otherwise evaporation would be necessary. It is scarcely worth while to evaporate, however; it is better in such case to add a few drops of concentrated acid, so as to bring the acid above decinormal strength, and then titrate the solution again and dilute it as may be required.

Having diluted the acid till it should be decinormal, store it in a stock bottle; but titrate it again into cold decinormal sodium carbonate solution, using methyl orange as indicator, to discover if it is exactly decinormal, or whether a small factor needs to be applied to it. The latter is generally the case. Calculate the factor, after having performed agreeing titrations, and label the bottle accordingly, adding the date. Thus if 20.2 c. c. of acid were required to neutralize 20.0 c. c. of decinormal sodium carbonate, the acid would be

$$\frac{20.0}{20.2} = 0.99 \frac{N}{10} \text{ or } 0.099N.$$

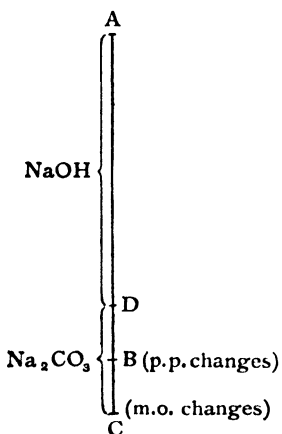
Standardization of Sodium Hydroxide Solution.

You have already titrated your approximately decinormal sodium hydroxide solution with decinormal oxalic acid solution, and from the figure obtained you could calculate a factor for the soda. The indicator used, however, was phenolphthalein, and the volume of acid added before the indicator changed has no precise significance as regards the alkali content of the solution, for the following reason. Sodium hydroxide readily absorbs carbon dioxide from the air, and therefore it is likely that your soda solution contained a mixture of sodium hydroxide with a little sodium carbonate. It will be worth while to consider how such a solution will react when an acid is added to it in presence of phenolphthalein.

First the sodium hydroxide will be neutralized by the acid, and then the carbonate will be attacked. This is necessarily the case, for if the carbonate were first decomposed, the liberated carbonic acid would react with the sodium hydroxide and reproduce carbonate, and this would amount to the same thing. When all the sodium hydroxide has been converted into neutral salt, the acid will next attack the carbonate; and when the carbonate has been half neutralized, the phenolphthalein will change its colour owing to the liberation of free carbonic acid, as in the case of litmus considered above. If now an acid is being used for the titration which reacts sharply with methyl orange, e.g. sulphuric acid, and this indicator is added after the phenolphthalein has been rendered colourless by the liberated carbonic acid, more acid will need to be added before the methyl orange changes if carbonate was present in the alkali. The difference between the volume of acid required to react with methyl orange and phenolphthalein respectively thus represents the second half of the carbonate in solution; and twice this difference is the acid equivalent of the sodium carbonate in solution, whilst

the remainder of the acid is equivalent to the sodium hydroxide present. The larger the amount of sodium carbonate present, the greater will be the difference between these volumes, and vice versa; so that if the solution is free from carbonate the indicators of acidity with phenolphthalein and methyl orange will coincide. These conclusions may be expressed graphically.

Suppose the line AB represents the volume of acid required to change phenolphthalein present in a certain volume of



alkali solution, and AC the volume required to change methyl orange. Make $BD = BC$. Then AD is the volume of acid corresponding with the sodium hydroxide in the solution, and DC that corresponding with the sodium carbonate; or stated otherwise: Twice the difference in volume of acid between methyl orange and phenolphthalein indications represents sodium carbonate.

Total volume of acid minus twice this difference represents sodium hydroxide.

It will be plain from the above that the titration figure for the alkali solution obtained when phenolphthalein is the indicator is of no permanent value, since it will gradually diminish as carbon dioxide is absorbed by the solution; but that the methyl orange titration figure remains constant so long as no water evaporates from the solution, since it is independent of the absorption of carbon dioxide by the alkali.

With these considerations in view, perform the following titrations:

(i) Titrate 20 c. c. of your sodium hydroxide solution with your standardized sulphuric acid, using phenolphthalein first; then, when the colour of this indicator has been discharged,

add methyl orange and continue the titration until the latter indicator changes colour. Thus the presence of sodium carbonate in the solution will be demonstrated, and its amount shown by twice the difference between the two indications.

(ii) Confirm the methyl orange value, and, if the soda is shown to be nearly decinormal, calculate a factor for it, remembering that the volume of acid used must be converted into volume of decinormal acid by employing the factor for the acid. If the soda is much stronger than decinormal, but not otherwise, dilute it appropriately, again titrate it, calculate a factor for it, and then label the bottle containing the solution.

Standard solutions of acid and alkali have now been prepared of very nearly decinormal strength, and these will be used for the estimations that follow.

EXERCISES IN ACIDIMETRY AND ALKALIMETRY.

The following is a list of exercises in the use of standard solutions of acids and alkalis.

1. Hydrogen chloride in solution.
2. Sodium hydroxide in solution.
3. Ammonia in solution.
4. Acetic acid in solution.
5. Strength of diluted sulphuric acid by density and titration.
6. Solubility of calcium hydroxide in water.
7. Percentage of Na_2CO_3 in "soda crystals".
8. Calcium carbonate in mixture of calcium carbonate and sodium chloride.
9. Hydrogen chloride and sodium chloride in solution by titration and evaporation.
10. Percentage of barium in $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ by estimation of sodium carbonate required for precipitation.
11. Equivalent weight of tartaric acid.
12. Ammonium sulphate in solution.
13. Phosphoric acid and phosphates (note on p. 154).

1. Estimation of Hydrogen Chloride in Solution.

Whenever possible, acid should be titrated into alkali. Therefore fill your burette with the hydrogen chloride solution of unknown strength, and titrate with it 20 c. c. of your standardized soda solution, or the same volume of decinormal sodium carbonate solution, using methyl orange as indicator. If the acid should be very much stronger than the alkali, so that a very small volume of it is required, dilute it before titrating by measuring, say, 20 or 40 c. c. with a pipette and diluting this to 100 c. c. in a graduated flask. It is desirable that the volume of acid used in the titration be not very far different from that of the alkali titrated. Several agreeing results should be obtained.

The calculation is very simple, for if a c. c. of acid are required to neutralize b c. c. of decinormal alkali, the acid solution contains $\frac{b}{a} \times 3.647$ gm. of hydrogen chloride per litre.

2. Estimation of Sodium Hydroxide in Solution.

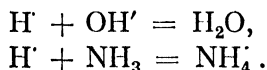
Measure 20 c. c. of the solution and titrate it with your standard sulphuric acid, using methyl orange as indicator. Dilute the solution an aliquot number of times, however, if it is found to be too strong, and use 20 c. c. of the diluted solution, so as not to waste your acid. In the calculation it is assumed that the sodium hydroxide solution contains no carbonate; that is to say the total alkali present, whether as hydroxide or carbonate, is expressed as hydroxide.

3. Estimation of Ammonia in Solution.

Ammonia solution is titrated in just the same way as sodium hydroxide, methyl orange being used as indicator. State the result as grams of NH_3 —not NH_4OH —per litre.

By far the larger proportion of ammonia in solution exists as NH_3 and not as NH_4OH . NH_4^+ and OH' ions must exist

in ammonia solution, since it is alkaline; but when an acid, i.e. a solution containing H^+ ions, is added to ammonia the reaction probably consists partly in the combination of H^+ and OH^- ions to form water, but chiefly in the union between H^+ ions and NH_3 molecules to form NH_4^+ ions; thus:



Since ammonia is continuously leaving the solution, as proved by the smell, the alkaline strength must decrease on keeping.

4. Estimation of Acetic Acid in Solution.

Acetic acid, like oxalic acid, gives no sharp end reaction with methyl orange, and consequently litmus or phenolphthalein must be used as indicator. The difficulty of carbonate in the alkali then arises. This may be overcome in either of two ways.

(i) The alkali solution may be boiled during the addition of acid to dispel carbon dioxide.

(ii) The alkali solution may be previously standardized cold by means of decinormal oxalic acid.

Method (i).—Use 20 c. c. of your sodium hydroxide solution which has been standardized in presence of methyl orange, add litmus to it, and titrate it with the acetic acid, finishing the titration in boiling solution.

Method (ii).—Titrate 20 c. c. of your sodium hydroxide solution first with decinormal oxalic acid, second with the acetic acid solution, using phenolphthalein as indicator in each case; the normalities of the two acid solutions are inversely as the volumes used to neutralize equal quantities of alkali. So the strength of the acetic acid is estimated.

Acetic acid, CH_3COOH , is a monobasic acid. Calculate the strength of the solution in grams per litre.

5. Estimation of Strength of Diluted Sulphuric Acid by its Density and by Titration.

The concentration of an aqueous solution of sulphuric acid can be determined (a) with a fair degree of accuracy by finding its density at a stated temperature and consulting published tables. The concentration of the same solution may also be determined (b) by suitably diluting a weighed quantity of it and titrating the diluted solution into standard alkali.

Prepare about 100 gm. of a solution containing about 30 per cent by weight of sulphuric acid by adding about 30 gm. of the concentrated acid to 70 gm. of water, and cool the solution to atmospheric temperature.

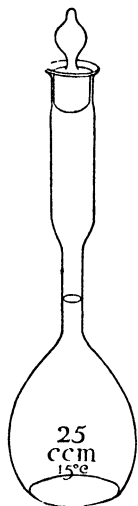


Fig. 11. — Specific Gravity Bottle (one-fourth actual size).

(a) Thoroughly clean and dry a specific gravity bottle, preferably of the shape shown in fig. 11 and of 25-gm. capacity, and carefully weigh it. Adjust the temperature of some distilled water to 15°C. , and fill the flask with the water so that the meniscus at the liquid surface is tangential to the etched ring on the narrow neck of the flask. Stand the flask full of water up to the neck in water, also at 15°C. , and leave it there for a few minutes to ensure adjustment of temperature. Then with a narrow glass tube or the tip of a small pipette add or remove water if necessary to bring the meniscus again to the mark. Dry the broader part of the neck of the flask with the corner of a duster or handkerchief, insert the stopper, remove the flask from the water, dry, and weigh it. Then empty the flask, rinse it with the dilute sulphuric acid, fill it with the same, and carefully adjust the temperature and the

level of the meniscus in the same way as before; dry, and again weigh. The ratio:

$$\frac{\text{weight of sulphuric acid}}{\text{weight of water}}$$

is the density of the diluted acid at 15° C. compared with that of water at 15°, i.e. $d_{15^\circ}^{15^\circ}$. If the density compared with water at 4° C. ($d_{4^\circ}^{15^\circ}$) is required the result may be multiplied by 0.9992, the density of water at 15° C. compared with that at 4° C. The correction, however, will make only about 0.1 per cent difference in the estimated strength of the sulphuric acid.

The percentage of sulphuric acid indicated by this density can be found by consulting tables*.

It will probably be discovered, however, that the density observed lies between two of the figures given in the table. The actual value must therefore be obtained by interpolation; it may be computed approximately by inspection, but an interesting exercise which will give the value more accurately consists in drawing a graph connecting together density and percentage of sulphuric acid. If a number of points on either side of the required value are thus located on graph paper it will be found that they can be joined by a straight line. The point at which this straight line intersects the co-ordinate of the density gives accurately the percentage of sulphuric acid required.

(b) To estimate the strength of the diluted sulphuric acid by titration weigh sufficient of it in a stoppered weighing bottle to make, say, 250 c. c. of an approximately decinormal solution. The quantity required is derived from the percentage of acid already shown to be present by the density determination. Dilute the weighed amount of acid to the volume decided upon,

* These will be found in the following books: Thorpe, *Dictionary of Applied Chemistry*; Landolt-Börnstein, *Physikalisch-Chemische Tabellen*; Castell-Evans, *Physico-Chemical Tables*.

and titrate the solution into your standard sodium hydroxide, using methyl orange as indicator. From the result calculate the percentage of H_2SO_4 in the prepared acid, and state the result side by side with that obtained by density determination. The agreement should be close.

6. Estimation of Solubility of Calcium Hydroxide in Water.

Calcium hydroxide, or slaked lime, shaken up with water until the water is saturated, produces lime-water. Owing to the sparing solubility of calcium hydroxide in water the alkaline solution which it yields must necessarily be dilute, but it has the advantage over sodium hydroxide solution that it cannot contain carbonate, for any carbon dioxide absorbed will necessarily produce a precipitate of calcium carbonate.

Procure some slaked lime and place some of it in a bottle of, say, a litre capacity provided with a cork or stopper. Now add distilled water so as nearly to fill the bottle, and having inserted the stopper shake the contents at intervals during a working day. Allow the undissolved matter to settle over night, note the temperature of the liquid, and pour off some of the clear lime-water into another bottle or flask, exposing it to the air as little as possible. Since the lime-water may be conveniently titrated with your decinormal sulphuric acid, and is itself a sufficiently strong alkali to react with phenolphthalein, it is of no consequence which indicator is used. Measure 20 c. c. of the lime-water and titrate it with your acid; perform the experiment several times, varying the indicator.

Now shake the bottle containing the lime-water with the excess of slaked lime and again allow time for subsidence. Then note the temperature, decant some of the clear solution, and again titrate it. Repeat these operations until agreeing results show that a saturated solution has been obtained. Calculate the normality of the lime-water, and thence the solubility

of calcium hydroxide, $\text{Ca}(\text{OH})_2$, in water at the observed temperature. This solubility varies little with temperature. Consult a dictionary of solubilities to discover whether your estimated solubility agrees with the observations of others.

7. Estimation of Sodium Carbonate in "Soda Crystals".

Decahydrated sodium carbonate, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, contains so much water of crystallization that it is likely to lose some, that is to effloresce, when exposed to moderately dry air.

The monohydrate is then produced according to the reaction:



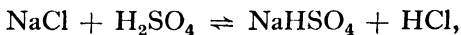
If this loss has taken place to any extent, the percentage of sodium carbonate found in soda crystals will be higher than that calculated from the formula for the decahydrate. The estimation of Na_2CO_3 by titration can be confirmed, however, by determining the residue which results from gently heating a weighed quantity of the hydrated salt in a crucible till it ceases to lose weight.

Obtain some soda crystals, and unless they are in a granular form, powder them, thoroughly mix the powder and place it in a dry test tube provided with a cork. Estimate the sodium carbonate in the specimen (a) *volumetrically*—by accurately weighing enough for 250 c. c. of an approximately decinormal solution, making up the solution to volume and titrating an aliquot part of it with your decinormal sulphuric acid, using methyl orange as indicator; and (b) *gravimetrically*—by weighing about 1 gm. of the salt in a porcelain or silica crucible, and very gently heating it until no further loss occurs. Sodium carbonate decahydrate melts in its water of crystallization at 35.1°C ., yielding a solution in which the monohydrate is suspended. Very careful heating is then necessary to evaporate the water, and so to dry the salt without causing loss by spurting.

Show that the percentages of Na_2CO_3 in the soda crystals estimated by the two methods agree.

8. Estimation of Calcium Carbonate in a Mixture of Calcium Carbonate and Sodium Chloride.

Calcium carbonate added to a solution of sulphuric acid may be regarded as neutralizing the acid, because the carbonic acid liberated, even if it remains in solution, does not affect methyl orange. Sodium chloride, being neutral already, does not neutralize an acid in dilute solution, for any hydrogen chloride liberated, as in the reaction



remains in solution in amount equivalent to that of the sulphuric acid originally present.

So the calcium carbonate present in a mixture of this salt with sodium chloride can be estimated in either of the two following ways:

(a) By direct titration.

Calculate the quantity of pure calcium carbonate which would neutralize 50 c. c. of decinormal acid; weigh this amount of the mixture and suspend it in about 20 c. c. of distilled water in a flask, or preferably in a suitable stoppered bottle. Add methyl orange, and titrate the turbid liquid with constant shaking until the change in the indicator shows the end of the reaction.

From the volume of acid used calculate the percentage of calcium carbonate in the mixture. If the calculated weight of mixture was used, and the acid was decinormal, twice the number of cubic centimetres of acid used is numerically equal to this percentage.

(b) By dissolving the powder in excess of acid and estimating this excess.

Take the same weight of the mixture as before, add to it exactly 50 c. c. of your standard acid, together with methyl

orange, and boil the liquid to complete the reaction.* Cool the solution to atmospheric temperature; calcium sulphate may crystallize from the solution, but this does not signify. Now add, by means of a pipette, 20 c. c. of your standard sodium hydroxide solution, or more, say another 10 c. c., if the solution does not otherwise become alkaline, as shown by methyl orange, and finally titrate the solution with your standard sulphuric acid. Correct the volumes of alkali and acid used by their respective factors, and subtract the one from the other. The excess of acid represents that used to neutralize the calcium carbonate, from which the percentage of this substance in the mixture can be calculated. The result should agree with that obtained by direct titration.

9. Estimation of Hydrogen Chloride and Sodium Chloride in Solution by Titration and Evaporation.

Since hydrogen chloride confers acidity upon a solution, its amount can be estimated by titrating the solution into standard alkali. The acid content of the solution being known, the amount of sodium chloride might be estimated in either of two ways: (a) by determining the total chloride present by precipitating it with silver nitrate, and either weighing the silver chloride or estimating its amount volumetrically by a process to be described later; or (b) by evaporating a measured volume of the solution to dryness and weighing the residual sodium chloride. The latter method will be adopted in the present case.

