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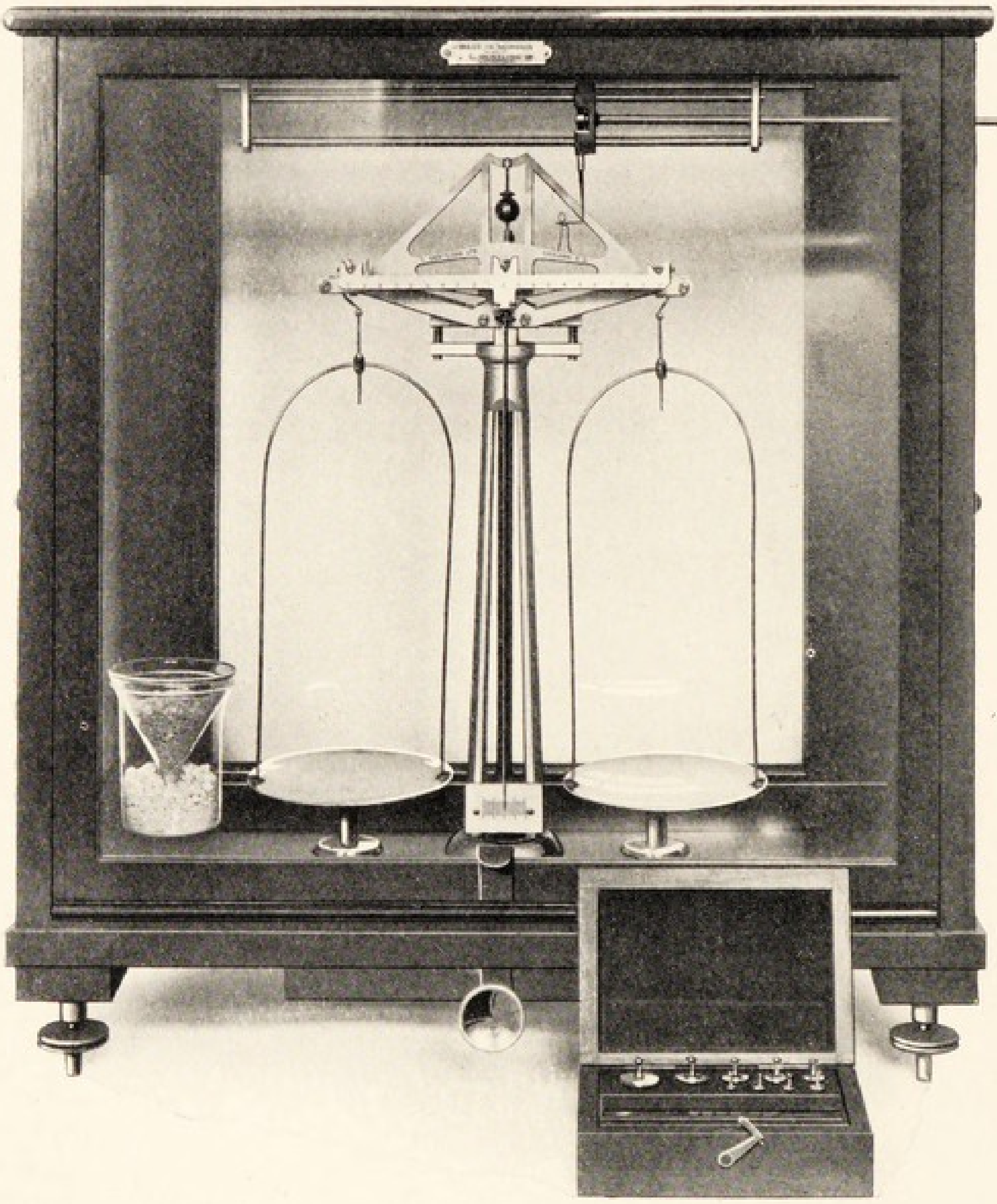

CHEMICAL BALANCE AND WEIGHTS

(See description on pp. 4–6)

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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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.

Revision of Part I has resulted in a few small alterations.

R. M. C.

June, 1934.

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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

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* 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.

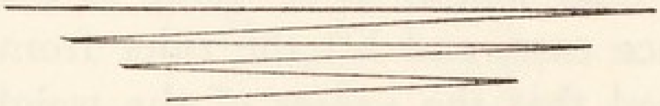
If the student possesses his own weights and rider he should see that the former always occupy their proper places in the box when not in use. There are only two proper places for the weights to occupy; one place is the box, the other is the balance pan; and the weights should be transferred from one 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:



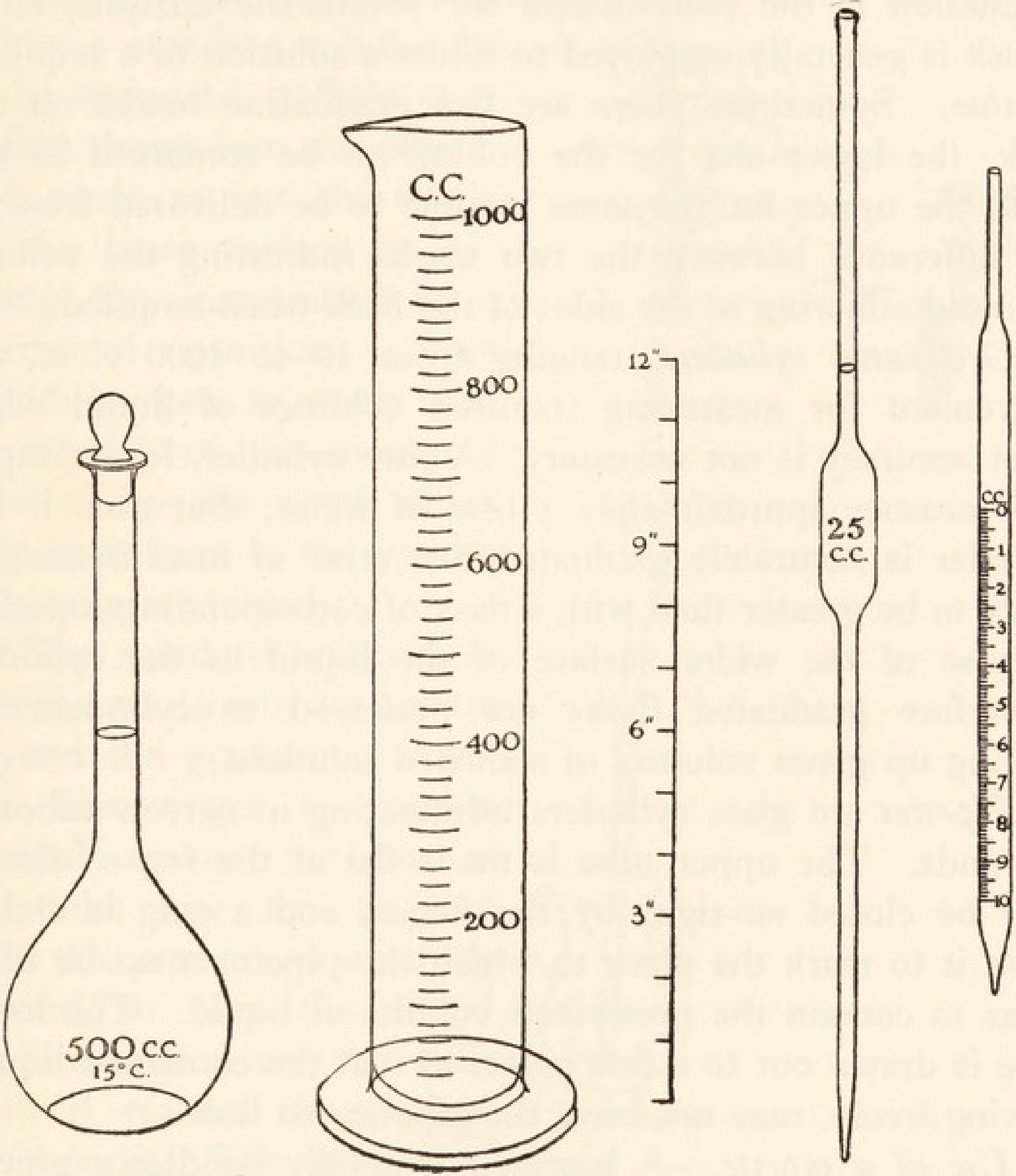
For general purposes of chemical analysis, however, when the weighing is carried to the nearest half-milligram, it is sufficient to observe equality of swing on either side. The pans should be brought to rest gently, so as not to jerk the balance.

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
16·8435

Graduated Vessels.

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



Flask Cylinder Pipettes

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

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* 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

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* 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.

plunged 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.

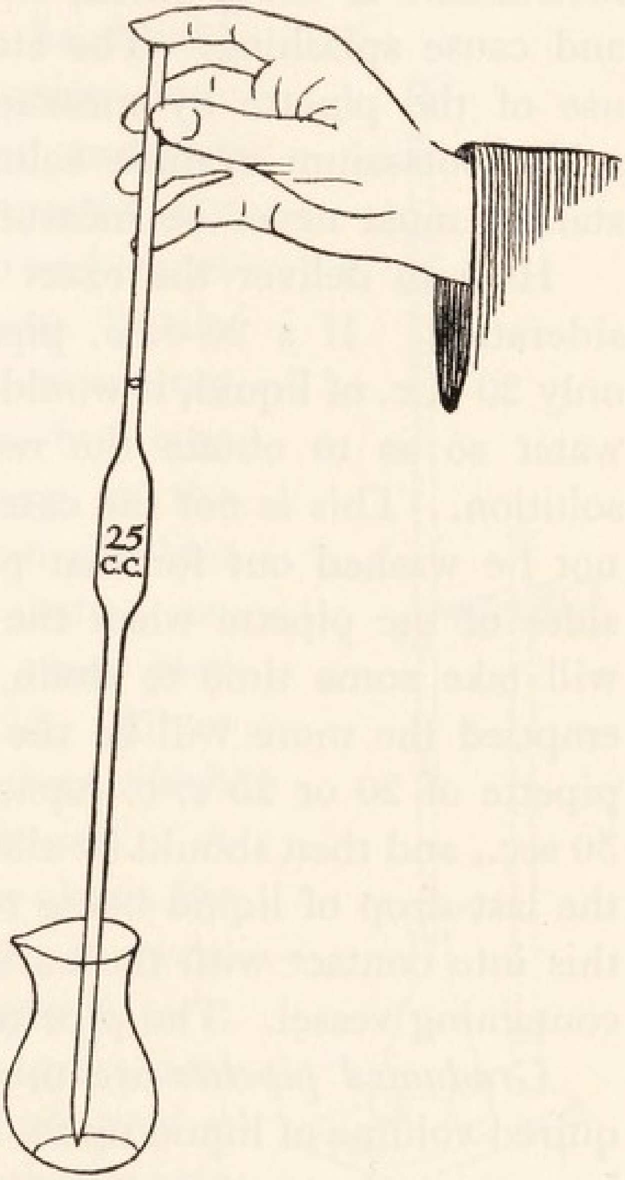

Fig. 2.—How to hold a Pipette

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 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.

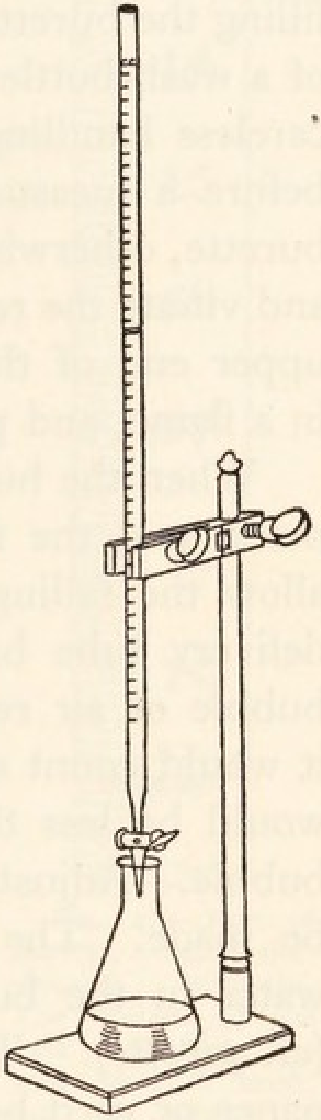
Fig. 3.—Burette in Stand

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 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.

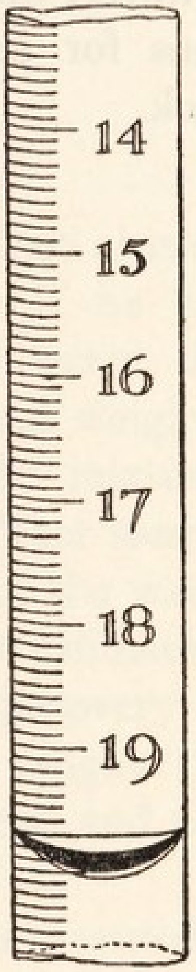

Fig. 4. — Part of Burette, full size, showing meniscus. The bottom of the dark curve is in line with 20-c. c. mark, but the number is omitted for the sake of clearness.

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.

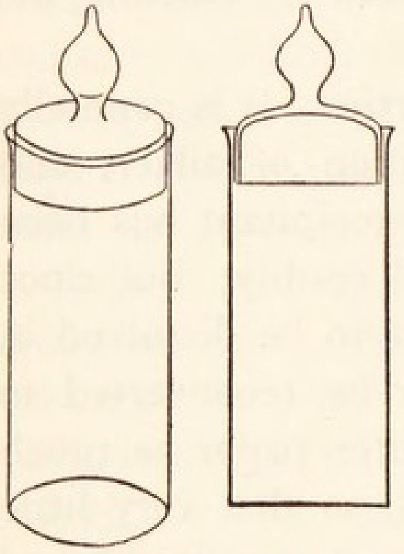

Fig. 5.—View and section of weighing bottle (one-fourth actual size).

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, $BaCl_2 \cdot 2H_2O$.

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

$$BaCO_3 + 2HCl = BaCl_2 + H_2O + CO_2.$$

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 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.

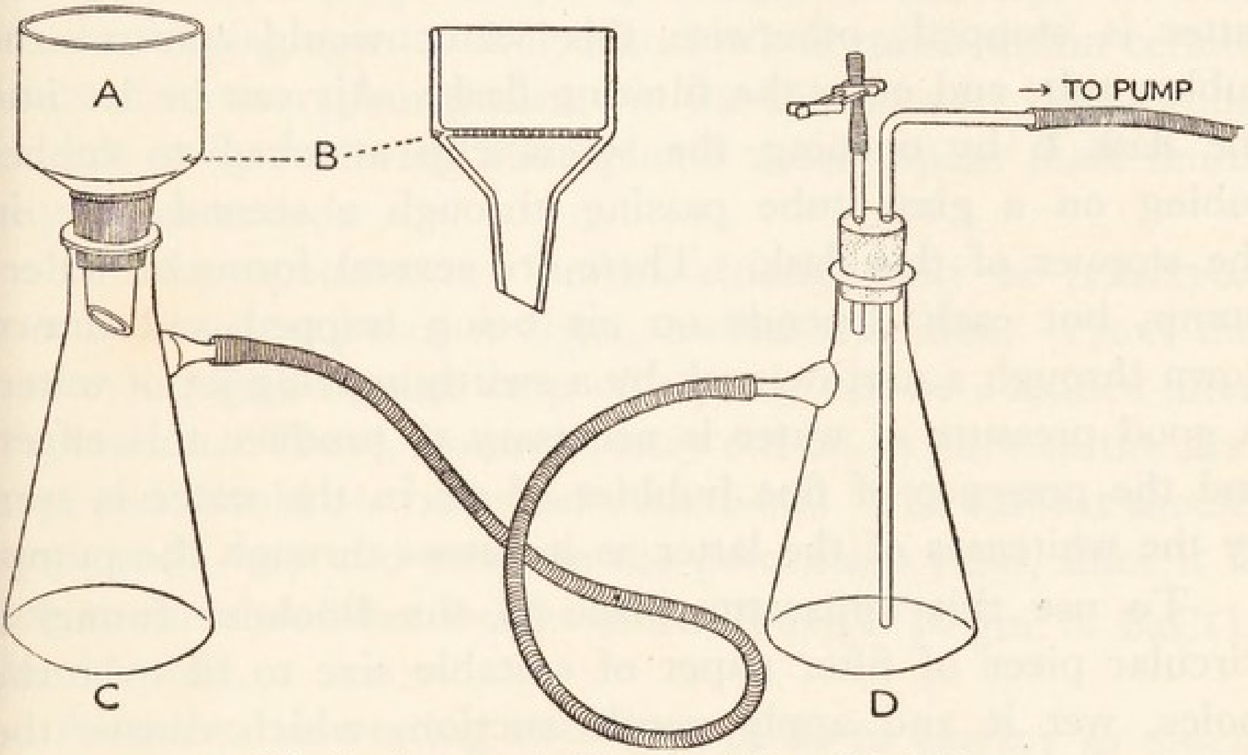

Fig. 6.—Apparatus for Filtration of Crystallized Salts

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

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 $BaCl_2 \cdot 2H_2O$ 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 $BaCl_2 \cdot 2H_2O$ 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.

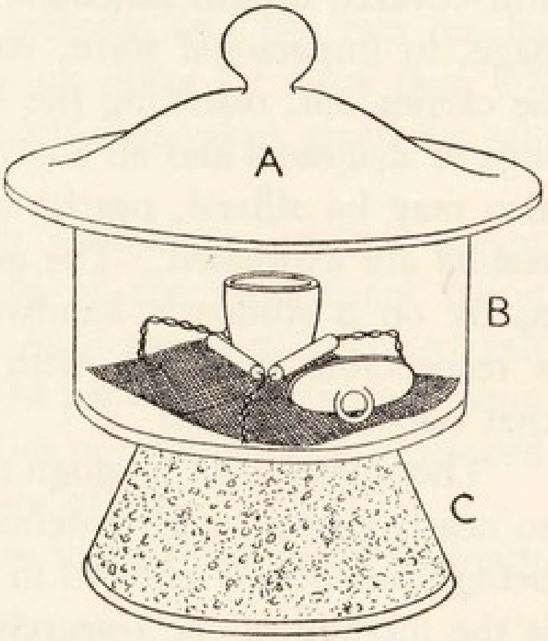

Fig. 7.—Desiccator

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 ½ 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.

I II

Weight of crucible + hydrated salt = gm.

Weight of crucible + salt after heating

$$\left.\begin{array}{r} = \text{(i)} \\ \text{(ii)} \\ \text{(iii)} \end{array}\right\} = \quad \text{gm.}$$

Loss of weight = water expelled = gm.

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

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 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 the filter may be prepared.

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, either with rubber tubing or by fusing it on to the glass, 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.

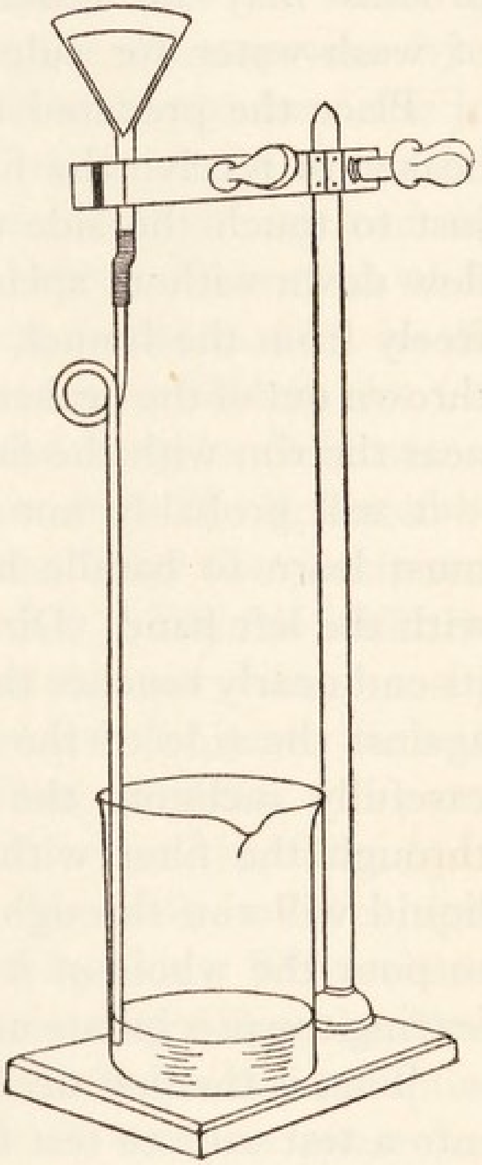

Fig. 8.—Accelerated Filtration

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* If an "ashless" filter cannot be obtained the weight of ash must be known, and subtracted finally from that of the crucible contents.

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

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* **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,

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cipitate 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

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* 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 mixture 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

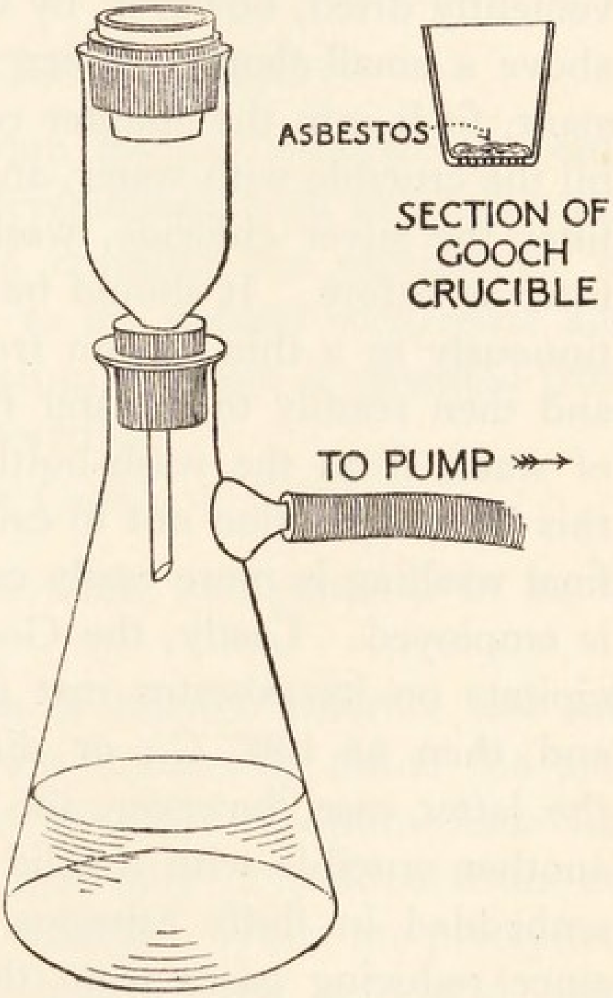

Fig. 9.—Asbestos Filter

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, $BaCl_2 \cdot 2H_2O$

	Found.	Calculated.	
$Ba^{\cdot\cdot}$			per cent.
Cl'			,,
H_2O			,,
		100·00	,,

II. Calcium Sulphate, $CaSO_4 \cdot 2H_2O$.

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:

$$CaCl_2 + H_2SO_4 \rightleftharpoons CaSO_4 + 2HCl.$$

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 $CaSO_4 \cdot 2H_2O$ 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, $CaCl_2 \cdot 6H_2O$, 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, $CaSO_4 \cdot 2H_2O$, is heated to 120° to 130° C. it is converted into plaster of Paris, $2CaSO_4 \cdot H_2O$, 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

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

the chloride which, for example, dissolves calcium carbonate. Like barium sulphate, however, calcium oxalate, $CaC_2O_4 \cdot H_2O$, 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

$$CaC_2O_4 \rightarrow CaCO_3 + CO,$$
$$CaCO_3 \rightleftharpoons CaO + CO_2.$$

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

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* 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 $(NH_4)_2C_2O_4{\cdot}H_2O$ 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 blowpipe, 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, and add excess of barium chloride,* both solutions being at the boiling-point. Then proceed as in the estimation of barium.

Tabulation of Results.

Tabulate the percentages of Cä, 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 $CaSO_4{\cdot}2H_2O$. The following are typical results:

	Found.			Theory.
Cä	23·32	..	..	23·26
SO_4''	55·75	..	..	55·81
$2H_2O$	20·89	..	..	20·93
	99·96	..	..	100·00

III. Copper Sulphate, $CuSO_4{\cdot}5H_2O$.

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

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* 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: $Cu_2O + H_2SO_4 = CuSO_4 + Cu + H_2O$.

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 $CuSO_4 \cdot 5H_2O$ per 100 gm. water.	Deg. C.	Grams $CuSO_4 \cdot 5H_2O$ 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 $CuSO_4 \cdot xH_2O$.

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

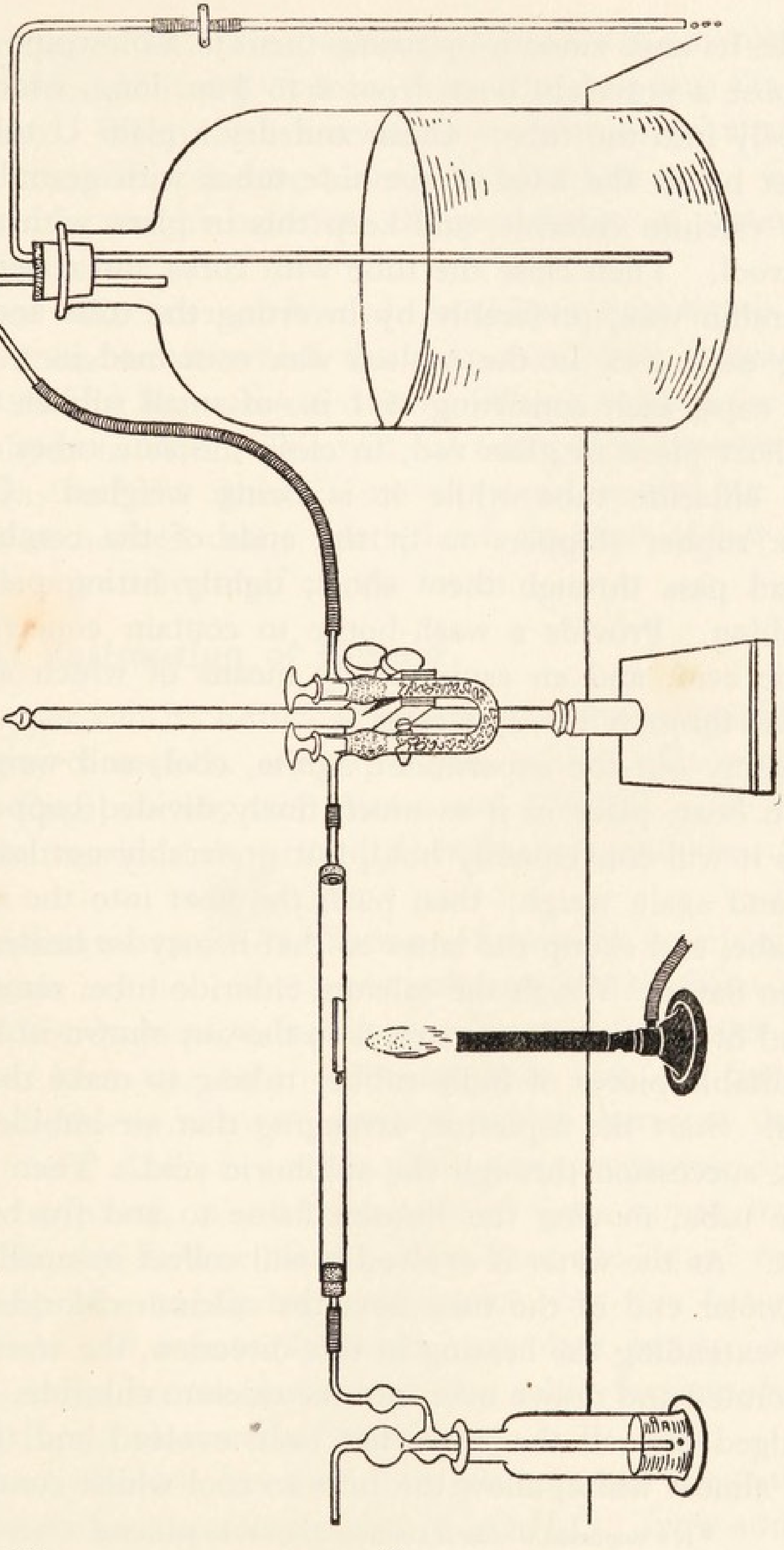

Fig. 10.—Apparatus for estimating water of crystallization in copper sulphate

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

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* 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, $Cu(OH)_2$, 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 $3CuO \cdot H_2O$. 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, $FeSO_4 \cdot 7H_2O$: Ferrous Ammonium Sulphate, $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$.

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 Fe : $(NH_4)_2SO_4$. 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

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* 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, $Fe(OH)_3$, 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 add a drop or two more nitric acid, and notice whether any further action takes place. 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, $Pb(NO_3)_2$.

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:

$$2Pb(NO_3)_2 = 2PbO + 4NO_2 + O_2.$$

Thus, since $Pb(NO_3)_2$ 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, $Na_2HPO_4 \cdot 12H_2O$.

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

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

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:

$$2[Na_2HPO_4\cdot 12H_2O] = Na_4P_2O_7 + 25H_2O.$$

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 ($Ag_4P_2O_7$), 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, $MgNH_4PO_4{\cdot}6H_2O$, and weighed as the pyrophosphate, $Mg_2P_2O_7$, 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 $MgNH_4PO_4{\cdot}6H_2O$, adopt the following procedure. Dissolve the salt in about 50 c. c. of water in a suitable beaker, add to the solution a little dilute hydrochloric acid, excess 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 to boiling, and then add to it with stirring dilute ammonia solution drop by drop until a crystalline precipitate begins to be formed. Con-

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* 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. $MgCl_2{\cdot}6H_2O$ 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.

tinue adding ammonia until the solution smells of the gas; then cool, add strong ammonia solution equal in volume to one-fifth that of the solution, and again stir. This quantity of ammonia is added because the precipitate is distinctly soluble in water, but much less soluble in ammonia solution. After ten minutes filter the precipitate through an asbestos filter, and wash it with dilute ammonia till it is free from chloride. Dry and strongly ignite the precipitate, having the Gooch crucible containing it inside an iron or nickel crucible. When the weight is constant, calculate from the amount of $Mg_2P_2O_7$ obtained the percentage of P_2O_5 in the sodium phosphate.

Express your results thus:*

Percentage Composition of $Na_2HPO_4 \cdot 12H_2O$

	Found.	Calculated.
H_2O ..		..
P_2O_5 ..		..
Na_2O (by diff.) ..		..
	100·00	100·00

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* 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:

$$\mathrm{NaOH + HCl = HOH + NaCl.}$$

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* $\left(\mathrm{N} \text{ or } \frac{\mathrm{N}}{1}\right)$ strength; solutions of one-tenth this strength are decinormal $\left(\frac{\mathrm{N}}{10}\right)$, and so on.

Now consider the reaction:

$$\mathrm{2NaOH + H_2SO_4 = 2HOH + Na_2SO_4,}$$

or say,

$$\mathrm{NaOH} + \frac{\mathrm{H_2SO_4}}{2} = \mathrm{HOH} + \frac{\mathrm{Na_2SO_4}}{2}.$$

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 $\left(\frac{H_2SO_4}{2} = \frac{98}{2} = 49 \text{ gm.}\right)$ of hydrogen sulphate per litre. Similarly normal sodium carbonate solution contains $\frac{Na_2CO_3}{2} = \frac{106}{2} = 53$ gm. of the pure salt per litre.

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

$$AgNO_3 + NaCl = AgCl + NaNO_3,$$

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, $K_2Cr_2O_7$, 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:

$$\frac{1}{10}\left(\frac{2KMnO_4}{10}\right) = 3{\cdot}16 \text{ gm. per litre.}$$

Similarly $K_2Cr_2O_7$ (M.W. 294) contains 3 available oxygen atoms, equivalent to 6 hydrogen atoms; therefore a decinormal solution contains:

$$\frac{K_2Cr_2O_7}{60} = 4{\cdot}9 \text{ gm. per litre.}$$

On the other hand, consider sodium thiosulphate, $Na_2S_2O_3 \cdot 5H_2O$ (M.W. 248), which is employed in the reaction:

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

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 $\frac{N}{10}$HCl or $\frac{N}{10}H_2SO_4$ 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:

$$\frac{4{\cdot}0 \times 15{\cdot}0}{20} = 3{\cdot}0 \text{ gm. NaOH per litre.}$$

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

Weight of acid used to neutralize the sodium hydroxide in 20 c. c. of solution

$$= 15{\cdot}0 \times 0{\cdot}00365 \text{ gm. HCl.}$$

Weight of sodium hydroxide equivalent to this acid

$$= \frac{15{\cdot}0 \times 0{\cdot}00365 \times 40}{36{\cdot}5}.$$

Weight of sodium hydroxide in one litre

$$= \frac{15{\cdot}0 \times 0{\cdot}00365 \times 40 \times 1000}{36{\cdot}5 \times 20} = 3{\cdot}0 \text{ gm.}$$

But why employ all these figures? The same principle may be applied to standard solutions of potassium permanganate of 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 $\frac{20{\cdot}0}{19{\cdot}8} = 1{\cdot}01$, for $19{\cdot}8 \times 1{\cdot}01 = 20{\cdot}0$.

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, $Na_2B_4O_7$, &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:

$H_2C_2O_4 \cdot 2H_2O$; $Ba(OH)_2 \cdot 8H_2O$; NH_3; HNO_3; $NaOCl$; $BaCl_2 \cdot 2H_2O$; 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 when it occurs.

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.

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* Dimethyl-amino-azo-benzene sulphonic acid, $(CH_3)_2NC_6H_4{\cdot}N{:}N{\cdot}C_6H_4SO_3H$.

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 $\frac{N}{1}H_2SO_4$ would be expected to produce a more marked colour change in an indicator than the same volume of $\frac{N}{10}H_2SO_4$, 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

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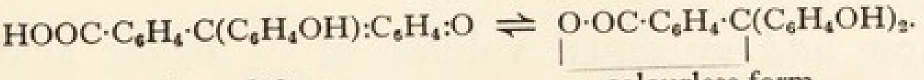
[*] 

$HOOC \cdot C_6H_4 \cdot C(C_6H_4OH) : C_6H_4 : O \rightleftharpoons O \cdot OC \cdot C_6H_4 \cdot C(C_6H_4OH)_2.$

coloured form. colourless form.

[†] 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 $\left(\frac{N}{10}\right)$ 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:

$$\underbrace{\mathrm{SO_3{\cdot}C_6H_4{\cdot}NH{\cdot}N:C_6H_4:N(CH_3)_2}}_{\text{red form.}} \rightarrow \underset{\text{yellow form.}}{\mathrm{HSO_3{\cdot}C_6H_4{\cdot}N:N{\cdot}C_6H_4{\cdot}N(CH_3)_2}}.$$

(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 phenolphthaleïn, 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, $H_2C_2O_4 \cdot 2H_2O$ (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 $Na_2CO_3 \cdot H_2O$. 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 $\frac{N}{10}$ 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 $\frac{N}{10}$ 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, $H_2C_2O_4 \cdot 2H_2O$, 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:

$$\begin{tikzcd} & \text{alkali} \\ & 20 \text{ c. c.} & \\ & \text{Indicator: phenolphthalein} & \\ \text{sulphuric acid } a \text{ c. c.} \arrow[uur] & \equiv & b \text{ c. c. } \frac{N}{10} \text{ oxalic acid} \arrow[uul] \end{tikzcd}$$

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, which may be a 4-oz. conical flask. Add a few drops of methyl orange, and titrate the alkali with the sulphuric acid (see p. 15). Repeat the operation several times, until by practice 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:

$$2\,Na_2CO_3 + H_2SO_4 = Na_2SO_4 + 2NaHCO_3,$$
$$2NaHCO_3 + H_2SO_4 = Na_2SO_4 + 2H_2CO_3.$$

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

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* 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

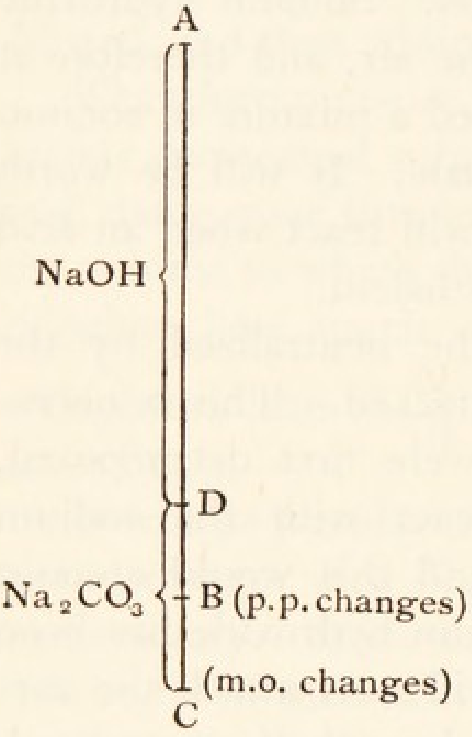
$$\frac{20{\cdot}0}{20{\cdot}2} = 0{\cdot}99\frac{N}{10} \text{ or } 0{\cdot}099N.$$

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 $BaCl_2{\cdot}2H_2O$ 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 $\frac{b}{a} \times 3{\cdot}647$ 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. $NH_4^{\cdot}$ and OH' ions must exist in ammonia solution, since it is alkaline; but when an acid, i.e. a solution containing $H^{\cdot}$ ions, is added to ammonia the reaction probably consists partly in the combination of $H^{\cdot}$ and OH' ions to form water, but chiefly in the union between $H^{\cdot}$ ions and NH_3 molecules to form $NH_4^{\cdot}$ ions; thus:

$$H^{\cdot} + OH' = H_2O,$$
$$H^{\cdot} + NH_3 = NH_4^{\cdot}.$$

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, $CH_3{\cdot}COOH$, 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.

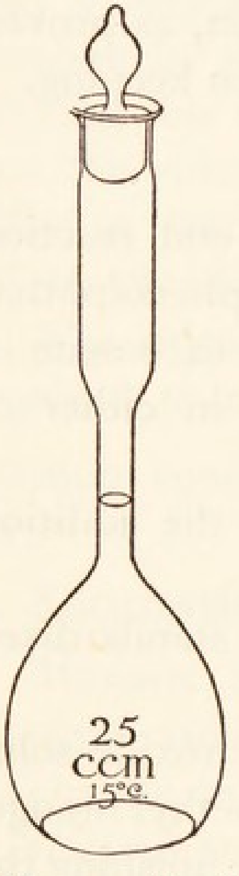


Fig. 11.— Specific Gravity Bottle (one-fourth actual size).

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.

(*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. $d\frac{15°}{15°}$. If the density compared with water at 4° C. $\left(d\frac{15°}{4°}\right)$ 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,

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* 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, $Ca(OH)_2$, 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, $Na_2CO_3 \cdot 10H_2O$, 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:

$$Na_2CO_3 \cdot 10H_2O \rightleftharpoons Na_2CO_3 \cdot H_2O + 9H_2O.$$

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

$$NaCl + H_2SO_4 \rightleftharpoons NaHSO_4 + HCl,$$

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

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* 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:

$$BaCl_2 + Na_2CO_3 = BaCO_3 + 2NaCl;$$

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:

$$Pb(NO_3)_2 + Na_2CO_3 = PbCO_3 + 2NaNO_3$$
$$PbCO_3 + 2H_2O \rightleftharpoons Pb(OH)_2 + H_2CO_3,$$

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 $\frac{5{\cdot}4}{0{\cdot}0857} = 63$.

To determine the equivalent weight of tartaric acid ($H_2C_4H_4O_6$), 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:

$$(NH_4)_2SO_4 + 2NaOH = Na_2SO_4 + 2H_2O + 2NH_3.$$

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

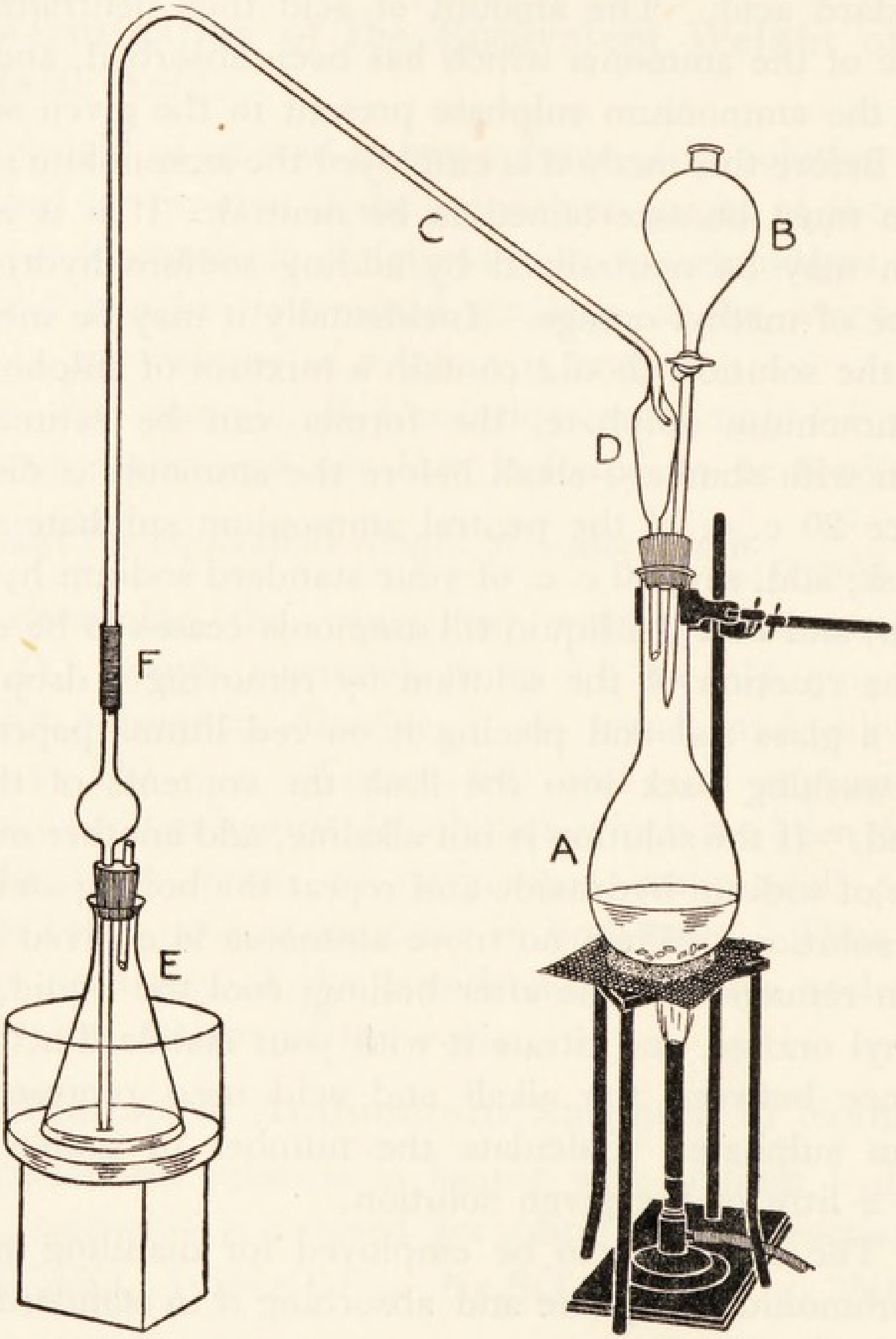

Fig. 12.—Estimation of Ammonia by Distillation

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

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:

$$MnO_2 + Na_2O_2 = Na_2MnO_4,$$

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* 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:

$$2MnO_3 + O = Mn_2O_7,$$

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,

$$3MnO_3 = MnO_2 + Mn_2O_7.$$

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

$$3H_2MnO_4 = MnO_2 + 2HMnO_4 + 2H_2O.$$

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:

$$\begin{aligned}\text{(i) } Mn_2O_7 &= 2MnO_3 + O,\\ \text{(ii) } Mn_2O_7 &= 2MnO_2 + 3O,\\ \text{(iii) } Mn_2O_7 &= 2MnO + 5O;\end{aligned}$$

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

$$\begin{aligned}&\text{(i) } 2KMnO_4 + Na_2SO_3 + 2KOH = 2K_2MnO_4 + Na_2SO_4 + H_2O;\\ &\text{(ii) } 2KMnO_4 + 3Na_2SO_3 + H_2O = 2MnO_2 + 3Na_2SO_4 + 2KOH;\\ &\text{(iii) } 2KMnO_4 + 5H_2SO_3 = 2MnSO_4 + K_2SO_4 + 2H_2SO_4 + 3H_2O.\end{aligned}$$

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

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* 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 $\frac{2KMnO_4}{10}$ gm., and a decinormal solution $\frac{2KMnO_4}{100}$ gm. per litre. The molecular weight of potassium permanganate is 158; therefore a decinormal solution of this salt contains $\frac{2 \times 158}{100} = 3{\cdot}16$ 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, $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$, (Mohr's salt).
Sodium oxalate, $Na_2C_2O_4$.
Oxalic acid, $H_2C_2O_4 \cdot 2H_2O$.