(a) Fill your burette with the given acid solution, and titrate it into 20 c. c. of your standard sodium hydroxide, using methyl orange as indicator. If the solutions of acid and alkali are very far from equivalent, either dilute the acid a suitable number of times before titrating with it, or take

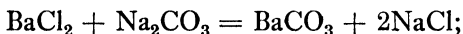
* If this is not done the result will be low, probably owing to protective crusts of calcium sulphate formed on the surface of particles of carbonate.

a smaller volume of standard alkali, as the case may require. Calculate the weight of hydrogen chloride per litre of the solution.

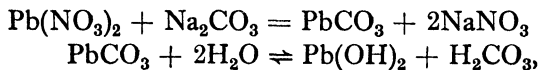
(b) Weigh a suitable porcelain dish, and place in it 20 c. c. of the given solution. Evaporate the solution to dryness on the water bath, when the sodium chloride will appear, and will probably be recognizable as crystallized in cubes. Then place the dish on your wire gauze on the tripod stand, and further heat it with a very small flame, the tip of which is kept 1 in. away from the dish. Continue heating until acid fumes cease to be evolved, but be very careful not to allow spurting, which would occasion loss of solid matter. Cool the dish in the desiccator and weigh it. Repeat the heating and weighing till a constant weight is obtained; thence calculate the weight of sodium chloride per litre of the solution.

10. Estimation of Barium Chloride in a solution by finding the amount of Sodium Carbonate required for Precipitation.

Barium is precipitated from solution by sodium carbonate thus:



so that when the barium carbonate has been filtered off and thoroughly washed, the solution will be poorer in alkalinity by the extent of the barium precipitated. The principle thus illustrated is of general application in cases where a normal salt in solution is converted into an insoluble carbonate by sodium carbonate. Moreover, it is immaterial whether the precipitate is that of a normal or basic carbonate. Lead nitrate, for example, yields a basic carbonate, which may be supposed formed by the partial hydrolysis of the normal carbonate thus:



the product being a compound of PbCO_3 and Pb(OH)_2 ; but the carbonic acid (H_2CO_3) liberated in the solution as the result of this hydrolysis has no effect upon the alkalinity of the latter, since the indicator employed is methyl orange.

There are cases, however, in which sodium carbonate is adsorbed from solution by the precipitated carbonate, so that less of it remains in the filtrate to be titrated, and the estimation consequently gives high results. This is the case when copper is precipitated from solution by sodium carbonate; therefore this metal cannot be estimated by the present process.

To carry out the estimation, measure, by means of a pipette, 20 c. c. of a prepared solution of barium chloride, placing this in a suitable beaker. Then add to the solution from a burette a volume of decinormal sodium carbonate solution sufficient to make the turbid liquid in the beaker decidedly alkaline. The liquid may be tested by stirring it with a glass rod and then bringing a drop of it into contact with litmus or turmeric paper, afterwards returning to the solution what was removed from it by a jet of water directed upon the paper from the wash-bottle. Then boil the liquid in the beaker to cause the precipitated barium carbonate to become granular. Filter the solution, receiving the filtrate in a flask, and washing the precipitate till it is free from alkali. Finally cool the solution in the flask, add methyl orange, and titrate it with your standardized sulphuric acid.

The difference between the volume of decinormal sodium carbonate used and that of decinormal acid required to neutralize what remained after precipitating the barium chloride, represents the volume of decinormal sodium carbonate used in precipitating the barium. From this figure the amount of barium chloride in 20 c. c., and so in 1 litre of the prepared solution, can be calculated directly, without bringing into the calculation the equivalent weight of sodium carbonate.

Soluble calcium salts can be estimated similarly to those of barium and lead.

11. Determination of the Equivalent Weight of Tartaric Acid.

The weight of an acid in any volume of its solution can be determined by titration if the equivalent weight of the acid is known; and conversely it follows that the equivalent weight of an acid can be determined similarly if the weight of it present in any volume of solution is known.

Thus, for example, if a solution containing 5.4 gm. of crystallized oxalic acid per litre is found to be 0.0857N, it follows that the equivalent weight of oxalic acid is $\frac{5.4}{0.0857} = 63$.

To determine the equivalent weight of tartaric acid ($\text{H}_2\text{C}_4\text{H}_4\text{O}_6$), weigh accurately from 1.5 to 1.75 gm. of the pure solid substance, dissolve it in water, and dilute the solution to 250 c. c. Titrate this acid into approximately decinormal sodium hydroxide solution, which has been recently standardized by means of decinormal oxalic acid, phenolphthalein being used as indicator in both cases. Thus determine the normality of the tartaric acid solution, and thence the equivalent weight of the acid.

12. Estimation of Ammonium Sulphate in Solution.

If ammonium sulphate is heated with sodium hydroxide solution, ammonia is evolved according to the reaction:



This suggests that there are two ways in which the amount of this salt in a solution might be estimated:

(a) By determining how much sodium hydroxide in standard solution is neutralized by being converted into sulphate when measured volumes of the two solutions are heated together till no more ammonia is evolved.

(b) By displacing ammonia from the solution by heating with it excess of alkali, and collecting the ammonia in excess of standard acid. The amount of acid thus neutralized is a measure of the ammonia which has been absorbed, and therefore of the ammonium sulphate present in the given solution.

(a) Before this method is employed the ammonium sulphate solution must be ascertained to be neutral. If it is acid the solution may be neutralized by adding sodium hydroxide in presence of methyl orange. Incidentally it may be mentioned that if the solution should contain a mixture of sulphuric acid and ammonium sulphate, the former can be estimated by titration with standard alkali before the ammonia is displaced.

Place 20 c. c. of the neutral ammonium sulphate solution in a flask; add, say, 30 c. c. of your standard sodium hydroxide solution, and boil the liquid till ammonia ceases to be evolved. Test the reaction of the solution by removing a drop on the end of a glass rod and placing it on red litmus paper, afterwards washing back into the flask the contents of the drop removed. If the solution is not alkaline, add another measured volume of sodium hydroxide and repeat the boiling and testing of the solution. When no more ammonia is evolved and the solution remains alkaline after boiling, cool the liquid, add to it methyl orange, and titrate it with your standard acid. The difference between the alkali and acid used represents ammonium sulphate. Calculate the number of grams of this salt in a litre of the given solution.

(b) The apparatus to be employed for distilling ammonia from ammonium sulphate and absorbing it in standard acid is shown in fig. 12.

A round-bottom flask A of about 1 litre capacity, and supported by wire gauze on a tripod stand, is fitted with a two-hole rubber stopper. Through one hole of the stopper passes a tap-funnel B, the lower end of which tapers in the manner shown; through the other hole passes a bent tube C,

cut off obliquely below the stopper, and carrying a trap or splash bulb D to prevent the possibility of alkaline liquid

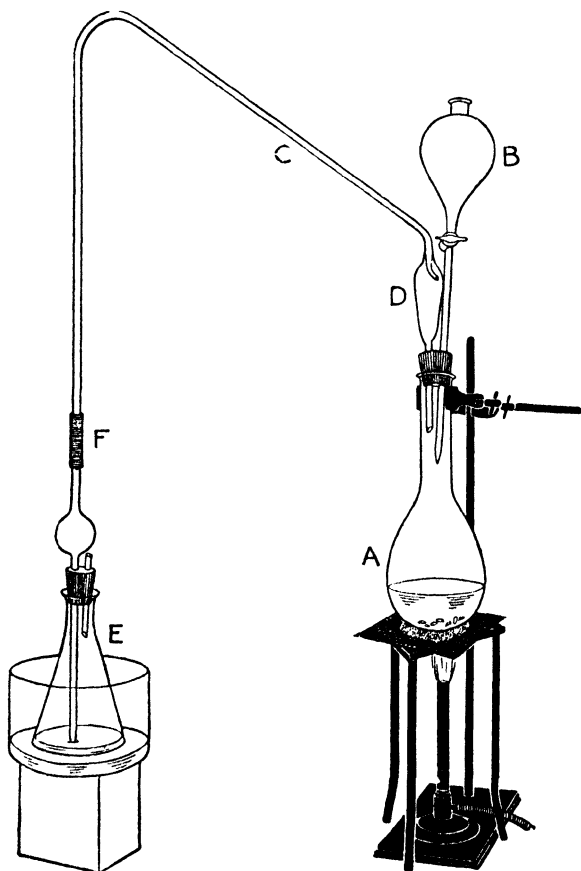


Fig. 12.—Estimation of Ammonia by Distillation

A, Flask. B, Tap-funnel. C, Bent tube. D, Splash bulb. E, Flask containing acid.
F, Rubber tubing.

being carried over into the flask E containing the acid in which the evolved ammonia will be absorbed. The tube ends at F, where another tube of similar bore meets it and is

joined to it with rubber tubing. This tube also carries a bulb to receive the liquid from the flask in case of sucking back, and is constricted at the lower end; it passes through one hole of a double-bored cork which closes the neck of the flask, whilst a short open piece of glass tubing passes through the other hole in the cork. Sometimes a condenser is introduced, so that the ammonia is delivered into the acid in cold solution; but this need not be employed if the flask E stands in a dish of cold water which can be renewed when necessary.

To carry out the estimation, place 20 c. c. of the ammonium sulphate solution in the flask A and dilute it to about 100 c. c. with water. At this stage add a little zinc dust; this substance reacts with caustic soda, causing a gentle evolution of hydrogen which effectively prevents bumping when the alkaline solution is boiled. In the flask E place a measured volume of standard acid, say 50 c. c., which is considerably in excess of what will be neutralized by the ammonia, and add to it a few drops of methyl orange. The result of the previous experiment will be a guide as to the volume of acid desirable. Stand the flask E in water, and fit the apparatus together, holding the distilling flask firm by means of a clamp. Half fill the tap-funnel with the bench caustic soda, and, by opening the tap, let all but a little of this solution run into the distilling flask, then close the tap again. The liquid remaining in the funnel serves as a seal.

Gradually heat the liquid in the flask and let it boil for half an hour, taking care to maintain a steady flame. Remember that after the air has been driven out of the apparatus by the evolved steam, any cessation of the boiling will bring about condensation followed by the rise of acid in the tube, and that if the flame is removed this acid may be driven right over into the distilling flask, and the estimation be ruined. Therefore when the boiling is finished turn on the tap of the funnel so that air may enter the flask as cooling takes place on the removal of the flame. This will prevent acid from rising in

the tube. Then separate the tubes at F, remove the lower tube from the acid, and wash down into the flask by a jet of water from the wash-bottle the acid solution which wets it. Finally cool the contents of the flask, which must still remain acid as shown by the colour of the methyl orange, and titrate the solution with your standard sodium hydroxide, or add a measured volume of the latter till the solution becomes alkaline and then titrate back with your standard acid. From the result obtained calculate as before the weight of ammonium sulphate in a litre of the given solution.*

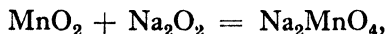
STANDARD POTASSIUM PERMANGANATE SOLUTION

Permanganates are oxidizing agents, and the use of potassium permanganate in volumetric analysis depends upon this fact. Before preparing and using a standard solution of potassium permanganate the student should study the reactions involved in the formation of this substance, and in its use as an oxidizing agent. The following experiments may be carried out.

(i) Formation of Permanganate.

Thoroughly mix a very little manganese dioxide with about six times its bulk of sodium peroxide, place the mixture in a small test tube, and heat it strongly in the Bunsen flame until a dark green fused mass is obtained. Allow this mass to cool, then dissolve it in a little water so as to produce a green solution in which there may be some unchanged manganese dioxide remaining suspended. Add dilute sulphuric acid to the green solution and observe that it changes to pink.

The compound present in the green solution is sodium manganate formed from manganese dioxide by oxidation thus:



* Ammonia in ferrous ammonium sulphate can be estimated similarly.

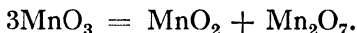
for the oxide of manganese corresponding with this salt, that is manganic anhydride, is MnO_3 . Acid changes green manganate into crimson permanganate; permanganic acid is HMnO_4 , with which the anhydride Mn_2O_7 corresponds.

The formation of permanganate from manganate thus again involves oxidation:

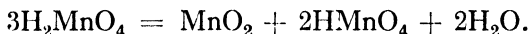


yet dilute sulphuric acid is not an oxidizing agent.

The oxygen comes from a molecule of manganate which is consequently reduced to manganese dioxide; thus, in terms of oxides,



The fact is that manganic acid, liberated from a manganate by dilute acid, is unstable, and undergoes self-oxidation and reduction in this way:



Excess of water alone is even able to bring about this change by hydrolysis, manganate solution being stable only in presence of free alkali.

(ii) Oxidation by Permanganate.

Prepare a dilute solution of potassium permanganate, and perform with it the following experiments:

(a) To some freshly prepared sulphurous acid in a test tube add permanganate solution drop by drop. Observe that the colour of the permanganate is quickly discharged, the solution remaining colourless; then prove the presence of sulphate in the solution by obtaining a white precipitate with barium chloride insoluble in hydrochloric acid.

(b) Mix together sulphurous acid and sodium hydroxide solutions, but leave the mixture slightly acid, as indicated by litmus paper. To this solution add dilute permanganate.

Observe that if the permanganate is very dilute the first few drops will be decolorized, but that a brown precipitate will soon appear and become permanent as more permanganate is added.

(c) Add sodium hydroxide to sulphurous acid till the solution is distinctly alkaline, and then permanganate. In this case the brown precipitate appears at once.

(d) Mix a little sulphurous acid with much sodium hydroxide so as to produce a strongly alkaline solution of sulphite, and to this add very dilute permanganate. Observe the appearance of a green colour due to manganate, followed by the brown precipitate as more permanganate is added and time elapses.

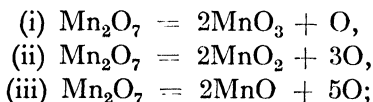
These experiments show that permanganate is reducible in three stages, which, taken in the reverse order of the above experiments, are:

(i) Reduction to manganate (green) in strongly alkaline solution.

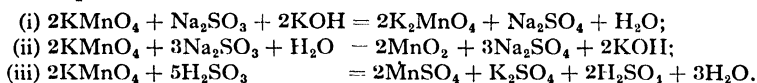
(ii) Reduction to hydrated manganese dioxide (brown) in alkaline or slightly acid solution.

(iii) Reduction to manganous salt (colourless) in acid* solution.

Expressed in terms of oxides the reactions are:



or in terms of reduction of permanganate by sulphurous acid or sulphite:



Reaction (iii) is typical of the kind of reaction almost exclusively employed in volumetric analysis; that is to say

* It is possible, however, to provide conditions under which permanganate is reduced to manganous salt in alkaline solution.

permanganate oxidizes in presence of excess of acid, being thereby reduced to colourless manganous salt. Owing to its deep colour, permanganate solution is its own indicator, a single drop of it being sufficient to produce a pink tint when no more oxidizable material remains.

The normality of a solution of potassium permanganate has reference to its available oxygen, since it is on account of this oxygen that the compound is employed. Now 2 molecules of potassium permanganate yield 5 atoms of available oxygen, which are equivalent to 10 atoms of hydrogen. Therefore a normal solution of potassium permanganate would contain $\frac{2\text{KMnO}_4}{10}$ gm., and a decinormal solution $\frac{2\text{KMnO}_4}{100}$ gm. per litre. The molecular weight of potassium permanganate is 158; therefore a decinormal solution of this salt contains $\frac{2 \times 158}{100} = 3.16$ gm. per litre.

Preparation and Standardization of Potassium Permanganate Solution.

Weigh 3.16 gm. of well-crystallized potassium permanganate and dissolve it in distilled water in the following way. Transfer the salt to a clean flask of 500 c. c. capacity or more. Add distilled water, and gently rotate the flask to assist the salt to dissolve. Allow time for undissolved crystals to settle; then decant the solution through a funnel into the litre flask, having first placed a little glass wool loosely in the neck of the funnel to strain off solid matter but not to retard the flow of the liquid. Add more water to the crystals remaining in the first flask, and repeat the process until all the permanganate is dissolved. This procedure avoids the introduction of solid permanganate into the graduated flask, where it might remain undissolved for a time, because unseen through the dark solution. Add water till the solution measures 1 litre, mix

thoroughly, and transfer it to a stock bottle. Flasks or bottles containing permanganate solution should have glass stoppers, because cork and rubber are attacked by this substance. For the same reason the burette used must be one with a glass tap.

Potassium permanganate, when supplied in well-formed crystals which dissolve in water without residue, is of a moderate degree of purity. Its purity cannot, however, be relied upon, nor can it be conveniently recrystallized by the student; and, moreover, there are other chemicals which, being more easily obtained in a state of purity, can be used to standardize a solution of this salt. These are:

Ferrous ammonium sulphate, $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$,
(Mohr's salt).

Sodium oxalate, $\text{Na}_2\text{C}_2\text{O}_4$.

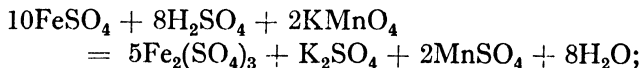
Oxalic acid, $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$.

Standardization of Permanganate Solution by Mohr's Salt.

A ferrous salt in solution is immediately oxidized at atmospheric temperature by permanganate in presence of sulphuric acid thus:



Since 2 molecules of potassium permanganate yield 5 atoms of available oxygen, the complete reaction is:



and since 2 atoms of iron are oxidized by 1 atom of oxygen, a solution of a ferrous salt equivalent to decinormal permanganate will contain one-tenth of a gram-molecule of the salt per litre. Calculate what weight of ferrous ammonium sulphate is required to make 100 c. c. of a decinormal solution. The salt employed must be pure and unoxidized. It should

be freshly prepared, according to the instructions given on p. 54, and used as soon as it is dry. If, however, the salt has been carefully protected from the air since it was made, that previously prepared may serve. Newly crystallized ferrous sulphate serves equally well for standardizing permanganate; indeed it is preferred by some chemists.

Weigh the calculated quantity of the salt, dissolve it in air-free distilled water * at atmospheric temperature, together with a few drops of dilute sulphuric acid to prevent the separation by hydrolysis of readily oxidizable basic salt, and dilute the solution to 100 c. c.

Take care that the burette to be used is scrupulously clean, rinse it with a little of the permanganate solution, and fill it in the usual way. Observe that, owing to the depth of colour of the solution, it is difficult to see the meniscus, unless the light is good. In this case the reading may be taken where the outer edge of the solution touches the glass.

Measure 20 c. c. of the ferrous solution, add to it a few drops only of concentrated sulphuric acid, or, if preferred, a few cubic centimetres of the dilute acid, and titrate the solution with the permanganate. Observe that the colour of the permanganate quickly disappears, but that a single drop is sufficient to produce a permanent pink colour when the oxidation is at an end. Repeat the titration, taking care to add the permanganate very slowly when the reaction is known to be nearly finished, so that a very pale pink tint may mark the end. Results concordant within 0.1 c. c. or even less should be readily obtained. These may be confirmed by titrating a single weighed quantity of the salt.

The relation between the volumes of permanganate and decinormal ferrous ammonium sulphate solutions indicates the normality of the former solution; calculate a factor for it.

* That is distilled water which has been boiled in a flask to expel all air, and quickly cooled in running water.

Note on titration with permanganate in presence of hydrochloric acid.

Titrate 20 c. c. of the above ferrous solution with permanganate, after acidifying it with hydrochloric instead of sulphuric acid. Observe that the liquid becomes yellow, owing to the formation of ferric chloride, that the pink colour is consequently more difficult to see, that it gradually fades so that more permanganate needs to be added, and that indeed no satisfactory end-point is ascertainable. At the same time an odour of chlorine can be perceived above the liquid in the flask.

It thus becomes evident that a ferrous solution cannot under ordinary circumstances be titrated by permanganate in presence of hydrochloric acid, because permanganate is slowly consumed in oxidizing this acid to chlorine and water.

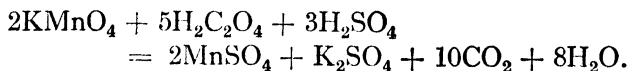
This difficulty can be overcome by a special procedure, but the student should, if possible, avoid the presence of hydrochloric acid or a chloride when titrating with permanganate.

Standardization of Permanganate Solution by Oxalic Acid.

Crystallized oxalic acid, $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, which has already served as a reliable reagent in acidimetry, can be employed in the standardization of permanganate solution, because it is quantitatively oxidized thereby to carbon dioxide and water according to the reaction:



or with potassium permanganate:



Thus oxalic acid solution, decinormal with reference to alkalimetry, is decinormal also with reference to oxidation by permanganate. Prepare 250 c. c. of decinormal oxalic acid solution.

In order to discover the conditions under which the reaction is carried to completion, perform the following experiments.

(i) Add a drop or two of decinormal permanganate solution to a few cubic centimetres of decinormal oxalic acid, without any other acid, and warm the mixture. Observe that the colour changes from pink to brown on warming, after which the solution gradually becomes colourless. The brown colour is due to manganous acid, i.e. hydrated, colloidal, manganese dioxide.

(ii) Add dilute sulphuric acid to some decinormal oxalic solution, and then a few drops of permanganate. Observe that the colour does not fade while the solution remains at atmospheric temperature, but that on heating the solution to 60° – 70° C. the colour is soon discharged.* It may be observed, however, that the manganese passes through the MnO_2 stage, as shown by the brown colour, before colourless manganous salt, corresponding with MnO , is reached.

(iii) Add decinormal permanganate drop by drop to hot oxalic acid solution containing sulphuric acid, and observe that the colour imparted by the first drop or two disappears slowly, but that after the first discharge of colour the colour of succeeding drops disappears more quickly. Since manganous sulphate is produced in the reaction it seems that it is the presence of this substance which promotes the reaction between permanganate and oxalic acid. To confirm this assumption add a little pure manganous sulphate to the solution of oxalic acid containing sulphuric acid, then heat and titrate as before. Observe that the colour of the permanganate fades sharply from the first drop. This proves that the presence of manganous sulphate is essential for the rapid oxidation of oxalic acid by permanganate. To discover the reason for this fact perform the following experiment.

(iv) Add very dilute solution of potassium permanganate to

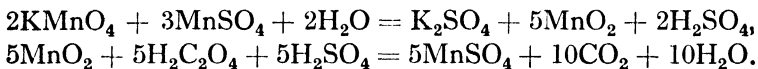
* This is a good example of the influence of temperature on the rate of chemical change.

manganous sulphate solution, and observe the appearance of a brown colour followed by a brown precipitate. This is hydrated manganese dioxide formed by a reaction represented in terms of oxides thus:

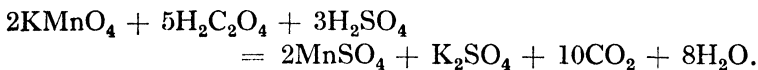


Now add the liquid containing this brown precipitate to hot oxalic acid solution containing sulphuric acid, and observe that the brown colour is instantly discharged. These experiments show that manganous sulphate promotes the oxidation of oxalic acid by permanganate, acting as a catalyst which is alternately oxidized to MnO_2 by permanganate, and reduced again to manganous salt by oxalic acid, or in other words that it acts as an oxygen carrier from permanganate to oxalic acid.

The reactions may be represented thus:



Adding eliminates the catalyst thus:



Standardize your potassium permanganate solution by means of your decinormal oxalic acid by placing 20 c. c. of the latter* in a flask, adding about 5 c. c. of dilute sulphuric acid, heating to $60^\circ\text{--}70^\circ\text{C.}$, and titrating with the permanganate till a pale pink colour remains. For a reason now understood the permanganate must be added slowly at first, and afterwards the rate of addition should not exceed that at which the colour fades, so that no brown colour may appear for more than an instant in the liquid.

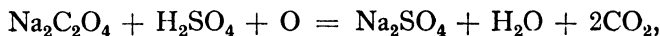
When agreeing results have been obtained, calculate a factor for the permanganate. This should agree with that obtained by means of Mohr's salt.

* It must be remembered that oxalic acid is poisonous. It is safer not to use a pipette, but to measure the oxalic acid from a second burette.

Standardization of Permanganate Solution by Sodium Oxalate.

Sodium oxalate, $\text{Na}_2\text{C}_2\text{O}_4$, can be readily obtained pure and crystallizes anhydrous. The salt, purchased as an analytical reagent or prepared by the student, should be heated in an air oven at 130°C . for two hours to expel any adventitious moisture, and then preserved in a desiccator or stoppered bottle.

In consideration of the reaction:



calculate what quantity of the salt is required to make 250 c. c. of a decinormal solution; prepare this solution and titrate it with your permanganate in presence of sulphuric acid as you titrated oxalic acid, and having obtained agreeing results calculate a factor for the permanganate.

Compare the factors for decinormal permanganate obtained by the three methods of standardization. These should agree closely, but, other things being equal, that obtained by the use of anhydrous sodium oxalate is the most reliable.

EXERCISES IN THE USE OF STANDARD POTASSIUM PERMANGANATE SOLUTION

The processes of oxidation which may be effected by potassium permanganate are manifold, and therefore a standard solution of this substance may be used for a considerable variety of exercises in volumetric analysis.

In his first year's course, however, the student may confine his attention to the following exercises:

1. Estimation of ferrous iron.
2. Estimation of ferric iron after reduction.
3. Estimation of metallic iron in iron wire.
4. Estimation of oxalate, e.g. ammonium oxalate,

5. Estimation of calcium by precipitating with excess of ammonium oxalate, and titrating the calcium oxalate or the excess of precipitant.

6. Estimation of hydrogen peroxide.

1. Estimation of Ferrous Iron.

If the ferrous iron is given in the form of a solution of ferrous salt this may be titrated directly at atmospheric temperature by standard potassium permanganate solution, after the addition of dilute sulphuric acid. The ferrous solution should be exposed to the air as little as possible, and should not contain chloride, or accurate results will not be obtained without special precautions.

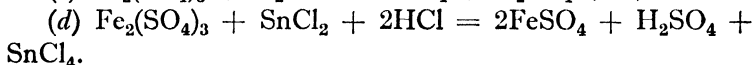
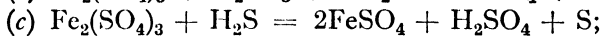
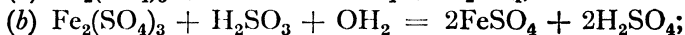
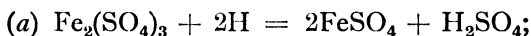
If a solid ferrous salt is provided, powder it and weigh sufficient of it to make, say, 100 c. c. of a solution of about decinormal strength. Dissolve the salt in air-free distilled water, together with a few drops of dilute sulphuric acid, which keeps the solution clear and retards atmospheric oxidation. Water is made air-free by boiling it briskly for a minute or two and then quickly cooling it with as little exposure to air as possible. It is best to use a narrow-necked flask, to invert a beaker over its mouth after the water has boiled, and then to allow cold water from the tap to run on to the beaker and so over the flask. When the solution has been diluted to 100 c. c., place 20 c. c. of it in a titrating flask, and titrate it cold with permanganate after the addition of about 5 c. c. of dilute sulphuric acid.

Instead of making 100 c. c. of the ferrous solution, successive weighed quantities of the salt may be dissolved in water and sulphuric acid in a small flask and directly titrated. The percentage of iron in the salt is readily calculated, since 1 c. c. of decinormal permanganate oxidizes 0.0056 gm.* of iron.

* Or more accurately 0.00584 gm.

2. Estimation of Ferric Iron after Reduction.

Various reagents are available for reducing ferric solutions to the ferrous state, as, for example, (a) zinc by nascent hydrogen, (b) sulphurous acid, (c) hydrogen sulphide, (d) stannous chloride, according to the following reactions:



The last reaction introduces chloride into the solution, and is therefore undesirable when permanganate is being employed. Either of the other three reactions may be used, the zinc sulphate which is present in solution after the first reaction, and the sulphur in suspension after the third, having no effect upon permanganate.

Ferric chloride is unsuitable to be estimated by permanganate for a reason already explained. Ferric sulphate, or better, ferric alum, i.e. ferric ammonium sulphate, is a suitable salt for the student to experiment upon.

Prepare, therefore, 250 c. c. of ferric alum solution containing about 0.0056 gm. Fe per cubic centimetre, having calculated the required amount of salt from the formula:



Choose transparent crystals of a pale violet colour.

When the salt is dissolved in water it produces a brown solution; this is due to incipient hydrolysis with the formation of basic ferric sulphate. Add a few drops of dilute sulphuric acid so as to reconvert the basic to normal salt. The solution will consequently become nearly colourless. Dilute the solution to the required volume, and mix its contents thoroughly. Use 25 c. c. for each of the following experiments.

(a) *Reduction by nascent hydrogen.*

The zinc employed may be in the form of rod or powder, or it may be granulated. The action is slowest with rod, and quickest with powder, owing to the large reacting surface in the latter case. Commercial zinc contains impurities, some of which remain when the metal is dissolved in dilute sulphuric acid. This residue generally contains lead and sometimes copper, which can be removed by filtration when the metal is used for reduction purposes. A more serious impurity than these may be iron, which if present passes into solution as ferrous salt, and necessarily invalidates the estimation. Therefore the zinc employed should be free from iron, but if such zinc cannot be obtained it is necessary to perform a "blank" experiment with the available zinc to determine the correction to be applied when it is used.

Reduction of ferric iron to the ferrous state takes place most rapidly in a hot solution which is only slightly acid. If too much acid is present hydrogen is wasted, and the reduction is not so effective.

The presence of sulphuric acid reduces the oxidizability of a ferrous solution; and a moderately acid solution is not perceptibly oxidized in air at atmospheric temperature. For the estimation, therefore, proceed as follows.

Measure 25 c. c. of the ferric solution, place it in a suitable flask, and dilute it to about 100 c. c. with water. Nearly neutralize the solution with ammonia, leaving it light brown, but containing no precipitate. Heat the solution to boiling, and add to it 0.5 gm. of zinc dust. Drop into the boiling solution, a little at a time, dilute sulphuric acid, so as to keep the solution pale, and promote the liberation of hydrogen. The iron is rapidly reduced, and in a minute or two the solution will become colourless. Add more dilute sulphuric acid, and boil briskly so as to dissolve all the zinc; then quickly cool the flask and its contents in running water; filter the

solution and wash the residual black powder, collecting filtrate and washings in another flask. Titrate the colourless solution with your standard permanganate. Repeat the experiment, using the same weight of zinc for reduction. If these instructions are carefully carried out, the results obtained will be concordant.

In case the zinc dust contains iron, perform a blank experiment thus: dissolve 1 gm. of the metal in boiling, dilute sulphuric acid, cool, filter, and titrate the solution with your permanganate. The volume required will indicate the correction to be applied when a ferric solution is reduced with a weighed quantity of this zinc.

(b) Reduction by sulphurous acid.

Sulphurous acid does not reduce a ferric solution in presence of much acid; neither does an alkaline sulphite solution effect reduction, because it causes a precipitate. Near the neutral point, however, ferric solution, when saturated with sulphur dioxide, is reduced on boiling. The reduction is easily carried out in the following way.

To 25 c. c. of the ferric solution contained in a convenient flask add sodium carbonate solution until the liquid turns reddish-brown, owing to the formation of basic salt, without actual precipitation. Next pass sulphur dioxide gas, from a siphon of the liquid, through this solution for a few minutes in order to saturate it; then heat the solution to boiling, adding to the hot liquid as much sulphuric acid as is necessary to prevent any precipitation. The solution will get paler, and eventually become colourless. When this takes place, add more dilute sulphuric acid, and boil briskly till sulphur dioxide is no longer smelt and the colour of potassium dichromate solution on filter paper held in the steam is not affected. Then quickly cool the solution, and titrate it with permanganate. Repeat the operation until agreeing results are obtained.

(c) *Reduction by hydrogen sulphide.*

When hydrogen sulphide gas is passed through a hot ferric solution in presence of acid, the gas is oxidized with the separation of white sulphur, and the solution becomes colourless owing to the reduction of the iron to the ferrous state.

For the estimation, measure 25 c. c. of the ferric alum solution, add to it an equal volume of dilute sulphuric acid, and heat the mixture to boiling. Then discontinue heating, and pass hydrogen sulphide gas through the solution. For this purpose it is best to have the solution in a flask fitted with a two-holed rubber stopper; through one hole passes a gas-delivery tube, bent at right angles, by which the gas is delivered into the liquid at the bottom of the flask; through the other passes an exit tube, also bent at right angles. Sulphur separates as the gas passes, and the yellow colour fades. Continue passing the gas until the liquid appears pure white, owing to the suspension of white sulphur in a colourless liquid. Then boil the liquid in the flask, and at the same time pass carbon dioxide through it. The carbon dioxide helps to displace hydrogen sulphide and at the same time excludes air. The sulphur gradually coagulates, and appears as a pale buff powder. Test the issuing gas with lead acetate paper, and, when it is free from hydrogen sulphide, quickly cool the solution, and titrate it with permanganate without filtering off the sulphur.

Estimate of Ferrous and Ferric Iron when Mixed.

If ferrous and ferric iron occur mixed in the solid state or in solution, the amount of iron in each state can be estimated by the application of the foregoing processes.

If a solid mixture is given, a weighed amount of it must be dissolved in air-free water, together with some dilute sulphuric acid, and the solution be diluted to a suitable volume.

The ferrous iron is then estimated by direct titration of 25 c.c. of the solution with permanganate; whilst the total iron is determined by reducing the ferric iron in another 25 c. c., by one or other of the above methods, and again titrating with permanganate. The ferric iron originally present is then ascertained by subtracting the original amount of ferrous iron from the total amount of the iron.