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:

$$2FeSO_4 + H_2SO_4 + O = Fe_2(SO_4)_3 + H_2O.$$

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

$$\begin{aligned} &10FeSO_4 + 8H_2SO_4 + 2KMnO_4 \\ &\quad = 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O; \end{aligned}$$

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.

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* 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 sáme 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, $H_2C_2O_4 \cdot 2H_2O$, 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:

$$H_2C_2O_4 + O = 2CO_2 + H_2O;$$

or with potassium permanganate:

$$\begin{aligned} &2KMnO_4 + 5H_2C_2O_4 + 3H_2SO_4 \\ &\qquad = 2MnSO_4 + K_2SO_4 + 10CO_2 + 8H_2O. \end{aligned}$$

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

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* 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:

$$Mn_2O_7 + 3MnO = 5MnO_2.$$

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:

$$2KMnO_4 + 3MnSO_4 + 2H_2O = K_2SO_4 + 5MnO_2 + 2H_2SO_4,$$
$$5MnO_2 + 5H_2C_2O_4 + 5H_2SO_4 = 5MnSO_4 + 10CO_2 + 10H_2O.$$

Adding eliminates the catalyst thus:

$$2KMnO_4 + 5H_2C_2O_4 + 3H_2SO_4 = 2MnSO_4 + K_2SO_4 + 10CO_2 + 8H_2O.$$

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°–70° 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.

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* 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, $Na_2C_2O_4$, 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:

$$Na_2C_2O_4 + H_2SO_4 + O = Na_2SO_4 + H_2O + 2CO_2,$$

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.

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* Or more accurately 0.005584 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:

(*a*) $Fe_2(SO_4)_3 + 2H = 2FeSO_4 + H_2SO_4$;
(*b*) $Fe_2(SO_4)_3 + H_2SO_3 + OH_2 = 2FeSO_4 + 2H_2SO_4$;
(*c*) $Fe_2(SO_4)_3 + H_2S = 2FeSO_4 + H_2SO_4 + S$;
(*d*) $Fe_2(SO_4)_3 + SnCl_2 + 2HCl = 2FeSO_4 + H_2SO_4 + SnCl_4$.

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:

$$Fe_2(SO_4)_3 \cdot (NH_4)_2SO_4 \cdot 24H_2O.$$

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

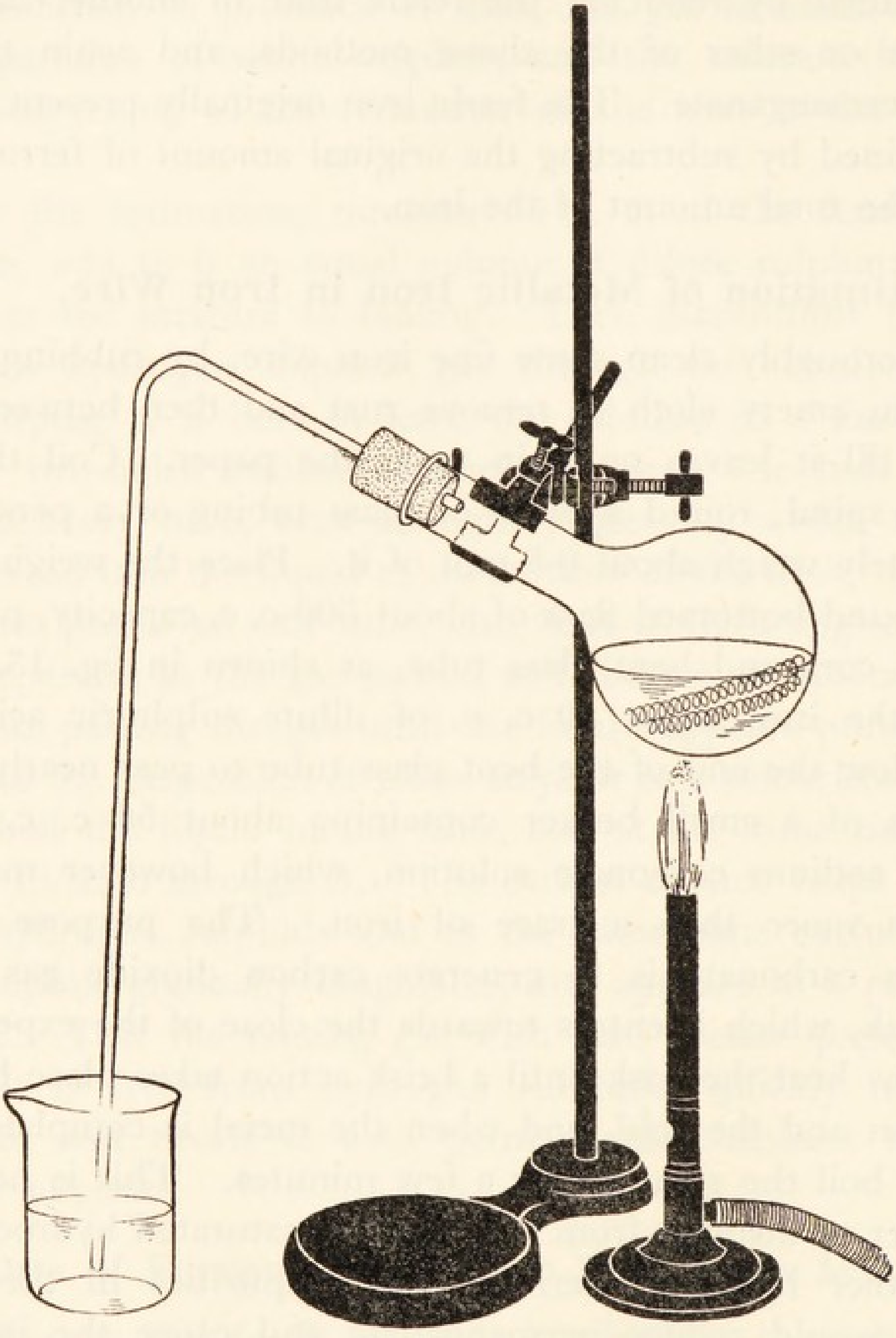

Fig. 13.—Solution of Iron Wire in dilute Sulphuric Acid

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 dioxide 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, $(NH_4)_2C_2O_4{\cdot}H_2O$.

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, $CaSO_4 \cdot 2H_2O$, 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:

$$Ca(NO_3)_2 + (NH_4)_2C_2O_4 = CaC_2O_4 + 2NH_4NO_3.$$

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

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* 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.†

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[*] 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:

$$H_2O_2 + O = H_2O + O_2,$$

or expressed fully:

$$\begin{aligned} 2KMnO_4 + 5H_2O_2 + 3H_2SO_4 \\ = K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2. \end{aligned}$$

1 c. c. of decinormal permanganate solution oxidizes

$$\frac{\text{m.w.}H_2O_2}{2 \times 10{,}000} = 0{\cdot}0017 \text{ gm. } H_2O_2.$$

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

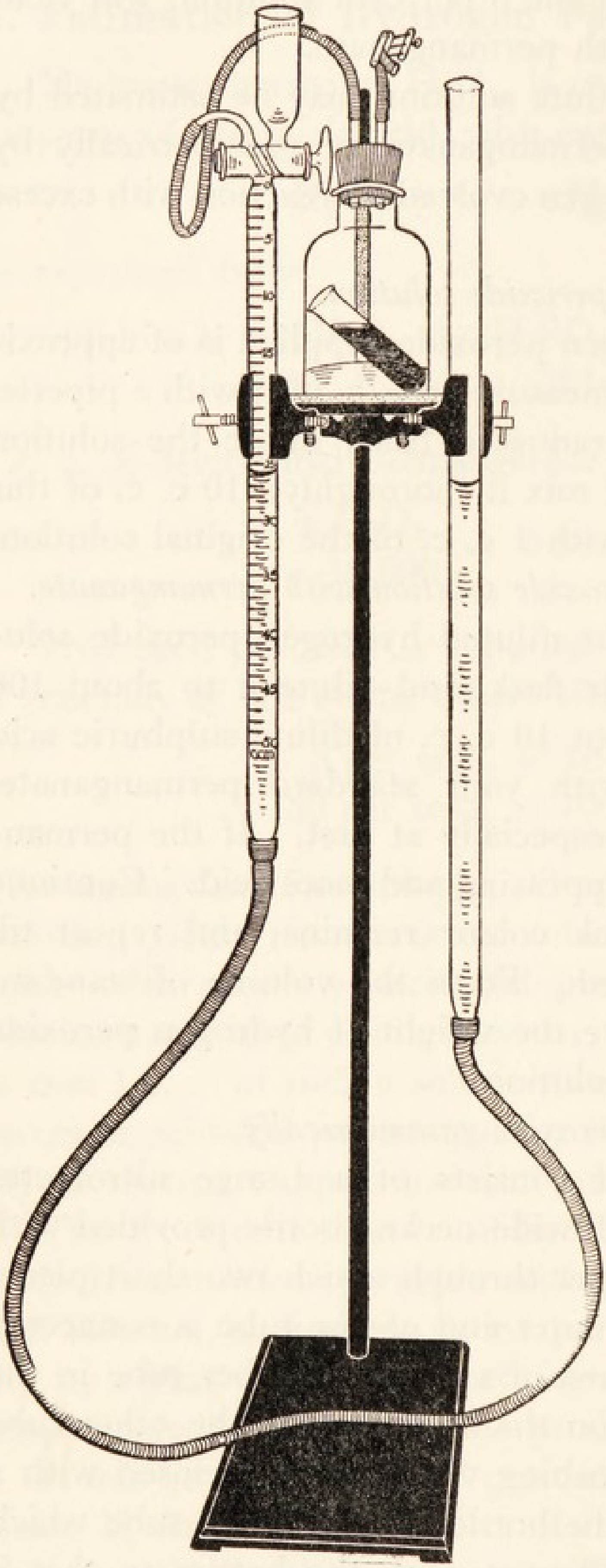

Fig. 14.—Gasometric Estimation of Hydrogen Peroxide

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.

$$= \frac{19{\cdot}8 \times 273 \times (754 - 12)}{287 \times 760} = 18{\cdot}4 \text{ c. c.}$$

Weight of oxygen = 18·4 × 0·00009 × 16 gm.; and since 32 gm. of oxygen are equivalent to 34 gm. of hydrogen peroxide.

$$\text{Weight of } H_2O_2 = \frac{18{\cdot}4 \times 0{\cdot}00009 \times 16 \times 34}{32} = 0{\cdot}0281 \text{ gm.}$$

∴ 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:

$$Cr_2O_3 + 3Na_2O_2 = 2Na_2CrO_4 + Na_2O.$$

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:

$$\begin{aligned} 2Na_2CrO_4 + 2HCl &= Na_2Cr_2O_7 + 2NaCl + H_2O, \\ Na_2Cr_2O_7 + 2NaOH &= 2Na_2CrO_4 + H_2O. \end{aligned}$$

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,

$$2CrO_3 \rightleftharpoons Cr_2O_3 + 3O,$$

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, $K_2Cr_2O_7$, is $K_2O{\cdot}2CrO_3$, 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:

$$K_2Cr_2O_7 + 4H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O;$$

but since iron is oxidized according to the scheme

$$2FeO + O = Fe_2O_3,$$

$$\text{or } 6FeSO_4 + 3H_2SO_4 + 3O = 3Fe_2(SO_4)_3 + 3H_2O,$$

the completed equation becomes:

$$\begin{aligned} &K_2Cr_2O_7 + 6FeSO_4 + 7H_2SO_4 \\ &\qquad = K_2SO_4 + Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 7H_2O. \end{aligned}$$

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

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

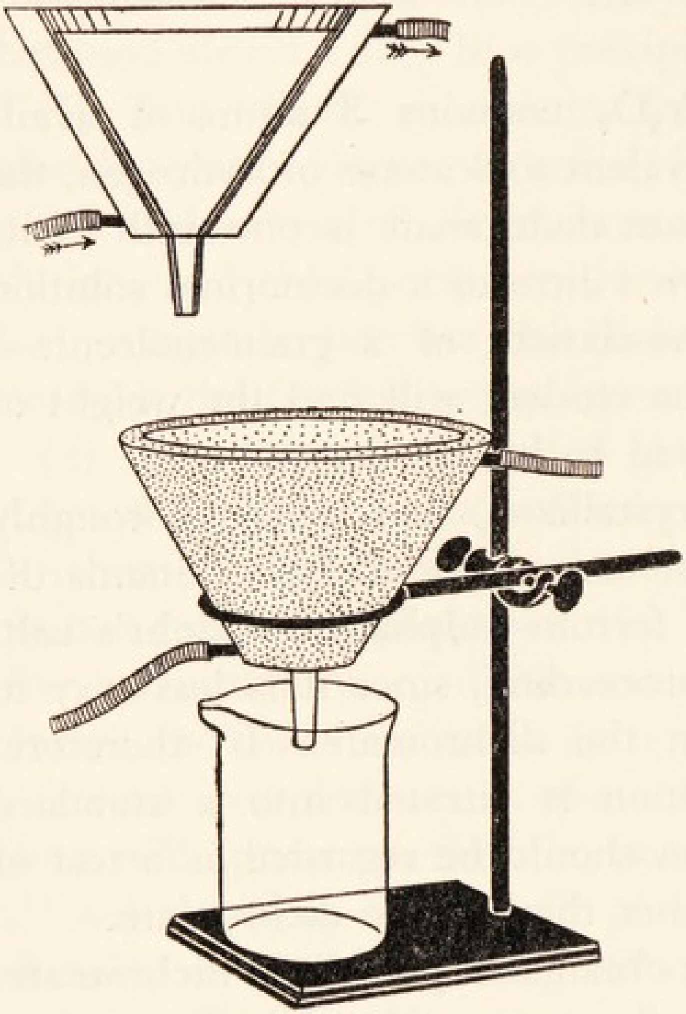

Fig. 15.—Funnel in Hot-water Jacket

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, however, 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, $SnCl_2 \cdot 2H_2O$, 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:

$$SnCl_2 + 2HgCl_2 = SnCl_4 + Hg_2Cl_2.$$

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:

$$Hg_2Cl_2 + SnCl_2 = SnCl_4 + 2Hg.$$

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,

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* 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. $2N.H_2SO_4$, 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.

STANDARD SOLUTIONS OF IODINE AND SODIUM THIOSULPHATE

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

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

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

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

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

$$\underset{I}{NaO{-}SO_2{-}SNa}\ \underset{I}{NaS{-}SO_2{-}ONa} \longrightarrow NaO{-}SO_2{-}S{-}S{-}SO_2{-}ONa + 2NaI$$

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 $Na_2S_2O_3{\cdot}5H_2O$ 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

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* 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:

$$\left\{\begin{array}{ll} K_2Cr_2O_7 + 14HCl + 6KI & = 8KCl + 2CrCl_3 + 7H_2O + 6I. \\ 6I + 6Na_2S_2O_3 & = 6NaI + 3Na_2S_4O_6 \end{array}\right.$$

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:

$$H_3AsO_3 + OH_2 + I_2 \rightleftharpoons H_3AsO_4 + 2HI.$$

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:

$$As_2O_3 + 2O = As_2O_5.$$

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, $\frac{197 \cdot 92}{400} = 0 \cdot 4948$ 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

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* 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:

$$H_2S + I_2 = 2HI + S.$$

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

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* 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

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* 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-

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* 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

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* 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:

$$NaCl + AgNO_3 = AgCl + NaNO_3.$$

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 $\frac{58{\cdot}46}{40} = 1{\cdot}461$ 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 $\frac{169{\cdot}9}{40} = 4{\cdot}248$ 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.

NOTE ON 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:

$$H_3PO_4 \rightarrow 3H^{\cdot} + PO_4{'''}.$$

Instead, ionization proceeds thus: $H_3PO_4 \rightarrow H^{\cdot} + H_2PO_4{'}$, and then thus: $H_2PO_4{'} \rightarrow H^{\cdot} + HPO_4{'}$ to a small extent.

Consider the salt Na_3PO_4, whose solution is alkaline because of hydrolysis, which takes place thus:

$$Na_3{}^{\cdots}PO_4{'''} + HOH = Na_2{}^{\cdot\cdot}HPO_4{''} + Na^{\cdot} + OH',$$

and thus:

$$Na_2{}^{\cdot\cdot}HPO_4{''} + HOH = Na^{\cdot}H_2PO_4{'} + Na^{\cdot} + OH';$$

or, to express the facts in another way:

$$\begin{aligned} Na_3PO_4 &\rightleftharpoons 3Na^{\cdot} + PO_4{'''}, \\ PO_4{'''} + HOH &\rightleftharpoons HPO_4{''} + OH', \\ HPO_4{''} + HOH &\rightleftharpoons H_2PO_4{'} + OH'. \end{aligned}$$

Now, since different indicators respond differently to the same degree of hydrion 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 normal soda 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:

$$H_3PO_4 + NaOH = NaH_2PO_4 + H_2O;$$

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

$$NaH_2PO_4 + NaOH = Na_2HPO_4 + H_2O.$$

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.

The titrations should be done in cold solution with 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.

In this way phosphoric acid, and sodium dihydrogen phosphate can be estimated by means of normal alkali, with suitable indicator, each substance being regarded as a monobasic acid.

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

APPENDIX

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

Temperature, Deg. Centigrade.	Pressure in Mm. Hg.	Temperature, Deg. Centigrade.	Pressure in Mm. Hg.	Temperature, 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	—	—

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	—	—

SULPHURIC ACID

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

Specific Gravity at 15°/4° in Vacuo.	Percentage H_2SO_4.	Specific Gravity at 15°/4° in Vacuo.	Percentage H_2SO_4.	Specific Gravity at 15°/4° in Vacuo.	Percentage H_2SO_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

SULPHURIC ACID—*Continued*

Specific Gravity at 15°/4° in Vacuo.	Percentage H_2SO_4.	Specific Gravity at 15°/4° in Vacuo.	Percentage H_2SO_4.	Specific Gravity at 15°/4° in Vacuo.	Percentage H_3SO_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	—	—

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						4	9	13	17	21	26	30	34	38
						0212	0253	0294	0334	0374	4	8	12	16	20	24	28	32	37
11	0414	0453	0492	0531	0569						4	8	12	15	19	23	27	31	35
						0607	0645	0682	0719	0755	4	7	11	15	19	22	26	30	33
12	0792	0828	0864	0899	0934	0969					3	7	11	14	18	21	25	28	32
							1004	1038	1072	1106	3	7	10	14	17	20	24	27	31
13	1139	1173	1206	1239	1271						3	7	10	13	16	20	23	26	30
						1303	1335	1367	1399	1430	3	7	10	12	16	19	22	25	29
14	1461	1492	1523	1553							3	6	9	12	15	18	21	24	28
					1584	1614	1644	1673	1703	1732	3	6	9	12	15	17	20	23	26
15	1761	1790	1818	1847	1875	1903					3	6	9	11	14	17	20	23	26
							1931	1959	1987	2014	3	5	8	11	14	16	19	22	25
16	2041	2068	2095	2122	2148						3	5	8	11	14	16	19	22	24
						2175	2201	2227	2253	2279	3	5	8	10	13	15	18	21	23
17	2304	2330	2355	2380	2405	2430					3	5	8	10	13	15	18	20	23
							2455	2480	2504	2529	2	5	7	10	12	15	17	19	22
18	2553	2577	2601	2625	2648						2	5	7	9	12	14	16	19	21
						2672	2695	2718	2742	2765	2	5	7	9	11	14	16	18	21
19	2788	2810	2833	2856	2878						2	4	7	9	11	13	16	18	20
						2900	2923	2945	2967	2989	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	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	3	4

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	2	2	2	2
·05	1122	1125	1127	1130	1132	1135	1138	1140	1143	1146	0	1	1	1	1	2	2	2	2
·06	1148	1151	1153	1156	1159	1161	1164	1167	1169	1172	0	1	1	1	1	2	2	2	2
·07	1175	1178	1180	1183	1186	1189	1191	1194	1197	1199	0	1	1	1	1	2	2	2	2
·08	1202	1205	1208	1211	1213	1216	1219	1222	1225	1227	0	1	1	1	1	2	2	2	3
·09	1230	1233	1236	1239	1242	1245	1247	1250	1253	1256	0	1	1	1	1	2	2	2	3
·10	1259	1262	1265	1268	1271	1274	1276	1279	1282	1285	0	1	1	1	1	2	2	2	3
·11	1288	1291	1294	1297	1300	1303	1306	1309	1312	1315	0	1	1	1	2	2	2	2	3
·12	1318	1321	1324	1327	1330	1334	1337	1340	1343	1346	0	1	1	1	2	2	2	2	3
·13	1349	1352	1355	1358	1361	1365	1368	1371	1374	1377	0	1	1	1	2	2	2	3	3
·14	1380	1384	1387	1390	1393	1396	1400	1403	1406	1409	0	1	1	1	2	2	2	3	3
·15	1413	1416	1419	1422	1426	1429	1432	1435	1439	1442	0	1	1	1	2	2	2	3	3
·16	1445	1449	1452	1455	1459	1462	1466	1469	1472	1476	0	1	1	1	2	2	2	3	3
·17	1479	1483	1486	1489	1493	1496	1500	1503	1507	1510	0	1	1	1	2	2	2	3	3
·18	1514	1517	1521	1524	1528	1531	1535	1538	1542	1545	0	1	1	1	2	2	2	3	3
·19	1549	1552	1556	1560	1563	1567	1570	1574	1578	1581	0	1	1	1	2	2	3	3	3
·20	1585	1589	1592	1596	1600	1603	1607	1611	1614	1618	0	1	1	1	2	2	3	3	3
·21	1622	1626	1629	1633	1637	1641	1644	1648	1652	1656	0	1	1	2	2	2	3	3	3
·22	1660	1663	1667	1671	1675	1679	1683	1687	1690	1694	0	1	1	2	2	2	3	3	3
·23	1698	1702	1706	1710	1714	1718	1722	1726	1730	1734	0	1	1	2	2	2	3	3	4
·24	1738	1742	1746	1750	1754	1758	1762	1766	1770	1774	0	1	1	2	2	2	3	3	4
·25	1778	1782	1786	1791	1795	1799	1803	1807	1811	1816	0	1	1	2	2	2	3	3	4
·26	1820	1824	1828	1832	1837	1841	1845	1849	1854	1858	0	1	1	2	2	3	3	3	4
·27	1862	1866	1871	1875	1879	1884	1888	1892	1897	1901	0	1	1	2	2	3	3	3	4
·28	1905	1910	1914	1919	1923	1928	1932	1936	1941	1945	0	1	1	2	2	3	3	4	4
·29	1950	1954	1959	1963	1968	1972	1977	1982	1986	1991	0	1	1	2	2	3	3	4	4
·30	1995	2000	2004	2009	2014	2018	2023	2028	2032	2037	0	1	1	2	2	3	3	4	4
·31	2042	2046	2051	2056	2061	2065	2070	2075	2080	2084	0	1	1	2	2	3	3	4	4
·32	2089	2094	2099	2104	2109	2113	2118	2123	2128	2133	0	1	1	2	2	3	3	4	4
·33	2138	2143	2148	2153	2158	2163	2168	2173	2178	2183	0	1	1	2	2	3	3	4	4
·34	2188	2193	2198	2203	2208	2213	2218	2223	2228	2234	1	1	2	2	3	3	4	4	5
·35	2239	2244	2249	2254	2259	2265	2270	2275	2280	2286	1	1	2	2	3	3	4	4	5
·36	2291	2296	2301	2307	2312	2317	2323	2328	2333	2339	1	1	2	2	3	3	4	4	5
·37	2344	2350	2355	2360	2366	2371	2377	2382	2388	2393	1	1	2	2	3	3	4	4	5
·38	2399	2404	2410	2415	2421	2427	2432	2438	2443	2449	1	1	2	2	3	3	4	4	5
·39	2455	2460	2466	2472	2477	2483	2489	2495	2500	2506	1	1	2	2	3	3	4	5	5
·40	2512	2518	2523	2529	2535	2541	2547	2553	2559	2564	1	1	2	2	3	4	4	5	5
·41	2570	2576	2582	2588	2594	2600	2606	2612	2618	2624	1	1	2	2	3	4	4	5	5
·42	2630	2636	2642	2649	2655	2661	2667	2673	2679	2685	1	1	2	2	3	4	4	5	6
·43	2692	2698	2704	2710	2716	2723	2729	2735	2742	2748	1	1	2	3	3	4	4	5	6
·44	2754	2761	2767	2773	2780	2786	2793	2799	2805	2812	1	1	2	3	3	4	4	5	6
·45	2818	2825	2831	2838	2844	2851	2858	2864	2871	2877	1	1	2	3	3	4	5	5	6
·46	2884	2891	2897	2904	2911	2917	2924	2931	2938	2944	1	1	2	3	3	4	5	5	6
·47	2951	2958	2965	2972	2979	2985	2992	2999	3006	3013	1	1	2	3	3	4	5	5	6
·48	3020	3027	3034	3041	3048	3055	3062	3069	3076	3083	1	1	2	3	4	4	5	6	6
·49	3090	3097	3105	3112	3119	3126	3133	3141	3148	3155	1	1	2	3	4	4	5	6	6

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	5	6	7
·53	3388	3396	3404	3412	3420	3428	3436	3443	3451	3459	1	2	2	3	4	5	6	6	7
·54	3467	3475	3483	3491	3499	3508	3516	3524	3532	3540	1	2	2	3	4	5	6	6	7
·55	3548	3556	3565	3573	3581	3589	3597	3606	3614	3622	1	2	2	3	4	5	6	7	7
·56	3631	3639	3648	3656	3664	3673	3681	3690	3698	3707	1	2	3	3	4	5	6	7	8
·57	3715	3724	3733	3741	3750	3758	3767	3776	3784	3793	1	2	3	3	4	5	6	7	8
·58	3802	3811	3819	3828	3837	3846	3855	3864	3873	3882	1	2	3	4	4	5	6	7	8
·59	3890	3899	3908	3917	3926	3936	3945	3954	3963	3972	1	2	3	4	5	5	6	7	8
·60	3981	3990	3999	4009	4018	4027	4036	4046	4055	4064	1	2	3	4	5	6	6	7	8
·61	4074	4083	4093	4102	4111	4121	4130	4140	4150	4159	1	2	3	4	5	6	7	8	9
·62	4169	4178	4188	4198	4207	4217	4227	4236	4246	4256	1	2	3	4	5	6	7	8	9
·63	4266	4276	4285	4295	4305	4315	4325	4335	4345	4355	1	2	3	4	5	6	7	8	9
·64	4365	4375	4385	4395	4406	4416	4426	4436	4446	4457	1	2	3	4	5	6	7	8	9
·65	4467	4477	4487	4498	4508	4519	4529	4539	4550	4560	1	2	3	4	5	6	7	8	9
·66	4571	4581	4592	4603	4613	4624	4634	4645	4656	4667	1	2	3	4	5	6	7	9	10
·67	4677	4688	4699	4710	4721	4732	4742	4753	4764	4775	1	2	3	4	5	7	8	9	10
·68	4786	4797	4808	4819	4831	4842	4853	4864	4875	4887	1	2	3	4	6	7	8	9	10
·69	4898	4909	4920	4932	4943	4955	4966	4977	4989	5000	1	2	3	5	6	7	8	9	10
·70	5012	5023	5035	5047	5058	5070	5082	5093	5105	5117	1	2	4	5	6	7	8	9	11
·71	5129	5140	5152	5164	5176	5188	5200	5212	5224	5236	1	2	4	5	6	7	8	10	11
·72	5248	5260	5272	5284	5297	5309	5321	5333	5346	5358	1	2	4	5	6	7	9	10	11
·73	5370	5383	5395	5408	5420	5433	5445	5458	5470	5483	1	3	4	5	6	8	9	10	11
·74	5495	5508	5521	5534	5546	5559	5572	5585	5598	5610	1	3	4	5	6	8	9	10	12
·75	5623	5636	5649	5662	5675	5689	5702	5715	5728	5741	1	3	4	5	7	8	9	10	12
·76	5754	5768	5781	5794	5808	5821	5834	5848	5861	5875	1	3	4	5	7	8	9	11	12
·77	5888	5902	5916	5929	5943	5957	5970	5984	5998	6012	1	3	4	5	7	8	10	11	12
·78	6026	6039	6053	6067	6081	6095	6109	6124	6138	6152	1	3	4	6	7	8	10	11	13
·79	6166	6180	6194	6209	6223	6237	6252	6266	6281	6295	1	3	4	6	7	9	10	11	13
·80	6310	6324	6339	6353	6368	6383	6397	6412	6427	6442	1	3	4	6	7	9	10	12	13
·81	6457	6471	6486	6501	6516	6531	6546	6561	6577	6592	2	3	5	6	8	9	11	12	14
·82	6607	6622	6637	6653	6668	6683	6699	6714	6730	6745	2	3	5	6	8	9	11	12	14
·83	6761	6776	6792	6808	6823	6839	6855	6871	6887	6902	2	3	5	6	8	9	11	13	14
·84	6918	6934	6950	6966	6982	6998	7015	7031	7047	7063	2	3	5	6	8	10	11	13	15
·85	7079	7096	7112	7129	7145	7161	7178	7194	7211	7228	2	3	5	7	8	10	12	13	15
·86	7244	7261	7278	7295	7311	7328	7345	7362	7379	7396	2	3	5	7	8	10	12	13	15
·87	7413	7430	7447	7464	7482	7499	7516	7534	7551	7568	2	3	5	7	9	10	12	14	16
·88	7586	7603	7621	7638	7656	7674	7691	7709	7727	7745	2	4	5	7	9	11	12	14	16
·89	7762	7780	7798	7816	7834	7852	7870	7889	7907	7925	2	4	5	7	9	11	13	14	16
·90	7943	7962	7980	7998	8017	8035	8054	8072	8091	8110	2	4	6	7	9	11	13	15	17
·91	8128	8147	8166	8185	8204	8222	8241	8260	8279	8299	2	4	6	8	9	11	13	15	17
·92	8318	8337	8356	8375	8395	8414	8433	8453	8472	8492	2	4	6	8	10	12	14	15	17
·93	8511	8531	8551	8570	8590	8610	8630	8650	8670	8690	2	4	6	8	10	12	14	16	18
·94	8710	8730	8750	8770	8790	8810	8831	8851	8872	8892	2	4	6	8	10	12	14	16	18
·95	8913	8933	8954	8974	8995	9016	9036	9057	9078	9099	2	4	6	8	10	12	15	17	19
·96	9120	9141	9162	9183	9204	9226	9247	9268	9290	9311	2	4	6	8	11	13	15	17	19
·97	9333	9354	9376	9397	9419	9441	9462	9484	9506	9528	2	4	7	9	11	13	15	17	20
·98	9550	9572	9594	9616	9638	9661	9683	9705	9727	9750	2	4	7	9	11	13	16	18	20
·99	9772	9795	9817	9840	9863	9886	9908	9931	9954	9977	2	5	7	9	11	14	16	18	20

ATOMIC WEIGHTS

(1934)

Aluminium,	Al	26·97
Antimony,	Sb	121·76
Arsenic,	As	74·91
Barium,	Ba	137·36
Bismuth,	Bi	209·00
Boron,	B	10·82
Bromine,	Br	79·916
Cadmium,	Cd	112·41
Calcium,	Ca	40·08
Carbon,	C	12·00
Chlorine,	Cl	35·457
Chromium,	Cr	52·01
Cobalt,	Co	58·94
Copper,	Cu	63·57
Fluorine,	F	19·00
Hydrogen,	H	1·0078
Iodine,	I	126·92
Iron,	Fe	55·84
Lead,	Pb	207·22
Magnesium,	Mg	24·32
Manganese,	Mn	54·93
Mercury,	Hg	200·61
Molybdenum,	Mo	96·0
Nickel,	Ni	58·69
Nitrogen,	N	14·008
Oxygen,	O	**16·0000**
Phosphorus,	P	31·02
Potassium,	K	39·096
Silicon,	Si	28·06
Silver,	Ag	107·880
Sodium,	Na	22·997
Strontium,	Sr	87·63
Sulphur,	S	32·06
Tin,	Sn	118·70
Uranium,	U	238·14
Zinc,	Zn	65·38

NOTE.—The atomic weights given in the above table are those published by the International Union of Chemistry, 1934. 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.

Index to Part I

QUANTITATIVE CHEMICAL ANALYSIS

AND

INORGANIC PREPARATIONS

BY

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In Two Parts

PART II

VOLUMETRIC ANALYSIS, GRAVIMETRIC SEPARATIONS, ANALYSIS OF MINERALS AND ALLOYS, PREPARATION OF INORGANIC COMPOUNDS

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Preface

This volume constitutes Part II of a textbook on quantitative analysis and inorganic preparations, and contains the exercises a candidate for a degree or the Associateship of the Institute of Chemistry should perform, after he has reached the standard of the first science or intermediate degree examination. The book is not a work of reference, but includes an extended course on volumetric analysis, gravimetric separations, and analysis of minerals and alloys, as well as a series of inorganic preparations arranged to illustrate important chemical principles and operations. Little scope is given for selection, as the intention of the author has been to provide a volume of moderate size containing nothing superfluous to the student's needs. Thus, while there is some room for choice in the sections dealing with the analysis of minerals, and the preparation of inorganic substances, because few students will have time to perform all the exercises, the sections on volumetric analysis and simple gravimetric separations should be worked through from beginning to end.

In the training of a student who is to become all that can be included in the term Chemist, the question inevitably arises as to how soon the guidance of the teacher should be relaxed, and the student be set free to go his own way, and evolve his own methods by judicious selection and appropriation of information drawn from all available literature. If the guidance is relaxed too soon the student may suffer from lack of soundness in his training, and so never learn those methods of precision and thoroughness which might have been acquired through the drilling and discipline which he has missed; but if the guidance is continued too long, if too much of the way is prepared for him, originality and resourcefulness may be hindered or destroyed, so that the student may never develop that faculty for research which a good teacher will hold before him as the highest attainment of a chemical career.

Two principles thus need to be kept in view by the teacher. One is that a student has the right to be told as plainly as possible how to do certain things. He cannot discover for himself everything in chemistry *de novo*, and he has a right to profit by the experience of those who have gone along the road before him. The other is that if he does only what he is told to do he will never become a chemist—he will hardly even become a man. Therefore he must be encouraged to make excursions away from the road, small at first, but increasing in range as he gains experience. He may, for example, try to improve on the methods described in his textbook; and perhaps he will succeed. In any case his experience will be salutary, and a precious bit of his chemical training; for is he not thus beginning research work?

How soon research work, in a definite sense, should commence is a question about which there is room for difference of opinion; but it is highly desirable that every student should conclude his course with a little problem upon which he may exercise his powers of investigation and insight. The problem may be related to some branch of chemical technology, of personal or local interest, it may have arisen out of some difficulty encountered in the course of the student's work, or it may be a question of purely scientific interest.

Whatever may be the nature of the chemical investigations in which a student engages at the end of, or subsequent to, his college career, it is hoped that the exercises described in the present volume will be found adequate for his previous training on the inorganic side.

The author desires to acknowledge his indebtedness, not only to a number of standard textbooks, but also to Miss M. M. J. Sutherland, D.Sc., F.I.C., who kindly read the MS. and made useful suggestions, to Dr. P. F. Gordon and Dr. Eric C. Pickering, for their practical help, as well as to his lecture assistant, Mr. J. Smith, and a number of students who have worked through those exercises which needed testing.

R. M. C.

Royal Technical College, Glasgow.

June, 1925.

NOTE TO SECOND EDITION

Advantage has been taken of a new edition of Part II of this book to incorporate a section on some Special Volumetric Processes. These include the use of potassium iodate and of adsorption indicators, and titration to a standard *p*H value.

Some of the reactions involved are of great theoretical interest as well as of practical importance. It has been thought well, therefore, to expound the underlying principles before describing the processes.

The author gratefully acknowledges the help of Dr. A. B. Crawford in elucidating the iodate reactions, of Dr. J. A. Cranston in the exposition of *p*H value, and of Mr. E. J. Schorn, Ph.C., in demonstrating the technique of the phosphate titration.

R. M. C.

Royal Technical College, Glasgow.
June, 1934.

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QUANTITATIVE CHEMICAL ANALYSIS

PART II

CALIBRATION AND STANDARDIZATION OF INSTRUMENTS

When beginning quantitative analysis the student generally proceeds on the assumption that the weights and measuring vessels with which he is provided are true, that is, that their real value corresponds with their designation. For ordinary purposes this assumption serves, and it is possible to carry out reliable analysis without giving a thought to the accuracy of the instruments employed. It will be understood, however, that more or less serious error may lurk in these instruments, and so give rise to discordant and puzzling results. Before proceeding to accurate work, therefore, it is well for the student to test his weights and graduated vessels, so as to be in a position to apply corrections to them if necessary.

The operations of *Calibration* and *Standardization* must be distinguished.

The calibration of instruments is the testing of them to discover errors, and so to provide a record of corrections by the use of which true values can be obtained.

The standardization of an instrument is the discovery of its error, followed by an alteration of the instrument so that it may give a true value.

Thus weights and burettes are calibrated; no alterations are made upon them, but a table of corrections is compiled for use with them. Flasks and pipettes, however, can be standardized; that is when they are found to be in error fresh graduation marks can be made upon them so that they will contain or deliver true volumes of liquid.

Examination of the Balance.

In order to familiarize himself with the chemical balance and judge of its capabilities, the student may examine it in the following way.

(i) *To find the zero-point of the balance.*

It was pointed out in Part I of this book (p. 7) that when the beam of the balance is swinging freely the pointer moves over the scale in the manner of a swinging pendulum, the amplitude of whose swing diminishes regularly as it approaches a condition of rest; and that consequently it is not strictly accurate to consider weights and object counterpoised when the pointer has been observed to swing equally on either side of the centre of the scale. True equipoise is indicated not by equality of swing in one case, but by equal diminutions of swing on either side, which end in the pointer coming to rest over the central point of the scale. On the scale there are ten divisions on each side of the centre, so that, counting from the left, the central mark is numbered 10. For 10 to be the zero-point of the balance, i.e. the mark towards which the pointer tends to settle down when swinging, the marks reached by the pointer must resemble those indicated in the following example:

Left.	Right.	Sum.	Mean = Zero-point.
4·6	—	—	—
(4·8)	15·2	20·0	10·0
5·0	(15·0)	20·0	10·0
(5·2)	14·8	20·0	10·0
5·4	—	—	—

The mean of two successive readings on left or right is shown by a figure in brackets, and it will be seen that in this case the mean of figures in each horizontal line is 10·0. This is the zero-point of the balance. The zero-point is altered, and the balance adjusted by moving to right or left a small metal flag fixed above the point of suspension, or else by rotating a screw at the end of the beam. It is unnecessary for the balance to be adjusted to give a zero-point at 10·0; this point may lie conveniently anywhere between say 8·0 and 12·0. It is only necessary to observe that the same zero-point is reached when the pans are loaded as when they are empty, to know that the total weight on one side of the balance is equal to that on the other.

The student should find the zero-point of the balance he is to use by observing the movements of the pointer when the beam is swinging, and recording them in the above manner. A distinction should be drawn between resting-point and zero-point. The *resting-point* is the point at which the balance will come to rest under any convenient condition; the *zero-point* is the resting-point when the balance is unloaded.

(ii) *To find the sensitiveness of the balance.*

The sensitiveness of a balance, that is the degree to which it responds to a very small change in weight, may be defined as the displacement of the resting-point caused by an alteration in weight of one milligram. Sensitiveness varies slightly with load and theoretically should increase with it, but it does not vary constantly because it is dependent not only on mechanical principles, but also on the material of which the balance is constructed. The variation of sensitiveness with load will probably be found to be negligible. The student should determine the sensitiveness with a load of 1 gm. on each pan, and also with the 50-gm. weight on one pan and the remainder of the brass weights on the other.

The following is a record of the sensitiveness of a balance carrying 1 gm. in each pan, the 10-mgm. rider being placed on the graduated scale first one division to the right, then one division to the left of the point of suspension.

SENSITIVENESS OF A BALANCE

1 Gm. in each Pan.		1 Mgm. on Right.		1 Mgm. on Left.	
Right.	Left	Right.	Left.	Right.	Left.
—	16·1	—	15·2	—	16·3
2·1	(15·7)	0·4	(15·0)	4·2	(16·15)
(2·4)	15·4	(0·7)	14·8	(4·45)	16·0
2·7	—	1·0	—	4·7	—
Resting-point $= \frac{17\cdot8}{2} = 8\cdot9$		Resting-point $= \frac{15\cdot4}{2} = 7\cdot7$		Resting-point $= \frac{20\cdot4}{2} = 10\cdot2$	
		Sensitiveness $= 8\cdot9 - 7\cdot7 = 1\cdot2$		Sensitiveness $= 10\cdot2 - 8\cdot9 = 1\cdot3$	
		Mean sensitiveness = 1·25			

Sensitiveness and Accurate Weighing.

Since an alteration of weight of 1 mgm. causes the resting-point to alter by, say, 1·25 scale divisions, an accurate estimation of the weight of an object can be made by counterpoising it with weights to the nearest milligram, and then seeing what ratio the difference between the resting-point when the pans are empty and the observed resting-point bears to 1·25. Thus if this difference is found to be $\pm 0\cdot25$ scale division, the weight to be added is $\pm\frac{0\cdot25}{1\cdot25} = \pm 0\cdot2$ mgm.

This principle is employed in the calibration of weights which follows.