3. Estimation of Metallic Iron in Iron Wire.

Thoroughly clean some fine iron wire, by rubbing it first between emery cloth to remove rust and then between filter paper till it leaves no stain upon the paper. Coil the wire into a spiral, round a piece of glass tubing or a pencil, and accurately weigh about 0.5 gm. of it. Place the weighed wire in a round-bottomed flask of about 500-c. c. capacity, provided with a cork and bent glass tube, as shown in fig. 13. Pour upon the iron about 50 c. c. of dilute sulphuric acid (2N) and allow the end of the bent glass tube to pass nearly to the bottom of a small beaker containing about 50 c. c. of the bench sodium carbonate solution, which however must not contain more than a trace of iron. The purpose of the sodium carbonate is to generate carbon dioxide gas within the flask, which it enters towards the close of the experiment,

Now heat the flask until a brisk action takes place between the iron and the acid, and when the metal is completely dissolved boil the solution for a few minutes. This is necessary in order to displace from the liquid unsaturated hydrocarbons, and other hydrides, derived from impurities in the metal, which would reduce permanganate and cause the indicated percentage of iron to be too high. That the escaping hydrogen is not pure is proved by the peculiar smell noticeable as the gas emerges from under the sodium carbonate solution.

Now remove the flame and allow the solution in the flask to cool. Steam will condense, and consequently sodium

carbonate solution will rise up the tube and enter the flask. Here carbon dioxide will be generated which will drive back

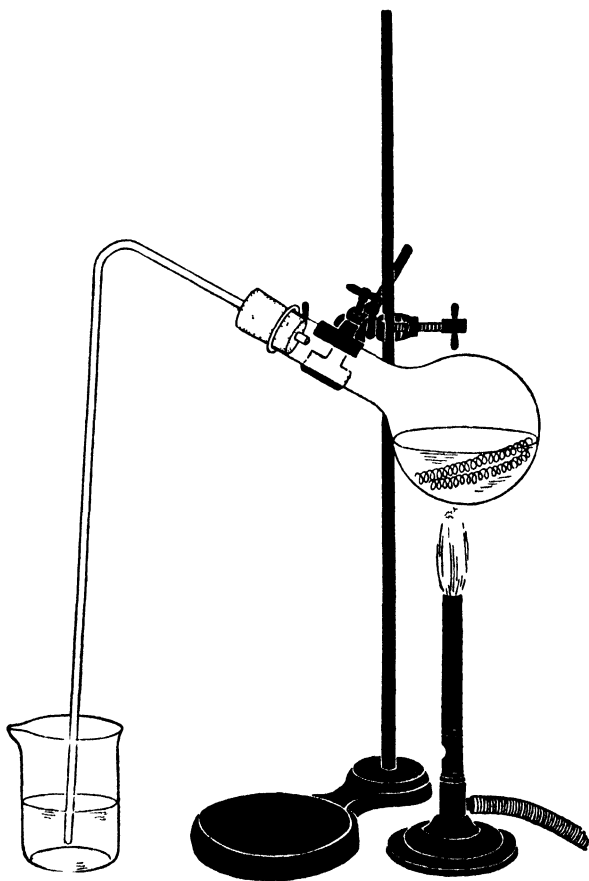


Fig. 13.—Solution of Iron Wire in dilute Sulphuric Acid

again the sodium carbonate. Cool the flask to atmospheric temperature, either by pouring water over it or by allowing it to stand in the air for some hours. By this time the space above the solution in the flask will be filled with carbon di-

oxide at nearly atmospheric pressure. Remove the cork from the flask, and test the acidity of the solution by adding to it a few drops of sodium carbonate solution. Unless effervescence is brisk, showing that a considerable excess of acid is present, add about 10 c. c. more of dilute sulphuric acid. There is now no fear that the cold acidified ferrous solution will undergo any perceptible atmospheric oxidation. In the solution will be seen suspended a residue of very fine particles of carbon which had been present in the free state in the iron. Since this residue has power to reduce permanganate slowly, filter the solution, receiving the filtrate in a 100-c. c. flask, and wash out the flask and the filter, so as to lose no ferrous sulphate. Dilute the filtrate to 100 c. c., thoroughly mix the solution, and titrate 20 c. c. of it with your standard permanganate. Repeat the titration, and then calculate the percentage of iron in the wire. This should be in the region of 99.5 per cent.

4. Estimation of Ammonium Oxalate, $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$.

This estimation is carried out in exactly the same way as that of oxalic acid or sodium oxalate.

It will be a useful exercise for the student to prepare his own specimen of ammonium oxalate, and then to prove its purity by analysis.

Weigh 5 gm. of commercial oxalic acid, dissolve it in a little hot water, and add ammonia to the solution with stirring, until the liquid smells of the gas. Evaporate the solution until from a few drops of it, poured into a test tube, crystals separate on cooling. Then quickly filter the solution, receiving the filtrate in a small flask. Cool the filtrate, so as to obtain the ammonium oxalate in the form of a crystalline meal, then filter off and dry the crystals in the usual way.

For the estimation, weigh accurately enough of the dry salt to furnish 100 (or 250) c. c. of an approximately decinormal solution, dissolve the salt in distilled water, dilute to the required

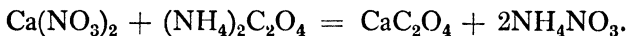
volume, and titrate an aliquot part of the solution with permanganate in presence of sulphuric acid, having first heated the solution to 60°–70° C., as was done in the case of oxalic acid.

From the result calculate the percentage of the pure hydrated salt in your specimen, or, assuming that no foreign matter is present, confirm the presence of one molecule of water of crystallization in a molecule of the salt.

5. Estimation of Calcium by Precipitation with Ammonium Oxalate, followed by Titration with Permanganate.

A soluble oxalate precipitates calcium as oxalate from a solution made alkaline with ammonia, or containing acetic acid but no mineral acid.*

The calcium salt employed for this estimation may be the crystallized sulphate, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, previously prepared, or Iceland spar, CaCO_3 , which is chemically pure. Weigh enough of the salt to yield 100 c. c. of a solution of about decinormal strength, dissolve it in dilute nitric acid, and dilute the solution to the required volume. The calcium salt is equivalent molecule for molecule to the ammonium oxalate, as the following equation shows:



It will be remembered that calcium oxalate is best precipitated by adding solid ammonium oxalate to a boiling solution of a calcium salt. Therefore proceed as follows.

Calculate what quantity of ammonium oxalate is necessary to make, say, 50 c. c. of a decinormal solution, and weigh accurately this amount of the salt. Measure 20 or 25 c. c. of your prepared calcium salt solution, dilute it to 100 c. c. in a suitable beaker, and add ammonium chloride. Then heat the liquid to boiling, add first the solid ammonium oxalate and

* Since calcium phosphate is freely soluble in acetic acid, the calcium present in bone-ash might be precipitated as oxalate, and so estimated by the process about to be described.

then ammonia in excess, boil for a minute, and allow the precipitated calcium oxalate to settle. Filter through paper, thoroughly wash the precipitate, and keep the filtrate. The calcium can be estimated in two ways.

(i) By titrating the calcium oxalate.

(ii) By titrating the excess of oxalate remaining in the filtrate.

(i) Wash the precipitated calcium oxalate into the apex of the filter, then boil a little dilute nitric acid in a test tube, and pour the acid on to the filter, below which a flask has been placed to receive the filtrate. The calcium oxalate readily dissolves, and when it has all disappeared, thoroughly wash the filter with hot water. Dilute the solution of calcium oxalate to about 50 c. c. with water, add some dilute sulphuric acid, heat the liquid to 60° – 70° C., and titrate it with decinormal permanganate. Calculate the amount of calcium in the volume of calcium salt solution taken, and thence the percentage in the original salt, remembering that 1 c. c. of decinormal permanganate corresponds with 0.0020 gm. of calcium.

(ii) Acidify the filtrate with dilute sulphuric acid, then heat and titrate it with permanganate. Subtract the volume of decinormal permanganate required from the volume which would be necessary to react with the quantity of ammonium oxalate originally taken. The difference is the volume of permanganate corresponding with the calcium precipitated, from which the weight of the latter can be calculated directly.*

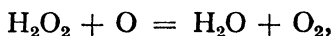
Repeat these experiments, precipitating the calcium in presence of acetic acid added in excess after mineral acid has been neutralized with ammonia.†

* The student may be inclined to calculate the weight of ammonium oxalate remaining, to subtract this from the weight taken, and then to calculate the calcium corresponding with the oxalate which left the solution. He will see, however, that if a weight of ammonium oxalate has been taken to correspond with a certain volume of decinormal permanganate solution, the calcium can afterwards be referred directly to permanganate, and a saving be made in the calculation.

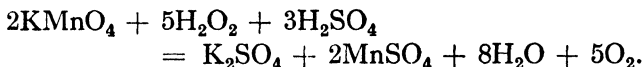
† Lead in a soluble salt can be estimated by the above process, lead oxalate being precipitated in presence of acetic acid.

6. Estimation of Hydrogen Peroxide.

Hydrogen peroxide, H_2O_2 , is oxidized by permanganate in presence of sulphuric acid, with evolution of oxygen, thus:



or expressed fully:



1 c. c. of decinormal permanganate solution oxidizes

$$\frac{\text{m.w. H}_2\text{O}_2}{2 \times 10,000} = 0.0017 \text{ gm. H}_2\text{O}_2.$$

Hydrogen peroxide is supplied in aqueous solution which is generally of one or the other following strengths:

3 per cent, or 10 volumes;
30 per cent, or 100 volumes.

This means that, for example, a 3 per cent solution of hydrogen peroxide yields ten times its volume of oxygen gas when it reacts with excess of acidified permanganate solution. The permanganate itself yields, however, a similar volume of oxygen, so that 1 c. c. of such a solution would yield, by reacting with excess of acidified permanganate, 20 c. c. of oxygen measured dry at normal temperature and pressure.

The 3 per cent solution of hydrogen peroxide is commonly made from barium peroxide without distillation; the 30 per cent solution, sometimes called perhydrol, is prepared generally by acting on sodium peroxide with sulphuric acid at low temperature and distilling the product *in vacuo*.

It will be seen that if a 3 per cent solution is diluted twenty times, if, for example, 5 c. c. of it are diluted with water to 100 c. c., the resulting solution will be a little less than equivalent to decinormal permanganate solution; and that 20 c. c.

of it, equivalent to 1 c. c. of the 3 per cent solution, will yield about 20 c. c. of oxygen with permanganate.

Hydrogen peroxide in dilute solution may be estimated by titration with decinormal permanganate, or gasometrically by measuring the volume of oxygen evolved on reaction with excess of acidified permanganate.

Preparation of hydrogen peroxide solution.

If the solution of hydrogen peroxide supplied is of approximately 3 per cent strength, measure 10 c. c. of it with a pipette, place this in a 100 c. c. graduated flask, dilute the solution with water to 100 c. c., and mix it thoroughly; 10 c. c. of this solution then corresponds with 1 c. c. of the original solution.

Titration of hydrogen peroxide solution with permanganate.

Measure 10 c. c. of your diluted hydrogen peroxide solution, place this in a suitable flask, and dilute it to about 100 c. c. with water. Add about 10 c. c. of dilute sulphuric acid and titrate the solution with your standard permanganate, adding the reagent slowly, especially at first. If the permanganate colour is slow in disappearing add more acid. Continue the titration till a pale pink colour remains, and repeat till agreeing results are obtained. From the volume of standard permanganate used, calculate the weight of hydrogen peroxide in 100 c. c. of the original solution.

Estimation of hydrogen peroxide gasometrically.

The apparatus required consists of a Lunge nitrometer containing water, and a small wide-necked bottle provided with a tightly fitting rubber stopper through which two short pieces of glass tubing pass. The outer end of one tube is connected with the nitrometer by means of a flexible rubber tube in the manner shown in fig. 14; on the outer end of the other tube is a short piece of rubber tubing which can be closed with a burette or screw clip. In the bottle is a specimen tube which is rather longer than the diameter of the bottle, so that it cannot slip down into a horizontal position. The apparatus

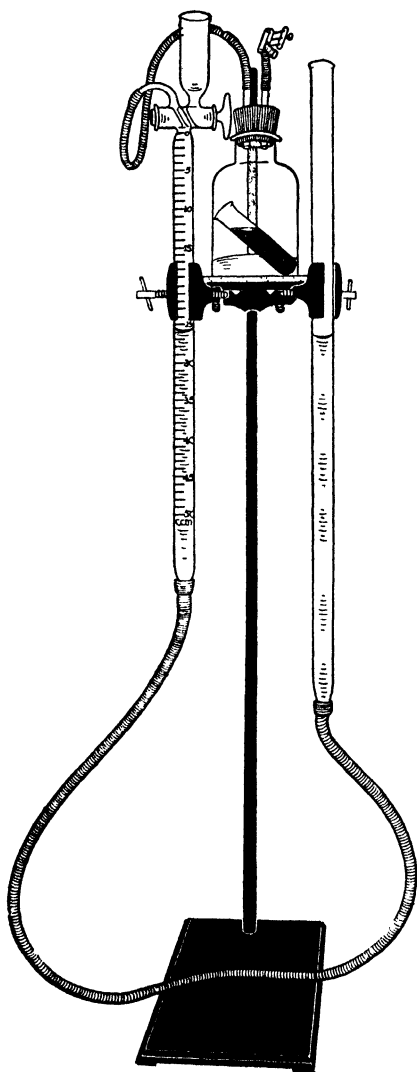


Fig. 14.—Gasometric Estimation of Hydrogen Peroxide

should be clamped so that the bottle can stand either on the shelf at the back of the bench, or preferably, if a double clamp is available, on a shelf made by placing a piece of wood or cardboard across the two arms of the clamp, as shown in the figure.

Before carrying out an estimation with this apparatus, discover whether it is air-tight in the following way. First see that the two-way tap of the nitrometer is properly greased; then fill the graduated measuring tube with water, first turning the tap so that the tube is connected with the cup above it. Water poured into the pressure tube will now rise into the graduated tube, driving out the air before it through the tap. It is not necessary for the water in the pressure tube to be finally at as high a level as that in the measuring tube, because

the pressure tube can be raised so as to fill the measuring tube, owing to the thick-walled rubber tubing which connects the two tubes. Now have the bottle attached and the exit from it closed by the clip. Let in some air through the two-way tap, then by rotating the tap through 180° connect the air in the bottle with that in the tube. Adjust the level of the water in the two tubes, so that the air contained in the bottle and measuring tube is at atmospheric pressure, and then read its volume. Now compress the air a little by raising the pressure tube; then bring it back to atmospheric pressure, and see if its volume remains unchanged. Also reduce the pressure on the air by lowering the pressure tube, and observe if the volume remains the same after the restoration of pressure.

When the apparatus is known to be air-tight proceed as follows. Prepare some cold saturated solution of potassium permanganate, by heating some of the salt with water and afterwards cooling. Then, by means of a funnel passing through the neck of the bottle into the specimen tube, pour the permanganate solution into the latter until it is two-thirds full. Let the funnel drain, then remove it and allow the specimen tube to take up an inclined position within the bottle. Take care not to spill any permanganate within the bottle itself. Now place 10 c. c. of dilute sulphuric acid in the bottle, and 10 c. c. of your diluted hydrogen peroxide solution; insert the rubber stopper into the bottle, and fix the clip on to the rubber tube; it is well to double over the tube before clipping it. See that the measuring tube of the nitrometer is full of water, then lower the pressure tube and turn the tap, so as to connect the measuring tube with the bottle. A little air will enter the measuring tube, because the air pressure is lower than that of the atmosphere.

Now tilt the bottle so as to pour the permanganate solution into the acidified hydrogen peroxide, and, as the evolved gas

enters the measuring tube, lower the pressure tube so as not to allow the pressure of the gas to exceed that of the atmosphere.

Shake the bottle so as to promote the disengagement of gas, and, when the reaction appears to be finished, bring the pressure tube against the measuring tube so that the water is at the same level in both tubes, and read the volume of gas. Again shake the bottle, and readjust and read the volume. When the volume is constant, record it, and ascertain the temperature and pressure of the atmosphere. What is actually measured is the increase in volume of the air originally in the bottle by the volume of oxygen evolved in the reaction.

Calculate the volume of oxygen at normal temperature and pressure, remembering that since the gas is measured over water, and is therefore saturated with water vapour, the pressure of this vapour at the observed temperature must be subtracted from the atmospheric pressure. From the volume of oxygen calculate its weight, and thence the weight of hydrogen peroxide in the volume of solution taken.

An example, showing the method of calculation, may be helpful.

10 c. c. of diluted hydrogen peroxide solution (= 1 c. c. of original solution) yielded 19.8 of oxygen measured over water at 14° C. and 754 mm. Pressure of water vapour at 14° C. = 12 m.m

Volume of oxygen at N.T.P.

$$= \frac{19.8 \times 273 \times (754 - 12)}{287 \times 760} = 18.4 \text{ c. c.}$$

Weight of oxygen = $18.4 \times 0.00009 \times 16$ gm.; and since 32 gm. of oxygen are equivalent to 34 gm. of hydrogen peroxide.

$$\text{Weight of H}_2\text{O}_2 = \frac{18.4 \times 0.00009 \times 16 \times 34}{32} = 0.0281 \text{ gm.}$$

∴ Weight of hydrogen peroxide in 100 c. c. of original solution = 2.81 gm.

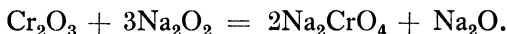
Repeat the experiment until agreeing results are obtained. These should coincide with those obtained by titration.

STANDARD POTASSIUM DICHROMATE SOLUTION

Potassium dichromate resembles potassium permanganate in being an oxidizing agent, and it is on account of its specific oxidizing properties that it is used in volumetric analysis. The chemistry of the preparation and reactions of dichromate will be elucidated by the following experiments.

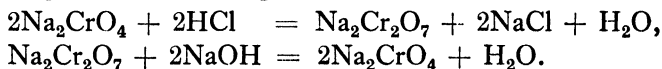
Formation of Chromate and Dichromate.

Mix a very little chromic oxide, which is green, or the hydrated oxide, which is grey, with excess of sodium peroxide; place the mixture in a test tube, and heat it till it fuses. Allow the mass to cool, and notice that it is lemon-yellow and easily soluble in water. Chromic oxide has been converted into chromate thus:



Chromate can be produced in solution thus: add some sodium peroxide to some dilute solution of chromic sulphate in a test tube, and boil the solution. Yellow sodium chromate is produced in solution, as before.

Add to the yellow solution dilute hydrochloric acid until the colour changes to orange-red; then add excess of sodium hydroxide, and observe that the yellow colour reappears. Chromate has been changed to dichromate, and vice versa, according to the following reactions:



Dichromates are less soluble in water than chromates; and potassium dichromate, being easily purified by crystallization, is chosen for use in volumetric analysis.

Oxidation by Dichromate.

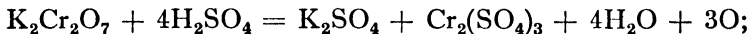
The formation of chromate or dichromate in the above experiments involves the oxidation of the basic oxide Cr_2O_3 to a salt derived from the acidic oxide CrO_3 ; oxidation by dichromate conversely involves the reduction of chromium from the state represented by CrO_3 to that represented by Cr_2O_3 . Thus the reversible reaction,



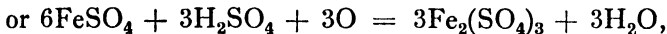
represents in terms of oxides what happens in the preparation and use of dichromate. Further, a salt of the acidic oxide CrO_3 , a dichromate, is formed when a base is present to promote its formation, and a salt of the basic oxide Cr_2O_3 , i.e. a chromic salt, when an acid is present.

Study oxidation by dichromate by means of the following experiments.

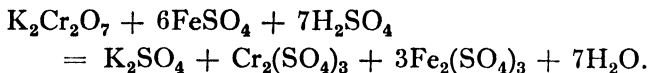
(a) Add potassium dichromate solution drop by drop to ferrous sulphate solution in presence of sulphuric acid. A green colour is produced due to chromic sulphate. Since potassium dichromate, $\text{K}_2\text{Cr}_2\text{O}_7$, is $\text{K}_2\text{O} \cdot 2\text{CrO}_3$, one molecule when reduced yields three atoms of oxygen, as the above simple equation shows. The formation of chromic sulphate, together with potassium sulphate, is therefore shown thus:



but since iron is oxidized according to the scheme



the completed equation becomes:



This reaction is the principal one for which dichromate is used in volumetric analysis, but there are others.

(b) Acidify some dilute dichromate solution with sulphuric or hydrochloric acid and divide the solution into two parts. Through one part pass hydrogen sulphide gas, through the other sulphur dioxide gas. In the case of hydrogen sulphide the colour of the dichromate changes gradually with separation of sulphur; by the sulphur dioxide the dichromate is rapidly reduced, a clear green solution resulting. The hydrogen sulphide is oxidized to water and sulphur, the sulphur dioxide in presence of water to sulphuric acid. The student should be able to construct the equations on the above model.

The following experiment is significant.

(c) Place some dilute hydrochloric acid in each of two test tubes; add a few drops of permanganate solution to one test tube and a few drops of dichromate to the other. Place the test tubes side by side in a beaker of water and heat the water. Notice that whilst the colour of the permanganate fades and disappears, that of the dichromate remains unchanged. This shows that dichromate is not so sensitive an oxidizing agent as permanganate, and since it does not oxidize dilute hydrochloric acid, estimation of iron by dichromate can be made in presence of hydrochloric acid. This is a distinct advantage.

Use of an Indicator with Dichromate.

It will be remembered that permanganate is its own indicator. Such, however, is not the case with dichromate, for it is not possible to see when the orange dichromate solution, added to a reducing agent, ceases to turn green. Since there is no indicator on the side of dichromate,* an indicator must be sought on the side of the substance undergoing oxidation. This is possible in the case of ferrous and ferric iron, for potassium ferricyanide solution gives a deep blue precipitate with

* Diphenylamine, which gives an intense violet-blue oxidation product with dichromate, is not oxidized in presence of ferrous iron; it can therefore be used as an internal indicator, if sulphuric and phosphoric acids are added to suppress the yellow of ferric chloride (J. Knop, *J. Amer. Chem. Soc.*, 1924, **46**, 263). For method, see p. 137.

ferrous iron and only a brown colour with ferric iron. The application of these facts to the use of dichromate is illustrated by the following experiments:

(a) Add dilute potassium ferricyanide solution to ferrous sulphate and obtain a deep blue precipitate of ferrous ferricyanide.

(b) Add dilute potassium ferricyanide to dilute ferric chloride solution; a brown colour is seen, but no precipitate.

(c) Add excess of dichromate to acidified ferrous sulphate solution, and then potassium ferricyanide. There will be no blue precipitate, because the dichromate has oxidized all the iron from the ferrous to the ferric state.

(d) By means of a rounded glass rod place out a series of drops of dilute potassium ferricyanide solution on a glazed tile; then mix dichromate solution drop by drop with some acidified ferrous sulphate solution in a test tube or small flask. After each addition of dichromate remove a drop of the iron solution and mix it with the ferricyanide on the tile. As long as ferrous iron remains in the solution a blue precipitate or colour will appear on the tile, but when the iron has all been oxidized the blue colour will give place to pale brown. An indication of the approaching end of the reaction will be shown by the blue colour becoming paler and somewhat green.

This illustrates the use of potassium ferricyanide as an external indicator for iron undergoing oxidation.

It may be objected to this method of indicating the end of the reaction that, since some solution is removed in order to test it for ferrous iron, less remains to be oxidized, and therefore the amount of iron found will be less than was originally present. To this objection the reply may be made that the amount of iron thus removed is almost negligible, and that it is towards the end of the reaction that the removal principally takes place, when the remaining ferrous solution is highly dilute; and further that in a second and confirmatory titration the iron may be almost completely oxidized before

any solution is removed, since the amount of standard dichromate solution required is already approximately known.

Preparation of Decinormal Potassium Dichromate Solution.

Since the molecule $K_2Cr_2O_7$ contains 3 atoms of available oxygen, which are equivalent to 6 atoms of hydrogen, the equivalent weight of potassium dichromate is one-sixth of its molecular weight. Therefore 1 litre of a decinormal solution of this reagent contains one-sixtieth of a gram-molecule—it is one-sixtieth molar. The student will find the weight of potassium dichromate required to be 4.903 gm.

The salt should be recrystallized, and when thoroughly dried may be regarded as pure enough for analysis. Standardization of the solution with ferrous sulphate or Mohr's salt, for example, is not a wise proceeding, since it is less easy to obtain these salts pure than the dichromate. If, therefore, decinormal dichromate solution is titrated into a standard ferrous solution, the operation should be regarded as a test of purity of the ferrous salt rather than of the dichromate.

Take 10 gm. of the purest obtainable potassium dichromate, powder it, dissolve it in the least quantity of boiling water, and filter the solution through a hot funnel. The purpose of the hot funnel is to prevent crystallization of the salt in the funnel. A large funnel, say 6 in. across, should be employed with filter paper to fit it, so that the whole of the solution may be poured into it at once. A jacket through which hot water runs, as shown in fig. 15, may be used, but it will probably suffice to heat the funnel in the steam oven immediately before using it.

Receive the filtrate in a flask, and cool it in running water so as to obtain the recrystallized salt in a finely granulated state. Filter the salt in the usual manner, pump it dry, and then leave it overnight on filter paper or a piece of porous

plate. When the salt seems crisp and dry, heat it in a porcelain dish till it turns darker but does not fuse, stirring all the while with a rounded glass rod. In the course of a few minutes the

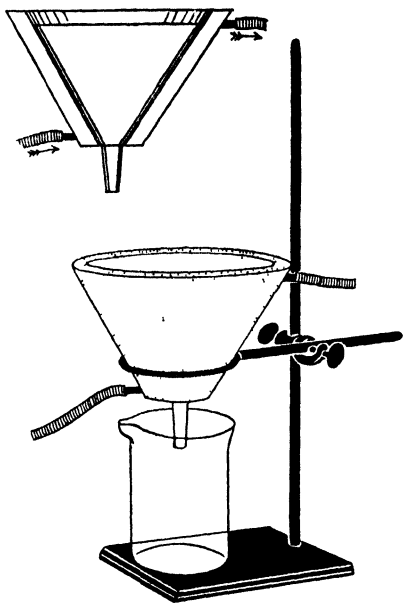


Fig. 15.—Funnel in Hot-water Jacket

dichromate will be quite dry, and after being allowed to cool should be transferred to a stoppered bottle or well-corked test tube.

Weigh the required amount of your potassium dichromate and make a litre of decinormal solution. The solution keeps indefinitely in a stoppered bottle. The only direct estimation for which standard potassium dichromate solution is used is that of iron, which it oxidizes quantitatively from the ferrous to the ferric state. Decinormal dichromate solution can be employed indirectly, how-

ever, for standardizing sodium thiosulphate solution (q.v.), since it liberates iodine quantitatively from an acidified solution of potassium iodide.

EXERCISES IN THE USE OF STANDARD POTASSIUM DICHROMATE SOLUTION

The following are the estimations to be carried out with decinormal potassium dichromate solution:

1. Iron in a ferrous solution or a solid ferrous salt.
2. Iron in a ferric solution or ferric salt, after reduction.
3. Iron in red hæmatite.

(1) Estimation of Iron in a Ferrous Salt.

If a ferrous solution is given for analysis, 20 c. c. of it may be directly titrated with decinormal dichromate in the following way.

First prepare a dilute solution of potassium ferricyanide by dissolving a fragment of the salt half the size of a pea in, say, 50 c. c. of water. Then by means of a thin rounded glass rod place a series of drops of the reagent at convenient intervals on a glazed white tile. Frequently tiles are provided for the purpose with rounded depressions on them in each of which a drop of the ferricyanide can be placed.

Acidify the measured volume of ferrous solution with dilute sulphuric or hydrochloric acid—it is the advantage of dichromate that it does not matter which acid is used—and titrate it with the dichromate. It will be seen, as the dichromate is added, that the solution becomes greener; this is due to the accumulation of chromic salt in the solution. When it is judged that the reaction is nearing completion, remove as little as possible of the solution on the end of the thin glass rod, and bring it into contact with a drop of the ferricyanide solution. Unless the reaction is already completed a blue colour will appear. Be careful to rinse the rod under the tap before bringing it again into the ferrous solution, for if ferricyanide reacted with ferrous iron in the titrating flask the estimation would be spoilt. Continue the addition of dichromate and the testing of the solution externally until no blue or green, but only a pale brown colour, marking the end of the reaction, is produced. After taking the reading repeat the estimation, quickly adding the dichromate to within 1 c. c. of what will be required, and then carefully finishing the titration a drop at a time.

When concordant results have been obtained, calculate the weight of iron, or of ferrous sulphate, in 100 c. c. of the given solution.

If a solid ferrous salt is given for estimation, dissolve a suitable weighed quantity of it in air-free distilled water, together with a little dilute sulphuric acid, and titrate as before. As regards the quantity of salt to be weighed, this may be either enough for a single titration, when the volume of water in which it is dissolved need not be measured, or 100 c. c. of a suitable solution may be prepared, and successive volumes of 20 c. c. titrated.

(2) Estimation of Ferric Iron after Reduction.

Study of Reduction Process.—For the use of permanganate in the estimation of iron, the following reducing agents were employed to reduce the iron when it existed in the ferric state: nascent hydrogen, sulphurous acid, hydrogen sulphide.

Either of these methods of reduction might be used with dichromate as the subsequent oxidizing agent, but a more convenient and rapid reducing agent exists in stannous chloride, which could not be used in conjunction with permanganate, because of the interaction between the latter and a chloride in solution.

Stannous chloride rapidly reduces ferric chloride in hot acid solution, as may be shown by the following experiment.

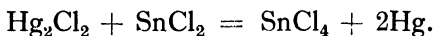
Place a few cubic centimetres of ferric chloride solution in a flask, add to it about 10 c. c. of dilute hydrochloric acid, dilute the solution to about 50 c. c. with water, and heat it to the boiling-point. Now add to the bright yellow liquid dilute solution of stannous chloride. This solution may be made from the crystallized chloride, $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, or may be prepared conveniently by heating a few pieces of granulated tin with concentrated hydrochloric acid for a few minutes, and then diluting with cold water the clear solution obtained. Add this solution to the ferric solution, a drop at a time, by employing a small pipette or a piece of glass tubing drawn out somewhat at the end. The yellow colour will fade and

disappear, though it will be observed that the change is not instantaneous. With care, and provided that the stannous solution is sufficiently dilute, reduction may be visibly completed with a single drop of the latter, so that very little excess need remain. Those who constantly use this reaction are able to complete the reduction and leave an excess of stannous chloride so small as to be negligible. It is usual, however, and advisable, to eliminate the excess of stannous chloride; and for this purpose the following reaction is employed.

Dilute a few cubic centimetres of stannous chloride solution to about 50 c. c. in a flask, and add to the liquid some mercuric chloride solution. Observe that a white precipitate gradually separates; this is mercurous chloride formed by the reaction:



Now repeat the experiment, using rather more stannous chloride, and heating the liquid to boiling before adding mercuric chloride to it. The precipitate thus obtained will be grey, for it contains finely divided mercury formed by the further reducing action of stannous chloride, the mercurous chloride first precipitated being reduced to metallic mercury thus:



The formation of this grey precipitate can be avoided, as appears from these experiments, by taking care to use as little excess as possible of stannous chloride, and cooling the solution before adding mercuric chloride.*

The Estimation.—Measure 20 c. c. of the given ferric solution, known to be in the region of decinormal strength,

* A brownish-grey turbid liquid, containing colloidal mercury, results when a drop of mercuric chloride is added to excess of cold dilute stannous chloride solution, but this product reacts with more mercuric chloride to form a white precipitate of mercurous chloride. If, however, the solution is heated to boiling before any mercuric chloride is added to it, the mercury separates as a grey coagulated precipitate which does not react with mercuric chloride.

add a few cubic centimetres of concentrated hydrochloric acid, then heat the solution to boiling and reduce the iron with the minimum amount of dilute stannous chloride solution; cool, and add a few cubic centimetres of mercuric chloride solution, observing that a faint white precipitate of mercurous chloride separates; then titrate the turbid liquid with decinormal dichromate solution, using potassium ferricyanide as external indicator. Repeat until agreeing results are obtained, and calculate the weight of iron in 100 c. c. of the solution.

(3) Estimation of Iron in Red Hæmatite.

The ease with which red hæmatite dissolves in concentrated hydrochloric acid depends upon its state of fine division. The coarsely powdered ore dissolves with difficulty, but the same ore reduced to a very fine powder dissolves readily, leaving behind only a small light residue of silica.

If the ore is supplied in lumps, these must first be crushed in a steel percussion mortar; the coarse material can then be ground to an impalpable powder in an agate mortar. Only a little of the substance should be placed in the agate mortar at a time, and this should be ground by the pestle held firmly in the hand and moved with pressure in a circular way. Grinding should be continued until no grittiness is felt when the powder is rubbed between the finger and thumb. It will be sufficient to grind finely 2 or 3 gm. of the hæmatite; this should be put into a stoppered weighing bottle, and weighed directly therefrom. Such a method of weighing is better than using a tared watch-glass, since it is difficult to remove completely from the glass such a very fine powder.

Weigh accurately, by difference, 0.8 to 1.0 gm. of the powdered hæmatite, dropping the powder directly into the flask in which it is to be dissolved. Add about 10 c. c. of concentrated hydrochloric acid, pouring the acid through a funnel which is allowed to remain in the neck of the flask;

this serves to condense some of the acid when it is boiled, and the condensed acid then carries down into the solution any of the powder which happened to adhere to the neck or sides of the flask. Support the flask on a tripod with asbestos-covered gauze, and apply heat so that the acid boils gently. After a few minutes all the oxide of iron will have been dissolved, leaving a floating residue of silica. More acid may, however, be added through the funnel, if necessary to effect solution. Pour a little water through the funnel so as to dilute the solution, then filter the latter into a 100-c. c. graduated flask, washing the flask and filter till the washings are colourless, taking care, however, that the volume of filtrate and washings does not exceed 100 c. c. If all the oxide of iron has been removed from it, the silica will appear on the filter as a grey, flocculent residue. Cool the solution to atmospheric temperature, and mix its contents by shaking.