Principles and Process of Calibration of Weights.

First it is necessary to distinguish between the three 1-gm. weights, and also between the two 10-gm. weights. In the better sets the weights will be found to be marked where necessary with asterisks, thus: 1, 1*, 1**; 10, 10*; otherwise the student must make faint scratches upon them with the tip of a knife-blade, for the purpose of indentification.

Since there is no pre-existing standard with which to compare any of the weights—unless an external standard is specially supplied

—the unmarked 1-gm. weight is chosen arbitrarily as the experimental standard of reference for all the other weights. As a matter of fact no external standard is needed, because what is required is not the value of each weight with reference to such a standard, but the relative values of the weights among themselves. For this an internal standard is needed, and is devised in the following way.

The sum of all the brass weights is nominally 100 gm., but will almost certainly be found not to be actually so with reference to the chosen 1-gm. standard. The procedure, therefore, is to correct every weight by the amount necessary to make the sum equal to 100 gm. Thus to each weight, except the chosen reference weight, are applied two corrections; first a correction to reduce the weight to the exact multiple of the 1-gm. weight which it is supposed to be; second a correction, which applies equally to the 1-gm. standard itself, of such a magnitude as to make the sum of the weights 100 gm.

For example, if the 20-gm. weight is found to be equal to 20 × 1 gm. $\pm x$ gm., a correction of $\mp x$ gm. will put the 20-gm. weight into a proper relation to the chosen 1-gm. weight; but when analogous corrections are applied to all the other weights the sum of the corrected values will not be equal to 100 gm. unless it should happen that the algebraic sum of these corrections is zero. Now suppose that this algebraic sum is not zero, but $\pm y$ gm.; then $\mp y$ gm. is an additional weight to be divided amongst the weights according to their magnitude, so that their sum may amount to exactly 100 gm. To the 1-gm. weight $\mp\frac{y}{100}$ must be added, to the 20-gm. weight $\mp\frac{20y}{100}$, and so on. For if the 1-gm. weight is $\pm\frac{y}{100}$ in error, the 20-gm. weight, whose value was computed with reference to this 1-gm. weight, must contain 20 times this error in addition to its own intrinsic error. So the total correction to be applied to the 20-gm. weight is $\left(\mp x \mp \frac{y}{5}\right)$. These considerations should be clear from the following table, which records the actual results of a calibration of weights, and shows first the errors on the weights with reference to the arbitrary standard, and the sum of these errors ($-0{\cdot}0040$ gm.), next the actual value of each weight adjusted so that the sum of the weights is equal to 100 gm., as the result of

Nominal Values of Weights.	Observed Results of Double Weighings.		Values in Terms of 1-gm. Weight.	Actual Values.	Error (to 4 Decimal Places).
1			1 Standard	1 +·00004= 1·00004	Nil
1*	1	—·0002	1—·0002	1 —·0002+·00004= 0·99984	—·0002
1**	1	±·0000	1±·0000	1 +·00004= 1·00004	Nil
2	1+1*	±·0000	2×1—·0002	2 —·0002+·00008= 1·99988	—·0001
5	2+1+1*+1**	+·0002	5×1—·0002	5 —·0002+·00020= 5·00000	Nil
10	5+2+1+1*×1**	+·0003	10×1—·0003	10 —·0003+·00040=10·00010	+·0001
10*	10	+·0004	10×1+·0001	10* +·0001+·00040=10·00050	+·0005
20	10+10*	—·0010	20×1—·0012	20 —·0012+·00080=19·99960	—·0004
50	20+10+10*+5+2+1+1*+1**	—·0010	50×1—·0020	50 —·0020+·00200=50·00000	Nil
100			100×1—·0040	100·00000	

distributing 0·0040 gm. between the weights according to their magnitude, and finally the error on each weight according to this adjustment.

The student will learn from the table opposite the actual mode of procedure. It will be noticed that each weight in turn is balanced against the sum of the weights which precede it. Double weighing is adopted to eliminate any error due to inequalities in the lengths of the balance arms, the recorded difference being the mean of the differences observed in the two weighings. Consider the two weights 1 and 1* gm. The sensitiveness of the balance was found to be 1·2 scale divisions per milligram, and the zero-point with empty pans was 8·7. The following observations were made:

	Left, 1 gm. Right, 1* gm.	Left, 1* gm. Right, 1 gm.
Resting-point	8·9	8·45
Whence	1^{*} gm. $= 1 - 0{\cdot}0002$ gm.	1 gm. $= 1^{*} + 0{\cdot}0002$ gm.

Since the mean of the two resting-points is practically equal to the zero-point, there is no appreciable difference in length between the balance arms.

In the case of the 1-gm. and 1**-gm. weights both resting-points were found to be 8·6, and that is why the weights were regarded as equivalent; for if weights after transposition give the same resting-points as before they must be equivalent whether the balance arms are of equal length or not.

The error on a weight in terms of the standard 1 gm. is obtained by adding the observed error, recorded in the second column, to the separate values, in terms of this 1 gm., of the weights which taken together counterpoise the weight in question. For example, consider the 5-gm. weight:

$$
\begin{aligned}
5\text{ gm.} &= 2 + 1 + 1^{*} + 1^{**} + 0{\cdot}0002 \\
&= 2 \times 1 - 0{\cdot}0002 + 1 + 1 - 0{\cdot}0002 + 1\,(\pm 0{\cdot}0000) + 0{\cdot}0002 \\
&= 5 \times 1 - 0{\cdot}0002.
\end{aligned}
$$

Again, since the sum of the weights in terms of the standard 1 gm. shows a deficiency in the above case of 0·004 gm., this weight is distributed between the weights as shown in the last column but one, the 1-gm. weights receiving 0·00004 gm., the 10-gm. weights 0·0004 gm., and so on. Consequently the sum of the finally corrected weights is necessarily equal to 100 gm. In the last column are the corrections for each weight to the fourth place of decimals.

Calibration of a Burette.

Graduated vessels are required to contain or deliver their stated volumes of liquids at an agreed temperature which is generally 15° C.*

Now suppose that a volume of water is delivered from a burette, which, according to the indication of the instrument, is 5 c. c.; how can it be determined whether this is the volume actually delivered?

The volume of 5 c. c. of water is determined by weighing it; but weight in grams expresses volume in cubic centimetres at 4° C., since it is at this temperature that 1 gm. of water measures 1 c. c. (see note). Therefore the volume of the water at t° C. is found by dividing its weight by the relative density of water at that temperature, or multiplying the same by the specific volume.

Two other considerations, however, enter into the problem of determining the correction to be applied to a burette or other graduated vessel after weighing a measured volume of water delivered from it. The first is a correction for the buoyancy of the air displaced by the weights and by the water at the time of weighing, since weighing is not performed *in vacuo*, nor is the water of the same density as the brass of which the weights are made. The second consideration has reference to the expansion of the glass from its state at 4° C. to that at the temperature of measuring and weighing (t° C.), since the vessel will hold a larger volume of water at t° C. than at 4° C.

---

* This statement is confusing because it is the mass of liquid delivered from the same burette which changes with temperature, not its volume, except that change of temperature causes a small change in the capacity of the containing vessel.

The chief requirement for graduated vessels used in ordinary volumetric analysis is that they agree among themselves, when their graduations are compared by means of water or other liquid whose temperature remains constant whilst the comparison is being made. It is only when the amount of substance in a stated volume of a given solution has to be found that the relation of the volumes indicated on the graduated vessels to true volumes need be known. Nevertheless, since it is convenient to calibrate a burette by weighing the water it contains, it becomes necessary to relate volume to mass.

The litre was originally supposed to be identical with the cubic decimetre or 1000 c.c.; and it was established by weighing water at 4° C., the temperature of maximum density, against the standard " kilogramme des Archives " in Paris. Accurate investigation, however, has shown the following discrepancy exists between the litre so established and the cubic decimetre:

1 litre = 1·000027 cubic decimetre = 1000·027 c. c.

To avoid this discrepancy it has been proposed to adopt the litre as the standard of volume and abolish the cubic decimetre as the standard, thus sacrificing the relation between mass and length, by referring the standard volume to the standard kilogram instead of the cubic decimetre. So the millilitre (ml.) would be substituted for the cubic centimetre (c. c.), which would disappear. Since, however, the difference between these two units is only 27 parts per million, it is far too small to affect the practical measurements of volumetric analysis. The Chemical Society advises chemists to use whichever unit is appropriate in any case. Generally they may be used indiscriminately, and no change from the c. c. has been adopted in this book.

It would be troublesome to have to apply all these corrections separately to the ascertained weights of certain volumes of water delivered from a graduated vessel; consequently a single correction has been calculated for each observed temperature, to include them all. The volumes occupied by 1 gm. of water at different temperatures, i.e. the specific volumes, as shown in the following table, provide factors by which the weights of water delivered from the glass vessel are converted into the cubic centimetres the water would occupy in the vessel at the temperature of measuring and weighing.

Temperature of Measuring and Weighing.	Cubic Centimetres occupied by 1 Gm.	Temperature of Measuring and Weighing.	Cubic Centimetres occupied by 1 Gm.
10° C.	1·0014	18° C.	1·0024
11	1.0015	19	1·0025
12	1·0016	20	1·0027
13	1·0017	21	1·0029
14	1·0018	22	1·0031
15	1·0019	23	1·0033
16	1·0021	24	1·0035
17	1·0023	25	1·0037

Procedure.—Thoroughly clean a burette by washing it with alkali or soap and water;* rinse it free from alkali, and ascertain that the tap is properly greased. Then fill the burette with distilled water, support it in a stand, hang a thermometer beside it, and bring the whole near to the balance case. Obtain a small, thin flask, to hold rather more than 50 c. c., and provide it with a rubber stopper.

After weighing the empty flask, allow to run into it from the burette successive volumes of 5 c. c. of water, weighing the flask and its contents after each addition so that the quantities of water weighed are approximately 5, 10, 15 . . . 50 gm.

Great care must of course be taken to measure the water accurately; it is well to fix a strip of white paper behind the burette, also to use a lens, and above all carefully to avoid parallax. Note

---

* Chromic acid mixture, i.e. a mixture of potassium dichromate solution and sulphuric acid, is useful for cleaning glass contaminated with oxidizable and especially organic matter. It may be used here if necessary.

the temperature at which the water is measured and weighed. Finally, convert each weight of water into the corresponding volume at t° C. by employing the factor appropriate to the temperature as shown in the above table. The following is an example of results that have been obtained.

CALIBRATION OF BURETTE (Temperature, 18° C.; factor, 1·0024)

Burette Reading.	Weight of Flask and Contents.	Weight of Water.	Volume Corrected to 18° C.
0	25·313	—	—
5 c. c.	30·315	5·002	5·014
10	35·302	9·989	10·013
15	40·337	15·024	15·06
20	45·337	20·024	20·07
25	50·350	25·037	25·10
30	55·352	30·039	30·11
35	60·336	35·023	35·11
40	65·359	40·046	40·14
45	70·381	45·068	45·18
50	75·413	50·126	50·25

The result of the calibration can be expressed graphically, the volumes being plotted as abscissæ and the errors as ordinates. If this is done the error on any volume between those in the table is easily found.

Standardization of a Pipette.

The standardization of a pipette consists in discovering if the graduation mark upon it is correct, and if not, correcting it.

A 20-c. c. pipette is the most useful for general purposes, and this may be standardized in the following way. First clean the pipette very thoroughly by washing it with soap solution, and then, after rinsing, with chromic-acid mixture, each solution in turn being allowed to remain in the pipette for a few minutes. To retain liquid in the pipette fix to its upper end a piece of rubber tubing provided with a screw clip or burette clip. After these solutions have been used, thoroughly cleanse the pipette with distilled water.

Now gum a strip of paper longitudinally on the upper part of the pipette, and across the graduation mark; on this paper marks will be made to indicate the levels of the meniscus when water is delivered in successive trials during standardization.

It is first necessary to decide how the pipette is to be used, that is how the liquid measured in it is to be delivered. The method described on p. 12 of Part I of this book should be followed; i.e. the liquid should be allowed to run out freely, a process which will occupy about 30 sec., and subsequently to drain for 15 sec., the delivery being finished by bringing the tip of the pipette into contact with the surface of the liquid, or against the wet side of the containing vessel. Unless a uniform method of delivery is adopted the refinement of standardizing a pipette is useless.

The pipette is standardized by the use of distilled water, which is delivered into a small stoppered and tared flask, and then weighed. It is necessary to observe the temperature of the water, and to correct its estimated weight by a factor given in the table on p. 9, in order to discover its volume. Therefore carry out the process near to the balance, having plenty of water in a vessel ready, and allowing it to stand for a sufficient time to attain the temperature of the balance room. A 100-c. c. stoppered flask is a convenient vessel in which to weigh the water.

Record the temperature of the water; then measure and deliver into the flask a volume indicated by the original graduation on the pipette. Correct the weight of the water for temperature; e.g. if the temperature was 18° C. the weight in grammes must be multiplied by 1·0024 to give volume in cubic centimetres. The allowable error for a 20-c. c. pipette is 0·025 c. c. If the error is not larger than this the original graduation mark may be taken as correct; but if it is draw a thin line on the paper above or below this mark as the case may require, and again measure and weigh the water. Continue these trials until a sufficiently correct result has been obtained. Then gum two strips of paper round the tube just above and below the correct graduation mark so as to leave a narrow space where the glass may be etched. Brush melted paraffin wax over the paper, and when this is set lay bare with a knife blade the glass where the graduation mark is to be. Then apply hydrofluoric acid solution with a camel-hair brush so as to etch the glass. In a few minutes remove the wax and paper; the operation is now finished.

Standardization of a Measuring Flask.

A measuring flask, say of 500 c. c. capacity, may be standardized in the following way.

First it is necessary to have a balance capable of weighing the flask full of water, and weights corresponding, so that the flask can be weighed accurately to a centigram or less, empty and when containing the water.

Thoroughly clean the flask, dry it, and weigh it empty without the stopper. Then place on the right-hand pan of the balance weights to counterpoise the flask containing 500 c. c. of water measured at the temperature of the balance room. The weight of this water is ascertained from the table given on p. 9; e.g. 500 c. c. of water at 18° C. will weigh in air against brass weights: $\frac{500}{1{\cdot}0024} = 498{\cdot}803$ gm.

Fill the flask with water at the observed temperature to within a short distance of the existing graduation mark, place it on the balance, and then by means of a pipette with a fine point, or a piece of glass tubing drawn out on purpose, add or remove water until the weights are counterbalanced. Take care, however, that the neck of the flask above the level of the water is dry. It is well to dry it with filter paper or a wad of cotton wool, and then to add the last drop or two of water required without touching the dry glass. When the adjustment has been made carefully gum a piece of paper round the neck of the flask so that its upper edge is horizontal and just tangential to the meniscus formed by the water; afterwards empty the flask and allow it to drain. Then cover the label, and the glass a little way above it, with paraffin wax. Next, by means of a knife make an incision in the wax all round the top of the label, and apply hydrofluoric acid. After a few minutes wipe off the acid, then warm the wax and remove it, leaving the flask clearly etched at the proper graduation mark.

VOLUMETRIC ANALYSIS

ACIDIMETRY AND ALKALIMETRY

The preparation, standardization, and use of a decinormal solution of sulphuric acid have been described in Part I of this book. A number of exercises, however, remain to be carried out by the student in order that he may learn more fully the scope of the processes of acidimetry and alkalimetry. Since decinormal solutions of acid and alkali have been employed hitherto, it will be convenient now to prepare a normal solution of acid, and then to dilute it to decinormal strength as required.

Preparation and Standardization of approximately Normal $\left(\frac{N}{1}\right)$ Hydrochloric Acid.

Preparation.—The strength of a solution of hydrochloric acid can be ascertained with considerable accuracy by determining its density, since tables connecting these two properties have been compiled with much care. Therefore it is possible to prepare a litre of hydrochloric acid solution of almost exactly normal strength by taking the density of the concentrated or diluted acid, calculating from its ascertained strength the volume of acid required, carefully measuring this volume, and diluting it to a litre.

Employ the purest hydrochloric acid obtainable, determine its density and its strength from tables. Calculate what volume of the acid will contain 36·47 gm. of hydrogen chloride; measure this volume by means of a burette, and dilute it with distilled water to a litre.

Standardization.—Hydrochloric acid solution can be standardized volumetrically by means of a solution of pure sodium carbonate, or gravimetrically by precipitating the chloride with silver nitrate and weighing the silver chloride; but a convenient method which introduces a fresh principle, consists in using pure Iceland spar, which by dissolving in hydrochloric acid produces a solution neutral to methyl orange. Thus the loss which a weighed mass of the spar undergoes when some of it dissolves in a measured volume of hydrochloric acid so as to neutralize the acid, represents a weight of calcium carbonate equivalent to the hydrogen chloride present.

To carry out the process select a clear crystal of Iceland spar weighing not less than 5 gm., wash it with a little dilute hydrochloric acid to remove any powder clinging to it, and then with water to remove the acid; dry the spar in the steam oven and weigh it when cold. Place 20 c. c. of the nearly normal hydrochloric acid in a narrow-necked flask, add a few drops of methyl orange, slide the spar down the side of the flask into the acid, quickly place a funnel in the neck of the flask to prevent loss of acid spray by effervescence, and allow the reaction to proceed. Place the flask on the water bath for a short time to hasten the reaction as it slows down, and when it is nearly over rinse down into the solution any acid spray on the funnel and sides of the flask.

Allow the spar to remain in the solution for some hours, or overnight, until the colour of the indicator shows that all the acid has been neutralized; then remove the spar, taking care that no small pieces remain in the flask, and wash, dry, and weigh it. Calculate from the loss in weight of the spar the normality of the acid. Since the equivalent weight of calcium carbonate is 50, just 1 gm. of the spar will be dissolved by 20 c. c. of normal acid.

Carry out the experiment in duplicate, and also confirm the result by titrating the acid into some normal sodium carbonate solution prepared from the pure ignited salt.

Dilution of Normal Hydrochloric Acid.

If reliable graduated vessels are available the $\frac{N}{1}$ acid can be diluted to $\frac{N}{2}$, $\frac{N}{5}$, or $\frac{N}{10}$ strength, without further standardization. Thus if the burette has been calibrated so that exactly 50 c. c. can be delivered from it, and the 500 c. c. flask has been standardized so as to contain the professed volume, 500 c. c. of $\frac{N}{10}$ acid can be quickly prepared by diluting 50 c.c. of the acid of $\frac{N}{1}$ strength. Even if the vessels have not been examined previously the error on dilution will probably be small if instruments of the best quality are used, though in this case it is wiser to standardize the diluted acid before use in order to secure accurate results.

EXERCISES IN ACIDIMETRY AND ALKALIMETRY

Certain exercises in the use of decinormal acid and alkali solutions have already been described, and a list of these is given on p. 87 of Part I. The following further estimations will now be described:

1. Alkali hydroxide and carbonate in solution.
2. Alkali carbonate and bicarbonate in solution.
3. Lime and chalk in a mixture of the two.
4. Temporary and permanent hardness of water.
5. Copper in copper sulphate solution by titrating sulphuric acid after precipitating copper with hydrogen sulphide.
6. Total alkali and combined boric acid in borax.
7. Potassium persulphate by titrating sulphuric acid developed on boiling.
8. Nitrate after reduction to ammonia.

1. Estimation of Alkali Hydroxide and Carbonate in Solution.

Two methods are available for estimating alkali hydroxide and carbonate when mixed in solution; they are those of (i) Winkler and (ii) Warder.

(i) *Method of Winkler.*—The student already knows that when a solution of alkali is titrated with standard acid in presence of methyl orange the total alkali is indicated irrespective of whether it is present as hydroxide or carbonate. If, therefore, a method of estimating the hydroxide alone can be found, the difference between total alkali and the hydroxide will be the carbonate. The method of Winkler depends upon precipitating the carbonate from solution by means of barium chloride, which does not affect the hydroxide. If the solution is then titrated with decinormal hydrochloric acid in presence of the precipitated barium carbonate, together with the excess of barium chloride, and with phenolphthalein as indicator, the colour of the indicator will be discharged when all the hydroxide has been neutralized, because the acid will only then begin to liberate carbonic acid from the precipitated carbonate. Care must be taken to add the acid slowly, and with shaking or stirring, so that the precipitate is not attacked and carbon dioxide lost.

Procedure (α).—Titrate 20 c. c. of the mixed solution of alkali hydroxide and carbonate with decinormal hydrochloric acid, using methyl orange as indicator. Let *a* c. c. of acid be used.

(β) Add to 20 c. c. of the mixed solution excess of a neutral solution of barium chloride followed by a few drops of phenolphthalein. Titrate the liquid slowly with decinormal hydrochloric acid, constantly rotating the flask, until the indicator is decolorized. Let *b* c. c. of acid be required.

Then *b* c. c. $\frac{N}{10}$ acid are equivalent to the alkali hydroxide, and $(a - b)$ c. c. to the alkali carbonate in 20 c. c. of solution.

From the results calculate the weights of alkali hydroxide and carbonate in a litre of the given solution.

An alternative method is to add excess of barium chloride solution to, say, 50 c. c. of the alkali solution, dilute to a suitable volume with air-free water, allow the precipitated barium carbonate to settle, or filter it off, and then titrate an aliquot portion of the supernatant liquid or the filtrate with decinormal acid, using methyl orange as indicator.

(ii) *Method of Warder.*—It was shown on pp. 85–6 of Part I of this book that when a mixed solution of alkali hydroxide and carbonate is titrated with standard acid, phenolphthalein and methyl orange being used successively as indicators, the phenolphthalein is decolorized when all the hydroxide and half the carbonate has been neutralized, and the methyl orange, added subsequently, indicates when the remaining half of the carbonate has been neutralized. The method of Warder consists in the use of the two indicators in this manner, the successive reactions being, in the case, for example, of the sodium compounds:

$$\begin{aligned} NaOH + HCl &= NaCl + H_2O \\ Na_2CO_3 + HCl &= NaCl + NaHCO_3 \\ NaHCO_3 + HCl &= NaCl + H_2CO_3. \end{aligned}$$

It must be remembered, however, that for phenolphthalein to indicate the proper point, the $NaHCO_3$ produced in the second reaction, and the H_2CO_3 in the third must remain undecomposed, i.e. no carbon dioxide must leave the solution. This condition is secured by having the solution highly diluted and by cooling it nearly to 0° C., by immersing the flask containing it in broken ice during titration. The presence of sodium chloride also promotes the stability of $NaHCO_3$ by suppressing its ionization.

Procedure. — Place 20 c. c. of the mixed solution of alkali hydroxide and carbonate in a suitable flask, dilute it to about 100 c. c. with ice-cold, air-free distilled water, and add about 5 gm. of pure neutral sodium chloride; then immerse the flask in broken ice, or in water cooled to 0° C. by pieces of floating ice, contained in a suitable trough. Add phenolphthalein, and titrate the solution with decinormal acid whilst carefully rotating the flask.* When the crimson colour of the phenolphthalein is discharged read the burette; then add methyl orange to the colourless solution and continue the titration until this indicator shows the sign of acidity.

Let *a* c. c. of decinormal acid be required to discharge the colour of phenolphthalein, and a further *b* c. c. to complete the titration after the addition of methyl orange, the total volume of acid used being $(a + b)$ c. c. Then according to the principle already explained in Part I (q.v.):

$2b$ c. c. $\frac{N}{10}$ acid are equivalent to the alkali carbonate in 20 c. c. of solution.

$[(a + b) - 2b] = (a - b)$ c. c. $\frac{N}{10}$ acid are equivalent to the alkali hydroxide in 20 c. c. of solution.

From these results calculate as before the weights of alkali carbonate and hydroxide in 1 litre of the given solution.

2. Estimation of Alkali Carbonate and Bicarbonate.

The mixture of alkali carbonate and bicarbonate may be given solid or in solution. If the former, the mixture must be dissolved in well-cooled air-free distilled water; for if the water is warm some of the bicarbonate will be decomposed, and if it contains dissolved

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* An additional refinement consists in attaching a narrow tube to the end of the burette, so as to deliver the acid beneath the surface of the solution in the flask.

carbon dioxide some of the carbonate will be converted into bicarbonate.

There are two methods of estimating carbonate and bicarbonate mixed in solution, also associated with the names of Winkler and Warder.

(i) *Method of Winkler.*—Barium chloride is used for the same purpose in this method as when alkali hydroxide and carbonate are being estimated; and in order that this may be done the mixture of carbonate and bicarbonate is converted into a mixture of carbonate and hydroxide by adding a known excess of alkali hydroxide to react with the bicarbonate thus:

$$NaHCO_3 + n\,NaOH = Na_2CO_3 + H_2O + (n - 1)\ NaOH.$$

A difficulty arises with regard to the alkali hydroxide solution, because this is very likely to contain a little carbonate. The presence of carbonate is immaterial, however, so long as the actual amount of hydroxide present is known. Therefore an approximately decinormal solution of sodium hydroxide is prepared, and 20 c. c. of it are titrated with decinormal acid with the use of the two indicators; the actual number of cubic centimetres of decinormal NaOH corresponding to the NaOH in 20 c. c. of the prepared alkali can then be calculated. It is convenient to add a volume of alkali solution containing NaOH equivalent to the acid required for complete neutralization of 20 c. c. of the mixed solution; the acid needed to neutralize the excess of NaOH is then equivalent to the sodium carbonate present, as will appear below:

Let a c. c. of $\frac{N}{10}$ acid be required to neutralize total alkali in 20 c. c. of given solution.

Let b c. c. of $\frac{N}{10}$ NaOH be added, followed by excess of barium chloride.

Let b_1 c. c. of $\frac{N}{10}$ acid be required to neutralize the excess of NaOH as indicated by phenolphthalein.

Then $(b - b_1)$ c. c. of $\frac{N}{10}$ acid represent the bicarbonate present, and $a - (b - b_1) = (a - b + b_1)$ c. c. of $\frac{N}{10}$ acid represent the carbonate present.

If b is made equal to a, then b_1 c. c. of $\frac{N}{10}$ acid represents the carbonate, as stated above.

Procedure.—Have the decinormal acid ready, and prepare a convenient quantity of nearly decinormal sodium hydroxide solution. Titrate this solution, cooled in ice, with the acid, using both indicators, and calculate how many cubic centimetres of $\frac{N}{10}$ NaOH 20 c. c. of it may be supposed to contain. Next titrate 20 c. c. of the mixed carbonate and bicarbonate solution with the acid (a c. c.), using methyl orange as indicator; then to another 20 c. c. of the mixed solution add from a burette as much of the prepared alkali solution as would contain a c. c. of $\frac{N}{10}$ NaOH solution, followed by barium chloride and phenolphthalein. Finally titrate the turbid liquid with the $\frac{N}{10}$ acid till the crimson colour of the indicator is discharged.

From the results obtained calculate the weight of Na_2CO_3 and $NaHCO_3$ in a litre of the solution, remembering that 1 c. c. of $\frac{N}{10}$ acid neutralizes 0·0053 gm. Na_2CO_3 and 0·0084 gm. $NaHCO_3$.

(ii) *Method of Warder.*—As in the case of estimating a mixture of alkali hydroxide and carbonate, this method consists in titrating the mixed solution with decinormal acid with the successive use of phenolphthalein and methyl orange. The reactions are:

$$Na_2CO_3 + HCl = NaCl + NaHCO_3$$
$$NaHCO_3 + HCl = NaCl + H_2CO_3.$$

Phenolphthalein loses its colour when free carbonic acid (H_2CO_3) appears in the liquid, i.e. immediately after all the carbonate has been turned into bicarbonate, which is when the former is half neutralized. From this it follows that twice the number of cubic centimetres required to decolorize the phenolphthalein stands for the sodium carbonate in the solution, and the remainder of the acid added before methyl orange changes stands for the bicarbonate. Thus if bicarbonate is present with carbonate the phenolphthalein change occurs before the half-neutralization point; whilst if the solution contains only carbonate this change occurs at the half-neutralization point.

Procedure.—Place in a flask 20 c. c. of the mixed solution to be titrated, dilute well, and add salt; then immerse the flask in ice-cooled water, and having added phenolphthalein slowly titrate the solution with decinormal acid; when the colour of this indicator has been discharged add methyl orange, and finish the titration. It is unnecessary in the latter part of the titration to maintain the solution below atmospheric temperature.

3. Estimation of Lime and Chalk in a Mixture of the two.

The method to be employed in this estimation is essentially that of Winkler as applied to alkali hydroxide and carbonate. It will be remembered that alkali hydroxide can be titrated in presence of carbonate when the latter has been converted into insoluble barium carbonate, phenolphthalein indicating when the latter begins to be attacked by the acid. Similarly lime can be titrated in presence of chalk; and then the total neutralizing power can be estimated separately by dissolving the mixture in excess of decinormal hydrochloric acid, and titrating the unneutralized acid with decinormal sodium hydroxide, methyl orange being the indicator.

Procedure.—If the specimen to be analysed is partially burnt limestone, in lumps, it must be reduced to an impalpable powder by first breaking it in a percussion mortar or clean iron mortar, and then grinding in an agate mortar the coarse powder thus produced. The thoroughly mixed powder must be preserved in a stoppered weighing bottle so that it may not absorb atmospheric water or carbon dioxide. Accurately weigh about 2 gm. of the powder, mix it into a paste with air-free cold water, and dilute the mixture to 500 c. c. with similar water.

Estimation of Free Lime.

Measure with a pipette 25 or 50 c.c. of the turbid liquid, in which the undissolved matter is uniformly suspended, add phenolphthalein, and titrate slowly with decinormal hydrochloric acid till the colour of the indicator disappears. Repeat the titration altering the volume of the liquid used, if necessary, so that about

20 c. c. of decinormal acid are required. From the result calculate the percentage of free lime (CaO) in the mixture, remembering that 1 c. c. $\frac{N}{10}$ acid neutralizes 0·0028 gm. of CaO.

Estimation of Chalk.

Measure 25 c. c. of the turbid liquid, containing 0·1 gm. of the powder; add to it 50 c. c. of $\frac{N}{10}$ hydrochloric acid, and boil until carbon dioxide gas ceases to be evolved. Cool, add methyl orange, which should show an acid reaction, and titrate the excess of acid with $\frac{N}{10}$ sodium hydroxide. From the volume of acid thus found to have been neutralized by the lime and chalk together, subtract that which was neutralized by the lime alone in the same volume of turbid liquid. The difference is the acid neutralized by the calcium carbonate, of which 0·005 gm. corresponds to 1 c. c. of $\frac{N}{10}$ acid. Calculate the percentage of calcium carbonate in the mixture.

4. Estimation of Temporary and Permanent Hardness of Water.

The student may be reminded briefly that the temporary hardness of natural waters is caused by calcium or magnesium carbonate held in solution by carbonic acid, i.e. by the bicarbonates of these metals; whilst the permanent hardness is due to the sulphates, or less frequently the chlorides of the same metals.

Temporary Hardness.—The temporary hardness of water is estimated directly by titrating a suitable volume of the water, usually 250 c. c., with decinormal acid, methyl orange being used as indicator. This hardness is usually expressed as parts of $CaCO_3$ per 100,000 of water. Thus suppose 10 c. c. of $\frac{N}{10}$ HCl were required to neutralize the $CaCO_3$ in solution in 250 c. c. of water, the parts per 100,000 of $CaCO_3$—since 1 c. c. $\frac{N}{10}$ acid neutralizes 0·005 gm. $CaCO_3$—

would be: $0{\cdot}005 \times 10 \times 400 = 20$ parts. If 500 c. c. of water are taken the volume of decinormal acid used is numerically equal to the temporary hardness expressed as parts of $CaCO_3$ per 100,000.

Procedure.—Carry out the titration by placing in a suitable flask 250 or 500 c. c. of the water—or less if the water is very hard—adding methyl orange to produce a very pale yellow colour before running in the acid. It is a little difficult to decide the end point, and it is therefore well to have alongside for comparison a similar flask with an equal volume of similarly coloured water.

Permanent Hardness.—The permanent hardness cannot be estimated directly by titration because the cause of it is a neutral salt; but it is determined by finding how much sodium carbonate is used up in precipitating the salt, thus:

$$CaSO_4 + Na_2CO_3 = CaCO_3 + Na_2SO_4.$$

The temporary hardness must be got rid of at the same time that the permanent hardness is precipitated; therefore excess of decinormal sodium carbonate solution is added to a measured volume of water, which is then boiled for half an hour; or if magnesium salts are present the liquid is evaporated to dryness, because these salts are more difficult to precipitate with sodium carbonate than calcium salts. The solution is then filtered, after the addition of water if necessary, the residue is washed with boiled water, and the filtrate, after cooling, is made up to the original volume with cold air-free water. It is necessary for the diluting water to be free from carbon dioxide, or it would redissolve some of the precipitated carbonate. The prepared solution now contains excess of sodium carbonate, which can be titrated with decinormal acid, methyl orange being the indicator. It is usual to titrate an aliquot part of this solution, corresponding to, say, 10 c. c. of the sodium carbonate added; if then a c. c. of $\frac{N}{10}$ acid are required, the amount of sodium carbonate used up in precipitating the permanent hardness in the corresponding volume of the water was $(10 - a)$ c. c.; and from this figure the permanent hardness in 100,000 parts of the water can be calculated, being expressed in terms of calcium carbonate.

Procedure.—Place 250 c. c. of the water in a suitable evaporating basin, add to it 50 c.c. of decinormal sodium carbonate solution, and boil gently for half an hour: if. however, magnesium salts are known or believed to be present evaporate the solution to dryness. Add boiled water and filter, receiving the filtrate in a 250-c. c. flask. Thoroughly wash the residue, and dilute the filtrate when cold to 250 c. c. Measure 50 c. c. of this solution, which corresponds with 50 c. c. of the water and 10 c. c. of the sodium carbonate solution added, and titrate it with decinormal hydrochloric acid in presence of methyl orange. Repeat the titration. If a c. c. of decinormal acid are required in each case, the permanent hardness of the water, expressed as parts of $CaCO_3$ per 100,000, is given by the expression:

$$(10 - a) \times 2000 \times 0{\cdot}005 = 10(10 - a).$$

5. Estimation of Copper in Copper Sulphate.

Various estimations of metals in their sulphates, chlorides, or nitrates can be carried out by precipitating the metallic sulphide by means of hydrogen sulphide, as for example with copper sulphate:

$$CuSO_4 + H_2S = CuS + H_2SO_4.$$

The precipitated sulphide is filtered off, and the free mineral acid estimated in the filtrate by titration with standard alkali in presence of methyl orange. This method is most suitably applied to normal salts which are soluble in water, and yield an insoluble sulphide. It cannot be applied to basic salts of unknown composition; for instance it could not be used to estimate the copper in a basic sulphate or carbonate of this metal, because the mineral acid produced by interaction with hydrogen sulphide would be a measure only of the amount of the corresponding acidic radicle in the salt. The method may of course be applied in such case to estimate this acidic radicle. The production of a basic salt by hydrolysis previous to reaction with hydrogen sulphide does not invalidate the method, however, because it is immaterial whether the free acid is liberated by means of water or hydrogen sulphide. Thus bismuthous nitrate, $Bi(NO_3)_3{\cdot}5H_2O$, would produce its equivalent of nitric acid by the successive action of water and hydrogen sulphide thus:

$$\begin{aligned} 2Bi(NO_3)_3 + 4H_2O &= 2Bi(OH)_2NO_3 + 4HNO_3 \\ 2Bi(OH)_2NO_3 + 3H_2S &= Bi_2S_3 + 4H_2O + 2HNO_3. \end{aligned}$$

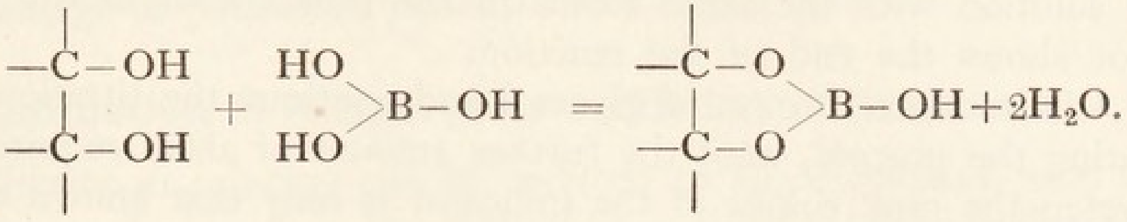
Procedure.—To estimate the percentage of copper in pure copper sulphate, weigh accurately from 1 to 1·5 gm. of the pure salt, dissolve it in water, and dilute the solution to 100 c. c. Place 25 c. c. of this solution in a beaker, saturate it with hydrogen sulphide and heat the liquid to help the precipitate to coagulate. A few grammes of pure, neutral sodium chloride may be added advantageously to aid the separation of the sulphide. Filter and wash the precipitate thoroughly till all the acid is removed from it, avoiding as much as possible exposing it to the air, which slowly oxidizes copper sulphide to sulphate. Collect filtrate and washings in a beaker, and boil the acid liquid till it ceases to smell of hydrogen sulphide. Cool and titrate the solution with decinormal sodium hydroxide in presence of methyl orange. From the result calculate the percentage of copper in the salt, remembering that 1 c. c. of decinormal acid is equivalent to 0·00318 gm. of copper.

6. Estimation of total Alkali and combined Boric Acid in Borax.

Borax, or sodium pyroborate, is represented by the formula $Na_2B_4O_7, 10H_2O$, which for analytical purposes is conveniently written $Na_2O, 2B_2O_3, 10H_2O$. Thus, if the alkali constituent is estimated as percentage of Na_2O, and the acid as percentage of B_2O_3, the percentage of water is given by the difference between 100 and the sum of these two percentages; or, alternatively, the percentage of water in the salt can be estimated by the loss on ignition, so that the analysis of each constituent of the salt is performed directly. The total alkali in borax is directly estimated by titrating, say, 20 c. c. of its solution with standard acid, methyl orange being used as indicator; for boric acid like carbonic acid is so weak an acid as to have no perceptible effect on this indicator. If the same amount of acid used in this titration is now added to a second 20 c. c. of the borax solution, the solution will contain a neutral sodium salt and free boric acid, thus:

$$Na_2B_4O_7 + 2HCl + 5H_2O = 2NaCl + 4H_3BO_3;$$

and the question is: how can this boric acid be estimated? The acid is too weak to give a sharp end point when titrated with decinormal alkali, even when phenolphthalein is the indicator, i.e. its alkali salt is hydrolyzed; it may, however, be fortified by the addition of glycerol or mannitol, for these compounds contain hydroxyl-groups which combine with the boric acid thus:



$$\begin{array}{l} | \\ -\mathrm{C}-\mathrm{OH} \\ | \\ -\mathrm{C}-\mathrm{OH} \\ | \end{array} + \begin{array}{l} \mathrm{HO} \\ \mathrm{HO} \end{array}\!\!>\mathrm{B}-\mathrm{OH} = \begin{array}{l} | \\ -\mathrm{C}-\mathrm{O} \\ | \\ -\mathrm{C}-\mathrm{O} \\ | \end{array}\!\!>\mathrm{B}-\mathrm{OH}+2\mathrm{H_2O}.$$

Thus if neutral glycerol (glycerine) is added to boric acid solution, glyceryl-boric acid is produced as a monobasic acid, which can be titrated with standard alkali in presence of phenolphthalein, since this indicator reacts sharply at the point indicated by the completion of the reaction:

$$C_3H_5(OH)O_2BOH + NaOH = C_3H_5(OH)O_2BONa + H_2O.$$

Procedure.—Prepare, say, 250 c. c. of a solution of borax decinormal with regard to its soda content, that is one-twentieth molar, or else containing a known weight of the salt giving a solution of approximately this strength. Titrate 20 c. c. of this solution with decinormal hydrochloric acid, using methyl orange as indicator, and from the result calculate the percentage of soda (Na_2O) in the salt.

Next proceed to estimate the boric acid in presence of glycerol.

Prepare, say, 250 c. c. of approximately decinormal sodium hydroxide solution by dissolving the required weight of the alkali in distilled water which has been recently boiled and cooled to eliminate carbonic acid. Standardize this solution by titrating it into decinormal hydrochloric acid in presence of phenolphthalein.

It is necessary for the glycerol to react neutral towards phenolphthalein. Therefore first test this reagent by measuring 10 c. c. of it in a small graduated cylinder, transferring the liquid to a suitable flask, diluting it with water, and titrating it with the recently prepared decinormal alkali in presence of phenolphthalein, till a pink colour just appears permanently. This titration will show how much alkali, if any, needs to be added to the volume of glycerol employed in titrating the boric acid.

To estimate the boric acid in the borax solution measure 20 c. c. of the solution and add to it the volume of decinormal hydrochloric acid known to be necessary to neutralize the soda; next add 10 c. c. of glycerol, followed by phenolphthalein and the volume of decinormal soda required to neutralize the glycerol; then titrate the solution with the same alkali till the pink colour of the indicator shows the end of the reaction.

Add another 10 c. c. of glycerol and continue the titration, repeating the process, 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 glycerol.

From the volume of alkali required to neutralize the boric acid calculate the percentage of B_2O_3 in the borax, remembering that:

$$NaOH \equiv H_3BO_3 \equiv \frac{B_2O_3}{2}.$$

Tabulate the result of the analysis of borax, showing the percentage of water either by difference, or after estimating it by igniting a weighed quantity of the salt in a capsule until it ceases to lose weight.

7. Estimation of Potassium Persulphate by titrating the Acid developed on boiling its solution.

Potassium persulphate, or perdisulphate, is formed by the electrolytic oxidation of potassium hydrogen sulphate thus:

$$2KHSO_4 = K_2S_2O_8 + H_2;$$

and when boiled with water degenerates to this salt with loss of oxygen thus:

$$2K_2S_2O_8 + 2H_2O = 4KHSO_4 + O_2.$$

This reaction, however, is slow, and even after lengthy boiling the acid produced is found to be less than equivalent to the persulphate originally present. If, however, a suitable reducing agent is added, the reaction is hastened, and the full degree of acidity quickly reached. For this purpose methyl alcohol is employed, and the formaldehyde produced eliminated by boiling.

Procedure.—Weigh about 0·25 gm. of potassium persulphate, dissolve it in 100 c. c. of water, add methyl orange, and, if the solution is acid, carefully neutralize it with decinormal alkali added drop by drop from a burette. Then add about 2 c. c. of pure methyl alcohol, and heat the mixture to 70° C. for five minutes. Afterwards boil for ten minutes, cool, and titrate with decinormal alkali. Repeat the estimation, and from the result calculate the percentage of potassium persulphate in the given salt.*

8. Estimation of Nitrate after reduction to Ammonia.

Nitrate in solution can be reduced to an ammonium salt, and the ammonia can then be estimated by distilling the solution with sodium hydroxide, and collecting the evolved gas in excess of standard acid. The reduction may be effected in various ways; e.g. in acid solution by zinc, aluminium, or iron, and in alkaline solution by zinc, aluminium, or Devarda's alloy. The methods adopted here will be (i) reduction by reduced iron in presence of dilute sulphuric acid, and (ii) reduction by **Devarda's** alloy in presence of sodium hydroxide.

(i) *Reduction by reduced iron in presence of acid.*

Zinc, aluminium, or iron may be used to generate hydrogen for the reduction of nitrate in solution, but it is found by experience that finely divided zinc and aluminium react so vigorously with acid that the hydrogen liberated is liable to escape as gas rather than to act as a reducing agent, and, moreover, that in the case of zinc there is much frothing. Reduced iron, however, reacts smoothly and effectively. For the estimation prepare a solution of potassium nitrate containing 20 gm. of the salt per litre, also standardized semi-normal solutions of sulphuric acid and sodium hydroxide, and sulphuric acid solution of 1·35 specific gravity made by mixing 40 c. c. of the concentrated acid with 100 c. c. of water, together with sodium hydroxide solution of 1·3 specific gravity, i.e. of 28 per cent strength. The apparatus shown in fig. 12, on p. 100 of Part I of this book, may be used. but the distilling flask must be fitted alternatively with a rubber stopper through which passes a small absorption-tube half filled with glass beads to retain any spray carried away with the evolved hydrogen.

Procedure.—Place in the litre flask 50 c. c. of potassium nitrate solution, 10 gm. of reduced iron, and 20 c. c. of sulphuric acid of 1·35 specific gravity; then add 50 c. c. of water, place in the neck

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* Another method for estimating persulphate will be found among the estimations by permanganate. The results of the two methods should agree.

of the flask the stopper carrying the absorption-tube with beads, raise the contents of the flask to boiling, and boil gently for five minutes. Remove the flame, wash the beads with water which is allowed to drain into the flask, and again boil for five minutes. By this time the nitrate will be completely reduced and the solution will contain in place of it ammonium sulphate.

Now arrange the apparatus, placing 50 c. c. of sodium hydroxide solution of 1·3 specfic gravity in the tap funnel, and 50 c. c. of semi-normal sulphuric acid in the receiving flask with a drop of methyl orange. Allow the soda to run from the tap funnel into the mixture in the flask, then add a further 100 c. c. of water, also through the tap funnel. Turn off the tap of the latter, and boil the liquid in the flask for three-quarters of an hour. Then turn on the tap to allow air to enter the flask before removing the flame, disconnect the apparatus at F, wash down the bulb into the flask, and titrate the unneutralized acid with semi-normal soda. From the volume of semi-normal acid neutralized by the evolved ammonia calculate the weight of potassium nitrate in the volume of the solution used, and thence the percentage of this salt in the specimen taken for analysis, remembering that since equimolecular solutions of KNO_3 and NH_3 are equivalent, 1 c.c. of semi-normal acid represents 0·0506 gm. of KNO_3.

(ii) *Reduction by Devarda's alloy in presence of alkali.*

Devarda's alloy is an alloy of 45 parts aluminium, 50 parts copper, and 5 parts zinc; and this when warmed with sodium hydroxide solution evolves hydrogen which reduces nitrate to ammonia. The alloy should be in the form of fine powder, and since the liquid froths during the first stage of the reaction, alcohol is added to prevent this as much as possible.

Complicated pieces of apparatus are sometimes recommended for this estimation; but if a trap is provided to prevent alkaline spray being carried over with the steam and ammonia the apparatus can be simple, so that that shown in fig. 12 on p. 100 of Part I of this book will suffice.

Procedure.—To estimate the purity of an alkali nitrate such as potassium nitrate, prepare, say, 100 c. c. of a semi-normal solution. Have ready also approximately semi-normal, standardized solutions of sulphuric acid and sodium hydroxide, and a solution of sodium hydroxide of about 1·3 specific gravity, i.e. of 28 per cent strength. Place 10 c. c. of the semi-normal potassium nitrate solution, 110 c. c. of water, 5 c. c. of alcohol, and 2·5 gm. of Devarda's alloy in a round-bottom " Kjeldahl " flask, of about one litre capacity, and 25 c. c. of the standardized acid in the receiving flask; then fit together the apparatus with trap, delivery tube, and tap funnel, as shown in the figure above referred to. Next add 5 c. c. of the concentrated soda solution by means of the tap funnel, rinsing the latter with a little water, which is allowed also to flow into the Kjeldahl flask. Gently warm the flask to start the reaction. Hydrogen will be evolved, and when the evolution of this gas slackens after about ten minutes, heat the contents of the flask to boiling, and boil for about half an hour. Keep the receiving flask cold during this time by immersing it in water. Then disconnect the apparatus, wash the acid from the delivery tube into the receiving flask, and titrate the remaining acid with the standardized sodium hydroxide, using methyl orange as indicator.

Repeat the estimation, and after obtaining agreeing results calculate the percentage purity of the potassium nitrate, one molecule of which yields by reduction one molecule of ammonia.

STANDARD POTASSIUM PERMANGANATE SOLUTION

The chemistry of potassium permanganate as an oxidizing agent and the preparation and use of a standard solution of this salt in volumetric analysis have been described on pp. 102–27 of Part I of this book. So varied are the oxidation processes that can be carried out with this reagent, however, that a number of these yet remain to be described. The following further estimations with decinormal potassium permanganate solution may now be carried out by the student; who must, however, first prepare and standardize his solution according to the instructions given on p. 105 of Part I.

1. Manganese dioxide and red lead.
2. Nitrite.
3. Hydroxylamine.
4. Persulphate.
5. Manganese when occurring with iron (Volhard).

1. Valuation of Manganese Dioxide and Red Lead.

Manganese dioxide and red lead are oxidizing agents and can oxidize oxalic acid by oxygen, which becomes available when they react with acids to form manganous and lead salts thus:

$$\begin{cases} MnO_2 + H_2SO_4 = MnSO_4 + H_2O + O \\ H_2C_2O_4 + O = H_2O + 2CO_2; \quad \text{and} \end{cases}$$

$$\begin{cases} Pb_3O_4 + 4HNO_3 = 2Pb(NO_3)_2 + H_2O + H_2PbO_3 \\ H_2PbO_3 + 2HNO_3 = Pb(NO_3)_2 + 2H_2O + O \\ H_2C_2O_4 + O = H_2O + 2CO_2, \end{cases}$$

or adding:

$$Pb_3O_4 + 6HNO_3 + H_2C_2O_4 = 3Pb(NO_3)_2 + 4H_2O + 2CO_2.$$

Dilute sulphuric acid can be used for the reaction with manganese dioxide, but dilute nitric acid should be employed for red lead. The latter reaction occurs in two stages, since dilute nitric acid removes 2PbO from Pb_3O_4 leaving hydrated PbO_2 (H_2PbO_3), which then oxidizes oxalic acid similarly to MnO_2.

The method of estimation in each case consists in having present a quantity of decinormal oxalic acid more than sufficient to react with the oxidizing agent in presence of mineral acid, and then titrating the remaining oxalic acid with standard permanganate solution.

Manganese Dioxide.

In order that manganese dioxide may oxidize oxalic acid readily it must be in a fine state of division. It is desirable, therefore, to grind the material in an agate mortar until it is of a floury consistence; and this is specially necessary if the natural pyrolusite rather than the artificial compound is being analysed.

Procedure.—Weigh accurately 0·1 to 0·15 gm. of the finely powdered manganese dioxide and place it in a flask of about 250 c. c. capacity. It is advisable to weigh by difference, having the material in a weighing bottle, and tipping into the flask the required amount of it. This avoids the loss likely to result in transferring a quantity of very fine powder from one vessel to another. Now run into the flask 50 c. c. of decinormal oxalic acid, preferably from a burette, and add about 10 c. c. of dilute sulphuric acid. Heat the mixture to boiling, and continue to heat it until no black particles remain; then titrate the oxalic acid remaining in the hot liquid with your decinormal permanganate. The difference between 50 and the number of cubic centimetres of decinormal permanganate required represents the volume of a decinormal solution of oxidizing agent which would correspond with the manganese dioxide employed. Thence calculate the weight of MnO_2 in the amount of material taken, and the percentage of this compound in the sample, remembering that the equivalent weight of MnO_2 as regards oxidizing power is half its molecular weight. Repeat the estimation until agreeing results are obtained.

Red Lead.

Red lead is already in a fine state of division, and can be used for the estimation without preliminary grinding.

Procedure.—Weigh 0·5 to 0·7 gm. of red lead " by difference " as before, and add to it in the flask 10 c. c. of dilute nitric acid. The colour of the solid will become dark brown owing to the removal of PbO and separation of hydrated PbO_2, according to the reaction on p. 30. Now add 50 c. c. of decinormal oxalic acid and boil the contents of the flask till a colourless and nearly or quite clear solution results. Then titrate the remaining oxalic acid with decinormal permanganate, and from the number of cubic centimetres of the former found to have been consumed by the red lead, calculate the weight of this oxidizing agent and the percentage of it in the specimen provided, remembering that the molecule Pb_3O_4 yields only one atom of available oxygen.

2. Estimation of Nitrite.

The student will remember that nitrous acid is both an oxidizing and a reducing agent; that it oxidizes by being reduced to nitric oxide and reduces by being oxidized to nitric acid. Nitrous acid is, however, exceedingly unstable, and must therefore be oxidized simultaneously with its liberation from a salt. Such oxidation is effected by titrating a solution of a nitrite of convenient strength into excess of acidified and well diluted potassium permanganate solution, containing a known quantity of the oxidizing agent. No gas must be evolved during the process, since the nitrite, instead of being decomposed by the acid present, is to be oxidized directly to nitrate, in accordance with the reaction:

$$\begin{aligned} &5NaNO_2 + 2KMnO_4 + 3H_2SO_4 \\ &\quad = 5NaNO_3 + K_2SO_4 + 2MnSO_4 + 3H_2O. \end{aligned}$$

It is possible to continue the titration of nitrite into permanganate until the colour of the latter is completely discharged, but the reaction becomes tedious towards the end. It is better, therefore, to add a measured volume of nitrite solution to a measured volume of standard permanganate which has been acidified, and then titrate the remaining permanganate with a solution of ferrous sulphate whose value with reference to the permanganate has been determined. The oxidation of nitrite by permanganate takes place most efficiently at about 65° C.

Procedure.—Weigh accurately about 1 gm. of sodium nitrite, dissolve the salt in water, and dilute the solution to 250 c. c.; also prepare a solution of ferrous sulphate containing a little sulphuric acid, and of about decinormal strength; say 7·0 gm. of the salt in 250 c. c. of solution. Standardize the ferrous solution by titrating 25 c. c. of it with decinormal permanganate in presence of sulphuric acid, remembering that what is required is not the iron value of the solution, but its value in terms of volume of permanganate solution.

Carry out the estimation thus: Measure into a flask of about 1-litre capacity, 50 c. c. of decinormal permanganate solution, dilute this with a mixture of 30 c. c. concentrated sulphuric acid with 300 c. c. water, and heat the solution to about 65° C. Then add slowly, from a burette, 25 c. c. of the nitrite solution, and finally cool and titrate the remaining permanganate with the standardized ferrous solution, until the pink colour is just discharged. Then subtract from 50 the permanganate equivalent of the ferrous solution employed; the remainder represents the volume of decinormal permanganate which oxidized the nitrite. Thence, after obtaining concordant results, calculate the weight of nitrite oxidized, and the percentage of $NaNO_2$ in the salt analysed, remembering that the weight of $NaNO_2$ equivalent to 8 parts by weight of oxygen is half its molecular weight.

3. Estimation of Hydroxylamine.

Various oxidizing agents oxidize hydroxylamine to nitrous oxide and water thus: *

$$2NH_2OH + 2O = N_2O + 3H_2O.$$

A ferric salt can be used conveniently for this purpose, and the ferrous salt resulting from the reduction can then be titrated with permanganate, the permanganate required being equivalent to the hydroxylamine which was oxidized. It will be observed that, in accordance with the above equation, a solution of a hydroxylamine salt needs to be one-twentieth molecular to be equivalent to decinormal permanganate solution. It is necessary to have present considerable excess of a ferric salt in order that the oxidation of hydroxylamine to nitrous oxide and water may proceed quantitatively.

Procedure.—Weigh accurately sufficient hydroxylamine hydrochloride to make, say, 250 c. c. of a decinormal solution; also prepare a convenient quantity of a solution of ferric alum, $(NH_4)_2SO_4 \cdot Fe_2(SO_4)_3 \cdot 24H_2O$, 400 gm. per litre strength.

Place in a flask of about 1-litre capacity 20 c. c. of the solution of hydroxylamine hydrochloride, 10 c. c. of the ferric solution, and 10 c. c. of dilute sulphuric acid. Boil the mixed solution for five minutes, then dilute it with 300 c. c. of air-free distilled water at room temperature, and titrate the ferrous iron produced with decinormal permanganate solution. Rather more care than usual is needed in judging the end point of the reaction owing to the excess of ferric salt present; nevertheless accurate results can be obtained. After obtaining concordant results calculate the percentage of hydroxylamine hydrochloride, $NH_2OH \cdot HCl$, in the salt provided.

4. Estimation of Persulphate.

Persulphate has already been estimated volumetrically by determining the acidity which is developed when its neutral aqueous solution is boiled. In this case the oxidizing power of the salt was not taken into account. Persulphuric acid, unlike hydrogen per-

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* It is convenient to remember that hydroxylamine, containing oxygen, yields as an oxidation product an oxide of nitrogen, whilst hydrazine, itself devoid of oxygen, yields when oxidized nitrogen gas.

oxide, does not react with permanganate, but it oxidizes ferrous salts in solution to ferric salts, even at atmospheric temperature, and the amount of such oxidation is a measure of persulphate, according to the following reaction:

$$H_2S_2O_8 + 2FeSO_4 = H_2SO_4 + Fe_2(SO_4)_3.$$

Since the molecule of $H_2S_2O_8$, $K_2S_2O_8$, or $(NH_4)_2S_2O_8$ contains one atom of oxygen available for oxidizing, one-twentieth of a gramme-molecule of either of the above alkali salts will be equivalent to 1 litre of decinormal permanganate solution.

Procedure.—Prepare 250 c. c. of ferrous sulphate solution, approximately equivalent to decinormal permanganate, adding dilute sulphuric acid in its preparation so as to inhibit atmospheric oxidation. Titrate 25 c. c. of this solution with decinormal permanganate; then place 50 c. c. of it in a suitable flask, and add to the solution not more than 0·5 gm. of the alkali persulphate, which has been finely powdered and then accurately weighed. Rotate the flask so as to promote the solution of the powder at atmospheric temperature. When all is dissolved, and the solution has become pale yellow in consequence, titrate the liquid with your permanganate till a pink colour remains permanently.

The difference between the volume of decinormal permanganate which was needed to oxidize 50 c. c. of the ferrous solution, and that required to oxidize the ferrous salt remaining after the addition of the persulphate, represents the oxygen equivalent of the persulphate. From this calculate the percentage of persulphate in the given salt.

5. Estimation of Manganese when occurring with Iron.

A. *Volhard's Method.*

Potassium permanganate reacts with manganous salt solution to produce manganese dioxide as follows:

$$2KMnO_4 + 3MnSO_4 + 2H_2O = 5MnO_2 + K_2SO_4 + 2H_2SO_4.$$

The hydrated manganese dioxide thus formed is in reality manganous acid; which may react with manganous salt to produce Mn_2O_3, or manganous manganite, thus:

$$H_2MnO_3 + MnSO_4 = Mn{\cdot}MnO_3 + H_2SO_4.$$

and so invalidate the process. If, however, sufficient zinc sulphate is present the precipitate will consist of zinc manganite of varying composition, but containing all the manganese in the quadrivalent condition.

If iron occurs in solution with manganese it must be eliminated, and this is done by means of precipitated zinc oxide, which precipitates the iron as hydroxide, zinc passing into solution as sulphate. It is well to standardize the permanganate directly by titrating it into a solution containing a known amount of manganese.

Standardization of Permanganate.

According to the ratio $2KMnO_4 : 3MnSO_4$ the weight of pure, anhydrous manganous sulphate required to make a litre of solution equivalent to decinormal permanganate is 4·53 gm. Manganous sulphate crystallizes in the hydrated state but is easily made anhydrous without decomposition by moderate ignition. Therefore powder some of the pure salt, and ignite it in a silica or porcelain crucible, with the tip of the Bunsen flame not quite touching the bottom of the crucible, until the salt ceases to lose weight. Preserve the salt in a stoppered weighing bottle, and prepare, say, 500 c. c. of solution of the required strength.

A zinc sulphate solution of convenient strength is made by dissolving 100 gm. of the salt in water and diluting to 500 c. c.

To standardize the permanganate solution proceed as follows:

To 25 c. c. of manganese sulphate solution contained in a large flask add 50 c. c. of zinc sulphate solution, and dilute the solution to about 250 c. c. with water; heat nearly to boiling, and titrate whilst hot with your nearly decinormal permanganate solution, thoroughly shaking the flask after each addition. When nearing the end add 1 c. c. of glacial acetic acid. A permanent pink tint, seen especially when the flask is held up to the light, marks the end of the reaction. Repeat the titration, and after obtaining consistent results calculate the manganese value of each c. c. of your permanganate solution.

Estimation of Manganese.

Prepare hydrated zinc oxide for precipitating the iron by adding caustic soda to zinc sulphate solution until the maximum precipitation has taken place; then filter and wash the precipitate free from alkali; keep the product suspended in water in a corked flask until it is required.

Measure 25 c. c. of the given solution containing ferric iron and manganese, nearly neutralize the acid in it by sodium hydroxide, then add sufficient of the prepared zinc oxide to leave some undissolved, heat the turbid liquid to boiling, filter and thoroughly wash the residue, collecting the iron-free filtrate and washings in a flask suitable for the titration. Add zinc sulphate and water, as before, then boil and titrate, adding 1 c. c. of glacial acetic acid near the end. Repeat the estimation until agreeing results are obtained, and calculate the manganese present.

B. *Bismuthate Method.*

Manganese is converted quantitatively into permanganate by sodium bismuthate in presence of nitric acid; iron does not interfere, but chloride must be absent. The method can be employed to estimate manganese in steel after the metal has been dissolved in nitric acid.

Procedure.

To 25 c. c. of the above manganese sulphate solution, placed in a stoppered bottle, add a cooled mixture of 30 c. c. concentrated nitric acid and 100 c. c. water, and then about 2 gm. of sodium bismuthate. Shake the mixture and allow it to stand for a few minutes. Then filter the crimson solution through asbestos with suction, and wash the residue by decantation and on the filter with dilute nitric acid until it is colourless. Meanwhile, have ready a standardized ferrous solution approximately equivalent to your decinormal permanganate. Add a measured volume of this solution in excess to the permanganate produced, and then titrate the excess with your decinormal permanganate. Thence derive the volume of decinormal permanganate equivalent to that produced, and calculate the corresponding amount of manganese, remembering that 1 c. c. N/10 $KMnO_4 = 0{\cdot}0011$ gm. Mn.

STANDARD POTASSIUM DICHROMATE SOLUTION

The preparation and use of decinormal potassium dichromate solution have been described in Part I of this book, pp. 127–37, but the only reactions in which this substance was there employed were the oxidation of ferrous iron, and the liberation of iodine from potassium iodide with a view to standardizing decinormal sodium thiosulphate solution. The applications of potassium dichromate are far more limited than those of the more sensitive potassium permanganate; indeed it is chiefly on account of its inferior sensitiveness that dichromate is employed as an oxidizing agent in volumetric analysis at all; thus it is useful in titrating ferrous iron in presence of dilute hydrochloric acid, because it does not oxidize the latter. It is possible, however, to employ chromate or dichromate solution in a reaction of precipitation. Thus if a metal forms a chromate, of definite and known composition, insoluble in a convenient reagent such as dilute acetic acid, it is possible to estimate the metal by precipitating it from solution by the addition of a measured volume of standard chromate or dichromate solution, filtering off the precipitate, and determining how much chromate remains in the filtrate. It will occur to the student that barium and lead could be estimated in this manner by precipitating their chromates in presence of acetic acid. The most convenient way of dealing with the excess of chromate, however, is to add potassium iodide to it in presence of acid, and then titrate with standard thiosulphate solution the iodine liberated.

Another exercise related to this is the estimation of the percentage of potassium chromate and dichromate in a mixture of the two pure salts. Since the ratios of basic and acidic oxides in the two salts are $K_2O : CrO_3$ and $K_2O : 2CrO_3$ respectively, the percentage of CrO_3 found in the mixture will lie between a minimum corresponding with chromate, and a maximum corresponding with dichromate, and the proportions of the two salts can be calculated from the relation of this percentage to the extreme percentages.

This estimation is most conveniently performed, however, by liberating and titrating iodine (see p. 52).

There remains to be carried out by means of standard dichromate the following estimation.

Estimation of Bleaching Powder by the Oxidation of Ferrous Iron.

A ferrous salt in acid solution is converted into ferric salt by bleaching powder. This reaction occurs at atmospheric temperature, and therefore the difference between the volume of decinormal dichromate solution required to titrate a certain volume of ferrous solution before and after the addition of bleaching powder solution is a volume equivalent in oxidizing power to the bleaching powder added. Since 1 c. c. of decinormal dichromate solution is equivalent to 0·00355 gm. of chlorine the percentage of chlorine in the bleaching powder is easily estimated.

Procedure.—Prepare 500 c. c. of ferrous sulphate solution containing about 14 gm. of the salt, adding a little dilute sulphuric acid before making up to volume; and 1 litre of bleaching powder solution containing 3·55 gm. of the powder (*vide* Part I, p. 147).

Titrate with decinormal dichromate solution, in the usual manner, 25 c. c. of the ferrous solution; then measure 50 c. c. of this solution, add to it dilute hydrochloric acid and, gradually, 100 c. c. of the bleaching powder solution. Finally titrate the remaining ferrous iron with dichromate. Subtract the volume of dichromate needed to complete the oxidation of the iron from the volume required to oxidize all the iron in the 50 c. c. of solution employed.

The difference represents, in terms of decinormal dichromate solution—1 c. c. of which is equivalent to 0·00355 gm. of chlorine—the amount of chlorine in the 100 c. c. of bleaching powder solution. Moreover, this volume of dichromate is numerically equal to the percentage of chlorine in the bleaching powder.

STANDARD IODINE AND THIOSULPHATE SOLUTIONS

The reaction between sodium thiosulphate and iodine, and the use of these reagents in volumetric analysis, have been studied to a limited extent in Part I of this book (pp. 138–48). Various reactions in which these substances participate, beyond those already described, are, however, available for volumetric processes. In the present section these processes will be described after alternative methods for standardizing sodium thiosulphate solution have been considered. The standardization of iodine solution, which is necessary from time to time, as the solution loses strength, is quite conveniently carried out by means of otherwise standardized sodium thiosulphate solution.

Standardization of Approximately Decinormal Sodium Thiosulphate Solution.

Prepare 1 litre of approximately decinormal sodium thiosulphate solution and let it stand for three or four days before use. This solution is necessarily standardized by titrating it into a known quantity of iodine. It has been seen that a definite quantity of iodine can be obtained in solution by causing a measured volume of standard potassium dichromate or permanganate solution to react in presence of acid with excess of potassium iodide. Either of two other methods may, however, be adopted, and these will now be described.

(i) *By means of pure iodine.*

Commercial resublimed iodine may contain chlorine, bromine, cyanogen, and water. It is freed from the first three of these by mixing it with potassium iodide and subliming, when potassium forms chloride, bromide, or cyanide, with liberation of iodine.

It is worth while to purify only enough iodine for the purpose of standardizing thiosulphate, since there is no purpose in employing the purified element to make a quantity of solution which needs to be restandardized at intervals. Proceed in the following way.

Intimately mix about 2 gm. of iodine with 0·5 gm. of potassium iodide by grinding the two solids together in a mortar. Procure two large porcelain crucibles of equal diameter; transfer the mixture to one of these crucibles, and support this on a triangle so that it can be heated with a flame; then invert the other crucible over the first one so that the two crucibles are rim to rim. Very gently heat the lower crucible with a small flame, removing the flame if iodine vapour is seen to escape. When all the iodine has sublimed into the upper crucible, place this vessel with its contained iodine in a desiccator over anhydrous calcium chloride, and leave it there overnight so as to remove all water from the iodine.

Because of the volatility of iodine it is difficult to weigh and dissolve in potassium iodide solution an accurately known amount of this substance. The following procedure will, however, be found satisfactory.

Accurately weigh a large size stoppered weighing bottle, place in it about 0·3 gm. of the dry, purified iodine, and again weigh. Crush coarsely about 2 gm. of potassium iodide, sprinkle it on the iodine in the weighing bottle, add a very little water, and replace the stopper. The iodine will soon dissolve in the concentrated solution of potassium iodide which is formed, but solution may be hastened by gently shaking the bottle. When solution is complete, add as much water as is convenient, then transfer the solution to a suitable flask, rinsing out the weighing bottle so as to lose no iodine. Dilute the solution to about 100 c. c., and titrate it with your thiosulphate solution, using starch as indicator.

Repeat the estimation with another weighed quantity of iodine, and calculate the iodine equivalent and normality of the thiosulphate, remembering that 1 c. c. of decinormal thiosulphate solution is equivalent to 0·01269 gm. of iodine.

(ii) *By means of potassium iodate.*

Neutral iodate and iodide have no action on one another in solution, but iodic and hydriodic acids react thus:

$$HIO_3 + 5HI = 3I_2 + 3H_2O.$$

Consequently, by means of a weighed quantity of pure potassium iodate, together with excess of potassium iodide in presence of dilute acid, an accurately known amount of iodine becomes available in solution for the standardization of sodium thiosulphate. Normal potassium iodate, KIO_3, or the bi-iodate, KHI_2O_6, may be used for this purpose; the equivalent weights of the salts being one-sixth and one-twelfth gramme-molecule respectively, so that the weights required per litre for decinormal solutions are 3·567 gm. KIO_3 and 3·250 gm. KHI_2O_6. Whichever salt is used, weigh enough of it to make 100 c. c. of a decinormal solution, and employ 25 c. c. for an estimation, adding to it excess of potassium iodide and dilute hydrochloric acid; then titrate the liberated iodine with your sodium thiosulphate solution, and calculate a factor for the latter.

The normalities of sodium thiosulphate solution estimated by various methods should agree closely.

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

The following estimations, in addition to those given in Part I of this book, can be carried out by means of a standard solution of iodine or of sodium thiosulphate, or of such solutions of the two reagents in conjunction.

1. Sulphurous acid and sulphite.
2. Antimony.
3. Tin.
4. Copper in copper salt and copper alloy.
5. Formaldehyde.
6. Potassium chlorate.
7. Manganese dioxide and red lead or lead peroxide.
8. Barium and lead by determination of iodine liberated by excess of chromate after their precipitation.
9. Potassium chromate and dichromate in a mixture of the two.

1. Estimation of Sulphur Dioxide Solution and Sulphites.

A solution of sulphur dioxide in water smells of the gas, and is thus continuously losing strength. This fact makes it difficult to obtain concordant results when estimating sulphur dioxide in solution by titration with iodine. The best procedure is to titrate the solution into a measured volume of standard iodine, and not *vice versa*. This reduces the time of exposure of the solution to the air; and if a thin glass tube is attached to the end of the burette, so as to lead the solution into the iodine without exposing it to the air, closely agreeing results are obtained. It has been supposed that errors in the estimation are due to atmospheric oxidation, or to a reaction in which sulphurous acid is reduced to sulphur; but it appears that evaporation of sulphur dioxide is the only appreciable cause of error.* The sulphur dioxide solution may be delivered into the iodine until the latter is completely decolorized, starch being used as indicator; or a measured volume may be added to excess of iodine, and the remaining iodine titrated with standard

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* R. M. Macaulay, *Trans. Chem. Soc.*, 1922, **121**, 552.

thiosulphate. The reaction is one of simple oxidation of sulphurous acid, thus:

$$SO_2 + H_2O = H_2SO_3;\ H_2SO_3 + OH_2 + I_2 = H_2SO_4 + 2HI.$$

Alkali sulphite in solution does not lose sulphur dioxide, but is very oxidizable; and on this account the solution must be protected from the air during titration. The same procedure as in the case of sulphur dioxide solution is therefore necessary, though from a different cause. In this case, however, dilute sulphuric acid must be added to the measured volume of iodine previous to the titration.

Estimation of Sulphur Dioxide.

Prepare a solution of sulphur dioxide in air-free water, and completely fill a stoppered bottle with it. The solution should not be stronger than decinormal; i.e. 3·2 gm. of SO_2 per litre, as with stronger solutions the risk of loss by evaporation is increased. If, therefore, on titration the solution is found much to exceed this strength it should be suitably diluted before the estimation is proceeded with.

Attach to the base of your burette by means of rubber tubing a piece of thin glass tubing long enough to reach nearly to the bottom of a stoppered bottle in which the titration will be performed. Place 20 c. c. of standard iodine solution in the bottle, and fill the burette and its extension with the sulphurous acid solution, taking care that no air bubbles remain in the tube below the tap. Perform the titration, finishing it in presence of starch, and, having obtained concordant results, calculate the weight of sulphur dioxide in 1 litre of the solution.

If some standardized sodium thiosulphate solution is available, modify the procedure by adding to a measured volume of iodine, less than sufficient sulphur dioxide solution to react with it. This may be done by the use of the burette, or a pipette. Then titrate the remaining iodine with standard thiosulphate, and from the result calculate the strength of the sulphur dioxide solution as before.

Estimation of Sulphite.

Sodium sulphite, $Na_2SO_3 \cdot 7H_2O$, is a convenient salt for analysis. Since it is liable to oxidation to sulphate, the quality of the salt should be tested by dissolving a little in dilute hydrochloric acid, and adding barium chloride. If much sulphate is shown to be present, the analysis will necessarily give a low result. Reduce to fine powder the sodium sulphite supplied, weigh accurately about 1·5 gm. of the salt, dissolve it in cold, air-free distilled water, and dilute the solution to 250 c.c. Attach to your burette the tube used in the previous experiment and fill the burette with the sulphite solution. Place 20 or 25 c.c. of standard iodine solution in a stoppered bottle, add a few cubic centimetres of dilute hydrochloric acid, and titrate the sulphite solution into the acidified iodine, adding starch as indicator before the reaction is finished. The titration may be varied by adding from a pipette to the same volume of acidified iodine solution a volume of sulphite solution less than sufficient to react with the iodine, or by employing a weighed quantity of the solid salt, and then titrating the remaining iodine with standard sodium thiosulphate. When concordant results have been obtained by the two methods, calculate the percentage of Na_2SO_3 in the salt analysed.

2. Estimation of Antimony.

The volumetric estimation of antimony depends upon its oxidation from the antimonious to the antimonic condition thus:

$$Sb_2O_3 + 2O = Sb_2O_5,$$

which is brought about by iodine:

$$Sb_2O_3 + 2OH_2 + 2I_2 = Sb_2O_5 + 4HI.$$

The reaction thus represented is, however, reversible; that is to say, antimonic acid will oxidize hydriodic acid, being thereby reduced again to antimonious acid. In the absence of acid, however, this reduction does not take place; that is to say, antimonate and iodide do not interact. Neither alkali hydroxide nor carbonate can be added, however, to neutralize the acids as they are formed, since these also react with iodine; but sodium hydrogen carbonate, whilst itself neutral and without action on iodine, serves to react with acid and keep the solution neutral. A difficulty is created, nevertheless, by the fact that sodium hydrogen carbonate precipitates from antimonious solutions either antimonious hydroxide or antimonyl chloride. Finally, this difficulty is overcome by having present a tartrate, which may be added in the form of tartaric acid or Rochelle salt, i.e. sodium potassium tartrate, since this forms with the antimonyl radicle, SbO, a soluble complex ion such as is present in tartar emetic, the potassium salt of antimonyl-tartaric acid, $K[(SbO)C_4H_4O_6]$. If tartar emetic itself is being estimated, no further tartrate need be added, because this salt is freely soluble in water, and is not precipitated therefrom by sodium hydrogen carbonate.

Incidentally it may be mentioned that pure crystallized tartar emetic, $[K \cdot SbO \cdot C_4H_4O_6]_2 \cdot H_2O$, can be used conveniently to standardize iodine solution.

Procedure.—For the estimation, weigh sufficient of the antimonious compound to make 250 c. c. of an approximately decinormal solution, remembering that the equivalent weight of Sb_2O_3, for the purpose of oxidation, is one-fourth of its formula weight. Dissolve the weighed amount in water if it is tartar emetic, or if otherwise in hydrochloric acid, and dilute the solution to the required volume. Place 20 or 25 c. c. of this solution in a titrating flask and nearly neutralize it with soda, adding the alkali until a small precipitate remains permanently. Then add some powdered Rochelle salt, heat the liquid until a clear solution is obtained, and cool it to atmospheric temperature again. Add to this solution solid sodium hydrogen carbonate until effervescence ceases, and some of the solid remains; then add starch solution (see Part I, p. 138) and titrate with iodine until a blue colour appears permanently. If there is difficulty in reaching an end point, that is because of an insufficiency of sodium hydrogen carbonate. It is well to allow some of this solid salt to remain in suspension throughout the titration, so as to keep the solution saturated with it, and thus secure the rapid neutralization of the hydriodic acid as it is formed. Concordant results should be obtained by repeating the titration, and from these the percentage of antimony or of antimonious oxide in the material taken can be calculated.

3. Estimation of Tin.

(*a*) *Metal or Stannous Salt.*

Tin is estimated by converting it from the stannous to the stannic state by means of iodine. This might be done by performing the reaction in neutral solution, as in the case of antimony, sodium bicarbonate being present to neutralize hydriodic acid as it is formed, and Rochelle salt to keep the tin in solution as a complex salt. There is no need, however, for this procedure, since tin in the form of stannous chloride, and in presence of hydrochloric acid, is directly convertible by iodine into the stannic state thus:

$$SnCl_2 + 2HCl + I_2 = SnCl_4 + 2HI.$$

Procedure.—Weigh accurately about 0·2 gm. of tin in the granulated form or as foil, place the metal in a flask of about 250 c. c. capacity and add about 50 c. c. of a mixture of concentrated hydrochloric acid with an equal volume of water. Arrange to pass a current of carbon dioxide gas on to the surface of the liquid in the flask so as to displace air, and then heat the liquid until all the tin has dissolved, leaving only a small grey or black residue. Do not filter, but continue to pass in carbon dioxide whilst the flask and its contents are cooled to atmospheric temperature. Then immediately titrate the solution with decinormal iodine, using starch as indicator, and passing in carbon dioxide gas during the titration. Calculate the percentage of tin in the sample; 1 c. c. $\frac{N}{10}$ iodine $\equiv$ 0·00594 gm. tin.

A stannous salt may be estimated similarly to tin, care being taken to dissolve the salt in air-free water, together with hydrochloric acid, and to exclude air from the flask during titration by means of carbon dioxide.

(*b*) *Stannic Salt.*

Ammonium stannichloride, or hexachlorstannate, $(NH_4)_2SnCl_6$, is a convenient salt in which to estimate the tin. It is easily prepared by mixing concentrated solutions of ammonium chloride and stannic chloride, and crystallizing.

The tin is reduced from the stannic to the stannous state by means of metallic antimony in presence of hydrochloric acid thus:

$$3SnCl_4 + 2Sb = 3SnCl_2 + 2SbCl_3,$$

and since iodine does not react with antimonious chloride in acid solution, and is almost without action on metallic antimony at atmospheric temperature, the stannous chloride in solution can be titrated directly with iodine without filtering off the excess of antimony.

Procedure.—Weigh accurately about 0·3 gm. of ammonium stannichloride, place it in a flask and dissolve it in a mixture of 50 c. c. concentrated hydrochloric acid and 50 c. c. water. Add about 1 gm. of powdered antimony and heat the liquid to boiling. Displace air from the flask by a current of carbon dioxide led by a tube on to the surface of the liquid, and continue boiling gently for thirty minutes, adding more hot water if necessary. Then cool the liquid, whilst continuing the passage of carbon dioxide, add starch, and titrate with decinormal iodine without filtering.

Calculate the percentage of tin or of ammonium stannichloride in the salt.

4. Estimation of Copper.

When potassium iodide is added in excess to a solution of a cupric salt the cupric iodide formed decomposes all but completely into cuprous iodide and iodine, thus:

$$CuSO_4 + 2KI = CuI_2 + K_2SO_4$$
$$CuI_2 = CuI + I.$$

Since the amount of cupric iodide remaining undecomposed in the solution is negligible, the copper present can be estimated by titrating the liberated iodine with standard thiosulphate solution. The method is serviceable for estimating the copper either in a cupric salt or mineral, or in an alloy.

Two precautions are necessary when the copper has been obtained in solution by the use of acid: (i) no free acid should be present except a little acetic acid in which cuprous iodide is not soluble; (ii) no nitrous acid or oxide of nitrogen which would oxidize hydriodic acid must be allowed to remain in the solution; consequently when copper or one of its alloys has been dissolved in nitric acid the solution must be boiled after the addition of a little urea, to destroy nitrous acid and expel oxides of nitrogen.

According to the above reactions one atom of iodine is equivalent to one atom of copper, so that 1 c. c. of decinormal sodium thiosulphate solution corresponds with 0·00636 gm. of copper.

Standardization of Sodium Thiosulphate Solution with Copper.

Unless the sodium thiosulphate solution has been recently standardized, it is convenient to standardize it by means of pure copper.

Weigh accurately about 0·636 gm. of pure copper in the form of foil, place it in a suitable flask with a little water; put a funnel in the neck of the flask, and pour a few cubic centimetres of concentrated nitric acid through the funnel. Warm the contents of the flask until the copper is dissolved, then add water if necessary, and boil the solution for several minutes to expel oxides of nitrogen; finally add about 0·5 gm. of urea and boil again so as to destroy nitrous acid according to the reaction:

$$2HNO_2 + CO(NH_2)_2 = 3H_2O + CO_2 + 2N_2.$$

Then transfer the solution to a 100-c. c. flask and dilute to volume.

To perform the titration, place 20 c. c. of the solution in a convenient flask, add sodium carbonate until a slight permanent precipitate remains, and then dissolve this precipitate by adding a little acetic acid. Next drop into the solution several crystals of potassium iodide, which has been proved to contain no iodate by not showing free iodine in presence of dilute acid. The proportion of potassium iodide to copper should not be less than 6 : 1.

A dark brown turbid liquid will be produced, which consists of cream-coloured cuprous iodide suspended in a solution of free iodine in potassium iodide. Titrate this liquid with approximately decinormal sodium thiosulphate, adding starch solution to indicate the end of the reaction. The titration is completed when the dark blue colour disappears, allowing the nearly white cuprous iodide to be seen. Calculate the weight of copper to which each cubic centimetre of thiosulphate solution corresponds.

Procedure to estimate Copper.

If the copper salt, or mineral containing copper, is soluble in water or dilute hydrochloric or sulphuric acid, all that is necessary is to dissolve a suitable weighed quantity of the material, to neutralize any free mineral acid with sodium carbonate, then to acidify with acetic acid, add potassium iodide, and titrate as above.

Estimate the copper in a copper salt by this means.

The copper in an alloy such as a bronze coin may be estimated by following the instructions for standardizing thiosulphate solution with pure copper, the small amounts of zinc in solution and hydrated stannic oxide in suspension in no way interfering with the titration. Iron, however, must not be present.

5. Estimation of Formaldehyde.

Formaldehyde is readily oxidized to formic acid in presence of alkali, with which the acid forms a salt, thus:

$$HCOH + O + NaOH = HCOONa + H_2O.$$

This oxidation is effected by iodine, which in presence of alkali forms iodide and hypoiodite thus:

$$I_2 + 2NaOH = NaI + NaOI + H_2O.$$

Thus it is hypoiodite which oxidizes the formaldehyde; but when the oxidation is completed, and the solution is acidified, the remaining hypoiodite produces free iodine again thus:

$$NaI + NaOI + 2HCl = 2NaCl + H_2O + I_2.$$

Consequently the difference between the iodine taken and that remaining represents an equivalent of formaldehyde oxidized to formate. Moreover, a decinormal solution of formaldehyde will be one-twentieth molecular and so contain 1·5 gm. per litre.

Procedure.—The solution of formaldehyde known as formalin contains about 40 per cent of this substance; therefore measure accurately 5 c. c. of the solution, and dilute it to 1 litre with water, so as to obtain a solution of rather more than decinormal strength. Measure 10 c. c. of this solution, add to it 25 c. c. of decinormal iodine, followed by concentrated sodium hydroxide solution, drop by drop, and in sufficient quantity to cause the liquid to become pale yellow. Allow the solution to stand at room temperature for ten minutes, then acidify it with dilute hydrochloric acid so as to liberate the remaining iodine. Titrate this iodine with decinormal thiosulphate, and from the volume of iodine consumed by the formaldehyde solution, calculate the original strength of the latter.

6. Estimation of Potassium Chlorate.

Potassium chlorate, and other oxidizing agents, can be estimated by heating them with hydrochloric acid, passing the evolved chlorine or oxide of chlorine into potassium iodide solution, and then titrating the liberated iodine with standard thiosulphate solution.

When potassium chlorate and hydrochloric acid are heated together, a mixture of chlorine and chlorine dioxide—the euchlorine of Davy—is evolved by a reaction which may be represented thus:

$$2KClO_3 + 4HCl = \overbrace{2ClO_2 + Cl_2} + 2KCl + 2H_2O.$$

Whether or not the actual proportion between the two gases evolved is that shown in this equation is, however, immaterial, since the iodine liberated from potassium iodide is in any case equivalent to the oxygen which the potassium chlorate loses, this equivalence being represented thus: $KClO_3 : 6I$.

Procedure.—Fit together the apparatus shown in fig. 1, consisting of the tap funnel A, the delivery tube of which passes, through a cork, nearly to the bottom of the distilling flask B, together with the absorption bulb-tube C, into which the bent delivery tube of the flask leads, and which is provided with a small bulb tube D, also fitted by means of a cork, and filled with glass beads. Provide a small weighing receptacle E to contain the potassium chlorate. This may be made of a piece of quill tubing, one end of which is sealed and flattened whilst plastic, the tubing being then cut off within half an inch of the sealed end. This little receptacle can then be stood upright on the balance pan to be weighed, and introduced into the distilling flask when it contains the weighed amount of potassium chlorate. Fit a cork to the top of the separating funnel, and pass through it a small piece of glass tubing bent at right angles, also similarly provide cork and glass tubing for the top of the bulb tube D. With this arrangement it is possible either to drive carbon dioxide gas through the apparatus, or to draw air through it by the use of an aspirator.

To carry out the estimation weigh accurately about 0·2 gm. of potassium chlorate in the little receptacle, and carefully slide the latter down inside the distilling flask. Dissolve about 2 gm. of potassium iodide in 10 c. c. of water, pour most of this solution into the bulb tube C, but reserve a little of it to wet the beads in the tube D. The solution in C should be diluted to occupy about the space shown in the figure, so that bubbles of gas can pass through it without risk of the liquid being splashed against the outer cork.