Measure 20 c. c. of this prepared solution, heat it to boiling, reduce the iron, and proceed subsequently in the manner already described. From the result of agreeing titrations calculate the percentage of Fe or of Fe_2O_3 in the hæmatite.

To confirm these results, enough hæmatite (about 0.2 gm.) for a single titration can be employed.

Keep your decinormal potassium dichromate solution, as it will be required subsequently.

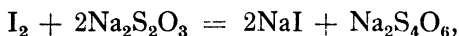
Use of Diphenylamine as Internal Indicator.

Solutions required.—A. 150 c. c. sulphuric acid (sp. gr. 1.84) mixed with 150 c. c. phosphoric acid (sp. gr. 1.7) and the mixture diluted to 1 litre. B. 1 gram. diphenylamine dissolved in 100 c. c. concentrated sulphuric acid.

Method.—To the solution of ferrous salt add 20 c. c. $2\text{N.H}_2\text{SO}_4$, 15 c. c. of solution A, and 3 drops of solution B, and dilute to 200 c. c. On titrating with standard potassium dichromate solution, the end point is shown by an intense blue colour. 0.05 c. c. should be allowed for the oxidation of the diphenylamine. The method may be used after the reduction of a ferric solution by stannous chloride, provided the reduction has been carefully performed and, therefore, only a slight precipitate of Hg_2Cl_2 is present.

STANDARD SOLUTIONS OF IODINE AND SODIUM THIOSULPHATE

Iodine and sodium thiosulphate * interact in solution in the following way:



producing sodium iodide and sodium tetrathionate;† and the amount of iodine present in any solution, whether liberated from an iodide by an oxidizing agent or not, can be estimated accurately by this reaction because of the delicate test for free iodine with starch, a deep blue colour being produced by the combination of very small amounts of these two substances in cold solution.

The chemistry of this subject may be studied experimentally in the following way.

Prepare a solution of iodine in potassium iodide by placing a fragment of iodine and a crystal of potassium iodide together in a test tube, and adding a few drops of water. A concentrated solution of potassium iodide is produced, in which the iodine easily dissolves. Dilute the solution to about 10 c. c.

Iodine is much more soluble in a solution of potassium iodide than in water, on the account of the formation of a polyiodide, e.g. KI_3 ; this compound dissociates, however, when the solution is much diluted, so that iodine is precipitated.

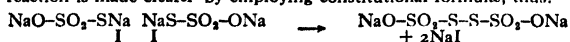
Prepare a dilute solution of sodium thiosulphate by dissolving a few small crystals of the salt in half a test-tubeful of water.

Preparation of Starch Solution.

Starch as ordinarily supplied consists of "grains" composed of starch "granulose" enclosed in an envelope of

* Commonly known as hyposulphite of soda or "hypo".

† The reaction is made clearer by employing constitutional formulæ, thus:



starch "cellulose". It is accordingly necessary to use boiling water in making "starch paste" in order to rupture the cellulose envelope and set free the granulose. Starch paste is therefore prepared by rubbing starch with cold water to make a cream, and then pouring this cream into boiling water so that it thickens as the colloidal granulose becomes diffused through the water. For the present purpose the starch paste, if made in this way, should be dilute. The objection to this starch paste, however, as a reagent for iodine, is that the fragments of cellulose remain in the paste, and that the granulose attached to them parts with its iodine less readily than the free granulose in colloidal solution. Consequently the starch loses in sensitiveness, and is less satisfactory to use than "soluble starch". The solution may, however, be filtered when dilute.

Soluble starch is made by filtering a dilute solution of starch so as to remove the cellulose fragments, and then precipitating the starch from its aqueous solution by alcohol. The white powder so obtained is collected and dried, and when boiled with water readily dissolves, yielding a liquid which gives a clear deep blue colour with a drop of iodine solution. On account of its superior sensitiveness, soluble starch should always be employed in preference to the ordinary kind. The solution should be dilute, since a very small quantity of starch is required to react with iodine.

Experiments.

(a) Place some dilute solution of iodine in a small flask and gradually add to it dilute solution of sodium thiosulphate. Observe that the colour of the solution becomes lighter with each addition of the thiosulphate until it quite disappears.

(b) Repeat the experiment, but add a little starch solution when the colour due to iodine has become faint. If more iodine is present than will combine with the starch the colour will appear somewhat green, a tint compounded of yellow

iodine and blue iodide of starch, but when almost sufficient thiosulphate has been added, the colour will be deep blue owing to iodide of starch alone, and this will suddenly disappear, leaving the liquid colourless when all the iodine has reacted with the thiosulphate. From this it appears that the compound of iodine with starch is an unstable one, since thiosulphate is able to decompose it and appropriate the iodine.

(c) An alternative to starting with free iodine is to liberate the iodine from hydriodic acid by an oxidizing agent. Thus a known quantity of potassium permanganate or dichromate may be caused to react with excess of potassium iodide in acid solution, and the liberated iodine can then react with sodium thiosulphate in solution. Show this with both the above oxidizing agents, using a few cubic centimetres of decinormal solutions of each; dilute these solutions, acidify them, and add in each case a few small crystals of potassium iodide, followed by starch, and then sodium thiosulphate solution drop by drop. Observe that in the case of potassium permanganate a colourless liquid remains when the blue of the iodide of starch disappears, but that with dichromate the blue colour gives place to green, which is the colour of chromic chloride. The latter colour change is sharp nevertheless, and therefore decinormal dichromate can be used to standardize sodium thiosulphate solution by means of the iodine it liberates from acidified potassium iodide. This is convenient, since decinormal dichromate solution is permanent, and that which remains from the former estimations can be employed.

Preparation of Sodium Thiosulphate Solution.

The equation given at the head of this section shows that 2 atoms of iodine react with 2 molecules of sodium thiosulphate; from this it follows that a decinormal solution of the latter is decimolecular. Crystallized sodium thiosulphate is $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ with molecular weight = 248.2; therefore a

decinormal solution of this reagent contains 24.82 gm. per litre. The salt can be obtained chemically pure, but its solution is decomposed by carbon dioxide dissolved in the water, for this liberates thiosulphuric acid from which sulphur is slowly deposited. It is well, therefore, to prepare a solution of strength slightly more than decinormal, and to allow it to stand for a few days before standardization to give time for its interaction with dissolved carbon dioxide.

Weigh, therefore, 25 gm. of sodium thiosulphate, dissolve it in distilled water, and dilute the solution to a litre. Transfer the solution to a suitable bottle,* and allow it to stand for three or four days before standardizing it.

Preparation of Iodine Solution.

The atomic weight of iodine, which is identical with its equivalent weight, is 126.92; therefore a decinormal solution of this substance contains 12.692 gm. per litre. The iodine usually supplied is not quite pure; it may be purified by special means, but this is unnecessary if the solution is to be standardized before use.

It has been seen that iodine dissolves much more readily in potassium iodide solution than in water; indeed the more concentrated the latter solution the more easily does iodine dissolve in it. The weight of potassium iodide required to dissolve and keep iodine in a solution of decinormal strength is about twice that of the iodine. The procedure is therefore as follows.

Since half a litre of solution will be sufficient for the present purpose, weigh 6.4 gm. of iodine on a tared clock-glass on the rough balance, and also about 12 gm. of potassium iodide.† Place the two solids together in a beaker and add a few cubic centimetres of water. Rotate the beaker so as to promote

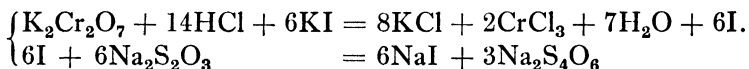
* Care must be taken that no trace of acid comes into contact with thiosulphate.

† If several students are to work with iodine it may be more economical for one of them to prepare a litre of the solution, which is then shared.

solution, adding a little more water if necessary. Potassium iodide is exceedingly soluble in water, and the iodine will quickly dissolve in its concentrated solution. When all is dissolved, transfer the solution to a 500-c. c. graduated flask, rinse the beaker with water, and pour the rinsings into the flask; then dilute to volume, mix thoroughly, and store the solution in a stoppered bottle.

Standardization of Sodium Thiosulphate Solution.

It has already been shown that decinormal potassium dichromate solution liberates its equivalent of iodine from acidified potassium iodide, and that sodium thiosulphate solution can be standardized by titration into the liberated iodine. This is expressed by the following equations, by which sodium thiosulphate is brought into relation with dichromate through the medium of iodine:



To standardize the sodium thiosulphate solution, therefore, proceed in the following manner.

Place 20 c. c. of decinormal potassium dichromate solution in a 500-c. c. flask, add not less than 10 c. c.* of concentrated hydrochloric acid, dilute the solution to about 200 c. c. and then drop into it about 0.5 gm. of crystallized potassium iodide. Iodine is quickly liberated and the solution becomes brown. Sufficient potassium iodide should be present to form a clear solution, so that no solid iodine separates. Now titrate the solution with your nearly decinormal sodium thiosulphate, interrupting the process to add starch when the end of the reaction is approaching. Then continue the titration until the bluish black colour formed on addition of the starch changes to the pale green due to chromic chloride.

* Sometimes the starch-iodide colour disappears too soon, but reappears on standing. This behaviour, which gives inaccurate results, is due to insufficiency of acid.

Repeat the titration, and when concordant results have been obtained calculate a factor for the sodium thiosulphate solution.

To confirm this result, decinormal potassium permanganate solution can be used in place of the dichromate.

Standardization of Iodine Solution.

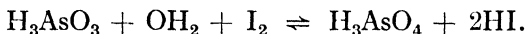
The prepared iodine solution can be standardized by means of the standard sodium thiosulphate solution, or by causing it to oxidize pure arsenious oxide contained in solution as arsenite.

Standardization by Thiosulphate.

Measure 20 c. c. of your iodine solution, preferably from a second burette, and titrate it with your standard thiosulphate solution, adding starch solution as indicator when the colour of the iodine has faded to a pale yellow. Confirm your result, and calculate a factor for the iodine solution.

Standardization by Arsenite.

Arsenious acid and iodine interact in aqueous solution thus:



This reaction is a reversible one, and the direction in which it proceeds depends upon the presence or absence of acid. If much hydrochloric acid is present, arsenic acid oxidizes hydriodic acid quantitatively, liberating free iodine; but if the solution is kept neutral the reaction proceeds to completion in the opposite direction. Thus arsenite, in neutral solution, can be titrated by iodine, provided a reagent is present to combine with the hydriodic acid produced and keep the solution neutral. Neither sodium hydroxide nor carbonate can be used for this purpose, because these are alkaline and react with iodine; but sodium hydrogen carbonate is neutral, and does not react with iodine, though it is decomposed by and so neutralizes hydriodic acid. Thus arsenite can be

titrated with iodine in presence of excess of sodium hydrogen carbonate.

Expressed in terms of oxides, the oxidation effected by iodine is:



Therefore a fourth of a gram-molecule of arsenious oxide represents the equivalent weight of the oxide; and, since the molecular weight of As_2O_3^* is 197.92, $\frac{197.92}{400} = 0.4948$ gm. of this oxide will be required for 100 c. c. of a decinormal solution.

Weigh 0.495 gm. of pure arsenious oxide on a tared watch-glass, transfer the powder to a small beaker, dissolve it in a little warm sodium hydroxide solution, add a drop of phenolphthalein to the liquid, and then dilute hydrochloric acid until the crimson colour is discharged. Then transfer the solution to a 100 c. c. graduated flask, dilute it to the mark, and mix thoroughly.

Prepare a cold saturated solution of sodium hydrogen carbonate by shaking the salt with water in a stoppered bottle. A solution of starch is required similar to that used previously. For the estimation two burettes must be employed, one to contain the iodine, the other the arsenite solution, for the latter must on no account be sucked up a pipette.

Measure 20 c. c. of the arsenite solution, running it from the burette into a suitable flask, add a few drops of starch solution, and say 10 c. c. of the cold solution of sodium hydrogen carbonate. Titrate the liquid with the standard iodine solution, observing that the blue colour which the iodine produces locally quickly disappears as the solution is shaken. The end of the reaction, shown by a permanent blue colour, should be sharp; if it is not so, i.e. if the blue colour appears too soon but does not last, this is due to deficiency of sodium hydrogen carbonate, and more of this

* The molecular formula is As_4O_6 , but the simpler formula suffices here.

reagent must be added. When the end point is reached, the addition of more sodium hydrogen carbonate will not affect the blue colour.

From agreeing results a factor can be calculated for the iodine which should agree with that obtained through standard thiosulphate solution.

EXERCISES IN THE USE OF STANDARD SOLUTIONS OF IODINE AND SODIUM THIOSULPHATE

Various estimations can be carried out with these two reagents, since iodine can be used for different processes of oxidation, and can also be liberated from acidified potassium iodide by a variety of oxidizing agents, and then titrated with sodium thiosulphate.

For the present purpose two estimations, one involving the use of standard iodine solution, the other of standard sodium thiosulphate, are chosen.*

(1) Estimation of hydrogen sulphide in aqueous solution by titration with standard iodine.

(2) Estimation of available chlorine in bleaching powder, by causing the bleaching powder to react with acidified potassium iodide, and titrating the liberated iodine with standard sodium thiosulphate.

(1) Estimation of Hydrogen Sulphide.

Hydrogen sulphide reacts with iodine thus:



The reaction proceeds quantitatively to completion whether hydrogen sulphide solution is added to iodine or vice versa. It is better, however, to add the prepared solution of hydrogen

* The uses of standard iodine and thiosulphate solutions will be dealt with more fully in Part II of this work.

sulphide to excess of standard iodine, and then to titrate the remaining iodine with sodium thiosulphate, than to proceed in the reverse order, since hydrogen sulphide solution loses strength by evaporation and atmospheric oxidation when it is exposed to the air during titration with iodine. Further, if the solution of hydrogen sulphide is too strong, the sulphur as it separates is liable to occlude iodine, which will then be unable to react with the thiosulphate, so that the amount of hydrogen sulphide indicated will be in excess of the truth; consequently the strength of the solution should not exceed about 0.4 gm. per litre, or 0.025-normal.

Prepare some cold, air-free, distilled water; place about 200 c. c. of it in a narrow-necked flask, and pass hydrogen sulphide through it for a few minutes. As a preliminary trial withdraw 20 c. c. of the solution,* place it in a titration flask with a little starch solution, and titrate it with your standard iodine solution until a permanent blue colour shows the end of the reaction. If not more than 5 c. c. of iodine are required, the solution is of suitable strength for accurate titration; if more than this amount of iodine is needed, dilute the hydrogen sulphide solution with air-free water, so that it may be of suitable strength. Since the purpose of the exercise is only to obtain a convenient solution and then to titrate it, and the amount of hydrogen sulphide originally dissolved was arbitrary, the dilution may be made roughly.

Having made a hydrogen sulphide solution which is known to be of suitable strength, place 20 c. c. of your standard iodine in a suitable flask, then fill a burette with the hydrogen sulphide solution, and quickly allow 50 c. c. of it to run down the side of the flask into the iodine. The solution should remain distinctly yellow with iodine, though turbid on account of separated sulphur. Now add starch solution, and titrate the remaining

* This may be done by the use of a small cylinder or a burette, since it is objectionable to fill a pipette with hydrogen sulphide solution by suction.

iodine with your standard thiosulphate solution. Convert the volumes of iodine and thiosulphate solutions used to decinormal strength by multiplying them by their respective factors; then the difference between them represents the volume of hydrogen sulphide solution of decinormal strength equivalent to that present in the 50 c. c. of the solution used. Repeat the titration, and, when concordant results have been obtained, calculate the strength of the hydrogen sulphide solution in grams per litre.*

(2) Estimation of Available Chlorine in Bleaching Powder.

The chlorine in bleaching powder, when set free by acid, liberates its equivalent of iodine from potassium iodide, which may then be estimated by titration with standard sodium thiosulphate solution. A weighed quantity of bleaching powder is rubbed into a paste with water, and the liquid is diluted to a suitable volume. An aliquot part of the turbid liquid is then placed in a flask, and crystals of potassium iodide are added to it, followed by dilute acid. This liberates the chlorine, which immediately displaces its equivalent of iodine from the iodide. Thus a clear brown solution of iodine results which can be titrated with thiosulphate.

To simplify the calculation it is convenient to weigh 3.55 gm. of bleaching powder, and, after rubbing it with water, to dilute the liquid to 1 litre. If then 100 c. c. of this solution are taken for a titration, the volume in cubic centimetres of decinormal sodium thiosulphate required to react with the liberated iodine is numerically equal to the percentage of chlorine in the bleaching powder. For 3.55 gm. of chlorine would make 1 litre of a decinormal solution of the element, and 100 c. c. of such a solution would liberate iodine requiring for decolorization 100 c. c. of decinormal thiosulphate. There-

* In practice this method is available for estimating the hydrogen sulphide present in certain mineral waters.

fore the percentage of this volume of thiosulphate employed represents the percentage of chlorine in the bleaching powder.

The acid used to liberate the chlorine from the bleaching powder may be dilute hydrochloric or acetic acid. If the bleaching powder contains any chlorate this may react with hydrochloric acid, yielding chlorine; it is therefore preferable to use acetic acid.