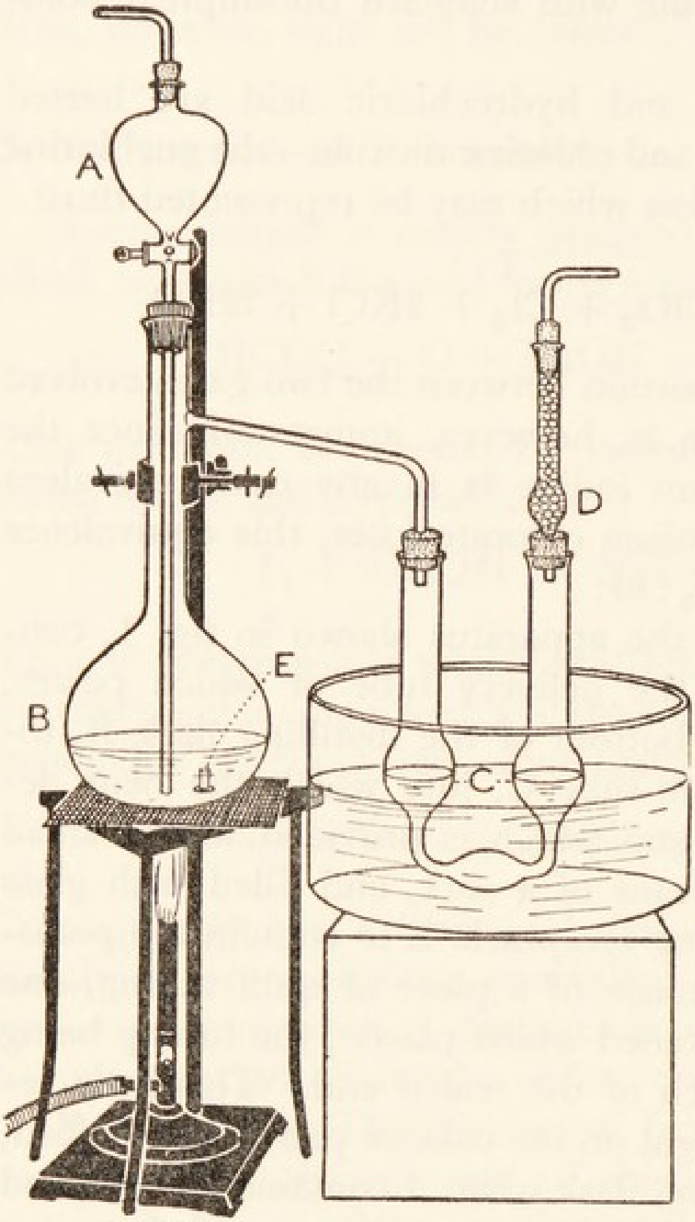

Fig. 1

Now place in the tap funnel about 25 c. c. of concentrated hydrochloric acid, and let this run down into the distilling flask. Turn off the tap, apply heat gently to the bottom of the flask, and gradually raise the liquid to boiling. Remember that at this stage, since by boiling most of the air in the flask has been displaced by steam and hydrogen chloride gas, there is danger of the liquid in the absorption tube being driven by atmospheric pressure into the distilling flask, if the temperature in the latter falls, and air does not otherwise take the place of the condensing steam and hydrogen chloride.

Therefore be ready to apply either suction at D by means of an aspirator or pressure at A by means of carbon dioxide from a Kipp's apparatus. It is immaterial which of these means is employed to remove the remaining chlorine from the distilling flask, but, when the arrangement is made, turn on the tap of the funnel and allow air or carbon dioxide to pass in a slow stream through the solution kept near its boiling-point, until after a few minutes the liquid and the atmosphere above it appear to be quite free from chlorine. Afterwards detach the absorption tube from the rest of the apparatus, transfer the brown iodine solution to a 100-c. c. flask, wash the beads with a little water which is also allowed to run into the flask, and dilute the liquid to volume at atmospheric temperature. Then titrate an aliquot volume of the solution with decinormal thiosulphate solution, and from the result calculate the percentage of potassium chlorate in the specimen of the salt employed.

7. Estimation of Manganese Dioxide and Red Lead or Lead Peroxide.

These oxidizing agents are best estimated in the same manner as potassium chlorate by determining the iodine liberated from potassium iodide by the chlorine evolved when suitable amounts are heated with concentrated hydrochloric acid in the apparatus above described. Since the molecules MnO_2, Pb_3O_4, and PbO_2 contain each one atom of oxygen available for oxidizing purposes, their equivalent weights are half the formula weights. It is convenient to employ quantities of these oxides sufficient to yield amounts of iodine equivalent to 100 c. c. of a decinormal solution, and otherwise to proceed just as in the case of potassium chlorate, but to continue the heating with hydrochloric acid until no solid particles remain. In the case of manganese dioxide there will probably be a little silica remaining in a solution which is yellow on account of ferric chloride present with manganous chloride, whilst the oxides of lead will yield lead chloride, crystallizing from the solution as it cools in white needles.

8. Estimation of Barium and Lead.

Since barium and lead are precipitated from aqueous solutions of their salts as the normal chromates $BaCrO_4$ and $PbCrO_4$, both these metals can be estimated by adding excess of a standard solution of potassium chromate to these solutions, filtering and washing the precipitated chromates, adding potassium iodide to the filtrate containing the excess of chromate, and titrating the liberated iodine with standard thiosulphate solution.

Crystallized barium chloride, $BaCl_2{\cdot}2H_2O$, and lead acetate, $Pb(C_2H_3O_2)_2{\cdot}3H_2O$, will serve for practice in the estimation. Prepare, say, 100 c. c. of a decinormal solution of each of these salts, and, say, 500 c. c. of an equivalent solution of potassium chromate, i.e. a twentieth-molecular solution. Standardize this solution by means of potassium iodide and decinormal thiosulphate,[*] remembering that a twentieth-molecular solution of K_2CrO_4 is $\frac{3}{2}$ times decinormal in oxidizing power, since a K_2CrO_4 solution, decinormal in oxidizing power, is thirtieth-molecular. Therefore the normality of the potassium chromate with reference to precipitation of barium or lead chromate is represented by two-thirds of the volume of decinormal thiosulphate required to react with the iodine it liberates.

Procedure.—Place 25 c. c. of the barium or lead salt solution in a suitable flask, in the case of the lead salt[†] add a little dilute acetic acid to prevent hydrolysis, and heat the solution to boiling. Add 50 c. c. of the potassium chromate solution, boil for a short time, and filter, receiving the clear yellow or orange filtrate in a titrating flask. Wash the precipitate thoroughly, so as to remove all soluble chromate, allowing the washings to run into the rest of the filtrate. Cool the filtrate, and add to it a few drops of concentrated hydrochloric acid and some crystals of potassium iodide. Titrate the liberated iodine as usual; subtract from 50 two-thirds of the volume of decinormal thiosulphate solution required to react with the liberated iodine, then calculate the amount of barium chloride, or lead acetate present in the solution, and therefore its percentage in the salt.

9. Estimation of Potassium Chromate and Dichromate in a mixture of the two.

Potassium dichromate, which may be regarded as a compound of potassium chromate, K_2CrO_4, and chromic anhydride, CrO_3, consequently contains a larger molecular proportion of oxygen available for oxidizing purposes than potassium chromate. Thus $K_2Cr_2O_7$, with molecular weight $= 294{\cdot}2$, contains $\frac{48 \times 100}{294{\cdot}2} = 16{\cdot}32$ per cent of available oxygen, whilst K_2CrO_4 contains only $\frac{24 \times 100}{194{\cdot}2} = 12{\cdot}36$ per cent. Therefore if the percentage of oxygen in a given mixture of the two salts is estimated, this per-

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[*] See Part I, p. 142.

[†] Acetic acid must not be added in the case of the barium chloride, because although barium chromate is practically insoluble in dilute acetic acid, it is perceptibly soluble when chloride is present in addition.

centage must necessarily be found to lie between these two extremes; and from the relation which it bears to them the proportion between the two salts in the mixture can be calculated. Thus, for example, let the available oxygen in the mixture be found to be 15·00 per cent, and let there be x per cent of $K_2Cr_2O_7$, and consequently $(100 - x)$ per cent of K_2CrO_4.

The dichromate thus yields $\frac{16{\cdot}32x}{100}$ per cent of available oxygen and the chromate $\frac{12{\cdot}36(100-x)}{100}$ per cent; and so:

$$\frac{16{\cdot}32x}{100} + \frac{12{\cdot}36(100 - x)}{100} = 15{\cdot}00, \text{ and } x = 66{\cdot}\dot{6}.$$

In this particular example, moreover, it is easy to see that two-thirds of the mixture will consist of potassium dichromate and one-third of potassium chromate, because 15·00 is at two-thirds the linear distance between 12·36 and 16·32.

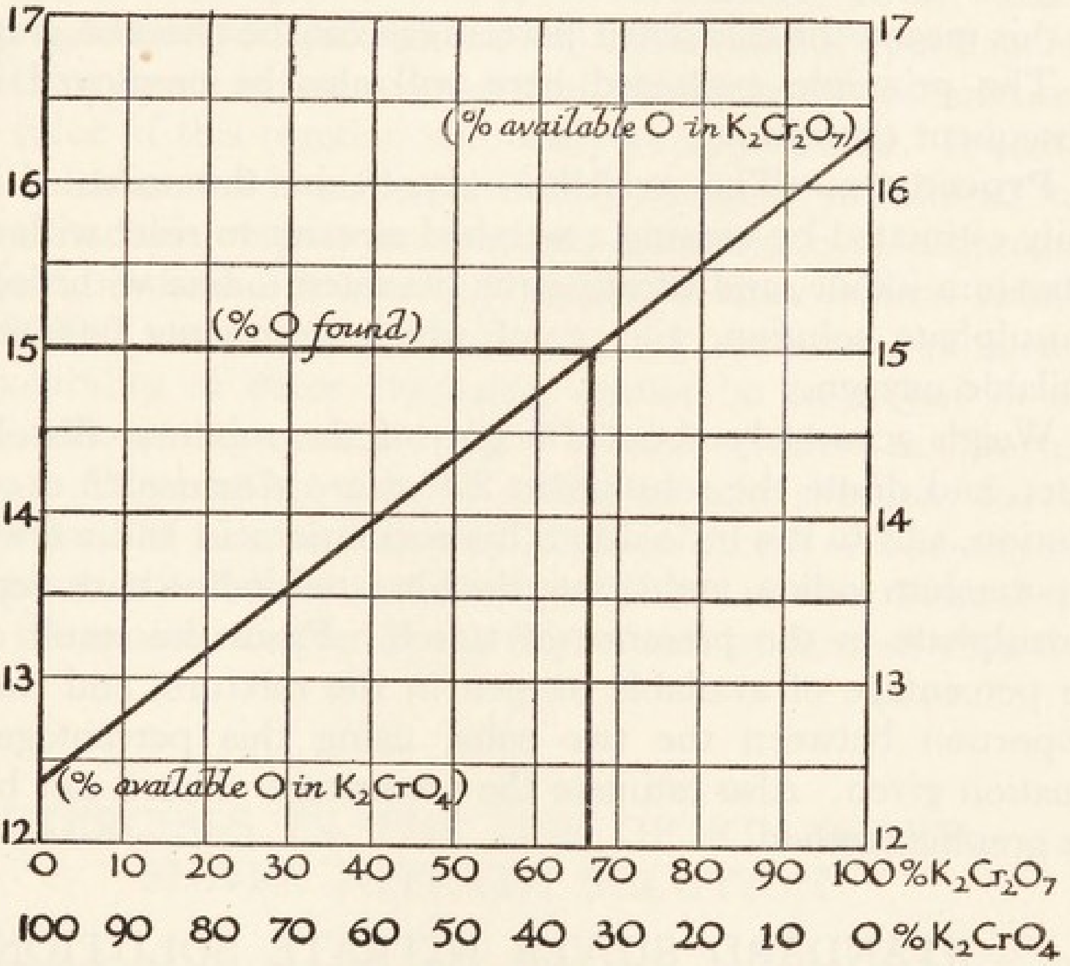

Fig. 2

In general, however, the result may be arrived at by a graphic method, thus:

Let the calculated percentages of oxygen in the two salts be plotted on two vertical axes, and the space between them be divided into 100 parts to represent percentages. Thus 12·36 per cent of oxygen shows zero per cent of potassium dichromate, and 16·32 per cent of oxygen 100 per cent of this salt, with reciprocal relationships for potassium chromate. Then since the variation is continuous, i.e. diminution in the percentage of one salt is identical with increase in the percentage of the other salt in any mixture, the co-ordinates of all points showing percentage of oxygen and percentage of one or other salt in the mixture lie along the straight line joining the points showing percentages of oxygen in the two pure salts. Thus it is seen from fig. 2 that 15·00 per cent of oxygen corresponds with $66 \cdot \dot{6}$ per cent of potassium dichromate. By this means the calculated percentage can be checked graphically.

The principle explained here will also be employed in some subsequent exercises.

Procedure.—The available oxygen in the mixture is most easily estimated by causing a weighed amount to react with acidified potassium iodide, and titrating the liberated iodine with decinormal thiosulphate solution, 1 c. c. of which represents 0·0008 gm. of available oxygen.

Weigh accurately about 1·5 gm. of the mixture, dissolve it in water, and dilute the solution to 250 c. c. Measure 25 c. c. of this solution, add to it a little dilute hydrochloric acid and a few crystals of potassium iodide, and titrate the liberated iodine with decinormal thiosulphate in the presence of starch. From the result calculate the percentage of available oxygen in the mixture, and thence the proportion between the two salts, using this percentage in the equation given. Also estimate the percentage of each salt by use of the graphic method.

STANDARD SILVER NITRATE SOLUTION

The principles underlying the use of standard silver nitrate solution have been discussed in Part I of this book, and estimations of chloride in neutral and acid solution and of silver in acid solution have been described (pp. 148–53).

There are other estimations, however, which may be carried out by the use of decinormal silver nitrate solution in conjunction with decinormal solution, either of sodium chloride or of ammonium thiocyanate.

Directions for preparing pure sodium chloride, and using it to standardize silver nitrate solution have already been given (Part I, pp. 149–52). The use of ammonium thiocyanate (sulphocyanide) may be illustrated qualitatively by the following experiment.

Place some silver nitrate solution in a test-tube, acidify it with nitric acid, and then add a few drops of a dilute solution of ferric alum, that is of a ferric solution containing no chloride. Now add to this mixture, drop by drop, a dilute solution of ammonium thiocyanate. Observe that a white, curdy precipitate, similar in appearance to silver chloride, is formed, and that if the deep red colour due to ferric thiocyanate is seen it disappears on shaking, until, when all the silver has been precipitated, the red colour appears permanently, because thiocyanate is free to react with the ferric salt in solution.

The value of this reaction will easily be appreciated. It enables silver to be estimated in acid solution by means of an internal indicator; and in this respect ammonium thiocyanate in conjunction with a ferric indicator is more advantageous than sodium chloride in conjunction with chromate indicator; for the latter, on account of the solubility of silver chromate, cannot be employed in acid solution. Moreover, standard silver nitrate solution can be used to estimate chloride, bromide, or iodide in acid solution; for if a known volume of silver solution is added in excess of that required to precipitate the halide, and the precipitate is then filtered and washed, the excess of silver in the filtrate can be titrated with thiocyanate.

EXERCISES IN THE USE OF STANDARD SILVER NITRATE SOLUTION

1. Estimation in neutral solution of mixtures of:
    (*a*) Sodium and potassium chlorides.
    (*b*) Potassium chloride and potassium bromide.
2. Estimation of cyanide.

3. Estimation of silver in acid solution by standard ammonium thiocyanate solution.
4. Estimation of chloride in acid solution.
5. Estimation of chloride and bromide when mixed.
6. Estimation of mercury in acid solution.

1 (*a*). Estimation of Sodium and Potassium Chlorides in a Mixture of the two Salts.

Since the atomic weight of sodium is less than that of potassium, sodium chloride contains a larger percentage of chlorine than potassium chloride; and thus the percentage of chloride found in a mixture of the two salts will lie between the maximum and minimum percentage corresponding with pure sodium chloride and potassium chloride respectively. The method of calculating the percentage of each salt from the percentage of chloride found is the same in principle as that explained under the estimation of chromate and dichromate (p. 52). The student should calculate these percentages according to this method, and confirm his result by means of a graph constructed similarly to that already shown.

Procedure.—Gently ignite the given mixture of sodium and potassium chlorides, to remove any adventitious water, and place it whilst warm in a stoppered weighing bottle. When the mixture is cold, accurately weigh by difference 0·6 to 0·7 gm., dissolve this in water, and dilute the solution to 100 c. c. Titrate 20 c. c. of this solution with decinormal silver nitrate solution, using potassium chromate as indicator, and perform the titration preferably in a porcelain dish, whilst stirring the liquid with a glass rod. Using the percentage of chloride found in the solid mixture, calculate the percentage composition of the mixture.

NOTE.—A little thought will show the student that no very great degree of accuracy in the determination of percentages of salts in a mixture is possible by this method. For example, the molecular weight of sodium chloride is 58·5, and that of potassium chloride 74·6; and the volumes of standard silver nitrate solution required to titrate equal weights of these two salts are inversely as the ratio of their molecular weights. If therefore the volume of decinormal silver nitrate solution used to titrate a certain volume of the mixed solution is in the region of 20 c.c., the difference between the extreme volumes needed when one or other salt alone is present does not exceed 5 c. c. That is to say 0·1 c. c. of silver nitrate solution corresponds with a 2 per cent difference in the proportion between the salts in the solid mixture.

1 (*b*). Estimation of Potassium Chloride and Potassium Bromide in a Mixture of the two Salts.

A mixture of potassium chloride and bromide can be estimated by the method and principle adopted in the case of the mixed chlorides above; though a mixture of potassium chloride and sodium bromide or of sodium chloride and potassium bromide could not be so estimated, because analysis does not determine how the basic and acidic radicles are distributed in such a mixture.

When a mixture of chloride and bromide is titrated the weight of silver nitrate used in the reaction is employed in the calculation, thus:

Let a gm. of the mixture of chloride and bromide require for complete precipitation b gm. of silver nitrate; and suppose x gm. of KCl is present, and therefore $(a-x)$ gm. of KBr. The amount of silver nitrate required to react with x gm. of KCl is $\frac{x \times \text{m.w.AgNO}_3}{\text{m.w.KCl}}$, and that required to react with $(a-x)$ gm. of KBr is $\frac{(a-x) \times \text{m.w.AgNO}_3}{\text{m.w.KBr}}$;

therefore:

$$\frac{x \times \text{m.w.AgNO}_3}{\text{m.w.KCl}} + \frac{(a-x) \times \text{m.w.AgNO}_3}{\text{m.w.KBr}} = b;$$

whence x, the proportion of KCl in a gm. of the mixture, and the corresponding percentage of this salt can be calculated.

Procedure.—Gently ignite the mixture of potassium chloride and bromide in a porcelain dish or crucible, and then preserve the dry mixture in a stoppered weighing bottle.* Accurately weigh about 1·0 gm. of the mixture, dissolve it in water, and dilute the liquid to 100 c. c. so as to obtain a solution of a strength in the region of decinormal.

Titrate 20 c. c. of this solution with decinormal silver nitrate, using neutral potassium chromate as indicator. Having obtained

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* If a solution is given for analysis, a measured volume of this must be evaporated to dryness and the weight of the quite dry solid ascertained.

agreeing results, calculate the percentage of chloride and bromide in the mixture by the method described above; also obtain the result by means of a graph.

2. Estimation of Cyanide.

Study the reaction by means of the following experiment. Add to a dilute solution of potassium cyanide silver nitrate solution drop by drop. The precipitate of silver cyanide dissolves in the excess of cyanide to form the soluble complex cyanide $KAg(CN)_2$, thus:

$$AgNO_3 + KCN = AgCN + KNO_3; \ AgCN + KCN = KAg(CN)_2.$$

Continue to add silver nitrate until a further drop causes a permanent precipitate. The formation of the complex cyanide has then come to an end, and consequently this reacts with more silver nitrate thus:

$$KAg(CN)_2 + AgNO_3 = 2AgCN + KNO_3.$$

Therefore the reaction the completion of which is indicated by the permanent precipitate is:

$$AgNO_3 + 2KCN = KAg(CN)_2 + KNO_3;$$

and a decinormal solution of silver nitrate is equivalent to a one-fifth molecular solution of potassium cyanide, 1 litre of which will contain 13·02 gm. of the salt.

The titration is done in presence of alkali, so that in the case of hydrocyanic acid the solution is first made alkaline with sodium hydroxide. The operation may be modified by adding a little potassium iodide as indicator. In this case the permanent precipitate consists of silver iodide, which is less soluble than silver cyanide, and consequently indicates the end of the reaction with more sensitiveness. This is unnecessary, however, unless ammonia is present in the solution, when the insolubility of silver iodide in this reagent secures a sharp end point which otherwise would not appear.

Procedure.—Commercial potassium cyanide is frequently highly impure, though specimens of this product containing upwards of 90 per cent, or even 98 per cent or more of the salt are obtainable. Carefully weigh in a weighing bottle about 1·5 gm. of the material provided;* dissolve the salt in water, and dilute the solution to 100 c. c. in a graduated flask. Procure two burettes; fill one of them with the cyanide solution, and the other with decinormal silver nitrate. Measure 20 c. c. of the cyanide solution into a stoppered bottle and titrate it with the silver nitrate, with shaking, until a faint permanent precipitate appears. Repeat the titration, and after obtaining concordant results calculate the percentage of potassium cyanide in the salt provided.†

3. Estimation of Silver in Acid Solution by Standard Solution of Ammonium Thiocyanate.

Silver can be estimated in acid solution by titrating it with standard sodium chloride, with shaking, until a further drop of the chloride solution is found to give no precipitate, and conversely chloride in acid solution can be estimated similarly by means of standard silver nitrate solution (Part I, p. 152).

This method, however, is tedious, and the method now to be described, in which an internal indicator is employed, is preferable.

Perform the following qualitative experiment. To a little silver nitrate solution in a test-tube add some dilute nitric acid and a few drops of a solution of ferric alum; then add gradually a solution of ammonium thiocyanate (sulphocyanide). White silver thiocyanate, insoluble in dilute nitric acid, is precipitated, any red colour due to ferric thiocyanate disappearing on shaking. When, however, with the continued addition of thiocyanate, all the silver has been precipitated, the red colour due to ferric thiocyanate will appear permanently. Thus silver can be estimated volumetrically in acid solution by means of standard ammonium thiocyanate, ferric sulphate serving as an internal indicator. The method may be employed to estimate the silver in a " silver " coin containing a little copper in addition to silver, because copper in dilute nitric acid solution gives no precipitate with thiocyanate. The same method is also available for estimation of chloride, bromide, or iodide

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* The student must remember that potassium cyanide is dreadfully poisonous, and that it evolves in the air vapours of hydrocyanic acid. The solid salt, therefore, must never be handled, and its solution must never be sucked up a pipette. Great care must be taken, also, not to leave any particles of the salt lying about.

† Potassium cyanide solution will be used later to estimate copper, but for this purpose it is standardized by means of a solution of a copper salt of known strength.

in acid solution; for if excess of standard silver solution is added to the halide solution the silver remaining unprecipitated can be estimated by means of thiocyanate; though in the case of chloride the precipitate must be filtered off and thoroughly washed, and the filtrate titrated with thiocyanate in presence of ferric salt, because silver chloride is sufficiently soluble to undergo double decomposition with ferric thiocyanate. If, however, the liquid containing the precipitate is heated to boiling before titration so as thoroughly to coagulate the silver chloride, this salt becomes less reactive and filtration is unnecessary.

Standardization of Ammonium Thiocyanate Solution.

Prepare 500 c. c. of approximately decinormal solution of ammonium thiocyanate, NH_4CNS, taking about 4 gm. of the salt, and standardize it by means of a decinormal solution of silver nitrate which has been standardized by the use of pure sodium chloride. To do this place 20 c. c. of the silver solution in a flask, add to it a few cubic centimetres of dilute nitric acid and about 1 c. c. of a moderately concentrated solution of ferric alum, or of ferric sulphate, made by heating ferrous sulphate solution with nitric acid until oxidation is complete and no nitrous fumes remain. Then titrate this solution with the thiocyanate solution until, after shaking so as to coagulate the precipitate, the supernatant liquid remains permanently red. Calculate the normality of the ammonium thiocyanate solution, and express it by means of a factor.

Estimation of Silver in a Coin.

Thoroughly clean with dilute nitric acid a small silver coin, such as a three-penny piece, accurately weigh it, and dissolve it in dilute nitric acid in a flask. Boil the solution to drive off nitrous fumes, transfer it to a 100-c. c. graduated flask, and dilute to volume.

Titrate the silver in 20 c. c. of this solution with your standardized thiocyanate solution, using ferric sulphate as indicator, and from the result calculate the percentage of silver in the coin.

4. Estimation of Chloride in Acid Solution.

As explained on p. 55, standard solutions of silver nitrate and ammonium thiocyanate may be used to estimate chloride in acid solution because the chloride can be precipitated by employing a known amount of silver nitrate in excess, and then titrating the excess of silver with thiocyanate after filtering off the silver chloride.

To estimate the hydrogen chloride in a solution of the gas known to be approximately decinormal, add to 20 c. c. of it, say, 40 c. c. of decinormal silver nitrate solution, and heat the liquid and precipitate so as to coagulate the latter. Filter the solution and thoroughly wash the precipitate. Then titrate the filtrate, containing excess of silver nitrate, with standard thiocyanate solution, and subtract the volume of silver nitrate, expressed in cubic centimetres of decinormal solution, which is found to remain from the volume originally taken. Repeat the estimation without filtering off the coagulated silver chloride. Calculate the weight of hydrogen chloride equivalent to the volume of decinormal silver nitrate solution required to precipitate it, and thence the weight of this compound in 1 litre of the solution.

5. Estimation of Chloride and Bromide when mixed.

Chloride and bromide can be precipitated together by excess of silver nitrate, and the silver equivalent of the two acidic radicles taken together estimated by determining the silver remaining. The bromide can then be oxidized and the liberated bromine removed without affecting the chloride, the amount of which remaining can subsequently be estimated.

A simple way of oxidizing bromide without appreciably oxidizing chloride is by means of suitably diluted nitric acid.

Mix nitric acid of 1·42 specific gravity with three times its volume of water, and add about 10 c. c. of this mixture to a few drops of a mixed solution of chloride and bromide contained in a boiling tube. Place the tube containing the colourless mixture in a beaker of water and then boil the water. An orange colour due to liberated bromine will gradually develop, and if a current of air is drawn through the solution it will carry the bromine with it, and in a few minutes leave the solution colourless. Chloride will then be found remaining in the solution. This reaction may be applied quantitatively to remove bromide before estimating chloride; and is useful to estimate a small amount of chloride present as an impurity in the bromide.

For an exercise in the estimation make a dry and intimate mixture of 1 gm. of potassium chloride with 9 gm. of potassium bromide.

Procedure.

(i) *Estimation of total Halide in terms of decinormal Silver Nitrate.*

Weigh accurately 1 gm. of the mixture, dissolve it in water, and dilute the solution to 100 c. c. Titrate 20 c. c. of this neutral solution with decinormal silver nitrate, employing potassium chromate as indicator. It is possible to calculate the proportion between the two salts from this result alone, as already shown; but in the present case what proportion of the silver nitrate solution used was required to precipitate the chloride will be determined by the second part of the estimation.

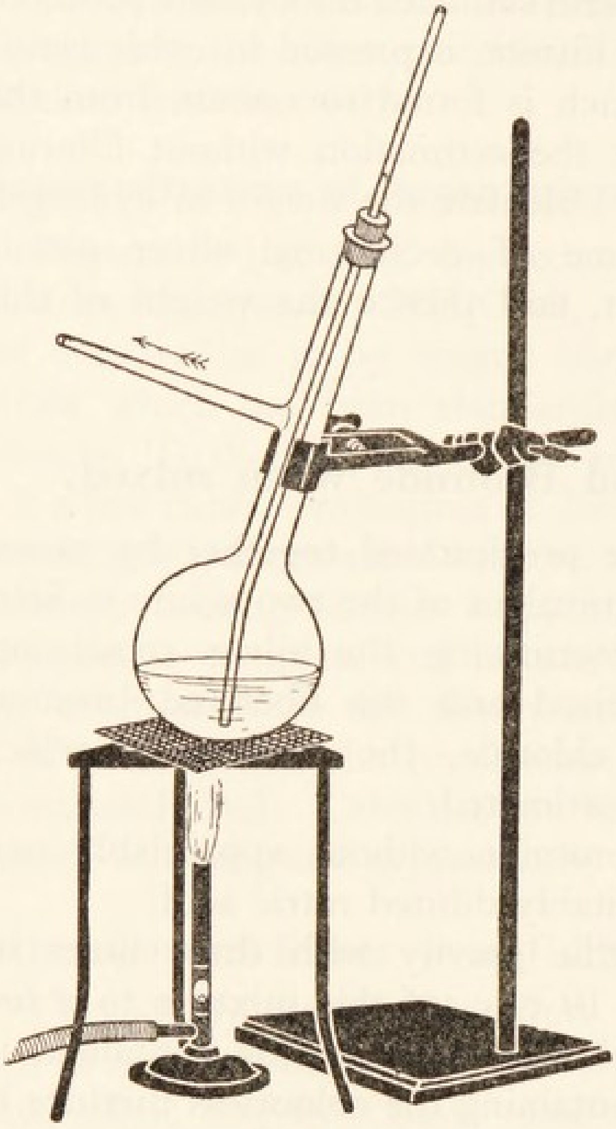

Fig. 3

(ii) *Removal of Bromide, and estimation of remaining Chloride.*

Fit a 500-c. c. distilling flask (fig. 3) with a cork through which passes a glass tube a little drawn out at the end, and bent at an obtuse angle so that when the flask is inclined with its side tube horizontal the bent tube nearly touches the bottom of the flask. Place in the flask 20 c. c. of the prepared solution of chloride and bromide and add to it a mixture of 30 c. c. of nitric acid 1·42 specific gravity and 70 c. c. water. Support the flask upon a tripod with gauze and heat its contents with a small flame, but do not allow the liquid to boil. Attach to the side tube of the flask a rubber tube leading to a water pump, and when bromine begins to be liberated, as shown by the colour of the solution, aspirate a slow current of air through the liquid so as to remove the bromine, keeping a very small flame under the flask all the while. When the solution is colourless, pour it out into a beaker, add to it a volume of decinormal silver nitrate solution known to be in excess of that required to precipitate the chloride, then filter and wash the precipitate, receiving the filtrate in a titrating flask. Titrate the remaining silver with decinormal ammonium thiocyanate, using the ferric indicator, and thence determine the volume of decinormal silver nitrate which was required to precipitate the chloride in the 20 c. c. of solution taken. The amount of silver nitrate corresponding with the total halide has already been determined, consequently that corresponding with bromide is found by difference. Thus calculate the proportion between potassium chloride and bromide in the mixture.

6. Estimation of Mercury in Acid Solution.

Add ammonium thiocyanate to mercuric chloride solution, and observe that no precipitate is formed;* repeat the experiment using mercuric nitrate, and notice that a white precipitate of mercuric thiocyanate, $Hg(CNS)_2$, is obtained which is soluble in excess of the thiocyanate. If the mercuric salt contains a trace of iron, the red colour of ferric thiocyanate will appear when the formation of mercuric thiocyanate is complete. It is concluded, therefore, that mercury obtainable in the form of mercuric nitrate can be estimated by standard thiocyanate in presence of ferric indicator.

Procedure.—To estimate the mercury in mercuric oxide, weigh accurately about 1 gm. of this compound, in the red or yellow form, dissolve it in nitric acid of 1·42 specific gravity and dilute the solution to 100 c. c. Titrate 20 c. c. of this solution with decinormal ammonium thiocyanate after adding to it about 50 c. c. dilute nitric acid and a little ferric indicator. From the result calculate the percentage of mercuric oxide in the specimen analysed.

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* This is due, probably, to the feeble ionization of mercuric chloride, in consequence of which it forms a complex salt with thiocyanate. It is well-known that mercuric chloride discharges the red colour of ferric thiocyanate from this cause.

MISCELLANEOUS EXERCISES

The following unclassified exercises will now be described:

1. Estimation of phosphate by standard uranyl acetate solution.
2. Estimation of zinc by standard potassium ferrocyanide solution.
3. Estimation of copper by potassium cyanide.

1. Estimation of Phosphate by Standard Uranyl Acetate* Solution.

Uranyl hydrogen phosphate, $(UO_2)HPO_4$, or in presence of ammonium salts uranyl ammonium phosphate, $(UO_2)NH_4PO_4$, is obtained as a greenish yellow precipitate when a solution of uranyl acetate* is added to a phosphate solution containing no free acid but acetic acid. The completion of the precipitation can be indicated by the use of potassium ferrocyanide externally because soluble uranyl salts give with this reagent a chocolate coloured precipitate. The reaction between the uranyl and phosphate solutions is completed by heating nearly to boiling the liquid being titrated; and it is necessary to standardize the uranyl solution with a known amount of a phosphate similar to that to be estimated. For example, if an alkali phosphate is to be estimated, the uranyl solution must be standardized by means of a pure alkali phosphate such as $Na_2HPO_4{\cdot}12H_2O$, $NaNH_4HPO_4{\cdot}4H_2O$, or KH_2PO_4. The latter salt is highly recommended because it crystallizes well without water, and can readily be obtained pure. If, however, calcium phosphate is being estimated, in bone ash for example, it is necessary first to standardize the uranyl solution with a specimen of calcium phosphate the phosphate content of which has been determined in another way.

To estimate phosphate in an alkali phosphate prepare the following solutions:

1. *Uranyl acetate solution.*—Dissolve about 18 gm. of uranyl acetate, $[UO_2(C_2H_3O_2)_2]{\cdot}2H_2O$, in water and dilute the solution to 500 c. c. 1 c. c. of this solution is equivalent to about 0·005 gm. P_2O_5.

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* If uranyl acetate is not available the nitrate may be employed.

2. *Potassium dihydrogen phosphate solution.*—Dissolve 1·916 gm. of pure KH_2PO_4 in water, and dilute the solution to 500 c. c. Unless the salt is of guaranteed analytical purity the solution must be standardized by precipitating the phosphate in a measured volume with magnesia mixture, and weighing as $Mg_2P_2O_7$ (see Part I, p. 62). The above solution, if the salt is pure, contains 0·002 gm. P_2O_5 in 1 c. c., so that 50 c. c. should be equivalent to 20 c. c. of the uranium solution.

3. *Ammonium acetate and acetic acid solution.*—Dissolve 50 gm. of ammonium acetate in a little water, add 50 c. c. of acetic acid of 1·04 specific gravity, and dilute the solution to 500 c. c.

4. *Potassium ferrocyanide* may be used in freshly prepared solution, or preferably as the powdered solid set out in little heaps.

Standardization of Uranium Solution.

To standardize the uranium solution proceed as follows. Place in a titration flask 50 c. c. of the standard phosphate solution and 10 c. c. of the solution of ammonium acetate and acetic acid. Powder some potassium ferrocyanide, and place tiny heaps of it at intervals on a white glazed tile. Titrate the cold phosphate solution with the uranyl acetate until a drop of the turbid liquid removed on a glass rod from the flask and brought into contact with the ferrocyanide turns it brown. Then heat the liquid to boiling and repeat the test; no brown colour will now appear because a little uranyl salt remaining uncombined with phosphate in the cold has been precipitated on boiling. Continue to add uranyl solution drop by drop to the phosphate solution, kept nearly boiling, until the external ferrocyanide is turned brown by a drop of the removed liquid. Repeat until constant results are obtained, and calculate the P_2O_5 value per cubic centimetre of the uranyl acetate solution.

Estimation of Alkali Phosphate.

The percentage of phosphate (PO_4) in an alkali salt such as ordinary sodium phosphate ($Na_2HPO_4 \cdot 12H_2O$), microcosmic salt ($NaNH_4HPO_4 \cdot 4H_2O$), or in free phosphoric acid, which can be neutralized by alkali, can be estimated by means of the uranyl solution standardized above. For comparable results to be obtained, however, it is necessary for the solution being estimated to be approximately equivalent as regards phosphate to that employed in standardizing the uranyl solution, and for the process to be carried out under conditions as similar as possible to those obtaining in the process of standardization. Bearing these requirements in mind the student can estimate the phosphate present in either of the above compounds.

Use of Uranium Solution to estimate Calcium Phosphate.

Phosphate as calcium phosphate, such as occurs in bone ash or superphosphate, cannot be estimated correctly by means of the uranium solution standardized with potassium phosphate. It is necessary for this purpose for the solution to have been standardized by means of calcium phosphate itself of known phosphate content.

To prepare a standard solution of calcium phosphate dissolve in dilute hydrochloric acid 4·4 gm. of the purest salt obtainable, add ammonia till the calcium phosphate begins to be precipitated, followed by acetic acid to make the liquid clear again; then dilute the solution to 1 litre.

This solution must now be standardized by estimating its P_2O_5 content by an independent process. To do this carry out a gravimetric estimation by either of the methods described under the analysis of basic slag (p. 125), using for this purpose 200 c. c. of the solution.

Now standardize the uranium solution by means of the standard calcium phosphate solution, using the same procedure as in its standardization by potassium phosphate.

The estimation of phosphate, reckoned as P_2O_5, in bone ash, superphosphate, &c., can now be carried out by means of the specially standardized uranium solution, care being taken that the concentration of the solution as regards phosphate is approximately the same as that of the standard calcium phosphate solution.

If iron or aluminium compounds are present in the material, however, a complication arises; because after the substance has been dissolved in dilute hydrochloric acid, and the solution made alkaline with ammonia and then acidified with acetic acid, phosphates of iron and aluminium will remain undissolved. If the quantity of this undissolved matter is appreciable it must be filtered off, and the phosphate estimated in the filtrate. The residue can then be dissolved in dilute nitric acid and the phosphate in it determined by one of the methods yet to be described. The analyst will probably prefer, however, under these circumstances to estimate the total phosphate by another method.

2. Estimation of Zinc by Standard Ferrocyanide Solution.

The formation of uranyl ferrocyanide, which was used in the previous exercise to indicate excess of uranyl salt solution, may be used reciprocally to indicate excess of ferrocyanide employed as a precipitating agent. Thus if zinc in solution is precipitated by ferrocyanide, excess of the latter is shown by uranium acetate solution used as an external indicator.

The reaction between zinc chloride and potassium ferrocyanide solutions takes place in two stages with the formation respectively of the single salt, $Zn_2Fe(CN)_6$, and the double salt, $K_2Zn_3[Fe(CN)_6]_2$ ($= 3Zn_2Fe(CN)_6 + K_4Fe(CN)_6$). Excess of ferrocyanide appears temporarily in the solution after the precipitation of $Zn_2Fe(CN)_6$, so that a drop of the solution removed colours uranyl acetate; but this ferrocyanide is soon absorbed to form the double salt, the formation of which is completed before the brown colouring of the external indicator appears permanently. Thus the complete reaction is represented by the equation:

$$3ZnCl_2 + 2K_4Fe(CN)_6 = K_2Zn_3[Fe(CN)_6]_2 + 6KCl.$$

The reaction is carried out near the boiling-point of the solution, in presence of an approximately constant amount of hydrochloric acid together with ammonium chloride, which sharpens the end point. It is well, however, to perform a blank experiment in order to determine what volume of ferrocyanide solution is required to produce the same effect with uranium as that observed in the estimation, and to subtract this volume from that of the standard solution used.

Solutions required.

Standard zinc solution.—It is convenient to prepare a solution of a zinc salt containing 10 gm. of zinc per litre. Ignited zinc oxide or recrystallized zinc sulphate is preferable to the metal for this purpose. Therefore prepare 500 c. c. of a standard zinc solution by dissolving 6·225 gm. of ignited zinc oxide in sufficient dilute hydrochloric acid or 21·985 of zinc sulphate, $ZnSO_4 \cdot 7H_2O$, in water, and dilute the solution to 500 c. c.

Potassium ferrocyanide solution.—A solution of potassium ferrocyanide equivalent to the above zinc solution will contain 43·06 gm. of the hydrated salt $K_4Fe(CN)_6 \cdot 3H_2O$ per litre. Therefore weigh about 22 gm. of the salt, dissolve it in water, and dilute the solution to 500 c. c.

Uranyl acetate solution.—A small quantity of a saturated solution.

Ammonium chloride solution.—Dissolve 20 gm. of ammonium chloride in water and dilute the solution to 100 c. c.

Standardization of Potassium Ferrocyanide Solution.

Place 20 c. c of the standard zinc solution in a flask of about 500 c. c. capacity; add to it 10 c. c. of the ammonium chloride solution and 10 c. c. of concentrated hydrochloric acid; then dilute the solution with water to about 200 c. c., and heat it to a temperature of 70° to 80° C. Titrate this solution with the ferrocyanide solution until, after shaking, a drop of it brought into contact with a drop of uranyl acetate solution on a glazed tile develops a permanent brown colour. The reaction of the zinc with the ferrocyanide is not instantaneous; therefore a minute or more should be allowed to elapse finally before bringing a drop of the solution in contact with the external indicator. From agreeing results the zinc value of 1 c. c. of the ferrocyanide solution can be calculated, after the value of the blank experiment now to be performed has been subtracted.

Blank Experiment.

In order to ascertain what volume of ferrocyanide solution is required to produce a standard brown colour with uranyl acetate, perform an experiment similar to that above, but without the zinc salt, and subtract the result, which will not amount to more than a few tenths of a cubic centimetre, from the figure obtained in the standardization.

The Estimation.

The standardized solution of potassium ferrocyanide can now be used to estimate zinc in a zinc compound of unknown composition. Commercial zinc oxide, or the basic carbonate or else a double salt of zinc is a suitable compound for the purpose. If hydrochloric acid is employed to dissolve the compound, the excess of it must be nearly neutralized with ammonia so that the amount of acid present during the titration may be as nearly as possible the same as in the standardization process; and care must be taken otherwise to fulfil the same conditions as in that process. Moreover, if metals such as copper and iron, which give precipitates with ferrocyanide in presence of hydrochloric acid, occur in the substance being analysed, these must be eliminated before the estimation of the zinc.

3. Estimation of Copper by Potassium Cyanide.

When a solution of potassium cyanide is added to the deep blue solution obtained by adding ammonia to a cupric salt, the solution containing the cuprammonium ion is decolorized with the formation of potassium or ammonium cuprocyanide, which may be $M_2Cu(CN)_3$, the copper being reduced to the cuprous condition and combining with the cyanide to form a complex salt. This reaction is employed in qualitative analysis to separate cadmium from copper because the cuprocyanide ion is not affected by hydrogen sulphide; and it may be used to estimate copper if potassium cyanide solution is first standardized by being titrated into a cuprammonium solution of known copper content until the colour of the latter is discharged. There is need for constant conditions, especially as regards the proportion of ammonia present, owing to the variability of the reaction with varying proportions of ammonia. It is well, therefore, to mix with the cupric solution sodium carbonate * until a precipitate begins to appear, then to add a measured volume, say 1 c. c., of dilute ammonia, sufficient to produce a clear blue solution, and finally, when the titration is nearly finished, to dilute the whole to a convenient measured volume, say 100 c. c.

The presence of iron does not interfere with this process, so that the copper in such a mineral as copper pyrites can be estimated by its means.

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* Sutton: *Volumetric Analysis*, 1924, p. 207.

Standard Copper Solution.

The standard copper solution may conveniently contain 5 gm. of copper per litre. Weigh 2·5 gm. of pure copper foil; place the metal in a flask and dissolve it in dilute nitric acid. Evaporate the solution to dryness in a dish to expel excess of nitric acid; dissolve the residue in water, adding a few drops of dilute nitric acid if this is necessary to produce a clear solution; then dilute the solution to volume in a 500-c. c. flask.

Potassium Cyanide Solution.

Weigh about 10 gm. of pure potassium cyanide,* or a proportionately larger quantity of the impure salt; dissolve the salt in water and dilute the solution to 500 c. c.

Standardization of the Potassium Cyanide Solution.

Mark a suitable flask to indicate 100 c. c., and measure into it 20 c. c. of the standard copper solution. Add sodium carbonate until a precipitate begins to form, and then 1 c. c. or other measured volume of dilute ammonia so as to produce a clear blue solution. Titrate this solution with the potassium cyanide, whilst rotating the flask, and when the colour has become pale, add water till the liquid measures 100 c. c. Then finish the titration, stopping when a very pale lavender colour remains. Repeat the titration, and after obtaining concordant results, calculate the copper value of 1 c. c. of the potassium cyanide solution.

Estimation of Copper in Copper Carbonate.

This process is suitable for the estimation of copper in a mineral, alloy, or salt of copper. The determination of the percentage of copper in precipitated copper carbonate, a basic salt of variable composition, is a suitable exercise.

Weigh accurately about 1 gm. of the salt in the form of a green powder, dissolve it in the least quantity of dilute nitric acid, and dilute the solution to 100 c. c. Then titrate 20 c. c. of this solution, first adding sodium carbonate and the same volume of ammonia, and diluting with water in the same way as in the process of standardization.

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* Remember the poisonous nature of this salt, and do not handle it.

COLORIMETRIC ESTIMATIONS

Certain metals yield intensely coloured compounds, soluble in water, by means of which they can be estimated. This is done by matching the colour produced by an unknown small quantity of the metal in the form of the chosen compound, with that produced by a known quantity. The estimation is generally carried out by employing flat-based test glasses, such as are used in the Nessler test for ammonia, standing on a white surface, and looking vertically downwards through the solutions.

Among the metals which, in minute quantities, can be estimated in this way are:

1. Iron as thiocyanate.
2. Copper as ferrocyanide.
3. Manganese as permanganate.

1. Colorimetric Estimation of Iron as Thiocyanate.

The blood-red colour which a solution of an alkali thiocyanate gives with ferric iron is well known. If the deeply coloured solution is poured into much water the colour fades but is restored by the addition of more thiocyanate. The colour is due, probably, to a complex salt which ferric thiocyanate forms with the alkali salt; and to the potassium complex salt the formula $Fe(CNS)_3 \cdot 9KCNS$ has been attributed. It is evident, therefore, that a large excess of thiocyanate must be present to secure the maximum colour, and that constant conditions must be maintained in the estimation of iron by means of this reaction.

Solutions required.

Standard ferric solution.—Weigh accurately 0·8630 gm. of ammonium ferric alum, dissolve the salt in water, adding just sufficient dilute iron-free hydrochloric acid to prevent the development of a brown colour by hydrolysis, and dilute the solution to 1 litre. This litre of solution contains 0·1 gm. of iron, i.e. 0·1 mgm. of iron per cubic centimetre.

Ammonium thiocyanate solution.—Solution of ammonium thiocyanate is conveniently made of normal strength; therefore dissolve 7·6 gm. of this salt in water and dilute the solution to 100 c. c.

Procedure. — Several 100-c. c. Nessler cylinders made of colourless clear glass and of equal cross-section are required. These stand upon a sheet of white paper or opalescent glass, or on a glazed tile. For practice measure 1 c. c. of the standard ferric solution, add to it in a cylinder 1 c. c. of concentrated iron-free hydrochloric acid, and dilute the mixture to 100 c. c. Then add 5 c. c. of the ammonium thiocyanate solution, and thoroughly mix the solutions by stirring. Note the colour developed, and repeat the experiment with other volumes of the ferric solution so as to have side by side several cylinders showing a gradation of colour intensity. The purpose of this experiment is to gain experience; the coloured solutions cannot be kept as standards, for the colours gradually fade owing to the oxidation of thiocyanate by ferric iron, which is thereby reduced to the ferrous state.

Estimation of Iron in Commercial Hydrochloric (Muriatic) Acid.

Numerous commercial chemicals that have not been purified contain small quantities of iron which can be estimated conveniently by the colorimetric method. Commercial hydrochloric acid, for example, is often yellow owing to ferric chloride, which forms with hydrogen chloride a bright yellow compound. The iron in this acid may now be estimated. It is necessary to find out what volume of the commercial acid will yield a suitable colour with thiocyanate; and for this purpose place 10 c. c. of the acid in a cylinder, dilute it with water to 100 c. c., and add 5 c. c. of the ammonium thiocyanate solution as before. If the colour after mixing is of a suitable depth to be matched, place in, say, three other cylinders different quantities of the standard ferric solution, which will yield colours approximating to the colour of the solution to be estimated. Add to each cylinder 10 c. c. of pure hydrochloric acid, being the same volume as that of the impure acid, dilute with water to 100 c. c., add 5 c. c. of the thiocyanate solution, and mix as before. It may be that the colour of the solution containing the iron to be estimated will be exactly matched by that of one of the three standard solutions; but if not, it will be easy to effect a match by taking some intermediate quantity of ferric solution. If it is necessary to use a larger volume than 10 c. c. of the impure hydrochloric acid to secure sufficient depth of colour to be matched, a corresponding volume of pure hydrochloric acid must be used in the standard solution.

When the colour given by the iron-containing acid has been matched by a measured volume of the standard ferric solution under similar conditions, repeat the experiment, and having obtained concordant results, calculate the weight of iron in 1 litre of the acid.

2. Colorimetric Estimation of Copper as Ferrocyanide.

When potassium ferrocyanide is added to copper sulphate solution a brown precipitate is obtained, but if the amount of copper present is very small a brown coloration appears instead of a precipitate, and the depth of this coloration furnishes a means of determining copper colorimetrically.

The test is carried out in neutral solution and in presence of ammonium nitrate, which enhances the colour. Iron and other metals which are precipitated by ferrocyanide must of course be absent. If iron is present it must be obtained in the ferric condition, and precipitated from solution by ammonia. The ferric hydroxide is then filtered off, dissolved in hydrochloric acid, reprecipitated with ammonia, and again filtered. The two filtrates now contain all the copper. They are mixed, and if necessary the solution is evaporated until it is sufficiently concentrated for the colorimetric estimation of copper.

Solutions Required.

Standard copper solution.—This solution, which is to contain 0·1 mgm. of copper per cubic centimetre, is made by dissolving 0·393 gm. of copper sulphate, $CuSO_4{\cdot}5H_2O$, in water, and diluting the solution to 1 litre.

Potassium ferrocyanide solution.—Dissolve 4 gm. of potassium ferrocyanide, $K_4Fe(CN)_6{\cdot}3H_2O$, in water, and dilute the solution to 100 c. c.

Ammonium nitrate solution.—The solution of ammonium nitrate should contain 10 gm. of the salt in 100 c. c.

Procedure.—1 c. c. of the potassium ferrocyanide solution and 5 c. c. of the ammonium nitrate are placed in a Nessler cylinder, and the mixture is diluted somewhat. The neutral copper solution is then added in sufficient quantity to produce a suitable coloration, and the whole is mixed after dilution to 100 c. c. When the standard copper solution is being used, successive quantities of it may be added to the same ferrocyanide solution until the required depth of colour is obtained.

This process is suitable for the estimation of copper present in water contaminated with this metal. To obtain such water add 1 c. c. of dilute sulphuric acid to 100 c. c. of water and allow this liquid to stand in the air in contact with some clean pieces of copper foil for a day. Then pour off the liquid, carefully neutralize the acid with ammonia, and dilute the solution to 1 litre. Determine how much of this solution should be used for the test by mixing 10 c. c. of it with potassium ferrocyanide and ammonium nitrate solutions in a cylinder. Then carry out the test according to the directions given above. Calculate the weight of copper per litre of the water.

3. Colorimetric Estimation of Manganese as Permanganate.

There are several reactions by which manganese in the form of a lower oxide or its derivative can be oxidized to permanganate. Heating with lead peroxide and concentrated nitric acid effects this change, as well as digestion with sodium bismuthate and diluted nitric acid. The first reaction has been used in qualitative analysis to detect manganese in presence of much iron, and the second has already been employed for the estimation of manganese. Another reaction, now to be employed colorimetrically, can be illustrated by the following experiment. Place in a test-tube a drop or two of the usual qualitative solution of manganese sulphate, fill up the tube with water, and mix. Prepare a solution of ammonium persulphate in cold water. Pour about 1 c. c. of the diluted manganese solution into each of two test-tubes, add to each an equal volume of the persulphate solution and a few drops of dilute sulphuric acid. Then add to the contents of one test-tube 1 c. c. of dilute silver nitrate solution, and to the other an equal volume of water, so that the contents of the two tubes are alike in all respects, except that to one and not the other has been added silver nitrate. Place the two tubes in a beaker of hot water, and observe that the solution containing the silver nitrate soon becomes pink, although it may go through the stage of brown hydrated manganese dioxide; whilst the other solution remains colourless, or at most develops a brown colour after some time.

This experiment shows that acidified manganous solution is oxidized to permanganate by ammonium persulphate in presence of silver nitrate as a catalyst. The reaction is quantitative, and may be carried out in presence of sulphuric or nitric acid, but not hydrochloric acid, which would precipitate the silver. It is valuable for the estimation of manganese in steel, because ferric iron does not interfere with the reaction. Moreover, this process has the advantage that when the manganese in the solution of a suitable weighed quantity of material has been oxidized to permanganate, that solution can then be diluted to a convenient volume and a measured proportion only of this taken to match a certain volume of a standard permanganate solution.

Solutions required.

Standard manganese solution.—Ignite in a crucible a small quantity of pure manganese sulphate so as to make it anhydrous, and when the salt is cold weigh 0·275 gm. of it; dissolve this in water, add 50 c. c. of dilute nitric acid, and dilute the solution to 1 litre. 1 c. c. of this solution contains 0·1 mgm. of manganese.

Silver nitrate solution.—A solution of convenient strength is made by dissolving 0·5 gm. of silver nitrate in water, and diluting the solution to 100 c. c.

Ammonium persulphate solution.—20 gm. in 100 c. c. of solution will be convenient. This solution should be made with cold water just before it is required.

Procedure.

Manganese in a mineral.—Manganese occurs in small quantities in various minerals, especially those containing allied elements which form compounds isomorphous with those of manganese. Thus manganese is found in minute quantities in limestone and dolomite, and also in spathic iron ore, i.e. ferrous carbonate, with which manganous carbonate is isomorphous. First test the mineral, e.g. spathic iron ore, for manganese, by mixing a little of it in the powdered state with lead peroxide and concentrated nitric acid, and heating the mixture to boiling.* After adding

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* This method of oxidation is a little more rapid than the persulphate method, and is more suitable for a qualitative test.

much water and allowing the undissolved lead peroxide to settle, the crimson colour of permanganate will be seen if an appreciable quantity of manganese was present. For the estimation weigh 1 gm. of the finely powdered ore and heat it with diluted nitric acid until effervescence ceases, and only a little siliceous matter remains. Dilute the solution to 100 c. c., filtering if necessary before making up to volume.

Place 10 c. c. of this solution in another 100-c. c. flask, then add to it 10 c. c. of silver nitrate solution and 5 c. c. (=1 gm.) of the ammonium persulphate solution, and heat the flask on the water bath or in a beaker of water, which is gradually brought to the boiling-point. A pink or crimson colour will gradually develop, but this may be preceded by the formation of a brown turbidity owing to the formation of hydrated manganese dioxide. If much manganese dioxide separates, and shows little sign of giving place to a crimson colour, too much manganese was present, and the experiment must be repeated with a smaller volume of the solution. When the liquid shows signs of developing a clear colour, and bubbles of oxygen make their appearance owing to the decomposition of the persulphate, remove the flask from the hot water and allow it to stand for the colour to develop completely.

Meanwhile prepare a standard of comparison by taking 10 c. c. of the standard manganese solution, containing 1 mgm. of manganese, and convert the manganese into permanganate in the same way. Dilute both solutions to 100 c. c. at atmospheric temperature, and compare their tints in Nessler cylinders. To do this it is convenient to place 50 c. c. of the paler of the two solutions in a cylinder; and having filled a burette with the deeper coloured solution to ascertain what volume of this solution, short of 50 c. c., matches in a similar cylinder the colour of the solution in the first cylinder.

The manganese content of the two solutions is obviously inversely proportional to the volumes required to produce the same depth of colour in the two cylinders, and from the observations made the percentage of manganese in the ore can be calculated. A repetition of the experiment should give the same result.

Manganese in steel.—Steel generally contains a few tenths per cent of manganese; if it contains 0·5 per cent 0·2 gm. will contain 1 mgm., a quantity suitable to be estimated by the colorimetric method. Weigh 0·2 gm. of the steel, dissolve it in a mixture of equal volumes of concentrated nitric acid and water, and heat the solution till nitrous fumes cease to be evolved. Place the solution in a 100-c. c. flask, and convert the manganese into permanganate as in the former estimation.

After diluting to volume, match the colour developed by comparison with the standard manganese solution, similarly converted into permanganate, or preferably by the use of a standard steel, similarly treated, the manganese content of which is accurately known.

SOME SPECIAL VOLUMETRIC PROCESSES

Use of Potassium Iodate in Volumetric Analysis

Introduction.

It is well known that iodic acid oxidizes hydriodic acid thus:

$$HIO_3 + 5HI = 3H_2O + 3I_2.$$

Free iodine may, however, be oxidized thus:

$$I_2 + O + 2HCl = H_2O + 2ICl,$$

so that it becomes basic. This oxidation is brought about by a further amount of iodic acid in presence of hydrochloric acid in quantity sufficient to stabilize the iodine monochloride, by preventing its hydrolysis. The successive reactions may, therefore, be represented thus:

$$\begin{array}{lr} & HIO_3 + 5HI = 3I_2 + 3H_2O \\ & HIO_3 = HI + 3O \\ & \underline{3I_2 + 3O + 6HCl = 6ICl + 3H_2O.} \\ \text{Adding:} & 2HIO_3 + 4HI + 6HCl = 6ICl + 6H_2O. \\ \text{Halving:} & HIO_3 + 2HI + 3HCl = 3ICl + 3H_2O; \end{array}$$

or, in terms of ions:

$$IO_3^- + 2I^- + 6H^+ = 3I^+ + 3H_2O;$$

or, considering the iodate ion only, which, in its reduction, consequent on the oxidation of $2I^-$ to $2I^+$, receives four electrons ($4e$):

$$IO_3^- + 6H^+ + 4e = I^+ + 3H_2O.$$

Iodic acid may, however, oxidize other substances besides HI, e.g. HCNS; and the use of the above ionic or electronic equation must not be allowed to obscure the fact that iodine is liberated in the course of all reactions on which the use of potassium iodate in volumetric analysis depends. Indeed, it is the disappearance of this free iodine which marks the end of every titration.

Consider the oxidation of HCNS by HIO_3:

$$2HIO_3 = H_2O + I_2 + 5O$$

$$2HCNS + 6O + 2H_2O = 2HCN + 2H_2SO_4$$

Thus:

$$\begin{aligned} 12HIO_3 &= 6H_2O + 6I_2 + 30O \\ 10HCNS + 30O + 10H_2O &= 10HCN + 10H_2SO_4 \\ 3HIO_3 + 6I_2 + 15HCl &= 15ICl + 9H_2O. \end{aligned}$$

Adding:

$$10HCNS+15HIO_3+15HCl$$

$$= 10HCN+10H_2SO_4+15ICl+5H_2O$$

1/5th: $2HCNS+3HIO_3+3HCl$

$$= 2HCN+2H_2SO_4+3ICl+H_2O;$$

or: $2HCNS + 3IO_3^- + 2H^+$

$$= 2HCN + 2SO_4^{=} + 3I^+ + H_2O.$$

It appears from this study that four-fifths of the HIO_3 is available to oxidize HCNS, whilst one-fifth reacts with the liberated iodine to form ICl. This relationship is always true; for, in terms of oxides:

$$[I_2O_5 = I_2 + 5O] + [I_2 + O = I_2O] = [I_2O_5 = I_2O + 4O].$$

The following explanation may help to an understanding of the above electronic equations:

First, it must be recognized that the terms oxidation and reduction are not absolute terms, since the former, at least, implies the addition of a particular element: oxygen. For example, the change of iron from the ferrous to the ferric state may involve oxygen, chlorine, or other element or radicle; thus the reactions:

$$2FeO + O = Fe_2O_3 \text{ and } 2FeCl_2 + Cl_2 = 2FeCl_3,$$

do not differ so far as the iron is concerned, since the compounds are ionized; for they both consist in a change from the ferrous to the ferric state, i.e. a change in the valency of the iron atom.

Now, a change in valency is a change in electronic content; and oxidation is equivalent to removal of electrons with increase of positive ionic charge, or decrease of negative charge, since an electron stands for one negative charge; whilst reduction is equivalent to addition of electrons or increase of negative ionic charge, thus:

$$\mathrm{Fe^{++}} - \mathrm{e} = \mathrm{Fe^{+++}} \text{ and } \mathrm{Fe^{+++}} + \mathrm{e} = \mathrm{Fe^{++}}.$$

Applying these principles to the case in hand, the electrically neutral atom of free iodine has seven electrons (.) in its outer orbit, i.e. seven valency electrons, thus: $\left[:\underset{\cdot}{\ddot{\mathrm{I}}}:\right]^{\circ}$, and this may undergo either reduction or oxidation:

$$\left[:\underset{\cdot}{\ddot{\mathrm{I}}}:\right]^{\circ} + \mathrm{e} = \left[:\underset{\times\,\cdot}{\ddot{\mathrm{I}}}:\right]^{-};\ \left[:\underset{\cdot}{\ddot{\mathrm{I}}}:\right]^{\circ} - \mathrm{e} = \left[:\ddot{\mathrm{I}}:\right]^{+}, \text{the added electron}$$

being shown temporarily by the sign ×.

In the first case the iodide ion is formed; in the second the positive basic ion of iodine monochloride.

The equation $IO_3^- + 6H^+ + 4e = I^+ + 3H_2O$ may now be represented pictorially thus:

$$\left[\begin{array}{lll} :\ddot{\mathrm{O}}: & & \\ :\ddot{\mathrm{I}}: & \ddot{\mathrm{O}}: & \\ \times\ \cdot & \cdot\cdot & \\ :\underset{\cdot\cdot}{\mathrm{O}}: & & \end{array}\right]^{-} + 4\mathrm{e} = \left[:\overset{\times\times}{\mathrm{I}}\substack{\times\\ \times}\right]^{+} + 3\left[:\underset{\cdot\cdot}{\ddot{\mathrm{O}}}:\right]^{=}$$

$$\text{and } 3\left[:\underset{\cdot\cdot}{\ddot{\mathrm{O}}}:\right]^{=} + 6\mathrm{H}^{+} = 3\left[\mathrm{H}:\underset{\cdot\cdot}{\ddot{\mathrm{O}}}:\mathrm{H}\right]^{\circ};$$

the double negative charges on the oxygen ions neutralizing the positive charges on the hydrogen ions in the formation of water.

Also the equation $IO_3^- + 2I_2 + 6H^+ = 5I^+ + 3H_2O$, to be employed later, may be expanded thus:

$$\left[\begin{array}{l} :\ddot{\mathrm{O}}: \\ :\underset{\cdot\cdot}{\ddot{\mathrm{I}}}:\underset{\cdot\cdot}{\ddot{\mathrm{O}}}: \\ :\underset{\cdot\cdot}{\mathrm{O}}: \end{array}\right]^{-} + 4\left[:\underset{\cdot}{\ddot{\mathrm{I}}}:\right]^{\circ} = 5\left[:\ddot{\mathrm{I}}:\right]^{+} + 3\left[:\underset{\cdot\cdot}{\ddot{\mathrm{O}}}:\right]^{=} \text{ and, as before:}$$

$$3\left[:\underset{\cdot\cdot}{\ddot{\mathrm{O}}}:\right]^{=} + 6\mathrm{H}^{+} = 3\left[\mathrm{H}:\underset{\cdot\cdot}{\ddot{\mathrm{O}}}:\mathrm{H}\right]^{\circ}.$$

It should be observed that in all cases the equations balance, both as regards charges, and total numbers of electrons.

Estimations

1. Iodide.

From the equation:

$$IO_3^- + 6H^+ + 4e = I^+ + 3H_2O,$$
$$\text{or } IO_3^- + 4I^\circ + 6H^+ = 5I^+ + 3H_2O,$$

it appears that a solution of potassium iodate decinormal with reference to free iodine will be 1/40th molecular.

From the equation:

$$IO_3^- + 2I^- + 6H^+ = 3I^+ + 3H_2O,$$

however, it appears that a M/40 solution of the iodate will be equivalent to only half its volume of N/10 potassium iodide solution, because in this case twice as many electrons need to be removed to produce the positive iodine ion, thus:

$$I^- - e = I^\circ, \text{ and } I^- - 2e = I^+.$$

So a M/40 solution of KIO_3, containing 5·351 gm. of this salt per litre, is equivalent to a solution of iodine containing 12·69 gm. per litre, and to one of potassium iodide containing 8·302 gm. (= 6·347 gm. iodide ion) per litre.

Prepare convenient quantities of these solutions of KIO_3 and KI, using pure (A.R.) KIO_3, which has first been dried at 120°; then proceed in the following manner.

Place a suitable volume, say 25 c. c., of the iodide solution in a stoppered bottle of 250 c. c. capacity, then add an equal volume of concentrated hydrochloric acid, and 5 c. c. of chloroform. Nearly this proportion of hydrochloric acid is necessary to prevent hydrolysis of the iodine monochloride into which all the iodine is finally converted, and thus to stabilize the I^+ ion. So that if in any case the solution becomes much diluted by the added iodate solution a compensating quantity of hydrochloric acid must be added.

Now titrate the iodate into the iodide solution with frequent shaking of the stoppered bottle. It will be observed by the changing colour of the solution that the iodine liberated in the earlier stages of the titration enters again into combination; and as the aqueous layer becomes pale the remaining iodine will be seen to colour the chloroform violet. The fading and disappearance of this colour can be well observed, and so the end of the reaction estimated accurately. The iodine monochloride is then seen to give a lemon-yellow colour to the aqueous solution. Thus the amount of iodide in any given solution can be estimated.

2. Iodide and Free Iodine.

It will be understood that since iodate liberates iodine from iodide solution, and then converts it into iodine monochloride, free iodine in potassium iodide solution will be titrated together with the iodide. And, moreover, since M/40 KIO_3 solution is equivalent to N/10 iodine, the free iodine in the mixed solution can be first titrated with N/10 sodium thiosulphate solution, and the number of c. c. thus required subtracted from the volume of iodate solution used in titrating an equal volume of the solution of iodine and iodide. The difference will then be the volume of iodate solution which reacted with the potassium iodide. Thus the amounts of both iodine and potassium iodide in a solution of the two can be ascertained; an important fact considering the analytical importance of such a solution.

3. Copper.

The oxidation of thiocyanic acid has been elucidated in the introduction to this section; and copper may be estimated by precipitating cuprous thiocyanate and titrating it with iodate. The oxidation involves conversion of cuprous into cupric, and the sulphur of thiocyanate into sulphate. The equation, which can be constructed similarly to that for thiocyanate only, is:

$$4CuCNS + 7HIO_3 + 7HCl = 4CuSO_4 + 4HCN + 7ICl + 5H_2O;$$

and thence it may be calculated that 1 c. c. of M/40 KIO_3 = 0·908 m.g.Cu.

For practice in the estimation, weigh accurately about 4 gm. of $CuSO_4 . 5H_2O$, dissolve it in water, and dilute the solution to 1 litre. Add to 25 c. c. of this solution sulphurous acid and a moderate excess of potassium or ammonium thiocyanate solution. Allow the mixture to stand at atmospheric temperature for 15 minutes for the complete precipitation of cuprous thiocyanate; then collect the precipitate on an asbestos or paper filter, wash it with water, and transfer it with the asbestos or paper to the stoppered bottle; add hydrochloric acid and chloroform, and titrate with the iodate solution as before. The filtering material does not influence the titration, and the end of the reaction is sharp. The method may be used for the estimation of copper in ores and alloys, or any material from which the copper can be obtained in solution and precipitated as pure cuprous thiocyanate.

N.B.—As hydrocyanic acid is liberated in this and other reactions in which thiocyanate is employed, care should be taken not to inhale any vapour arising from the solution.

4. Zinc.

When a mixture of mercuric chloride and ammonium or potassium thiocyanate is added to a neutral or slightly acid solution of a zinc salt, the zinc is quantitatively precipitated as the double thiocyanate $ZnHg(SCN)_4$. This can be titrated with iodate solution, the reaction being:

$$\begin{aligned}&ZnHg(SCN)_4 + 6HIO_3 + 6HCl \\ &\qquad = ZnSO_4 + HgSO_4 + 2H_2SO_4 + 6ICl + 4HCN + 2H_2O.\end{aligned}$$

It will be observed, however, that the ratio of iodate to zinc being much greater than in, say, the preceding case of iodate to copper, a M/40 solution of potassium iodate will not suffice for this reaction. A convenient solution is a M/5 one, containing 42·806 gm. KIO_3 per litre, 1 c. c. of which is equivalent to 0·00218 gm. Zn. It must be remembered, however, that with an iodate solution of this concentration the end of the reaction is reached more suddenly, so that there is danger of adding too much iodate if care is not exercised.

Prepare the precipitating solution so as to contain 39 gm. of potassium thiocyanate or an equivalent quantity of the ammonium salt, and 27 gm. of mercuric chloride per litre; for practice, also prepare a solution of pure zinc sulphate containing about 2 gm. of zinc per litre.

Place, say, 25 c. c. of the zinc solution in a suitable beaker, add 25 c. c. of the precipitating solution and 20 c. c. of water, stir, and let stand. A crystalline precipitate of the required double salt gradually separates, but an hour should be allowed for complete precipitation. Then collect the precipitate on an asbestos or paper filter, wash it, first with cold water containing a very little of the precipitating solution, and then with a little pure water. Transfer it to the stoppered bottle by means of a mixture of 35 c. c. of concentrated hydrochloric acid and 10 c. c. water, add 5 c. c. of chloroform, and titrate the mixture with the standard potassium iodate solution.

The results are accurate, and the method is general for the estimation of zinc. Salts of bismuth, cadmium, copper, cobalt, manganese, and mercurous mercury, must, however, be absent, and ferric iron, if present, must first be reduced to the ferrous state by sulphur dioxide. If acid is present in the original solution it must not exceed 5 per cent.

5. Mercury.

In view of the method of estimating zinc described above, it is obvious that mercuric mercury can be estimated by precipitating and titrating the same double salt, $ZnHg(SCN)_4$. The precipitating solution in this case should contain 39 gm. of KSCN, or an equivalent quantity of NH_4SCN, and 29 gm. of $ZnSO_4 . 7H_2O$ per litre; and the same M/5 KIO_3 solution is equivalent to 0·006682 gm. of mercury per c. c.

The method may be used to estimate mercuric oxide, which can be dissolved in dilute nitric acid, as well as other mercuric compounds, provided they can be obtained in solution containing not more than about 5 per cent of acid.

6. Sodium thiosulphate.

The reaction between thiosulphuric and iodic acids forms an interesting study, though the method based upon it is not to be preferred for the purpose of standardizing sodium thiosulphate solution to the direct method of titrating iodine liberated from iodide by dichromate.

The oxidation of $H_2S_2O_3$ is thus represented:

$$H_2S_2O_3 + 4O + H_2O = 2H_2SO_4,$$

and therefore the reaction with iodic acid is as follows:

$$H_2S_2O_3 + 2HIO_3 + 2HCl = 2H_2SO_4 + 2ICl + H_2O.$$

Now it was seen above, under the estimation of iodine, that M/40 KIO_3 is equivalent to N/10 iodine; but in the reaction between iodic and thiosulphuric acids four atoms of oxygen are provided by the iodate instead of the one atom of free iodine per molecule of thiosulphate in the familiar titration. It follows, therefore, that a M/5 solution of KIO_3 will be equivalent to a N/10 solution of sodium thiosulphate. Prepare these solutions and proceed as follows:

Place 20 or 25 c. c. of N/10 sodium thiosulphate solution in the stoppered bottle, add an equal volume of concentrated hydrochloric acid, and 5 c. c. of chloroform, and titrate as usual. No sulphur will appear to be liberated immediately by the concentrated acid in the cold, nor will sulphur dioxide leave the solution. When a little iodate solution has been added, iodine will appear locally in the solution, but will disappear again. This will necessarily occur so long as thiosulphate remains in the solution, for free iodine cannot coexist with thiosulphate. Thus iodide and tetrathionate are formed as intermediate products in the reaction, but disappear before the final stage is reached, so that their formation need not be represented in the equation. When, however, no more thiosulphate remains, iodine appears in the solution, and the titration is continued until the violet colour it imparts to the chloroform has been discharged. The two solutions, viz. M/5 potassium iodate and N/10 sodium thiosulphate, should thus be proved equivalent.

A number of other estimations can be carried out by means of standard potassium iodate solution; *vide*, *Volumetric Iodate Methods* by G. S. Jamieson, Chemical Catalog Co., New York, 1926; also *Modern Methods of Quantitative Chemical Analysis* by Mitchell and Ward, Longmans, 1932.

ESTIMATIONS DEPENDING ON THE FORMATION OF POTASSIUM MERCURI-IODIDE

Mercuric iodide dissolves in excess of potassium iodide to form potassium mercuri-iodide thus:

$$HgI_2 + 2KI = K_2HgI_4;$$

and basic mercuric compounds behave similarly, with liberation of alkali which may be titrated.

1. Mercuric Oxide.

Yellow mercuric oxide reacts with excess of potassium iodide thus:

$$HgO + 4KI + H_2O = K_2HgI_4 + 2KOH;$$

and the liberated alkali can be titrated with standard acid, methyl-orange being the indicator.

For practice in the estimation weigh accurately about 0·2 gm. of pure, yellow mercuric oxide, suspend it in water in a stoppered bottle, add potassium iodide crystals, and shake until all solid has disappeared. Then add methyl-orange and titrate with N/10 acid.

The method is accurate, and it is possible, though rather extravagant, to use it to standardize acid, if pure mercuric oxide is employed.

2. Infusible White Precipitate: Mercuric Aminochloride, $HgNH_2Cl$.

This compound reacts with excess of potassium iodide in solution as follows:

$$HgNH_2Cl + 4KI + H_2O = K_2HgI_4 + KCl + KOH + NH_3.$$

Thus, as before, two equivalents of alkali are liberated for each atom of mercury, and these may be titrated with N/10 acid, with methyl-orange as indicator.

Have the white precipitate in a dry and finely divided state; weigh accurately about 0·25 gm. of it, suspend this in water in a stoppered bottle, add solid potassium iodide, and shake until all is dissolved. The solution should be diluted to 30–40 c. c. to avoid loss of the liberated ammonia. Add methyl-orange and titrate with N/10 acid as before. This method provides a convenient, rapid, and accurate assay of " white precipitate ".

USE OF ADSORPTION INDICATORS

Certain organic colouring matters are adsorbed by some precipitates formed in volumetric analysis, and for this reason may be used to indicate the end of a reaction.

For example, if a few drops of an alcoholic solution of fluorescein are added to a neutral solution of sodium chloride, and the solution is then titrated with silver nitrate, the fluorescein produces no permanent effect so long as chloride remains in excess, but when the precipitation of silver chloride is finished and silver ions are available in the solution, the fluorescein combines with them forming a red salt whose characteristic colour indicates the end of the reaction. Indeed the whole of the precipitated silver chloride, which by shaking is made to coagulate, is coloured pink by the adsorbed colouring matter, which has been removed from the solution.

Chlorides, bromides, and iodides, in N/10 neutral solution, can be estimated by N/10 silver nitrate, with use of suitable adsorptive indicators, which are used in 1 per cent alcoholic solution, one or two drops sufficing for an estimation. The following are suitable indicators:

For chloride: fluorescein or dichlorofluorescein.
For bromide: eosin or a 1 : 10 solution of red ink.
For iodide: di-iodofluorescein.

It is said to be possible by the use of a combination of indicators to estimate chloride and iodide, or bromide and iodide, when occurring together; but the right conditions are difficult to arrange (see Mitchell and Ward, p. 12).

For the estimation of chloride and bromide adsorption indicators have no advantage over chromate; but for experience the student may prepare the necessary solutions and compare the two methods.

For the estimation of iodide, however, the adsorptive method is valuable, since this estimation cannot be performed accurately in neutral solution with potassium chromate as indicator.

Estimation of Iodide.

Prepare a 1 per cent solution of di-iodofluorescein in alcohol, also N/10 solutions of silver nitrate and potassium iodide. Place 20 c. c. of the iodide solution in a suitable stoppered bottle, dilute it to about 100 c. c., add 2 or 3 drops of the solution of di-iodofluorescein, and titrate it with the silver nitrate solution with frequent shaking. As the reaction is finishing the precipitated silver iodide will coagulate, and at the end the precipitate will collect together and be seen coloured pink by the adsorbed indicator.

If an unknown iodide solution is given for estimation, the student may compare this method with that of precipitating the iodide with excess of standard silver nitrate in nitric acid solution, filtering, washing, and titrating the excess of silver nitrate with ammonium thiocyanate with ferric alum indicator. Thus it will be found that the adsorptive method, while equally accurate, is more expeditious than the indirect method.

INDICATORS AND *p*H VALUE

Introduction.

The beginner in chemistry learns to use moistened litmus paper to discover whether a substance is acid or alkaline in reaction, and gains the impression that there is a sharp boundary line between the two states. That early impression has, however, to be modified when in the beginning of volumetric analysis more than one indicator is employed, and a choice of indicator has to be made according to the kind of acid or alkali that is being titrated. Thus, it has been observed that the colour of methyl-orange changes gradually when the point of neutrality is being reached by titrating an alkaline solution with oxalic acid; and so it is concluded that methyl-orange is an unsuitable indicator to use with that acid. For the same reason it has been found that phenolphthalein is an unsuitable indicator to use when titrating ammonia solution.

More striking is the difference between these two indicators as regards carbonic acid, for it has been observed that the proportion of hydroxide and carbonate in a solution can be found with moderate accuracy by reason of the fact that phenolphthalein reacts to carbonic acid but methyl-orange does not. It has also been shown (Part I, p. 155) 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.

Lastly, it has been proved that the degree of dilution of a solution affects the indicator; for if a small volume of a solution containing methyl-orange has been made sufficiently acid for the colour to change a little towards pink, dilution will cause it to revert to yellow (Part I, p. 74).

Evidently these phenomena need to be carefully considered; and since different indicators give different signs of neutrality, the question arises: what is absolute neutrality?

The answer is that a solution which contains H^+ and OH^- ions in equivalent amounts is ideally neutral. It is true that these ions can coexist only to a minute extent in any solution; and they coexist in water at atmospheric temperature each to the extent of 10^{-7} normal. Water, then, is ideally neutral; and in water:

$$[H]^{+} = [OH]^{-} = 10^{-7}, \text{ so that } [H]^{+} \times [OH]^{-} = 10^{-14}.$$

Here, then, we have a definition of absolute neutrality: a solution is absolutely neutral when its hydrogen-ion (hydrion) concentration is 10^{-7}. Of such a solution the *p*H value is said to be 7; i.e. the power of the normality is used with the sign changed. Moreover, according to the law of mass action, the product of hydrogen- and hydroxyl-ion concentration is always the same, in acid and alkaline, as well as in neutral solutions; it is, therefore, unnecessary to specify the hydroxyl-ion concentration. Thus, if a solution has a *p*H value of 6, the corresponding value for its hydroxyl-ion concentration is 8, and so on.

The following study will elucidate the subject:

	N/1 NaOH added	N/1 HCl left	$[H]^{+}$	$[OH]^{-}$	*p*H
1	0	100	10^{-1}	10^{-13}	1
2	90	10	10^{-2}	10^{-12}	2
3	99	1	10^{-3}	10^{-11}	3
4	99·9	0·1	10^{-4}	10^{-10}	4
5	100	0·0	10^{-7}	10^{-7}	7
		N/1 NaOH in excess			
6	100·1	0·1	10^{-10}	10^{-4}	10
7	101	1·0	10^{-11}	10^{-3}	11
8	110	10·0	10^{-12}	10^{-2}	12
9	200	100·0	10^{-13}	10^{-1}	13

Let 100 c. c. N/1 HCl be diluted to 1000 c. c., so that it becomes N/10; then, assuming the acid to be fully ionized, the hydrogen-ion concentration is 10^{-1}, the hydroxyl-ion concentration 10^{-13}, and the *p*H value 1.

In successive experiments let the quantities of N/1 NaOH shown in the first column be added to the 100 c. c. N/1 acid before dilution. Then, in the second column the HCl left, expressed as c. c. N/1 acid, is shown until the neutral point is passed and NaOH is present

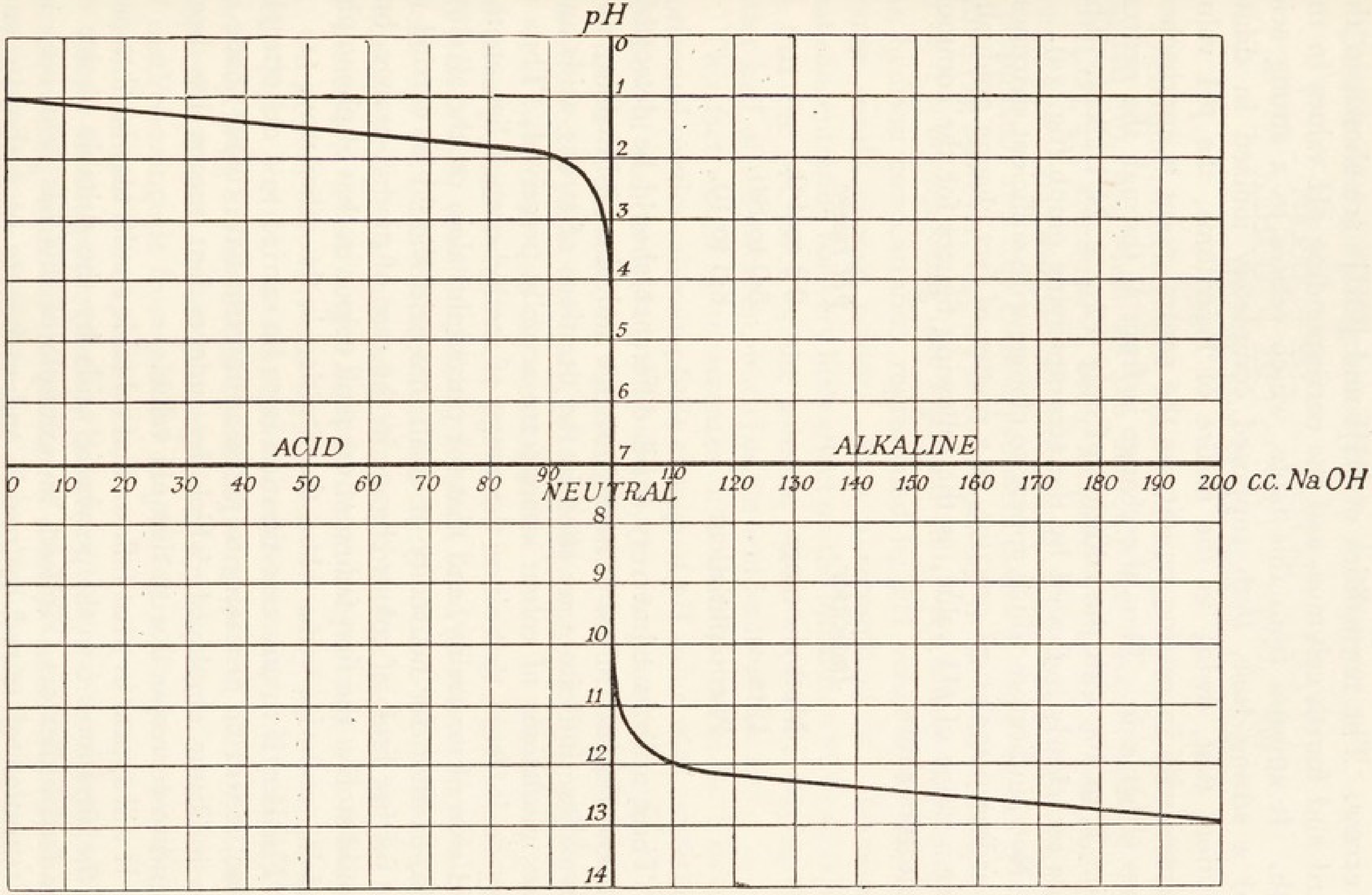
pH
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
ACID
ALKALINE
NEUTRAL
0
10
20
30
40
50
60
70
80
90
110
120
130
140
150
160
170
180
190
200
c.c. Na OH

Fig. 3a

in excess. The normalities of $[H]^+$ and $[OH]^-$ are shown in the third and fourth columns, and the corresponding *p*H values in the fifth. It appears from this table, which relates to a strong acid and a strong base, both supposed completely ionized in dilute solution, that, owing to the nature of logarithms, the *p*H value changes with increasing rapidity as the neutral point is approached from either side. Thus the change is from 4, through the neutral point 7, to 10, with the addition of only 0·2 c. c. N/1 alkali. The facts are clearly indicated by the accompanying graph (fig. 3*a*).

Now, indicators which appear to change with sufficient sharpness in ordinary analytical practice, as a matter of fact change gradually over a range of *p*H value, as the following figures for the common indicators show:

Indicator	*pH range*
Methyl-orange	2·9 to 4·0.
Litmus	5·0 to 8·0.
Phenolphthalein	8·3 to 10.

Thus, a distinct but very small difference should be detectable between the indications of methyl-orange and phenolphthalein; and when these indicators are used in the titrations of strong acids and bases gradations of colour change are actually perceived. Thus it may be inferred that since the range of methyl-orange lies on the acid side of neutrality, and that for phenolphthalein on the alkaline side, titration for neutrality of alkali into acid should be carried to the further limit of colour change in the case of methyl-orange, but should stop at the first fading of the pink colour in that of phenolphthalein; and vice versa when the titration is the other way.

Further, if in any case titration is to be carried to a definite *p*H value, it will be necessary to judge an intermediate colour shade in the indicator employed, which by independent means has been found to correspond with that *p*H value.

It will appear in what follows that valuable results may be obtained in the titration of weak, polybasic acids by the suitable choice of standard indicators. Indeed, an example of this has been seen in the titration of mixed hydroxide and carbonate or carbonate and bicarbonate solutions, by the combined use of phenolphthalein and methyl-orange indicators.

Consider the following reactions:

$$Na_2CO_3 + HCl = NaHCO_3 + HCl \quad (1)$$
$$NaHCO_3 + HCl = NaCl + H_2CO_3 \quad (2)$$
$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \quad (3)$$

Phenolphthalein changes when hydrion is liberated as shown in reaction (3), i.e. when all the Na_2CO_3 has been converted into $NaHCO_3$, and the latter is being attacked by the HCl; yet methyl-orange does not change until conversion of carbonate into chloride is completed, and free HCl is present. During the progress of reaction (2), however, H_2CO_3 is accumulating in the liquid, except so far as it is decomposing into H_2O and CO_2; yet it does not produce the hydrion concentration represented by *p*H value 4, or methyl-orange would change colour. It is a recognized fact, however, that concentration has very little effect on the ionization of weak acids, so that the *p*H value of the solution varies very little during the latter half of the titration, but changes suddenly at the end.