Carry out the estimation in accordance with the above suggestions, but on no account put the turbid bleaching powder into a burette. If a litre of the solution is made, 100 c. c. may be measured in a cylinder or flask. Bleaching powder itself dissolves in water; the residue is unchanged slaked lime with perhaps a little siliceous impurity.

STANDARD SILVER NITRATE SOLUTION

The use of silver nitrate in volumetric analysis differs from that of the foregoing reagents because it depends upon the precipitation of an insoluble salt carried to completion. For example, chloride in solution can be estimated by means of standard silver nitrate solution, provided there is a way of indicating the point at which precipitation of silver chloride is complete. That this point is easily indicated when the reacting solutions are neutral is shown by the following experiments.

(i) Add to a little silver nitrate solution a few drops of potassium chromate. A deep red precipitate is formed. Now add some sodium chloride solution and shake. Observe that the red silver chromate is converted into white silver chloride, which remains suspended in the yellow chromate solution. The reason for this transformation is that silver chloride is less soluble in water than silver chromate, and that any change that takes place in presence of a solvent is in the direction of forming the compound least soluble in that solvent. The same fact is

illustrated by the transformation of silver chloride suspended in water into the less soluble iodide by the addition of potassium iodide.

(ii) Add to a little neutral sodium chloride solution a drop of potassium chromate, and then silver nitrate drop by drop. Notice that the first permanent precipitate is that of sodium chloride, any silver chromate which may be formed locally owing to the exhaustion of the chloride in solution being transformed to chloride on shaking the liquid.

As the addition of silver nitrate is continued, however, there comes a stage when the precipitate becomes permanently ruddy owing to the formation of silver chromate. This point is that at which all the chloride in solution has been converted into silver chloride, so that silver chromate is necessarily formed by the addition of more silver. Thus it is seen how potassium chromate serves as an internal indicator of the complete precipitation of chloride in solution by means of silver nitrate.

(iii) Repeat experiment (ii), but adding a little dilute nitric acid to the mixture of sodium chloride and potassium chromate solutions before the addition of silver nitrate. It will be found that the chromate is useless to indicate the end of precipitation of the chloride, for no red colour of silver chromate appears; that is because this salt, being soluble in dilute nitric acid, is not precipitated in its presence. It is evident therefore that the chromate indicator can be used only in neutral solution.

Preparation of Pure Sodium Chloride.

Pure sodium chloride is needed to make a standard solution by reference to which a solution of silver nitrate can be standardized. Since sodium chloride is but slightly more soluble in hot water than cold, this salt cannot be recrystallized by cooling its hot saturated solution. It is, however, less soluble in concentrated hydrochloric acid than in water.

Show this by adding to a cold concentrated solution of

salt in a test tube an equal volume of concentrated hydrochloric acid. A white crystalline precipitate falls which is sodium chloride; for on diluting with water the precipitate disappears, passing again into solution. Barium chloride behaves similarly, and such behaviour is characteristic generally of chlorides which do not combine chemically with hydrogen chloride. This behaviour is accounted for by the law of solubility-product, which states that in a condition of equilibrium with the solid salt the product of the concentrations of the two ions of the salt in the solution is constant. If, therefore, hydrogen chloride is added to a saturated solution of sodium chloride so as to increase the concentration of chloride ions, that of the sodium ions must be proportionately decreased; that is to say, sodium chloride must separate from solution until the product of the concentrations of sodium and chloride ions is the same as before. It will be understood that whilst the concentrations of sodium and chloride ions in a neutral salt solution are equal, their concentrations in acid solution are unequal, deficiency of sodium ions being compensated for by excess of hydrogen ions.

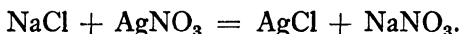
Prepare about 100 c. c. of a saturated solution of common salt and filter it if necessary. Place the solution in a beaker a little broader than the diameter of a funnel. Fix the funnel in an inverted position so that its rim touches the surface of the solution in the beaker,* and lead hydrogen chloride gas from a Kipp's apparatus through the stem of the funnel so that it reaches the surface of the water and there dissolves. A crystalline precipitate of sodium chloride will be formed and will accumulate on the bottom of the beaker. When sufficient sodium chloride has been separated, filter it from the mother liquor by means of suction, wash the salt in the funnel with concentrated hydrochloric acid, and then pump it as dry

* This arrangement is adopted rather than the simpler procedure of leading hydrogen chloride gas into the solution by means of a tube, because the latter would soon become clogged with sodium chloride crystals.

as possible; further dry it on a porous plate, and finally ignite it gently in a porcelain dish until water vapour and hydrogen chloride cease to be evolved. Keep the salt in a stoppered bottle or tightly corked test tube.

Preparation of Decinormal Sodium Chloride Solution.

The reaction between sodium chloride and silver nitrate is:



Thus the molecules of the two reacting salts are chemically equivalent, and decimolecular solutions are decinormal. Prepare 250 c. c. of a decinormal solution of sodium chloride by dissolving $\frac{58.46}{40} = 1.461$ gm. of your prepared salt in water and diluting the solution to volume in a 250-c. c. flask.

Preparation and Standardization of approximately decinormal Silver Nitrate Solution.

250 c. c. of silver nitrate solution will be sufficient for the present purpose. Therefore weigh $\frac{169.9}{40} = 4.248$ gm. of the crystallized salt, dissolve it in water, and make 250 c. c. of solution. It is important for the distilled water employed to be quite free from chloride. The stock of water should be tested with silver nitrate before use, and if an opalescence appears, enough water for the present purpose should be redistilled.

Measure 20 c. c. of decinormal sodium chloride solution, placing the solution in a flask, or preferably in a porcelain basin 6 in. in diameter provided with a stirring rod of convenient length with rounded ends. Add to the solution two or three drops of potassium chromate solution which has been proved to be free from chloride, and then titrate the pale yellow liquid until the accumulating silver chloride just begins to appear ruddy. When agreeing results have been

obtained, calculate a factor for your silver nitrate solution. This will be very nearly unity, because the solid silver salt will have been nearly pure.

EXERCISES IN THE USE OF STANDARD SILVER NITRATE SOLUTION

1. Estimation of chloride in neutral solution.
2. Estimation of hydrogen chloride in solution.
3. Estimation of silver in acid solution.

1. Estimation of Chloride in Neutral Solution.

A metallic chloride which dissolves in water, yielding a neutral solution, can be estimated by means of standard silver nitrate solution, provided its chromate is also soluble. The percentage of chloride in the crystallized barium chloride prepared by the student earlier in his course cannot be estimated directly in this way because of the insolubility of barium chromate in water. The barium must therefore first be removed from solution.

Excess of neutral potassium sulphate is consequently to be added to the measured quantity of barium chloride solution. The chloride can then be titrated after the addition of chromate without filtering off the barium sulphate precipitate.

2. Estimation of Hydrogen Chloride in Solution.

A solution of hydrogen chloride, or of another chloride in presence of acid, may be estimated by first carefully neutralizing the acid with ammonia and then titrating the solution with standard silver nitrate, using potassium chromate as indicator.

3. Estimation of Silver in Acid Solution (Method of Gay-Lussac).

Silver in acid solution, e.g. a solution made by dissolving silver foil or a silver coin in nitric acid, can be estimated directly

by titration with decinormal sodium chloride by taking advantage of the property of silver chloride to coagulate and leave the supernatant liquid clear. Thus if sodium chloride solution is added to a warm solution of silver nitrate containing nitric acid, and the mixture is shaken, the precipitate, which at first appears cloudy and uniformly dispersed through the liquid, begins to coagulate on shaking when the precipitation of silver is approaching completion, so that it becomes easy to see whether or not a drop of chloride solution allowed to run down the side of the containing vessel produces a further precipitate when it reaches the surface of the almost clear supernatant liquid above the silver chloride. This method of estimating silver, which seems rather tedious to the beginner, gives accurate results in expert hands.

For practice in the estimation, weigh accurately about 1 gm. of silver foil, dissolve it in dilute nitric acid, and boil the solution to expel nitrous fumes. Transfer the solution to a 100-c. c. flask, and dilute to volume. Place 20 c. c. of this solution in a white glass stoppered bottle, add 2 or 3 c. c. of concentrated nitric acid, and heat the liquid in the water bath to 50° or 60° C. Then titrate the solution with decinormal sodium chloride, shaking the liquid in the bottle after each addition of chloride. When the precipitate begins to coagulate and the liquid consequently to clear, add the precipitant more slowly, and finally let each drop run down the side of the bottle into the liquid, shaking between each addition till precipitation is at an end. Repeat the titration, and when agreeing results have been obtained, calculate the percentage of silver in the foil, remembering that 1 c. c. of decinormal sodium chloride precipitates 0.01079 gm. of silver.

APPENDIX I

1. Volumetric estimation of phosphoric acid and phosphates.

2. Volumetric estimation of boric acid.

3. Note on "screened" methyl orange.

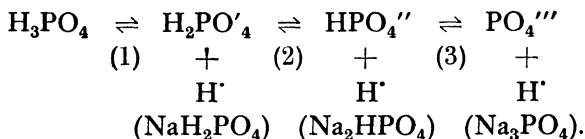
4. Gravimetric estimation of sodium as sulphate.

1. Estimation of Phosphoric Acid and Phosphates.

Phosphoric acid, H_3PO_4 , is not an acid of sufficient strength to be ionized in solution according to the scheme:



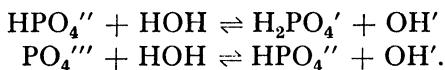
Instead, ionization proceeds thus:



In aqueous solution the first dissociation proceeds to a considerable extent, the second to a small extent, and the third scarcely occurs. If alkali is added to this solution it is found that neutralization occurs in three stages, at each of which is formed the corresponding alkali salt (as shown in brackets). Indeed, an aqueous solution of phosphoric acid behaves almost as a mixture of three independent acids of progressively weaker strength, for the ions $\text{H}_2\text{PO}_4'$ and HPO_4'' are considered to be acids, since they can ionize to give hydron.

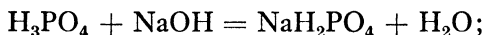
Consider now the effect of water on the salts produced. The monosodium salt NaH_2PO_4 is scarcely hydrolysed by

water; rather does its ion $\text{H}_2\text{PO}_4'$ dissociate as in (2), and its solution is weakly acidic in consequence. An aqueous solution of the disodium salt is weakly, and one of the trisodium salt strongly, alkaline because of hydrolysis, thus:

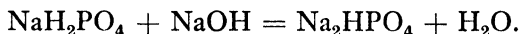


Therefore, as one, two, or three equivalents of alkali are added to a quantity of phosphoric acid, the resulting solution will be, respectively, weakly acidic, weakly alkaline, and strongly alkaline.

Now, since different indicators respond to a different degree of hydron or hydroxidion concentration, the indication of a particular phase of neutralization of phosphoric acid depends on what indicator is employed. The following are the relevant facts. When semi-normal alkali hydroxide solution is added to phosphoric acid in presence of methyl orange, this indicator changes from pink to yellow when the following reaction has been completed:



and if phenolphthalein is now added it changes from colourless to crimson when the following reaction has been completed:



Thence it follows that NaH_2PO_4 is acid to phenolphthalein, but neutral to methyl orange, whilst Na_2HPO_4 is alkaline to methyl orange, but neutral to phenolphthalein. With a suitable indicator, therefore, phosphoric acid and sodium dihydrogen phosphate can be estimated by means of standard alkali. Phosphoric acid is never directly titrated to trisodium phosphate, for no satisfactory indicator is known.

The titrations should be done in cold solution with semi-normal alkali, free from carbonate, and in the second reaction

some sodium chloride should be added to prevent hydrolysis of Na_2HPO_4 , and make the end-point sharp.

A further study of the titration of alkali phosphate, from the standpoint of *pH* value, will be found in Part II of this book.

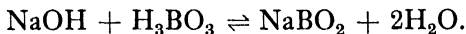
Estimation of Phosphoric Acid.—Weigh accurately in a weighing bottle not more than 7 gm. of syrupy phosphoric acid, then carefully wash the acid into a 250 c. c. graduated flask and dilute to the mark. Measure 25 c. c. of this solution into a flask, cool in ice, add 10 gm. of pure sodium chloride and a few drops of phenolphthalein, then titrate with semi-normal sodium hydroxide solution to the dibasic end-point at which the indicator turns pink.

Alternatively, titrate 50 c. c. of the cooled solution with the alkali in presence of methyl orange (without adding sodium chloride) until the indicator turns yellow at the monobasic end-point. Screened methyl orange (p. 159) may be used.

From your results calculate the percentage of phosphoric acid in the sample.

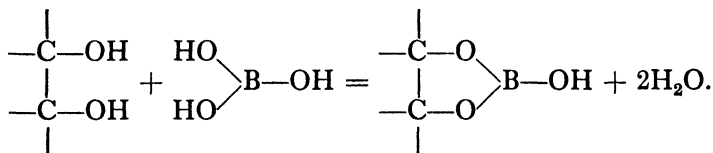
2. Estimation of Boric Acid.

Boric acid, H_3BO_3 , and its salt, sodium pyroborate (borax), $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, are important commercial products. (For the analysis of borax, see Part II, p. 24.) Boric acid, or more accurately, orthoboric acid, is a very weak acid which does not affect methyl orange, but is acidic to phenolphthalein. Towards alkali hydroxide it reacts as a monobasic acid, thus:



The sodium metaborate formed, being the salt of a weak acid, is appreciably hydrolysed by water (i.e. the reaction reverses), so that phenolphthalein will turn pink before one equivalent of alkali has been added. Certain polyhydroxy

compounds such as glycerol or mannitol react with boric acid to form a somewhat stronger monobasic glycerol- or mannito-boric acid, thus:



This acid can be titrated with alkali in presence of phenolphthalein, which reacts sharply when one equivalent of alkali has been added. Glycerol is used in the procedure given below; mannitol may be used in the same way (1 gm. to each 20 c. c. of solution), except that no correction for acidity will be necessary.

Procedure.—Weigh accurately 1.2 to 1.4 gm. of boric acid and dissolve it in water, diluting the solution to 200 c. c. in a graduated flask.

If the glycerol to be used contains free acid, a correction will be required. Therefore, measure 10 c. c. of glycerol in a small graduated cylinder, transfer it to a suitable flask, dilute with water, and titrate with decinormal sodium hydroxide solution in presence of phenolphthalein. This titration gives the volume of alkali, if any, required by each 10 c. c. of glycerol in the titration of boric acid.

Measure 25 c. c. of the prepared boric acid solution into a flask, add 10 c. c. of glycerol and a few drops of phenolphthalein, then titrate the solution with the standard sodium hydroxide solution until the indicator turns pink. Add another 10 c. c. of glycerol and continue the titration, repeating the addition of glycerol until the further amount of alkali required to develop the pink colour of the indicator is only that known to be necessary to neutralize the last volume of glycerol added.

From the total volume of alkali used subtract the volume

required to neutralize the total amount of glycerol added, and thence calculate the percentage purity of the boric acid.

3. Screened Methyl Orange.

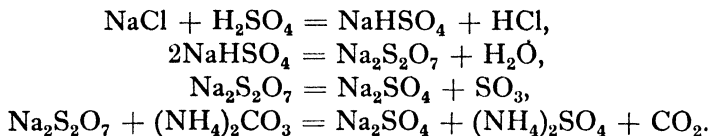
The colour changes of methyl orange, pink $\rightleftharpoons$ orange $\rightleftharpoons$ yellow, are not too readily distinguished by the eye, particularly in artificial light. Hickman and Linstead (1922) proposed the addition to methyl orange solution of the blue dyestuff known as Xylene Cyanol FF to act as a "screen", in the presence of which the methyl orange colour changes, from the acid to the alkaline side, appear as magenta $\rightarrow$ grey $\rightarrow$ green. The end-point is given by the grey colour. The "screened" indicator may with advantage replace the simple solution of methyl orange, particularly for titrations done in artificial light. It is prepared by dissolving 0.2 gm. of methyl orange and 0.28 gm. of Xylene Cyanol FF in 100 c. c. of 50 per cent aqueous alcohol.

4. Estimation of Sodium.

In general, the determination of an element by gravimetric methods of analysis requires its precipitation from solution as a sparingly soluble compound, which can be filtered off and weighed in the same or in a modified, but definite, form after suitable treatment.

There are few insoluble sodium compounds; those which may be used are complex and give accurate results only in the hands of an experienced operator. If, however, sodium (but no other metal) is present as the salt of an acid more volatile than sulphuric acid, repeated evaporation with sulphuric acid and subsequent heating of the residue will form sodium sulphate, from the weight of which the amount of sodium originally present can be calculated. During the process the bisulphate NaHSO_4 is formed, which on heating forms the pyrosulphate $\text{Na}_2\text{S}_2\text{O}_7$, and this in turn decomposes

at a red heat to form sodium sulphate with loss of sulphur trioxide. To ensure completion of the last stage a little solid ammonium carbonate is added: this forms ammonium sulphate, which is volatilized on further heating. Assuming that sodium chloride has been given for the analysis, the following equations represent the changes:



Procedure.—Ignite a silica crucible, allow it to cool in a desiccator and then weigh it (cf. p. 26). Into the crucible place about 0.3 gm. of the given sodium salt and accurately weigh the crucible and its contents. (If a solution of a sodium salt is given, place a measured volume in a clean porcelain dish and heat on a water bath, or over a small flame, until the volume of the solution is reduced sufficiently for it to be transferred, using a glass rod, to the weighed crucible. Rinse the dish thoroughly with small amounts of hot water and add the rinsings carefully to the crucible. Evaporate the contents to dryness on the water bath.)