This fact would be represented on a titration curve by a nearly horizontal portion, showing little change of *p*H value with continued addition of standard HCl, followed by a change to vertical on the conclusion of the reaction. A similar condition of things occurs in the titration of phosphoric acid, as the following graph (fig. 3*b*) shows.

It is here seen that the neutralization curve for phosphoric acid contains two almost vertical portions, indicating rapid change of *p*H value with small addition of alkali; and these correspond respectively with the formation of the mono- and di-basic phosphate. These two stages of neutralization are therefore shown by the use of indicators whose ranges include the corresponding *p*H values.

On p. 154, Part I, it was shown that N/10 H_3PO_4 can be titrated with N/10 NaOH, so that points corresponding with NaH_2PO_4 and Na_2HPO_4 are indicated by methyl-orange and phenolphthalein respectively; and this is now explained by the fact that the range of methyl-orange is from *p*H 2·9 to *p*H 4·0, and that of phenolphthalein from *p*H 8·3 to *p*H 10.

Closer investigation shows, however, that the actual *p*H value corresponding with the formation of NaH_2PO_4 is 4·5, which lies a little beyond the methyl-orange range; so that an indicator within whose range *p*H 4·5 is included would be preferable. Such an indicator is bromo-cresol green, with *p*H range of 3·6 to 5·2. Nevertheless this indicator changes over this range from yellow to blue, or vice versa, with an intermediate green shade; therefore, for accuracy in its use it is necessary to have for comparison a standard tint produced by a solution of known *p*H value of 4·5. This explains why the following procedure is adopted.

A solution of *p*H value of 4·5 is made by mixing in suitable proportions solutions of sodium acetate and acetic acid. Such a solution is called a " buffer " solution. A buffer solution may be defined as a solution of a weak acid and its alkali salt, or an equivalent combination, whose *p*H value undergoes very little change by the addition of small quantities of strong acids or alkalis. That this is possible by an adjustment which occurs within the solution the following consideration will show. Suppose that a drop of dilute hydrochloric acid is added to the mixed solution of sodium acetate and acetic acid. If it is remembered that sodium acetate is largely ionized but acetic acid scarcely at all, it will be understood that

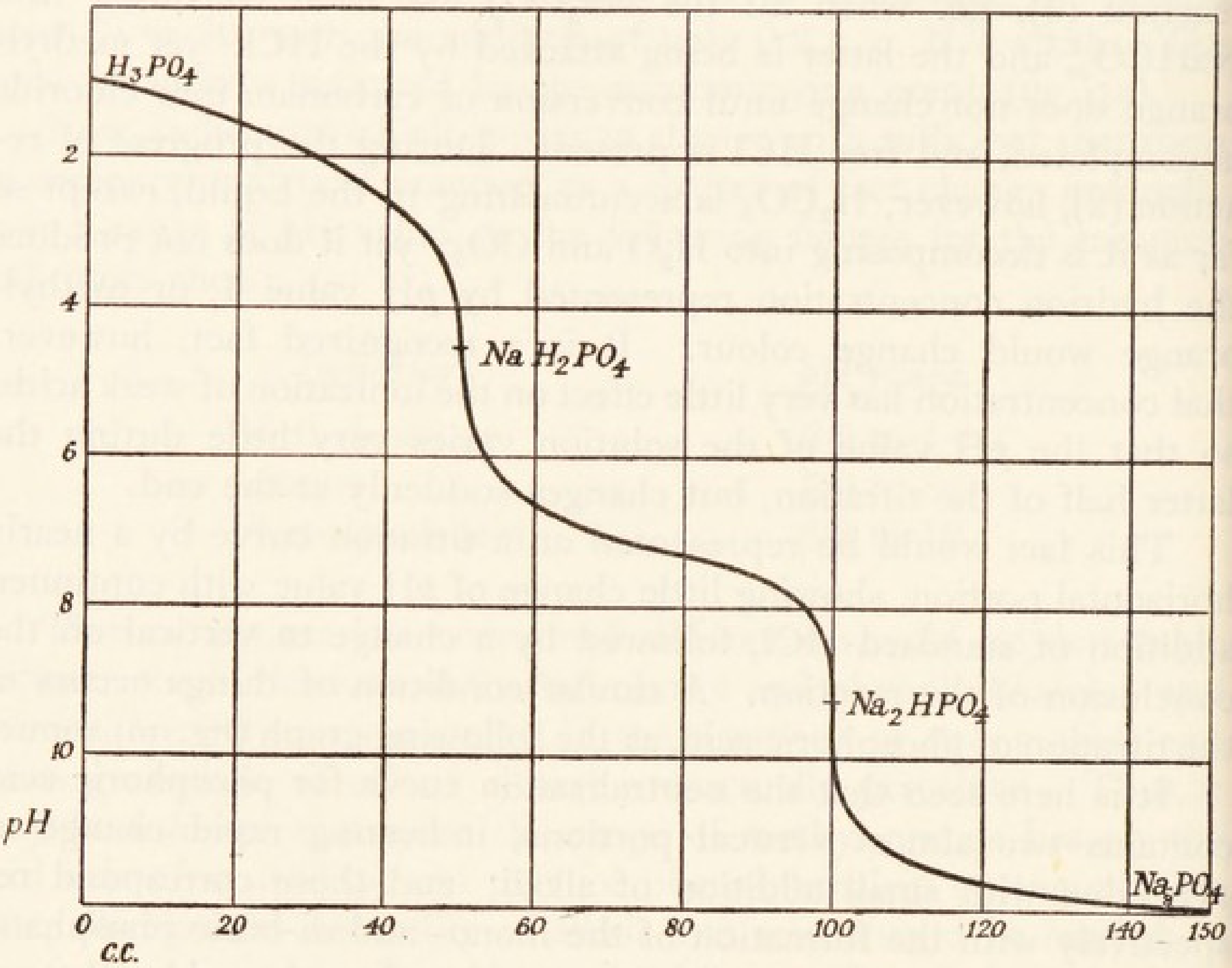

Fig. 3*b*.—Titration Curve of Phosphoric Acid
50 c. c. M/10 H_3PO_4 titrated with N/10 NaOH

the hydrogen ions of the added acid will combine with acetate ions from the sodium salt to produce almost non-ionized acetic acid, so that there will be a scarcely perceptible increase in the hydrogen-ion concentration, i.e. the *p*H value of the solution. Just as a cushion or buffer softens the impact of a colliding body, so the sodium acetate in solution reduces the effect of the added hydrogen-ions.

Further, since the addition of the alkali salt of an acid to a solution of that acid diminishes the ionization of the acid, according to the principles of mass action, it is possible to prepare mixed solutions of definite *p*H values by employing a weak acid and its alkali salt in various proportions. Thus, Walpole, by electrometric methods, found *p*H values and molar-concentrations of sodium acetate and acetic acid mixed in solution to be related as follows:

Molar concentration of

Acetic Acid	Sodium Acetate	*p*H
0·147	0·053	4·2
0·126	0·074	4·4
0·102	0·098	4·6
0·080	0·120	5·8

It will be observed that in each case the total acetate concentration is M/5, and by interpolation it appears that a solution of *p*H value, 4·5, which is that required, will contain 0·114 M of acetic acid and 0·086 M of sodium acetate.

Thus the required reference solution will be obtained by mixing 57 volumes of M/5 acetic acid solution with 43 volumes of M/5 sodium acetate solution.

Estimation of common Sodium Phosphate, $Na_2HPO_4{\cdot}12H_2O$.

The estimation of sodium phosphate to be described depends on the conversion of Na_2HPO_4 into NaH_2PO_4, i.e. the estimation of the extent of the middle third of the way between Na_3PO_4 and H_3PO_4.

Prepare and standardize some approx. N/10 H_2SO_4 or HCl, and a convenient volume of a solution of pure disodium hydrogen phosphate containing 1 M. $Na_2HPO_4 . 12H_2O$ per litre. Also have at hand methyl-orange solution and a solution of bromo-cresol green (B.D.H. reagent), and a glass tube by means of which counted drops can be delivered into a solution.

Titrate separate quantities of 25 c. c. of the phosphate solution with the acid, first with methyl-orange as indicator, and then with 2 or 3 drops of bromo-cresol green. Stop in the latter case when the blue colour of the indicator has changed to green. The volumes of acid used in the two cases will agree to within about 0·1 c. c. They serve as a rough indication of the amount of acid that will be required in the more refined procedure which follows.

Thoroughly cleanse two test-tubes of equal cross-section, and indicate on each the level to which 20 c. c. of liquid will reach. Place in one of the test-tubes 20 c. c. of the prepared reference solution and add 2 drops of the bromo-cresol green indicator. This is the solution whose colour has to be matched in the titration.

Now indicate on a titration flask the level reached by 100 c. c. of liquid; and place in it 25 c. c. of the phosphate solution and 10 drops of the indicator. Thus, when the flask is made to contain 100 c. c. of liquid the state of dilution of the indicator will be the same as in the reference solution. Now add from the burette a volume of standard acid about 0·5 c. c. short of that required according to the rough titration already done, and dilute the liquid in the flask to nearly 100 c. c. Transfer 20 c. c. of this solution to the prepared test-tube, and add to it a drop or two more acid until the colour of the indicator has gone beyond that of the reference solution towards yellow. Then return this solution to the flask. Excess of acid will not be indicated when the solutions are mixed, because the solution in the test-tube has been added to four times its volume of a solution which did not contain enough acid. Remove another 20 c. c. to the test-tube and repeat the addition of acid as many times as necessary, with diminishing amounts, until, when the volume in the flask has been diluted to 100 c. c., 20 c. c. of it in the test-tube exactly match in colour the same volume of the reference solution. The best way to compare the colours is to hold the two test-tubes side by side in the line of vision, and look through the whole depth of the solutions on to a sheet of white paper.

In an actual experiment the following results were obtained:

8·95 gm. of A.R. sodium phosphate, which had effloresced slightly, was dissolved in water, and the solution diluted to 250 c. c.
25 c. c. were titrated, and required:
With methyl-orange indicator 25·40 c. c. N/10 acid.
With bromo-cresol green indicator 25·45 c. c. N/10 acid.
With bromo-cresol green indicator titrated in the special way, to a shade matched against the reference solution 25·38, 25·38 c. c. ,,

Thus the percentage of Na_2HPO_4 found = 40·27
theory for $Na_2HPO_4 . 12H_2O$ = 39·67
The percentage is high owing to efflorescence.

It appears from the above figures that the result of titration with methyl-orange is sufficiently accurate, and is probably superior to that with bromo-cresol green used without a reference solution, because of a doubt as to the shade of green at which to stop. Yet when the reference solution is used, the titration can be carried out with extraordinary precision, so that more error is like to result from inaccuracy in the instruments or the methods of using them than from the delivery of an incorrect volume of acid from the burette.

The practical utility of this method for the assay of sodium phosphate, however, is limited. The salt must contain no Na_3PO_4, or, if it does the amount of this must first be ascertained by titration with phenolphthalein as indicator, in presence of sodium chloride, to prevent hydrolysis of Na_2HPO_4, and the volume of acid required when this indicator is used subtracted from the total volume required in the above experiment.

The exercise is useful, however, to give a practical introduction to the conception of *p*H value; and, incidentally, it may be remarked that the same technique might be applied to ordinary titrations with common indicators, though it is tedious and generally unnecessary.

SIMPLE GRAVIMETRIC SEPARATIONS AND RELATED PROCESSES

The student has become familiar in the course of his qualitative analysis with methods of separation of two or more metals in a solution which depend upon converting the metals into compounds of widely different properties. Some of these methods are suitable with modification for quantitative analysis, though in some cases methods of separation not generally employed in qualitative work are necessary. Separations in qualitative analysis are sometimes imperfect owing to co-precipitation, i.e. the association with the precipitate of a small quantity of the material all of which was expected to remain in solution and to be found in the filtrate. When such a separation is to be used quantitatively it is necessary to dissolve in acid the precipitate first obtained, and to repeat the precipitation and filtration. The second precipitate is then practically free from impurity, and the two filtrates together contain the whole of the other constituent.

For example, when iron is to be separated from zinc and manganese it is precipitated as basic ferric acetate from a solution containing a little acetic acid, but the precipitate carries down with it a little zinc and manganese. It is therefore dissolved in hydrochloric acid, and the iron precipitated from the solution in the same way as before. The combined filtrates then contain the whole of the zinc and manganese, the second precipitate consisting of basic ferric acetate only.

A little different is the case of the separation of iron from aluminium and chromium, which are obtained in solution as aluminate and chromate by the action of soda, and hydrogen peroxide and ammonia, respectively. It is not possible in this case completely to remove soda from the ferric hydroxide precipitate, so that it is necessary to dissolve this precipitate in hydrochloric acid and reprecipitate the iron by means of ammonia.

The gravimetric separation of the constituents of a complex mineral or alloy is a lengthy process; and the estimation of a particular constituent is often necessarily preceded by the elimination of other constituents whose presence would interfere with this estimation. When, however, this constituent can be estimated in presence of the others by a reaction applicable to it alone, the analysis may be shortened.

Calcium, for example, can be estimated by precipitation as oxalate in acetic acid solution, although phosphate may be present; for calcium phosphate is soluble in acetic acid, and phosphate ions in solution do not interfere with the precipitation of calcium oxalate. Phosphate, too, can be estimated as magnesium ammonium phosphate in presence of ferric iron and calcium, after the addition of excess of ammonium citrate, for this reagent prevents the precipitation of phosphates of iron and calcium by ammonia.

As already mentioned in Part I, p. 20, organic chemistry has provided the analyst with specific reagents for precipitating individual metals in presence of the salts of other metals. Besides dimethyl glyoxime, which precipitates nickel, there is "cupferron", which is the ammonium salt of nitrosophenyl-hydroxylamine. This reagent, as its name indicates, precipitates copper and iron, and does so from acid solution in which other metals remain dissolved.

In this section, which is introductory to one dealing with the analysis of minerals and alloys, the separations of the following pairs of metals will be described.

Simple Gravimetric Separations.

1. Iron from aluminium.
2. Iron from chromium.
3. Iron from manganese.
4. Zinc from nickel.
5. Calcium from magnesium.
6. Potassium from sodium.

Also, 7. Estimation of nitrate in nitrometer.

8. Estimation of nitrite and nitrate in nitrometer.

1. Separation of Iron from Aluminium.

From ferric and aluminium salts ferric and aluminium hydroxides are precipitated both by ammonia and by sodium hydroxide solution. The latter solution, however, when added in excess, dissolves aluminium hydroxide, forming sodium aluminate in solution, while leaving ferric hydroxide undissolved. From the sodium aluminate solution aluminium hydroxide can be reprecipitated by excess of acid followed by ammonia; the acid first precipitates the hydroxide by decomposing the aluminate, and redissolves it when added in excess, forming aluminium chloride from which ammonia precipitates the hydroxide again. This precipitate, however, is colloidal and will be slow in filtering unless the conditions described below are observed; an alternative way of precipitating the alumina is that shown by the following experiment.

Mix together dilute solutions of common alum and sodium thiosulphate, and boil the liquid. A white precipitate forms which is a mixture of hydrated alumina and sulphur resulting from the formation and hydrolytic decomposition of aluminium thiosulphate thus:

$$Al_2(SO_4)_3 + 3Na_2S_2O_3 \rightleftharpoons Al_2(S_2O_3)_3 + 3Na_2SO_4$$
$$Al_2(S_2O_3)_3 \rightarrow Al_2O_3 + 3SO_2 + 3S.$$

As may be shown, this precipitate, being denser, filters more rapidly than the gelatinous hydroxide, and after the combustion of its contained sulphur by ignition in the air leaves a residue of pure alumina.

Procedure.—The material given for analysis may be solid, as for example an intimate mixture of ferric and aluminium alums, it may consist of a mixture of ferric and aluminium salts in solution, or it may contain iron in the ferrous state, either solid or in solution. It is desirable to take for analysis a quantity of the mixture sufficient to yield not less than 0·2 gm. of each oxide to be weighed; though if there is a great disproportion between the iron and aluminium there will be less than this amount of the smaller constituent, for it is undesirable to deal with a bulk of precipitate corresponding with the larger constituent more than sufficient to be contained in one filter, with room for washing.

Unless it is already in solution, dissolve the material taken in water or dilute hydrochloric acid, and if it contains ferrous iron oxidize this by means of a little concentrated nitric acid. Have the solution in a porcelain, or preferably silver, dish, and add to it, with stirring, a concentrated solution of sodium hydroxide free from alumina.* When the ferric hydroxide is precipitated add more soda, say 10 c. c., sufficient to redissolve the aluminium hydroxide precipitated with the iron, and, whilst stirring, heat the liquid in the dish to boiling. Add hot water if desirable, and filter through a large filter. Wash the dish, the precipitate, and the filter with hot water, until the wash water gives at most a faintly alkaline reaction, collecting the filtrate and washings in a suitable beaker. Deal further with the precipitate and filtrate as follows.

Estimation of Iron.

Place the dish under the filter, and pour upon the filter some hot dilute hydrochloric acid, so as to dissolve the ferric hydroxide. Make sure that all the precipitate is dissolved, and that all the solution of ferric chloride finds its way into the dish, the paper being thoroughly washed with hot water till no yellow colour remains upon it. Then add ammonia to the contents of the dish to reprecipitate ferric hydroxide, filter and wash the precipitate, dry and ignite it in the usual manner, and from the weight of ferric oxide obtained calculate the percentage of iron in the solid, or the weight of this metal in 100 c. c. or 1 litre of the solution.

Estimation of Aluminium. Use either method (i) or (ii).

(i) Add dilute hydrochloric acid to the solution of sodium aluminate in the beaker until the aluminium hydroxide at first precipitated is just redissolved. Then add several grammes of ammonium chloride in concentrated solution, and heat the liquid to 66° C. To the solution, kept at 66° C., add ammonia until the liquid smells faintly of the gas, and the alumina has been reprecipitated. Boil until the smell of ammonia is no longer perceived; then filter, wash, and dry the precipitate. Ignite the precipitate with the filter paper at a bright red heat until its weight is constant.

(ii) Add to the solution of sodium aluminate in the beaker dilute hydrochloric acid until the aluminium hydroxide at first precipitated is just redissolved. Then add sodium thiosulphate

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* Use "soda by alcohol" or potassium hydroxide, which is generally purer than soda of ordinary quality.

solution in excess, and heat the liquid to boiling. Precipitation of alumina with sulphur takes place, and when this is judged to be complete, filter and wash the precipitate until the wash water is free from chloride. Place the moist filter containing the precipitate in a weighed silica or platinum crucible, dry, and ignite it, and roast the alumina at a bright red heat until its weight is constant. Calculate the percentage of aluminium in the material analysed.

2. Separation of Iron from Chromium.

When sodium peroxide is added to a solution containing ferric and chromic salts, and the liquid is heated till oxygen ceases to be evolved, the iron is precipitated as ferric hydroxide, and the chromium oxidized to soluble sodium chromate. The student has already used this reaction to separate iron and chromium in qualitative analysis; he may refresh his memory by mixing together very small quantities of ferric and chromic alum in dilute solution, adding sodium peroxide little by little until the liquid becomes brown and turbid, and then boiling so as to eliminate superfluous oxygen. It is necessary to do this, because if any hydrogen peroxide, derived from sodium peroxide, remained in the solution, this would react with the chromate when the solution was acidified, and some of the latter might eventually be reduced again to chromic salt. The ferric hydroxide so precipitated, however, carries down a little chromium with it, and a double precipitation is necessary to effect a complete separation. Moreover, ammonia is a cleaner precipitant than soda, and a more perfect oxidation of the chromic salt is effected by adding hydrogen peroxide to the mixed acid solution, pouring the mixture in a thin stream into excess of ammonia, and boiling. Even in this case, however, a double precipitation is necessary. After filtering and washing, the ferric precipitate is ignited and weighed as Fe_2O_3, and the chromium in the filtrate estimated either gravimetrically Cr_2O_3, or volumetrically as chromate.

Procedure.—Take of the mixture, supplied either in the solid state or in solution, sufficient to yield not more than 0·5 gm. of either ferric or chromic oxide. When the substance has been obtained in solution, nearly neutralize the liquid with ammonia and then add 20 c. c. of 3 per cent hydrogen peroxide solution. This will have no chemical action so long as the solution remains acid. Now pour the mixture in a thin stream into dilute ammonia contained in another beaker whilst constantly stirring the ammoniacal liquid. Brown ferric hydroxide is precipitated, and the solution becomes yellow owing to the formation of chromate. Then heat the liquid to boiling, and observe that a gas, which is oxygen, is evolved, proving that excess of hydrogen peroxide was present. Filter off and wash the precipitate until the wash water is colourless, and set aside the yellow filtrate and washings. Dissolve the ferric hydroxide in a little hot, dilute hydrochloric acid poured upon the filter, receiving the solution in a beaker, and washing the filter paper with hot water until it is free from ferric solution. If difficulty is found in dissolving all the precipitate from the filter paper, this may be digested separately with a little hot, dilute hydrochloric acid and the solution added to the rest; but this difficulty is less likely to occur with ammonia than with soda as precipitant. Now add another 5 c. c. of hydrogen peroxide to the solution, and repeat the process of nearly neutralizing, pouring into excess of ammonia, boiling, filtering, and washing, adding the filtrate if perceptible yellow, to the rest of the chromate solution.

Estimation of Iron.

The precipitate on the filter is pure, clean ferric hydroxide. Therefore ignite it in a crucible, and weigh the resulting Fe_2O_3. Then calculate the percentage of iron in the mixture.

Estimation of Chromium.

The chromium, present now as chromate, can be estimated either (*a*) gravimetrically or (*b*) volumetrically. Add concentrated hydrochloric acid to the solution until the colour changes from yellow to orange, showing the conversion of chromate into dichromate, and then dilute the solution to 250 c. c.—or 500 c. c.—in a graduated flask, and take a measured proportion of the whole volume for each estimation.

(*a*) *Gravimetric Estimation.*

Reduction by Alcohol.—To a measured volume, say 50 c. c., of the acidified dichromate solution contained in a beaker, add 20 c. c. of alcohol, and heat the solution to boiling. The colour of the solution gradually passes through olive green to a vivid green as the reduction proceeds, and meanwhile the smell of aldehyde, formed by oxidation of the alcohol, can be perceived. If necessary, add more alcohol, and boil again until the full green colour has been reached. Then add ammonia solution in sufficient quantity to precipitate chromic hydroxide completely; boil the turbid liquid until it ceases to smell of ammonia, and the precipitate quickly settles, when the liquid is quiescent, leaving the solution colourless. The student will remember that excess of ammonia dissolves chromic hydroxide, producing the violet coloured ammine $[Cr(NH_3)_6](OH)_3$; this is why it is necessary to add as little ammonia as possible, and to expel the excess by boiling. Filter and wash the chromic hydroxide; transfer the filter whilst moist to a weighed porcelain, silica, or platinum crucible, and after drying and burning the filter paper, ignite the precipitate at a bright red heat until its weight is constant. From the weight of Cr_2O_3 obtained, calculate the percentage of chromium in the mixture.

(*b*) *Volumetric Estimation.*

Prepare a solution of ferrous ammonium sulphate of about decinormal strength, and also an accurately decinormal solution of potassium dichromate. Titrate the prepared dichromate solution of unknown strength, and the decinormal dichromate solution successively into equal volumes of the ferrous ammonium sulphate solution (Part I, p. 133). The strengths of the two solutions are in the inverse ratio of their volumes required to effect equal oxidations. Therefore calculate from the normality of the dichromate solution thus found, the percentage of chromium in the mixture.

3. Separation of Iron from Manganese.

In the separation of ferric iron from manganese, advantage is taken of the fact that the salts of trivalent iron are more hydrolyzable than those of bivalent manganese, and that by means of this property ferric iron can be precipitated when manganous salts remain in solution. Thus if calcium or barium carbonate or zinc oxide is added in excess to a mixed solution of salts of ferric iron and manganese, all the iron is precipitated on neutralization of the acid present, and is found mixed with the other insoluble material, whilst the manganous salt remains in solution and can be obtained free from iron. Also when the only acid present is acetic acid, and sodium or ammonium acetate is added to suppress as much as possible the ionization of this acid, insoluble basic ferric acetate is precipitated on boiling a solution containing iron and manganese, whilst manganous acetate, not being hydrolyzed, remains in solution. The two processes of separating iron from manganese now to be described depend upon the precipitation of ferric iron, (*a*) as hydroxide in association with zinc oxide, and (*b*) as basic acetate which separates on boiling a suitably prepared solution.

(*a*) *Precipitation of Iron as Ferric Hydroxide by Zinc Oxide.*

Barium carbonate has generally been used for the separation of iron and manganese, but zinc oxide is preferable because of the solubility of zinc sulphate.

Dilute a measured volume of the solution in a flask to about 100 c. c., add excess of a fresh suspension of hydrated zinc oxide, made by mixing solutions of sodium hydroxide and zinc sulphate until the maximum precipitation has taken place, filtering, and washing the precipitate free from alkali; and shake the mixture. All the iron will be at once precipitated making the suspension brown, and when this has settled somewhat the supernatant liquid will be seen to be clear and colourless. Filter, and wash the solid on the filter once with hot water, and reserve the filtrate and washing. Transfer the residue to a suitable beaker or flask and dissolve it in hot dilute hydrochloric acid. Add more suspension of zinc oxide and again shake, filter, and wash the residue. Mix the two filtrates and washings and reserve them for the estimation of manganese. Dissolve the residue in dilute hydrochloric acid, and heat to boiling; then add ammonium chloride and ammonia, collect the ferric hydroxide, ignite it, and weigh the Fe_2O_3 obtained.

(*b*) *Precipitation of Iron as Basic Acetate.*

Great care needs to be taken to obtain the basic ferric acetate in a flocculent condition suitable for filtration, for if the precipitate is allowed to become slimy filtration is almost impossible.

Place a measured volume of the mixed solution of ferric and manganous chlorides * in a large beaker and add ammonia till a slight permanent precipitate forms; dissolve this in the least possible amount of hydrochloric acid. To this solution add a concentrated solution of ammonium acetate containing about 5 gm. of the salt. Dilute the deep red solution to about 400 c. c. with boiling water, then boil it for a minute or two only, and filter while hot. In order to filter as expeditiously as possible it is wise to use a filter of not less than 11 cm. diameter, and to surround the funnel with a hot-water jacket (see Part I, p. 132). After quickly washing the precipitate on the filter, dissolve it in hot dilute hydrochloric acid, by pouring this on the filter; and when all the iron has been obtained again in solution, and the filter washed free from it, repeat the process of neutralizing and precipitating the iron as basic acetate. After filtering again and washing the precipitate ignite it and weigh the Fe_2O_3 obtained. Reserve the two filtrates for the estimation of the manganese.

Estimation of Manganese.

(i) *Determination as* Mn_3O_4.

The filtrates from the iron precipitates should be clear and colourless. Mix them, add ammonia, free from carbonate, till the liquid is alkaline, followed by hydrogen peroxide,† and heat to boiling. A dark brown precipitate of hydrated manganese dioxide will separate.‡ Filter, wash, dry, ignite, and weigh the residue of Mn_3O_4.

(ii) *Determination as Pyrophosphate*, $Mn_2P_2O_7$.

To the mixed filtrates containing the manganese, and made slightly acid with acetic acid, add ammonium chloride, and about 10 c. c. of a concentrated solution of sodium or ammonium phosphate, followed by ammonia until the formation of the precipitate of manganous ammonium phosphate, $MnNH_4PO_4{\cdot}H_2O$, is complete.

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* Sulphate must be absent, or basic ferric sulphate may be precipitated.

† Bromine water or ammonium persulphate can be used in place of hydrogen peroxide, though if persulphate is used barium if present must first be eliminated.

‡ In the presence of alkali MnO_2 is liable to form manganite, that is to form a compound from which alkali is not removed by washing. In this case, however, no fixed alkali is present. In the absence of alkali the precipitate contains some manganous manganite, $MnMnO_3$ or Mn_2O_3. This, however, is immaterial, since Mn_2O_3 is converted to Mn_3O_4 by ignition in the air.

Boil the liquid until it is apparent that the precipitate separates easily from the solution and will filter well. Filter through an asbestos filter in a Gooch crucible (Part I, p. 39), and, after washing the precipitate with hot water, place the crucible inside a larger crucible and ignite it strongly till the weight is constant, the manganese being thus obtained in the form of pyrophosphate, $Mn_2P_2O_7$.

4. Separation of Zinc from Nickel.

There are various forms in which zinc and nickel may be precipitated and weighed. Zinc can be precipitated as sulphide, which by roasting is converted into oxide, in which form the metal is weighed; or it may be precipitated as zinc ammonium phosphate, $ZnNH_4PO_4$, and weighed as this or the pyrophosphate, $Zn_2P_2O_7$. Nickel can be precipitated as the hydroxide by alkali, or as the hydrated dioxide by alkali in presence of bromine or persulphate used as an oxidizing agent. Both of these precipitates are converted by ignition into the monoxide, but since it is difficult to free them from alkali, neither of these methods of precipitation is to be recommended. Dimethyl glyoxime, however, is a useful precipitant for nickel, with which, in presence of ammonia or a little acetic acid, it forms a red crystalline insoluble salt thus:

$$NiSO_4 + 2(CH_3)_2C_2(NOH)_2 = Ni[(CH_3)_2C_2NOH{\cdot}NO]_2 + H_2SO_4.$$

This reaction furnishes so valuable a method for estimating nickel gravimetrically, either alone or in presence of zinc, cobalt, or manganese, that no other method need be considered here.

Two methods of separating and estimating zinc and nickel will be described.

I. (*a*) Precipitation of zinc from a suitably acidified solution as sulphide by hydrogen sulphide, whilst nickel remains in solution, followed by (*b*) the precipitation of nickel from the filtrate as the dimethyl glyoxime compound.

II. Precipitation of (*a*) nickel as the dimethyl glyoxime compound, and of (*b*) zinc from the filtrate as zinc ammonium phosphate.

I. (*a*) Precipitation of Zinc as Sulphide.

Precipitation of zinc as sulphide, in presence of nickel, is effected by passing hydrogen sulphide into a solution containing as the only acid a small amount of acetic or preferably formic acid (Waring's method). The amount of zinc present in solution should not exceed 0·3 gm.

Measure out a suitable volume of the solution containing zinc and nickel, add to it a few drops of methyl orange, and, if it is acid, just enough sodium hydroxide to restore the yellow colour of the indicator. Then add drop by drop a 50 per cent solution of formic acid until the indicator becomes fully pink again, followed by 0·5 c. c. more of the acid. The acid may be added conveniently from a burette. Dilute the solution to about 150 c. c., heat it to 80° C., and pass through it a rapid stream of hydrogen sulphide gas. Allow the white precipitate of zinc sulphide to settle, and, after ascertaining that precipitation is complete by allowing a little of the gas to bubble through the clear supernatant liquid, filter and wash the precipitate by decantation and on the filter with hot water, and preserve the filtrate and washings for estimation of the nickel. Dry the filter and detach from it as much as possible of the precipitate. Moisten the filter with concentrated solution of ammonium nitrate, then dry it and burn it in a weighed silica or porcelain crucible. By roasting, the zinc sulphide which remained on the filter will be converted completely into oxide, reduction to metal which would be volatilized being prevented by the oxidizing agent. Now put into the crucible the main portion of the zinc sulphide precipitate, and roast it for an hour, beginning with a low red, and ending with a bright red heat. Thus the zinc sulphide will be converted completely into oxide, in which form the zinc is weighed.

(*b*) Precipitation of Nickel as Dimethyl Glyoxime Salt.

Add to the solution containing the nickel a little dilute hydrochloric acid, then boil it to expel the hydrogen sulphide left in it after precipitation of the zinc. Add to the liquid a 1 per cent alcoholic solution of dimethyl glyoxime in rather more than sufficient quantity to precipitate the nickel; the volume of the alcoholic solution added should not, however, be more than half that of the aqueous solution, owing to the solubility of the nickel compound in alcohol. Then add ammonium acetate so as to replace free hydrochloric acid by acetic acid. The nickel salt of dimethyl glyoxime separates as a scarlet precipitate, but the liquid should be kept hot for twenty minutes to complete the precipitation. Collect the precipitate on a weighed asbestos filter in a Gooch crucible (see Part I, p. 38), wash it with hot water, and dry it in an air oven at 110° C. until its weight is constant. The percentage of nickel in its dimethyl glyoxime compound is 20·33.

II. (*a*) Precipitation of Nickel as Dimethyl Glyoxime Salt.

Carry out this process according to the directions given above under I (*b*), having the mixed solution of nickel and zinc salts slightly acid, and adding ammonium acetate after the dimethyl glyoxime. When it is ascertained that precipitation is complete, filter, dry, and weigh the precipitate as before.

(*b*) Precipitation of Zinc as Zinc Ammonium Phosphate, and Weighing as Pyrophosphate.

Before the zinc is precipitated, it is necessary to destroy the excess of dimethyl glyoxime remaining in the filtrate from the nickel. To do this add to the liquid about 20 c. c. of concentrated hydrochloric acid, and boil for about fifteen minutes. Then neutralize the solution with ammonia, add about 5 gm. of solid ammonium phosphate, $(NH_4)_2HPO_4$, and a few drops of acetic acid. Heat the liquid nearly to boiling, stir well, and allow it to stand on the water bath until the precipitate has settled and appears crystalline. Filter the precipitate through an asbestos filter in a Gooch crucible, and wash it with hot water. The precipitate may be weighed either as $ZnNH_4PO_4$ or $Zn_2P_2O_7$. For the former, dry the Gooch crucible and its contents in an air oven at 110° to 120° C., till the weight is constant; for the latter place the crucible inside an iron or nickel crucible, so that the flame gases cannot reach the precipitate through the holes in the base of the crucible, and heat it gradually to redness.

5. Separation of Calcium from Magnesium.

Calcium is separated from magnesium in qualitative analysis by precipitation as carbonate or oxalate,* the magnesium being detected in the filtrate from the calcium by precipitation as mag-

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* The precipitation of calcium as molybdate in slightly ammoniacal solution has recently been recommended (R. C. Wiley, *Industrial and Engineering Chemistry*, 1931, *3*, 127–9), one precipitation being sufficient to separate calcium completely from magnesium.

nesium ammonium phosphate. This oxalate method is available for the quantitative separation of these two metals provided ammonium oxalate is added in considerable excess to secure the complete precipitation of the calcium, and also that the precipitated calcium oxalate is dissolved in hydrochloric acid, and reprecipitated by ammonia and a little more ammonium oxalate, on account of the tendency for a little magnesium oxalate to be precipitated with the calcium oxalate.

Procedure.

Estimation of Calcium.

Measure or weigh sufficient of the mixed solution or solid containing the equivalent of not more than 0·25 gm. each of CaO and MgO. Dissolve the solid, if necessary, in dilute hydrochloric acid, and dilute the solution to about 100 c. c.; then make the liquid alkaline with ammonia, heat it to boiling, and add 1·5 gm. of finely powdered solid ammonium oxalate. Keep the liquid hot while the precipitate subsides, filter through paper and wash the precipitate with hot water by decantation and on the filter. Set aside the filtrate, which contains nearly all the magnesium. Dissolve the precipitate on the filter by pouring upon it hot dilute hydrochloric acid, and receive the filtrate in a suitable beaker. When care has been taken to leave no calcium oxalate, either solid or in solution, on the filter, heat the solution in the beaker to boiling, make it alkaline with ammonia, and add a little more ammonium oxalate, either as powder or in solution. Keep the liquid hot while the precipitate settles; then filter and wash the precipitate with hot water by decantation and on the filter, ascertaining finally that the wash water is free from chloride. Dry the calcium oxalate precipitate, and ignite and weigh it as carbonate or sulphate (Part I, p. 44).

Estimation of Magnesium.

Mix the filtrates from the calcium oxalate precipitate, and make the solution distinctly acid with hydrochloric acid. Add 5 gm. of ammonium chloride dissolved in a little water, followed by excess of sodium or ammonium phosphate. Heat the liquid to boiling, and add dilute ammonia solution until a crystalline precipitate of magnesium ammonium phosphate is formed. When precipitation is complete, and the liquid smells of ammonia, allow it to cool, and then add, with stirring, strongest ammonia solution equal in volume to about one-fifth of that of the liquid containing the precipitate. Take care not to scratch the sides of the beaker with the glass rod, and after ten minutes filter through an asbestos filter and wash the precipitate with dilute ammonia solution. Place the Gooch crucible inside a nickel crucible without previous drying, and ignite, very gradually increasing the temperature to a full red heat. The magnesium pyrophosphate should be quite white before it is weighed.

6. Separation of Potassium from Sodium.

It has already been seen (p. 56) that the proportion of each salt in a mixture of sodium and potassium chlorides can be estimated by determining the chloride in the mixture. The same estimation might be effected by converting a weighed quantity of the mixed chlorides into sulphates, or, if the mixed sulphates were given, by determining the percentage of sulphate in the mixture.

These methods are open to the objection, however, that the estimation of a percentage depends upon the determination of a point between two extremes which may not be very far distant from one another; and therefore that a small intrinsic error may lead to a large percentage error.

Potassium, can, however, be separated from sodium by the precipitation of a sufficiently insoluble salt. The method employed before platinum became too expensive, consisted in forming potassium platinichloride, K_2PtCl_6, which is insoluble in alcohol, while the sodium salt is soluble. The precipitation of potassium cobaltinitrite ($K_3Co(NO_2)_6$) has also been suggested, but not found satisfactory; potassium perchlorate, however, is one of the least soluble potassium salts, and moreover it is almost completely insoluble in 97 per cent alcohol containing 0·2 per cent of perchloric acid, whilst sodium and other perchlorates are soluble in this mixture. The method is applicable when nitrates, chlorides, or phosphates of sodium and potassium, as well as of the alkaline earth metals and magnesium are present, but sulphates must be absent.

Procedure.—When it is necessary to estimate sodium and potassium chlorides, derived say from the soda and potash present in felspar, the procedure is as follows.

By preliminary operations (see under felspar) a solution will have been obtained containing sodium and potassium chlorides, together with ammonium oxalate. Evaporate this solution to dryness in a porcelain or silica, or preferably a platinum dish, and then very gently heat the dish so as to volatilize all the ammonium chloride, taking great care not to overheat, because potassium chloride is rather easily volatilized. Allow the dish to cool and dissolve its contents in a little hot water. A small black residue of carbon will remain. Filter this off, taking care not to lose any of the solution. Collect the filtrate and washings in a small beaker, and again evaporate to dryness in a weighed dish. Gently ignite the residue, and after cooling the dish and its contents in a desiccator, weigh them. This residue consists of sodium and potassium chlorides.

Estimation of Potassium.

Dissolve the mixture of sodium and potassium chlorides in a little water in a dish, and add to the solution about twice as much perchloric acid as is necessary to convert the two alkali salts into perchlorates, say about 3 c. c. of 20 per cent perchloric acid for each 0·2 gm. of the mixed chlorides present. Evaporate the liquid, with stirring, on the sand bath, or over a very small flame which does not touch the bottom of the dish. Hydrogen chloride will first be evolved, with the steam, and afterwards heavy fumes of perchloric acid will appear provided the latter has been added in excess. Very carefully continue the evaporation until the mass is almost dry, then add to it a convenient quantity of a mixture of 100 c. c. of 97 per cent alcohol and 1 c. c. of 20 per cent perchloric acid solution. Stir gently with a glass rod so as to break up the solid mass, taking care, however, not to grind the potassium perchlorate to a powder which might be difficult to filter. Allow the solid to settle and decant the supernatant liquid through a prepared asbestos filter; repeat the washing and decantation two or three times, then transfer the residue to the filter and also wash it there, using in all about 100 c. c. of the washing liquid. Dry the Gooch crucible and contents at 120° C., and weigh. From the weight of $KClO_4$ found, calculate according to requirements the percentage of K, K_2O, or KCl present.

Estimation of Sodium.

Determine the sodium present as sodium chloride by subtracting the weight of potassium chloride found from the weight of the mixed chlorides.

7. Estimation of Nitrate in Nitrometer.

As its name indicates, the nitrometer was devised for measuring nitrous gas. When a nitrate or nitrite, in presence of sufficient sulphuric acid, is shaken with mercury, the nitric or nitrous acid liberated is reduced by the mercury to nitric oxide, and the measurement of this gas under observed conditions of temperature and pressure serves to estimate the nitrate or nitrite. By this means " nitrous vitriol " is estimated (Lunge).

A nitrometer has already been used for the gasometric estimation of hydrogen peroxide (Part I, p. 124). For the present purpose the bottle attached at the side will not be necessary.

Procedure.—Thoroughly clean the nitrometer, and see that it is supported by clamps strong enough to hold it when filled with mercury. The stand on which the nitrometer is held must be placed within a tray with upturned edges to catch mercury if any should be spilled.

Let the tap of the nitrometer be open, and pour in mercury through the pressure tube until the graduated tube appears about half full. Next raise the pressure tube so as to cause the mercury, by ascending, to drive out the air from the graduated tube, either through the cup at the top or through the side tube; then close the tap. There will be sufficient mercury if its level in the pressure tube is now an inch or two above the rubber connection.

The nitrate to be estimated may be solid or in aqueous solution. In the former case place the weighed amount directly in the cup of the nitrometer, and there dissolve it in 1 c. c. of warm water; in the latter deliver 1 c. c. of the solution into the cup from a burette or small pipette. The amount of nitrate taken must yield a volume of gas not in excess of that provided for by the graduations of the instrument. If sodium nitrate is being used, not more than 0·1 gm. of the salt should be taken unless the nitrometer is provided with a bulb so that it will hold upwards of 100 c. c., in which case about 0·4 gm. should be employed.

Carefully turn the tap so as to allow the nitrate solution to flow slowly into the measuring tube above the mercury, then rinse the cup with 1 c. c. of water and let the rinsings flow also into the tube. See that there is no air in the measuring tube, or displace any that has been allowed to enter accidentally; then pour about 15 c. c. of concentrated sulphuric acid into the cup, and allow this to flow gently into the tube.

Now remove the graduated tube from the clamp, and, clasping the upper part of it in the right hand, with fingers round the cup and side tube and the palm of the hand holding the tap in its place, gently give to the tube a rotatory motion whilst holding it obliquely, so as to mix some of the mercury with the acid and thus cause interaction between the metal and the nitric acid in solution. The mercury will break into small globules, and nitric oxide gas will accumulate. When the evolution of gas has ceased, clamp the measuring tube, and allow the apparatus to stand for an hour, or until the mercury has assumed atmospheric temperature, arranging the pressure tube, however, so that the gas is at approximately atmospheric pressure. Then carefully adjust the pressure tube so that the gas is under exactly atmospheric pressure. This will be the case when the column of concentrated sulphuric acid is about seven times the length of the balancing column of mercury in the pressure tube. To prove that the gas is at atmospheric pressure, or to adjust it accurately to this pressure, place a few drops of water in the cup of the nitrometer, and very carefully turn the tap, observing whether there is a tendency for water to enter or gas to leave the tube. Very small movement of the pressure tube up or down will suffice to adjust the pressure so that there is no motion of water or gas when the tap is opened, showing that the gas has been brought exactly to atmospheric pressure. Read the volume of the nitric oxide gas, the barometric pressure, and the temperature.