The subsequent operations should be done in a fume cupboard. For each 0.1 gm. of sodium salt present add 0.5 c. c. of 10N sulphuric acid to the crucible, support the latter in a slightly inclined position on a triangle, partially cover it by the lid and carefully expel all the liquid by gently heating the upper portion of the crucible. Cool the crucible, add half the original volume of 10N sulphuric acid, and repeat the evaporation, finally heating the base of the crucible at a dull red heat. Allow the crucible to cool, add a few pieces of solid ammonium carbonate and again ignite the residue by heating the base of the crucible, at first gently, then for 15 minutes at a dull red heat. Allow the crucible to cool

sufficiently, transfer it to a desiccator, and when it is quite cold weigh it. Repeat the ignition and weighing until the weight remains constant. From the weight of Na_2SO_4 obtained calculate the percentage of sodium present in the given substance, or the weight of sodium present per litre of the given solution.

APPENDIX II

PRESSURE OF AQUEOUS VAPOUR FROM 0° TO 30° C.

Tempera- ture, Deg. Centigrade.	Pressure in Mm. Hg.	Tempera- ture, Deg. Centigrade.	Pressure in Mm. Hg.	Tempera- ture, Deg. Centigrade.	Pressure in Mm. Hg.
0.0	4.6	10.5	9.5	21.0	18.5
0.5	4.8	11.0	9.8	21.5	19.1
1.0	4.9	11.5	10.1	22.0	19.7
1.5	5.1	12.0	10.5	22.5	20.3
2.0	5.3	12.5	10.8	23.0	20.9
2.5	5.5	13.0	11.2	23.5	21.5
3.0	5.7	13.5	11.5	24.0	22.2
3.5	5.9	14.0	11.9	24.5	22.9
4.0	6.1	14.5	12.3	25.0	23.5
4.5	6.3	15.0	12.7	25.5	24.3
5.0	6.5	15.5	13.1	26.0	25.0
5.5	6.8	16.0	13.5	26.5	25.7
6.0	7.0	16.5	14.0	27.0	26.5
6.5	7.2	17.0	14.4	27.5	27.3
7.0	7.5	17.5	14.9	28.0	28.1
7.5	7.8	18.0	15.4	28.5	28.9
8.0	8.0	18.5	15.8	29.0	29.8
8.5	8.3	19.0	16.3	29.5	30.7
9.0	8.6	19.5	16.9	30.0	31.5
9.5	8.9	20.0	17.4	—	—
10.0	9.2	20.5	17.9	—	—

QUANTITATIVE ANALYSIS

HYDROCHLORIC ACID

Specific Gravity and Concentration at 15° C. (Lunge and others)

Specific Gravity at 15°/4° in Vacuo.	Percentage HCl by Weight.	Specific Gravity at 15°/4° in Vacuo.	Percentage HCl by Weight.
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	—	—

APPENDIX

SULPHURIC ACID

Specific Gravity and Concentration at 15° C. (Lunge and Others)

Specific Gravity at 15°/4° in Vacuo.	Percentage H ₂ SO ₄ .	Specific Gravity at 15°/4° in Vacuo.	Percentage H ₂ SO ₄ .	Specific Gravity at 15°/4° in Vacuo.	Percentage H ₂ SO ₄ .
1.000	0.09	1.165	22.83	1.330	42.66
1.005	0.83	1.170	23.47	1.335	43.20
1.010	1.57	1.175	24.12	1.340	43.74
1.015	2.30	1.180	24.76	1.345	44.28
1.020	3.03	1.185	25.40	1.350	44.82
1.025	3.76	1.190	26.04	1.355	45.35
1.030	4.49	1.195	26.68	1.360	45.88
1.035	5.23	1.200	27.32	1.365	46.41
1.040	5.96	1.205	27.95	1.370	46.94
1.045	6.67	1.210	28.58	1.375	47.47
1.050	7.37	1.215	29.21	1.380	48.00
1.055	8.07	1.220	29.84	1.385	48.53
1.060	8.77	1.225	30.48	1.390	49.06
1.065	9.47	1.230	31.11	1.395	49.59
1.070	10.19	1.235	31.70	1.400	50.11
1.075	10.90	1.240	32.28	1.405	50.63
1.080	11.60	1.245	32.86	1.410	51.15
1.085	12.30	1.250	33.43	1.415	51.66
1.090	12.99	1.255	34.00	1.420	52.15
1.095	13.67	1.260	34.57	1.425	52.63
1.100	14.35	1.265	35.14	1.430	53.11
1.105	15.03	1.270	35.71	1.435	53.59
1.110	15.71	1.275	36.29	1.440	54.07
1.115	16.36	1.280	36.87	1.445	54.55
1.120	17.01	1.285	37.45	1.450	55.03
1.125	17.66	1.290	38.03	1.455	55.50
1.130	18.31	1.295	38.61	1.460	55.97
1.135	18.96	1.300	39.19	1.465	56.43
1.140	19.61	1.305	39.77	1.470	56.90
1.145	20.26	1.310	40.35	1.475	57.37
1.150	20.91	1.315	40.93	1.480	57.83
1.155	21.55	1.320	41.50	1.485	58.28
1.160	22.19	1.325	42.08	1.490	58.74

QUANTITATIVE ANALYSIS

SULPHURIC ACID—*Continued*

Specific Gravity at 15°/4° in Vacuo.	Percentage H ₂ SO ₄ .	Specific Gravity at 15°/4° in Vacuo.	Percentage H ₂ SO ₄ .	Specific Gravity at 15°/4° in Vacuo.	Percentage H ₂ SO ₄ .
1.495	59.22	1.630	71.27	1.765	83.01
1.500	59.70	1.635	71.70	1.770	83.51
1.505	60.18	1.640	72.12	1.775	84.02
1.510	60.65	1.645	72.55	1.780	84.50
1.515	61.12	1.650	72.96	1.785	85.10
1.520	61.59	1.655	73.40	1.790	85.70
1.525	62.06	1.660	73.81	1.795	86.30
1.530	62.53	1.665	74.24	1.800	86.92
1.535	63.00	1.670	74.66	1.805	87.60
1.540	63.43	1.675	75.08	1.810	88.30
1.545	63.85	1.680	75.50	1.815	89.16
1.550	64.26	1.685	75.94	1.820	90.05
1.555	64.67	1.690	76.38	1.825	91.00
1.560	65.20	1.695	76.76	1.830	92.10
1.565	65.65	1.700	77.17	1.835	93.56
1.570	66.09	1.705	77.60	1.840	95.60
1.575	66.53	1.710	78.04	1.8405	95.95
1.580	66.95	1.715	78.48	1.8410	96.38
1.585	67.40	1.720	78.92	1.8415	97.35
1.590	67.83	1.725	79.36	1.8410	98.20
1.595	68.26	1.730	79.80	1.8405	98.52
1.600	68.70	1.735	80.24	1.8400	98.72
1.605	69.13	1.740	80.68	1.8395	98.77
1.610	69.56	1.745	81.12	1.8390	99.12
1.615	70.00	1.750	81.56	1.8385	99.31
1.620	70.42	1.755	82.00	—	—
1.625	70.85	1.760	82.44	—	—

APPENDIX

SODIUM HYDROXIDE SOLUTION

Specific Gravity and Concentration at 15° C. (Lunge)

Specific Gravity.	Percentage NaOH by Weight.	Specific Gravity.	Percentage NaOH by Weight.
1.007	0.61	1.220	19.58
1.014	1.20	1.231	20.59
1.022	2.00	1.241	21.42
1.029	2.71	1.252	22.64
1.036	3.35	1.263	23.67
1.045	4.00	1.274	24.81
1.052	4.64	1.285	25.80
1.060	5.29	1.297	26.83
1.067	5.87	1.308	27.80
1.075	6.55	1.320	28.83
1.083	7.31	1.332	29.93
1.091	8.00	1.345	31.22
1.100	8.68	1.357	32.47
1.108	9.42	1.370	33.69
1.116	10.06	1.383	34.96
1.125	10.97	1.397	36.25
1.134	11.84	1.410	37.47
1.142	12.64	1.424	38.80
1.152	13.55	1.438	39.99
1.162	14.37	1.453	41.41
1.171	15.13	1.468	42.83
1.180	15.91	1.483	44.38
1.190	16.77	1.498	46.15
1.200	17.67	1.514	47.60
1.210	18.58	1.530	49.02

LOGARITHMS

	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4	9	13	17	21	26	30	34	38
											4	8	12	16	20	24	28	32	37
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	12	15	19	23	27	31	35
											4	7	11	15	19	22	26	30	33
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3	7	11	14	18	21	25	28	32
											3	7	10	14	17	20	24	27	31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	7	10	13	16	20	23	26	30
											3	7	10	13	16	19	22	25	29
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3	6	9	12	15	18	21	24	28
											3	6	9	12	15	17	20	23	26
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	6	9	11	14	17	20	23	26
											3	5	8	11	14	16	19	22	25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	14	16	19	22	24
											3	5	8	10	13	15	18	21	23
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	3	5	8	10	12	15	17	19	22
											2	5	7	10	12	15	17	19	22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16	19	21
											2	5	7	9	11	14	16	18	21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	7	9	11	13	16	18	20
											2	4	6	8	11	13	15	17	19
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

LOGARITHMS

	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
50	9990	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
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	6	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	8898	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	8978	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	0	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	4	4

ANTILOGARITHMS

	0	1	2	3	4	5	6	7	8	9	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	1	2	2	2
05	1122	1125	1127	1130	1132	1135	1138	1140	1143	1146	0	1	1	1	1	1	2	2	2
06	1148	1151	1153	1156	1159	1161	1164	1167	1169	1172	0	1	1	1	1	1	2	2	2
07	1175	1178	1180	1183	1186	1189	1191	1194	1197	1199	0	1	1	1	1	1	2	2	2
08	1202	1205	1208	1211	1213	1216	1219	1222	1225	1227	0	1	1	1	1	1	2	2	2
09	1230	1233	1236	1239	1242	1245	1247	1250	1253	1256	0	1	1	1	1	1	2	2	2
10	1259	1262	1265	1268	1271	1274	1276	1279	1282	1285	0	1	1	1	1	1	2	2	2
11	1288	1291	1294	1297	1300	1303	1306	1309	1312	1315	0	1	1	1	1	2	2	2	2
12	1318	1321	1324	1327	1330	1334	1337	1340	1343	1346	0	1	1	1	1	2	2	2	2
13	1349	1352	1355	1358	1361	1365	1368	1371	1374	1377	0	1	1	1	1	2	2	2	2
14	1380	1384	1387	1390	1393	1396	1400	1403	1406	1409	0	1	1	1	1	2	2	2	2
15	1413	1416	1419	1422	1426	1429	1432	1435	1439	1442	0	1	1	1	1	2	2	2	2
16	1445	1449	1452	1455	1459	1462	1466	1469	1472	1476	0	1	1	1	1	2	2	2	2
17	1479	1483	1486	1489	1493	1496	1500	1503	1507	1510	0	1	1	1	1	2	2	2	2
18	1514	1517	1521	1524	1528	1531	1535	1538	1542	1545	0	1	1	1	1	2	2	2	2
19	1549	1552	1556	1560	1563	1567	1570	1574	1578	1581	0	1	1	1	1	2	2	2	2
20	1585	1589	1592	1596	1600	1603	1607	1611	1614	1618	0	1	1	1	1	2	2	2	2
21	1622	1626	1629	1633	1637	1641	1644	1648	1652	1656	0	1	1	1	1	2	2	2	2
22	1660	1663	1667	1671	1675	1679	1683	1687	1690	1694	0	1	1	1	1	2	2	2	2
23	1698	1702	1706	1710	1714	1718	1722	1726	1730	1734	0	1	1	1	1	2	2	2	2
24	1738	1742	1746	1750	1754	1758	1762	1766	1770	1774	0	1	1	1	1	2	2	2	2
25	1778	1782	1786	1791	1795	1799	1803	1807	1811	1816	0	1	1	1	1	2	2	2	2
26	1820	1824	1828	1832	1837	1841	1845	1849	1854	1858	0	1	1	1	1	2	2	2	2
27	1862	1866	1871	1875	1879	1884	1888	1892	1897	1901	0	1	1	1	1	2	2	2	2
28	1905	1910	1914	1919	1923	1928	1932	1936	1941	1945	0	1	1	1	1	2	2	2	2
29	1950	1954	1959	1963	1968	1972	1977	1982	1986	1991	0	1	1	1	1	2	2	2	2
30	1995	2000	2004	2009	2014	2018	2023	2028	2032	2037	0	1	1	1	1	2	2	2	2
31	2042	2046	2051	2056	2061	2065	2070	2075	2080	2084	0	1	1	1	1	2	2	2	2
32	2089	2094	2099	2104	2109	2113	2118	2123	2128	2133	0	1	1	1	1	2	2	2	2
33	2138	2143	2148	2153	2158	2163	2168	2173	2178	2183	0	1	1	1	1	2	2	2	2
34	2188	2193	2198	2203	2208	2213	2218	2223	2228	2234	1	1	1	1	1	2	2	2	2
35	2239	2244	2249	2254	2259	2265	2270	2275	2280	2286	1	1	1	1	1	2	2	2	2
36	2291	2296	2301	2307	2312	2317	2323	2328	2333	2339	1	1	1	1	1	2	2	2	2
37	2344	2350	2355	2360	2366	2371	2377	2382	2388	2393	1	1	1	1	1	2	2	2	2
38	2399	2404	2410	2415	2421	2427	2432	2438	2443	2449	1	1	1	1	1	2	2	2	2
39	2455	2460	2466	2472	2477	2483	2489	2495	2500	2506	1	1	1	1	1	2	2	2	2
40	2512	2518	2523	2529	2535	2541	2547	2553	2559	2564	1	1	1	1	1	2	2	2	2
41	2570	2576	2582	2588	2594	2600	2606	2612	2618	2624	1	1	1	1	1	2	2	2	2
42	2630	2636	2642	2648	2655	2661	2667	2673	2679	2685	1	1	1	1	1	2	2	2	2
43	2692	2698	2704	2710	2716	2723	2729	2735	2742	2748	1	1	1	1	1	2	2	2	2
44	2754	2761	2767	2773	2780	2786	2793	2799	2805	2812	1	1	1	1	1	2	2	2	2
45	2818	2825	2831	2838	2844	2851	2858	2864	2871	2877	1	1	1	1	1	2	2	2	2
46	2884	2891	2897	2904	2911	2917	2924	2931	2938	2944	1	1	1	1	1	2	2	2	2
47	2951	2958	2965	2972	2979	2985	2992	2999	3006	3013	1	1	1	1	1	2	2	2	2
48	3020	3027	3034	3041	3048	3055	3062	3069	3076	3083	1	1	1	1	1	2	2	2	2
49	3090	3097	3105	3112	3119	3126	3133	3141	3148	3155	1	1	1	1	1	2	2	2	2

ANTILOGARITHMS

	0	1	2	3	4	5	6	7	8	9	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	6	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	6	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	6207	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

ATOMIC WEIGHTS

(1940)

Aluminium,	Al	..	26·97	Lead,	Pb	..	207·21
Antimony,	Sb	..	121·76	Magnesium,	Mg	..	24·32
Arsenic,	As	..	74·91	Manganese,	Mn	..	54·93
Barium,	Ba	..	137·36	Mercury,	Hg	..	200·61
Bismuth,	Bi	..	209·00	Molybdenum,	Mo	..	95·95
Boron,	B	..	10·82	Nickel,	Ni	..	58·69
Bromine,	Br	..	79·916	Nitrogen,	N	..	14·008
Cadmium,	Cd	..	112·41	Oxygen,	O	..	16·0000
Calcium,	Ca	..	40·08	Phosphorus,	P	..	30·98
Carbon,	C	..	12·01	Potassium,	K	..	39·096
Chlorine,	Cl	..	35·457	Silicon,	Si	..	28·06
Chromium,	Cr	..	52·01	Silver,	Ag	..	107·880
Cobalt,	Co	..	58·94	Sodium,	Na	..	22·997
Copper,	Cu	..	63·57	Strontium,	Sr	..	87·63
Fluorine,	F	..	19·00	Sulphur,	S	..	32·06
Hydrogen,	H	..	1·0080	Tin,	Sn	..	118·70
Iodine,	I	..	126·92	Uranium,	U	..	238·07
Iron,	Fe	..	55·85	Zinc,	Zn	..	65·38

NOTE.—The atomic weights given in the above table are those published by the International Union of Chemistry, 1940. For analytical purposes it is generally sufficient to employ figures accurate to one place of decimals; e.g. Mg = 24·3, Na = 23·0, &c.

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