The gas is dry because it is contained over nearly concentrated sulphuric acid. The nitrogen present in this gas would measure half its volume; so after reducing the gas to its volume at 0° C. and 760 mm. pressure, calculate the weight of nitrogen, and thence the percentage of this element in the nitrate analysed. 1 c. c. of nitrogen at normal temperature and pressure weighs 0·00125 gm.

8. Estimation of Nitrite and Nitrate in Nitrometer.

Whether nitrite or nitrate is present in solution it is converted into nitric oxide by mercury in presence of sulphuric acid. Nitrite, however, can be estimated by measuring the nitrogen evolved in the following reaction with urea, which occurs in presence of dilute sulphuric acid, and is not interfered with by nitrate:

$$CO(NH_2)_2 + 2HNO_2 = 2N_2 + CO_2 + 3H_2O.$$

Half the nitrogen evolved in this reaction was present in the nitrite. Therefore if from half the volume of gas evolved in the reaction of the mixed nitrite and nitrate with mercury is subtracted half the volume of gas obtained by reaction with urea, the remaining gas represents the nitrogen which was originally present as nitrate.

Procedure.—(*a*) Place in the nitrometer cup 1 c. c. of a solution of the mixed nitrite and nitrate of suitable concentration. Allow this solution to run into the measuring tube, and rinse out the cup with 1 c. c. of water as before. Add 15 c. c. of sulphuric acid, and, after causing nitric oxide gas to be evolved by shaking, measure the gas under observed conditions of temperature and pressure as when nitrate alone was being estimated.

(*b*) Place, as before, 1 c. c. of the mixed solution in the cup, and allow the solution to run into the nitrometer on the top of the mercury. Rinse the cup with 1 c. c. of water, and add the rinsings. Then place in the cup 1 c. c. of saturated solution of urea and allow the solution to enter the measuring tube. Finally introduce 5 c. c. of dilute sulphuric acid. Nitrogen gas is quickly evolved together with carbon dioxide. When the reaction is over, introduce into the measuring tube some sodium hydroxide solution coloured with litmus, allowing enough to enter to make the mixed solution alkaline. Shake the gas with the alkali to promote absorption of carbon dioxide, and when the volume has become constant, read it and correct it to standard temperature and pressure, regarding the gas as saturated with water vapour.

Subtract half this volume from half the volume of gas obtained from the 1 c. c. of mixed nitrate and nitrite solution, and calculate the weights of the volumes of nitrogen representing nitrite and nitrate respectively. Thence estimate the weight of nitrite and nitrate in a given quantity of the original solution or mixture.

QUANTITATIVE ANALYSIS OF MINERALS, ORES, AND ALLOYS

The quantitative analysis of complex inorganic products, whether of natural or artificial origin, should always be preceded by a careful qualitative analysis; and an attempt should be made in this analysis to gain an approximate idea of the proportions in which the various constituents are present.

Since many minerals are obtained in solution with difficulty, it is essential to reduce them to a very fine state of subdivision before attempting to dissolve them. This is done by crushing the mineral to coarse powder in a steel percussion mortar, and then grinding it in an agate mortar until no gritty particles can be felt between the fingers. An alloy, if brittle, can be treated in the same way, but otherwise drillings should be obtained from it, or if it is in the shape of foil this may be cut with scissors into small pieces.

The results of the analysis of a mineral may frequently be expressed with convenience in terms of oxides, according to the dualistic system of Berzelius. For example, dolomite may be said to contain the following oxides: CaO, MgO, Fe_2O_3, Al_2O_3, SiO_2, CO_2; and felspar the oxides: K_2O, Na_2O, CaO, MgO, Fe_2O_3, Al_2O_3, SiO_2. Objection may be taken to this scientifically; but there is really no alternative, since even if silicate and carbonate ions exist in these minerals, the nature of the silicate ion is not certainly known, and neither is it known whether all the metals present can be regarded as combined with carbonate or silicate radicles.

Sometimes, however, as in the case of sulphide ores, the metals present can be reported as such; e.g. the analysis of zinc-blende will show insoluble matter, and then Zn, Fe, and S.

To obtain the substance in solution there are various methods of procedure. Some minerals, and artificial products such as dolomite and spathic iron ore, as well as superphosphate of lime and basic slag, do not require an oxidizing agent to dissolve them and can therefore be dissolved in moderately concentrated hydrochloric acid, what remains undissolved being reported as insoluble residue. Other minerals such as zinc-blende and pyrites, as well as alloys, require an oxidizing agent to dissolve them, so that nitric acid, potassium chlorate, or bromine must be employed in addition to hydrochloric acid. Siliceous minerals, such as felspar, and artificial products such as glass and pottery, require processes of fusion in order to obtain their constituents in a form suitable for analysis.

In a complex analysis the presence of volatile products, which include water and carbonaceous matter, as well as carbon dioxide, which will be displaced by acid, must not be overlooked.

It is highly desirable to perform analyses in duplicate.

The analysis of the following minerals or ores and alloys will be described in this section.

1. Dolomite or limestone.
2. Spathic iron ore.
3. Zinc-blende.
4. Galena.
5. Copper pyrites.
6. Serpentine.
7. Felspar.
8. Basic slag and other phosphatic manures.
9. Silver coin.
10. German silver.
11. Solder.
12. Brass or bronze.

1. ANALYSIS OF DOLOMITE OR LIMESTONE

Dolomite or magnesian limestone consists chiefly of calcium and magnesium carbonates; but it will contain also small amounts of iron and aluminium oxides, and of silica and insoluble siliceous matter. A little water will probably be present also, and possibly a very little manganese, and phosphate. Limestone is similar to dolomite, but contains little or no magnesium carbonate.

Reduce about 10 gm. of the sample to be analysed to a fine powder in the agate mortar; then analyse it qualitatively, obtaining a rough idea of the proportions in which the constituents are present.

The method of quantitative analysis for the insoluble matter and metallic constituents is shown in the following scheme, from which it is seen to be similar to that employed in qualitative analysis.

<table>
<tr><td colspan="4">Dissolve the finely powdered mineral in hydrochloric acid, evaporate solution to dryness, and ignite residue on sand bath. Digest with hydrochloric acid, dilute, and filter.</td></tr>
<tr><td rowspan="3">*Residue,*
Silica and insoluble silicate.</td><td colspan="3">*Filtrate.*—Add ammonium chloride and ammonia, heat to boiling, and filter. Dissolve precipitate in hydrochloric acid, reprecipitate with ammonia, and filter.</td></tr>
<tr><td rowspan="2">*Residue,*
Hydrated $Fe_2O_3 + Al_2O_3$ ($?P_2O_5$).</td><td colspan="2">*Mix Filtrates*, heat to boiling, add solid ammonium oxalate, and filter. Dissolve precipitate in dilute hydrochloric acid, and reprecipitate with ammonia and a little ammonium oxalate. Filter.</td></tr>
<tr><td>*Residue,*
Calcium oxalate.</td><td>*Mix Filtrates*, and precipitate magnesium with microcosmic salt.</td></tr>
</table>

The above scheme serves to show the scope of the analysis, but further details of instruction are necessary, with regard to separate determinations.*

Water.—Dolomite or limestone contains little moisture and the amount present is of no significance. If, however, this is not estimated the sum of the analytical figures obtained may fall short of 100 per cent. The finely ground specimen of the mineral should be kept in a closely stoppered weighing bottle so that the amount of moisture present in it may not alter during the analysis. Weigh 5 gm. of the mineral in tared watch glasses with clamp. These are two watch glasses with edges ground so that when clamped together they fit nearly air-tight (fig. 4). Slide the watch glasses a little apart to allow for the passage of air, and place them in an air oven heated to 110°. After an hour,

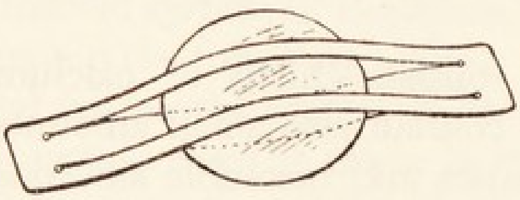

Fig. 4

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* Methods of quantitative analysis frequently have no counterpart in qualitative analysis, and therefore no attempt will be made in other cases to present tabulated schemes of analysis.

remove them from the oven, push them together again, cool in the desiccator and weigh. Repeat heating and weighing until the weight is constant, and from the loss in weight calculate the percentage of moisture in the mineral.

Silica and Insoluble Matter.—Silica and insoluble matter are distinguished because the silica found may have been present as a silicate soluble in hydrochloric acid, then separated as silicic acid, and finally obtained as insoluble silica by evaporation and ignition.

If much silica were present as silicate a double evaporation would be necessary to obtain it all in an insoluble form. This, however, need not be carried out in the present case, since most if not all of the silica found will have been present in the mineral in the free state or as an insoluble silicate.

Weigh accurately 1·0 to 1·5 gm. of the powdered mineral, placing the weighed portion in a large porcelain dish provided with clock glass which fits it closely except at the lip. Provide a suitable glass rod, moisten the powder with water, and stir it well so that it may become thoroughly wetted. Then through the lip of the dish introduce dilute hydrochloric acid by means of a pipette. The clock glass prevents loss of liquid as spray during the effervescence as the powder dissolves. When effervescence has ceased, wash into the dish by means of a jet of water any liquid on the convex surface of the clock glass, and then carefully evaporate the solution. The water bath may be used at first, followed by the sand bath, or the dish may be placed on gauze which is heated directly by a minute flame the tip of which does not reach the gauze. This way of heating is in some respects preferable to the use of the sand bath, because the heating is under direct control, and can be stopped instantly by removal of the flame. When the mass is nearly dry it must be stirred carefully with the glass rod. Finally heat the dish until fumes of hydrochloric acid cease to be evolved, and the contents are quite dry. During this final heating place the clock glass over the dish. Allow the dish to cool, and then add to the dry residue a few cubic centimetres of concentrated hydrochloric acid. Stir with the glass rod, and dilute with a convenient volume of hot water, wash into the dish any particles of solid that may be on the surface of the clock glass, and digest the liquid until all soluble matter has been dissolved. Filter through a quantitative filter paper, and wash the filter first with a little warm dilute hydrochloric acid, and finally with hot water until the washings are colourless. Allow the filter to drain and ignite it together with its contents, moist, in a silica or preferably platinum crucible. Weigh the insoluble matter, and reserve the filtrate and washings for subsequent estimations.

Ferric Oxide and Alumina.—Ferric and aluminium hydroxides are precipitated together from the filtrate from the silica by ammonia added after ammonium chloride, but a little calcium carbonate is likely to be precipitated with them. To ensure the complete separation of iron and aluminium it is necessary, therefore, to dissolve the precipitate in dilute hydrochloric acid after filtration, and then to reprecipitate the hydroxides with ammonia added after ammonium chloride.

Place the filtrate and washings from the insoluble matter in a beaker, or preferably a large evaporating dish provided with a rubber-tipped glass rod of suitable length, add, say, 10 c. c. of ammonium chloride solution from the bench, and ammonia with stirring, until the precipitate is formed, and the liquid smells faintly of ammonia. Large excess of this reagent must be carefully avoided because aluminium hydroxide is distinctly soluble in it. Heat the liquid to boiling, filter, and wash the precipitate with hot water; but do not attempt to remove that part of it which adheres to the beaker or dish. Set aside the filtrate and washings, place the beaker or dish under the filter, heat some dilute hydrochloric acid in a small flask or boiling tube and pour this upon the filter so as to dissolve all the precipitate. Wash the filter in order to lose none of the solution, then add ammonia again just in excess, heat, filter through a fresh filter paper and wash the precipitate, adding the second filtrate and washings to the first. Allow the filter to drain thoroughly, then place it moist in a weighed crucible and ignite it, reheating it until the weight is constant. From the result calculate the percentage of ($Fe_2O_3 + Al_2O_3$) in the dolomite.

It is not usual to estimate separately the ferric oxide and alumina occurring in dolomite. In order to do so, however, it is convenient to prepare a fresh solution in hydrochloric acid of a weighed quantity of the powdered mineral, and to titrate with standard dichromate solution an aliquot part of this solution after reduction with stannous chloride (Part I, p. 135). The iron thus found is calculated to

Fe_2O_3, and the amount of this subtracted from that of the (Fe_2O_3 + Al_2O_3) present in an equal quantity of the mineral to give the amount of alumina present.

Lime.—Lime is estimated in the mixed filtrates obtained after the double precipitation of ferric and aluminium hydroxides, by a double precipitation with ammonium oxalate.

Heat the solution to boiling in a beaker, add excess of solid ammonium oxalate, allow the precipitate to settle and decant the clear supernatant liquid through a filter. Wash the precipitate once with hot water, pouring the wash water through the same filter after the precipitate has settled in the beaker. Set aside the combined filtrate and washings. Then pour a little hot dilute hydrochloric acid upon the filter so as to dissolve any calcium oxalate there, and receive the solution in the beaker, which contains the main portion of the calcium oxalate; this will quickly dissolve in the acid. Wash the filter thoroughly with hot water.

Now heat the solution and reprecipitate the calcium oxalate by making the liquid alkaline with ammonia and adding a few cubic centimetres of ammonium oxalate solution to secure presence of excess of oxalate. Filter and wash the calcium oxalate, and convert it into carbonate, oxide, or sulphate before weighing (Part I, p. 44).

Magnesia.—The combined filtrates and washings from the calcium oxalate precipitate contain considerable quantities of ammonium salts, and it has been customary to evaporate such a solution to dryness and ignite the residue so as to volatilize these salts, which, it has been considered, interfere with the complete precipitation of magnesium.

Fortunately this troublesome operation can be avoided by adopting the method of B. Schmitz,* carried out in the following way.

Acidify the solution with hydrochloric acid, add microcosmic salt in excess followed by a few drops of phenolphthalein solution; then heat to boiling and, with stirring, add dilute ammonia solution until the indicator shows an alkaline reaction. Thus magnesium ammonium phosphate will be precipitated. Allow the liquid to cool, and add to it, while stirring, one-fifth of its volume of concentrated ammonia solution. This is added because magnesium am-

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* *Zeitsch. anal. Chem.*, 1906, **45**, 512.

monium phosphate is less soluble in ammonia solution of moderate concentration than in water. After ten minutes filter the precipitate through an asbestos filter, wash it with dilute ammonia solution until it is free from chloride; then dry and ignite it, gently at first and then at a bright red heat, having the Gooch crucible inside an iron or nickel crucible. From the weight of $Mg_2P_2O_7$ obtained, calculate the weight and percentage of MgO.

Manganese.—If a trace of manganese has been found in the dolomite, and it is desirable to estimate it, this may be done colorimetrically by oxidizing it to permanganic acid by ammonium persulphate in presence of silver nitrate as catalyst. See p. 74.

Phosphate.—If phosphate is present in appreciable quantity, it can be estimated by the method described under the analysis of basic slag (p. 125), but in this case the whole analysis will need to be conducted according to that method.

Carbon Dioxide.—Several methods for estimating carbon dioxide in a mineral containing it can be suggested.

(*a*) In the absence of organic matter and ferrous iron, the loss on ignition will be due to water and carbon dioxide. If, therefore, this is determined, and the water present has been estimated in another way, the difference between the two losses represents carbon dioxide.

(*b*) The carbonate may be dissolved in an acid in a weighed apparatus containing the carbonate and the acid, and the loss in weight determined. This method is sometimes employed, Schrötter's apparatus being used; but the results are approximate only.

(*c*) The carbon dioxide evolved by the action of an acid may be dried, and then absorbed in potash solution or soda lime. This method, which gives the best results, will be described here.

The question of the acid to be used in liberating carbon dioxide gas from the carbonate remains, however, to be considered. If hydrochloric acid is used, moist hydrogen chloride gas will accompany the carbon dioxide, and it will be necessary to remove this gas from the carbon dioxide before the latter enters the alkali absorbent. This might be done, if necessary, by the use of pumice impregnated with anhydrous copper sulphate. Sulphuric acid is free from the objection of evolving an acid vapour with the carbon dioxide, but its use is limited on the account of the insoluble sulphates which it forms. For example, its use in the case of limestone or dolomite is to be avoided because of the formation of a layer of crystallized calcium sulphate which inhibits the reaction. Phosphoric acid, however, is free from both of these objections; it evolves no acid vapours, and when added in excess forms soluble acid phosphates with the bases present. Thus when finely divided dolomite is dissolved in excess of dilute phosphoric acid, it forms a nearly clear solution from which all the carbon dioxide is readily displaced.

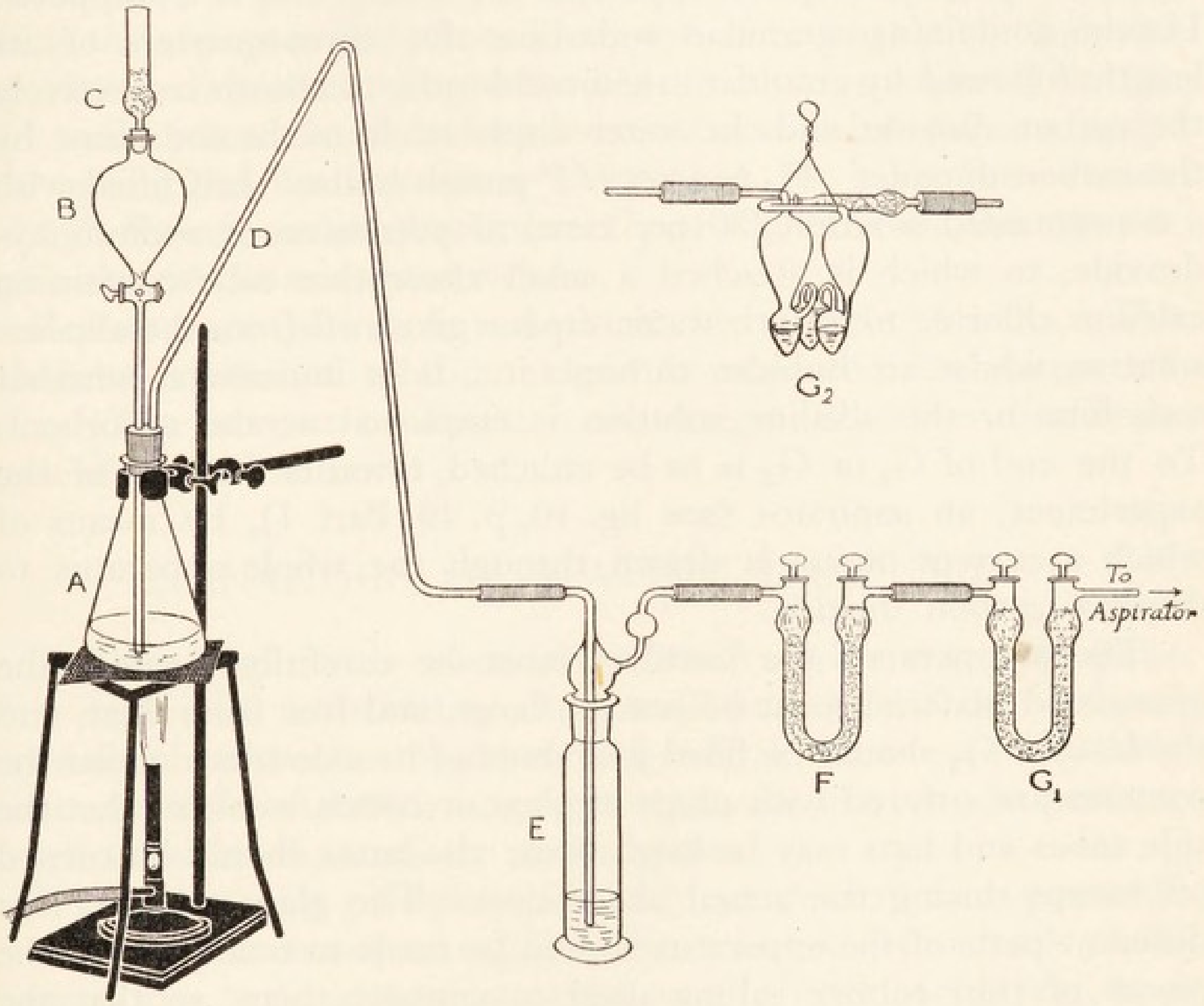

Fig. 5

Apparatus and Procedure.—A flask A, of not less than 500 c. c. capacity, is provided with a doubly-bored rubber stopper, through one hole of which passes the tap funnel B; to this funnel is attached a soda-lime tube C, to absorb carbon dioxide from the air which is drawn through the apparatus at the end of the experiment. It is well for the end of the delivery tube of the tap funnel to be drawn out and turned upwards within the liquid, so that no carbon dioxide gas can possibly escape by means of it. Through the other hole in the stopper passes a glass tube D, which is bent obliquely upwards, and then downwards to the wash bottle E, containing concentrated sulphuric acid. By this means the carrying over of liquid water into the sulphuric acid is prevented. Attached to the wash bottle is a stoppered U-tube F, containing fragments of pumice stone soaked in concentrated sulphuric acid, to complete the drying of the carbon dioxide begun in the wash bottle. This is followed by the absorption apparatus G_1 or G_2. G_1 is a stoppered U-tube containing granular soda-lime for three-quarters of its length, followed by granular calcium chloride, to absorb respectively the carbon dioxide, and the water displaced from the soda-lime by the carbon dioxide. G_2 is a set of " potash bulbs " half filled with a concentrated solution (30 per cent) of potassium or sodium hydroxide, to which is attached a small absorption tube containing calcium chloride to absorb water vapour given off from the alkaline solution whilst air bubbles through it. It is immaterial whether soda-lime or the alkaline solution is employed as the absorbent. To the end of G_1 or G_2 is to be attached, towards the end of the experiment, an aspirator (see fig. 10, p. 49, Part I), by means of which a current of air is drawn through the whole apparatus to displace carbon dioxide.

The stoppers of the U-tubes must be carefully greased, the granulated material must be not too large, and free from dust, and the U-tube G_1 should be filled just short of its side tubes whilst the contents are covered with plugs of glass or cotton wool, so that the side tubes and taps may be kept clean; the latter should be turned off except during the actual absorption. The glass tubes of the different parts of the apparatus should be made to touch within the pieces of thin rubber tubing used to connect them, so that the whole may be air-tight. If G_2 is employed, its open ends, when it is not in use, should be covered with caps of thin rubber tubing stopped with small pieces of glass rod, and these should be weighed with the apparatus.

Fit together the apparatus except for attaching the absorption tube or bulbs, and the aspirator. Weigh accurately about 1 gm. of the powdered dolomite, and in order to introduce it easily into the body of the flask, screw it up in a little piece of thin paper so that it can be dropped in quickly. Dilute about 5 c. c. of syrupy phosphoric acid to 25 c. c. with water, pour this solution into the tap funnel, attach the soda-lime tube to the top of the latter, and see that the drawn-out end of the delivery tube of the tap funnel reaches nearly to the bottom of the flask, when the stopper is in position. Weigh and attach the absorption apparatus, and turn on the taps of the U-tube or tubes. Allow all the acid to flow gently into the flask, then warm the liquid to promote disengagement of gas. Observe that the U-tube containing soda-lime becomes warm as carbon dioxide is absorbed. Finally heat the liquid in the flask just to boiling, attach the aspirator and draw a current of air slowly through the apparatus. See that the powder has dissolved completely in the acid; and when the soda-lime tube—if used—has become quite cold again, and not less than 2 litres of air have been drawn through the apparatus, disconnect G_1 or G_2, turn off the taps or attach the rubber ends, and weigh.

Repeat the experiment, and obtain two agreeing results. The soda-lime or alkaline solution should be renewed after being used twice. The increase in weight is the weight of carbon dioxide in 1 gm. of the dolomite.

2. ANALYSIS OF SPATHIC IRON ORE

Spathic iron ore is essentially ferrous carbonate, with some ferric oxide due to oxidation, and small amounts of calcium and magnesium carbonates, together with a little water and insoluble siliceous matter. A little manganese carbonate may also be present, as well as traces of phosphate and sulphate.

If manganese or phosphate, or both, are present in appreciable amounts it is necessary to separate ferric iron together with phosphate as the basic acetate in presence of a little acetic acid, and then to precipitate the manganese from the filtrate as hydrated dioxide by means of hydrogen peroxide in presence of ammonia, calcium and magnesium being estimated in the usual way in the filtrate from the manganese.

If manganese and phosphate are absent the procedure is simpler, since the iron is precipitated from the ferric solution by ammonia as $Fe(OH)_3$ and weighed as Fe_2O_3, calcium and magnesium being estimated as before in the filtrate from the iron. If phosphate is present in sufficient quantity to be estimated it must be precipitated from acid solution by ammonium molybdate, and it may be weighed as phosphomolybdic anhydride, $24MoO_3, P_2O_5$.

Since iron is present in both the ferrous and the ferric condition, and the total iron will have been determined gravimetrically, it is desirable to determine the ferrous iron by dissolving a fresh portion of the powdered ore in hydrochloric acid in absence of air, and titrating with standard dichromate solution the ferrous chloride produced.

The water present is estimated by heating a weighed amount of the powdered ore in an air oven at 110° C. until it ceases to lose weight; and the carbon dioxide by displacing it from the ore by phosphoric acid, and absorbing it in a soda-lime tube or potash bulb. Sulphate if present is precipitated and weighed as $BaSO_4$.

Procedure.—Reduce to fine powder, by grinding in an agate mortar, not less than 10 gm. of the ore; then make a careful qualitative analysis, looking specially for manganese, phosphate, and sulphate.

Not only does the qualitative analysis of a mineral necessarily precede its quantitative analysis, but it is often a useful guide to the latter, since by careful observation a judgment may be formed of the relative proportions in which the different components are present. The components to be estimated will be included amongst the following: FeO, Fe_2O_3, (MnO), CaO, MgO, CO_2, H_2O, insoluble matter, (P_2O_5).

Water.—Weigh accurately between watch glasses and clamp 2 gm. of the finely powdered ore, and heat it in an air oven at 110° C. until it ceases to lose weight. From the loss of weight calculate the percentage of water present.

Carbon Dioxide.—The dried ore after the estimation of water serves for determining the carbon dioxide. Introduce it into the apparatus described under the analysis of dolomite, and estimate the carbon dioxide similarly by direct weighing.

Insoluble Matter.—The insoluble matter includes not only matter directly insoluble in hydrochloric acid, but also any silica derived from silicic acid and rendered insoluble by evaporation with hydrochloric acid followed by ignition.

Weigh 2·5 gm. of the powdered ore and place it in a large evaporating dish provided with a clock glass and stirring rod. Pour over it dilute hydrochloric acid, and heat so as to dissolve the ore; then add a little concentrated nitric acid to oxidize the ferrous iron; carefully evaporate the solution to dryness, and ignite the residue gently over a small flame until it is dry. Add a little dilute hydrochloric acid, stir well, and repeat the evaporation and ignition. Finally digest the mass with dilute hydrochloric acid, then filter and wash the residue with hot water by decantation and on the filter till the washings are colourless. Let the filter drain, place it whilst damp in a weighed crucible, dry and ignite it, and weigh the residue.

Ferric Oxide.—Place the filtrate and washings from the insoluble matter in a 250-c. c. flask, dilute to the graduation mark and thoroughly mix the solution by shaking; 100 c. c. of this solution corresponds with 1 gm. of the ore. As explained above, the next procedure depends upon whether either manganese or phosphate or both are present.

A. *Manganese* (*and Phosphate*) *Present.*

Neutralize the solution with ammonia and precipitate the iron as basic acetate according to instructions on p. 85, carrying out a double precipitation. If any P_2O_5 is present it will be precipitated and weighed with the Fe_2O_3. If phosphate is present although manganese is absent the ammonium acetate method of separating iron together with phosphate should still be adopted.

B. *Manganese* (*and Phosphate*) *Absent.*

Add ammonium chloride and ammonia to precipitate the iron as $Fe(OH)_3$. Filter, dissolve the precipitate in dilute hydrochloric acid, and reprecipitate $Fe(OH)_3$ with ammonia. Wash, ignite, and weigh as Fe_2O_3. The result gives the total iron in terms of Fe_2O_3. From this must be subtracted Fe_2O_3 equivalent to FeO in the ore to be found by volumetric analysis.

Manganous Oxide.—If manganese is present in appreciable quantity, add to the faintly acid filtrate from the iron ammonia and hydrogen peroxide, and heat to boiling. Filter off the hydrated manganese dioxide, ignite and weigh the manganese as Mn_3O_4; then calculate this weight to MnO. If the amount of manganese present is very small it may still be possible to estimate it colorimetrically after converting it into permanganic acid according to the method described on p. 74.

Lime.—Estimate the lime in the filtrate from the iron or manganese precipitate by a double precipitation with ammonium oxalate according to the method described under the analysis of dolomite, p. 101.

Magnesia.—Estimate the magnesia in the mixed filtrates from the lime by precipitating it as magnesium ammonium phosphate, which is converted by ignition into pyrophosphate according to the method described under the analysis of dolomite, p. 101.

Ferrous Oxide.—Dissolve 1 gm. of the powdered ore by heating it with dilute hydrochloric acid free from iron in a flask through which a current of carbon dioxide gas is made to pass. It is convenient to close the neck of the flask with a cork with three holes through which pass a tap funnel to deliver the acid, and the inlet and outlet tube for the carbon dioxide, the former extending nearly to the bottom of the flask and the latter ending just through the cork. When the ore has been dissolved and the liquid cooled to atmospheric temperature in a stream of carbon dioxide, the solution may be filtered without fear of oxidation. Collect the filtrate and washings in a 100-c. c. flask, dilute to volume, and titrate 20 or 25 c. c. of the solution with decinormal dichromate solution. From the result calculate the percentage of FeO in the ore; then convert this into percentage of Fe_2O_3 and subtract the figure obtained from the percentage of Fe_2O_3 found by gravimetric analysis, thus obtaining the percentage of Fe_2O_3 present as such in the ore.

Phosphate.—If an appreciable amount of phosphate has been found by qualitative analysis it may be estimated by precipitation with ammonium molybdate. The following reagents are required:

1. Ammonium molybdate: a 3 per cent aqueous solution of the crystallized salt.
2. Nitric acid: 25 per cent strength.
3. Ammonium nitrate: a 30 per cent solution.
4. Wash liquid containing 5 gm. of ammonium nitrate and 4 c. c. of concentrated nitric acid per 100 c. c.

Procedure.—Dissolve 1 gm. of the finely powdered ore in twice N nitric acid, evaporate the solution to dryness in a porcelain dish and ignite the residue. Digest this residue with very dilute nitric acid, then filter and wash it, receiving the filtrate and washings, which should amount to about 50 c. c., in a beaker. Add to this solution 15 c. c. of the ammonium nitrate solution and 5 c. c. of the nitric acid. Heat the solution nearly to boiling; also heat to boiling 10 c. c. of the ammonium molybdate solution, and add the latter whilst stirring. Be careful, however, not to touch the sides of the beaker with the stirring rod. Precipitation of ammonium phosphomolybdate is complete, and after settling filtration may be proceeded with.

Filter the precipitate through an asbestos filter, washing it several times by decantation, and on the filter, with the prepared solution. Place the Gooch crucible inside a nickel or platinum crucible and ignite to dull redness so as to convert the yellow precipitate into greenish black phosphomolybdic anhydride. Repeat the heating till the weight is constant.

Ammonium phosphomolybdate has the composition: $(NH_4)_3PO_4$, $12MoO_3$, xH_2O, and phosphomolybdic anhydride, formed from this salt by ignition, is P_2O_5, $24MoO_3$, containing 3·947 per cent of P_2O_5.

The percentage of P_2O_5 found in this estimation must be subtracted from the percentage of what has been regarded as Fe_2O_3 in order to obtain the true percentage of the latter, since all phosphate present is precipitated as ferric phosphate when the faintly acid solution is boiled with ammonium acetate.

Sulphate.—If sulphate is present it may be precipitated by barium chloride from a solution of 1 gm. of the ore, after oxidation of the ferrous iron. The iron, however, should first be precipitated by ammonia, and redissolved by acid after the precipitation of the sulphate, so that adsorption of ferric iron from solution by the precipitate may be avoided.

3. ANALYSIS OF ZINC-BLENDE

Zinc-blende is essentially zinc sulphide, but with this there generally occur the sulphides of lead and iron, and occasionally those of copper, cadmium, and manganese. Siliceous matter is also present, and a little carbonate may also be found; if the latter is present it must be reckoned as CO_3''.

Procedure.—Conduct carefully a qualitative analysis of the finely powdered mineral; and for the quantitative analysis follow the detailed instructions given below so far as they are applicable.

The ore is dissolved in hydrochloric acid, and after the evolution of hydrogen sulphide a little nitric acid is added to oxidize the iron. The lead, if present, is weighed as sulphate together with the insoluble matter, the lead sulphate being then removed by ammonium acetate. Copper is precipitated by hydrogen sulphide from the filtrate containing sulphuric acid and heated to boiling, and cadmium similarly, if present, from the filtrate from the copper after cooling, according to the method of Hofmann, modified by Treadwell. The iron is then removed by precipitation with cupferron and the manganese as hydrated dioxide, the zinc being estimated in the filtrate by precipitation as zinc ammonium phosphate. Sulphur is estimated as barium sulphate, after oxidation, either by fusion of the ore with sodium peroxide or its treatment with nitric acid; and carbonate, if present, by displacement of carbon dioxide, and weighing after absorption in alkali.

Solution of Ore: Estimation of Insoluble Matter and Lead.—Weigh accurately about 1 gm. of the finely powdered ore, and act upon it in a 5-in. evaporating dish with concentrated hydrochloric acid, keeping the dish covered with a clock glass whilst the mixture is heated, and evolution of hydrogen sulphide continues. When the reaction appears to be finished, add a few drops of nitric acid, evaporate the contents of the dish to dryness, and ignite the residue to render the silica insoluble. Then add a few cubic centimetres of concentrated hydrochloric acid and a little water, and warm the mixture so as to dissolve all soluble matter. Next carefully add 5 c. c. of concentrated sulphuric acid, and proceed as directed on p. 60, Part I, in order to precipitate the lead completely as sulphate, but collect the insoluble mixture on filter paper instead of asbestos. Preserve the filtrate and washings for the estimation of the other constituents of the ore. Dry the filter, and ignite the paper and contents separately in a porcelain or silica crucible. Convert into sulphate any reduced lead from the filter by treating the ash with a drop of nitric acid, and then a drop of sulphuric acid, followed by gentle ignition, before the main quantity of the solid is placed in the crucible. Gently ignite the whole, and weigh the mixture of lead sulphate and insoluble matter. Then turn out into a beaker the contents of the crucible, add ammonium acetate solution and a little ammonia, and boil to dissolve the lead sulphate. Collect the residue on another filter, after washing it by decantation with more ammonium acetate solution; then wash it on the filter with the same solution until the filtrate shows no reaction for lead with potassium chromate. Finally wash the residue with hot water, place the damp filter in the crucible, ignite it and weigh the residue. The difference between the two weighings is the weight of lead sulphate. Estimate the insoluble residue as such, and the lead as metal.

Estimation of Copper (if necessary).—Add to the filtrate and washings from the lead sulphate about 20 c. c. of concentrated sulphuric acid, dilute the solution to 100 c. c., and heat it to boiling. Pass hydrogen sulphide through the boiling solution for 20 min., then keep the liquid boiling for a further 15 min. Filter off and wash the precipitated copper sulphide, carefully protecting it from atmospheric oxidation. Then dissolve this precipitate in dilute nitric acid, add a few drops of sulphuric acid, and evaporate the solution in a dish to remove nitric acid; dilute the solution with (1:4) sulphuric acid, using, so far as can be judged, about 50 c. c. of this diluted acid for every 0·1 gm. of copper present. Again heat to boiling and pass hydrogen sulphide gas as before. Filter off the precipitate, and weigh the copper as cuprous sulphide (see p. 117).

Estimation of Cadmium (if necessary).—Two precipitations of copper sulphide were necessary to separate copper completely from cadmium. Mix the filtrates and saturate the cold solution with hydrogen sulphide. This will precipitate the cadmium in a dense, orange form, less soluble than the yellow sulphide. Filter off, and wash the precipitate, and reserve the filtrate and washings. Place the filter and contents in a porcelain dish, and dissolve the precipitate by heating it with dilute hydrochloric acid (1:3). Filter the solution in which the disintegrated filter paper is suspended, and wash the paper thoroughly on the filter. Receive the filtrate in a small, weighed, porcelain dish, and evaporate it to dryness. Then add a little dilute sulphuric acid and again evaporate. Ignite the residue and weigh the anhydrous cadmium sulphate. Add a little more dilute sulphuric acid, and again evaporate, ignite, and weigh, repeating these operations until the weight is constant. From the weight of $CdSO_4$ calculate the percentage of cadmium in the ore.

NOTE.—Conversion of cadmium sulphide into sulphate is necessary because the precipitate is impure, containing Cd_2Cl_2S, or Cd_2SO_4S (Treadwell).

Estimation of Iron.—Iron is conveniently separated* from manganese and zinc by precipitation with "cupferron" †. Evaporate the filtrate from the cadmium, if necessary, until its volume does not exceed 80 c. c.; add 20 c. c. of concentrated hydrochloric acid, and dilute with water to 100 c. c. Add to the cold solution with constant stirring a solution of about 3 gm. of cupferron in 50 c. c. of cold water. A dark red precipitate of the iron compound will be formed, and when a white precipitate begins to appear the separation of the iron is completed. Add the precipitant in slight excess, and then allow the mixture to stand for about ten minutes. Filter the bulky precipitate through paper with slight suction, and wash it with cold water till the washings are free from chloride. Reserve the filtrate and washings for the estimation of manganese and zinc. Then treat the precipitate on the filter with dilute ammonia solution (1:4), which hydrolyzes the cupferron compound, and if the reaction is complete, converts it into ferric hydroxide. This is an advantage, since the latter is more easily ignited to oxide than the organic compound. Afterwards wash again with water, and then ignite precipitate and filter together in a porcelain or silica crucible; weigh the ferric oxide, and calculate the percentage of iron present.

Estimation of Manganese.—Precipitate the manganese from the above filtrate as peroxide, and weigh it as Mn_3O_4 according to the method described on p. 125.

Estimation of Zinc.—Precipitate the zinc from the filtrate from the manganese as zinc ammonium phosphate, and weigh it as pyrophosphate according to the method given on p. 107.

Estimation of Sulphur.—Use method (i) or method (ii). (i) Weigh about 1 gm. of the finely powdered ore, and mix it with six times its weight of sodium peroxide in an iron or nickel crucible. Heat the mixture cautiously until it fuses, and keep it just fused for a few minutes, until all reaction is at an end. Allow the mass to cool and then extract it with water. The extract will contain some

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[*] The basic acetate method of separation may be employed (see p. 85), but a double precipitation is necessary, not only on account of manganese, but also because much sulphate is present in solution, and basic ferric sulphate is liable to be precipitated in the first case instead of acetate.

[†] "Cupferron" is the ammonium salt of nitrosophenyl hydroxylamine, $C_6H_5 \cdot N(NO) \cdot ONH_4$. The shorter name indicates that this compound is a reagent for copper and iron, since it precipitates these metals from acid solution in which all other metals remain soluble. In order to preserve the compound it is necessary to store it in a stoppered bottle in an atmosphere of ammonia, secured by suspending in the bottle a lump of ammonium carbonate contained in a muslin bag.

suspended matter, but should be free from particles of the ore. Dilute the liquid to about 300 c. c. in a 500-c. c. beaker, and heat it to boiling. Then add to the turbid liquid* boiling barium chloride solution to precipitate the sulphate, and when precipitation is complete, acidify with hydrochloric acid so as to dissolve all solid except barium sulphate. Filter, wash, ignite, and weigh the barium sulphate, then calculate the percentage of sulphur in the ore.

(ii) Place 1 gm. of the very finely powdered ore in a small conical flask provided with a funnel. Pour concentrated nitric acid through the funnel so as to cover the ore, and allow the action to proceed for a time without heat. Then gently heat the mixture, and keep it hot until, except for siliceous matter, the ore has been completely dissolved. Thus by taking care not to overheat the mixture it is possible to oxidize the sulphur of the ore direct to sulphate without separation of globules of the element. Filter off and wash the insoluble matter, receiving the filtrate in a beaker. Since the solution from which sulphate is to be precipitated contains iron it is necessary first to precipitate this to prevent its adsorption by the barium sulphate. Therefore make the liquid alkaline with ammonia, and heat it to boiling whilst it contains the precipitate which has been formed. Precipitate the sulphate by adding boiling barium chloride solution; then add acid so as to redissolve all except barium sulphate. Filter, wash, ignite, and weigh the barium sulphate.

Estimation of Carbonate.—If carbonate is present it may be estimated in 5 gm. of the ore by the direct weighing of carbon dioxide (p. 102). Hydrogen sulphide, which would be liberated by the action of acid on the ore, must, however, first be oxidized by chromic acid. In this case dilute sulphuric acid, in which some chromic anhydride has been dissolved, may be used to decompose the ore; and the gas should also pass through a wash bottle containing chromic acid, so that no hydrogen sulphide may escape oxidation.

4. ANALYSIS OF GALENA

Galena is essentially lead sulphide, PbS. It is generally argentiferous, i.e. it contains a minute proportion of silver which is worth extracting. There may also be present in addition to insoluble

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* The precipitation of barium sulphate from solutions containing salts of heavy metals, and especially ferric iron, is avoided so as to prevent adsorption of these salts by the precipitate.

matter small amounts of the sulphides of the following metals: copper, antimony, iron, manganese, zinc.

Procedure.—In the analysis of zinc-blende it was necessary to perform a separate operation on the ore for the estimation of the sulphur, because lead was estimated as sulphate after the addition of sulphuric acid; but in this case the lead sulphide of the ore can be converted into sulphate which is held in solution by hydrochloric acid. The lead is then precipitated as hydrated peroxide, and the sulphate determined in the filtrate from this precipitate. If iron and manganese are present, however, these will be precipitated with the lead, and in this case it will be necessary subsequently to separate the lead as sulphate and to estimate the iron and manganese in the filtrate from the lead sulphate. As a rule silver, copper, antimony, and zinc, if present, are in such small quantities as to be negligible for present purposes. Make a careful qualitative analysis looking for all the metals named.

Solution of the Ore and Estimation of Insoluble Matter.—Weigh accurately about 1 gm. of the finely powdered ore; place it in a 5-in. porcelain dish provided with a clock glass; then moisten it with water, and act upon it with concentrated nitric acid, heating the mixture upon the water bath. Commence with 10 c. c. of the acid, and add more if necessary, together with a few drops of bromine, to aid its action. When the residue is white, because all the lead sulphide has been converted into sulphate, carefully evaporate to dryness over a minute flame, and then digest the residue with hot dilute hydrochloric acid (1 to 3) so as to dissolve the lead sulphate. Decant through a filter, digest the residue again with acid, and finally wash it on the filter with hot water until the washings are free from chloride. Ignite the filter wet in a crucible, and weigh the insoluble siliceous matter.

Estimation of Lead, with Iron and Manganese, if present.

(*a*) *Iron and Manganese are absent.*

Lead chloride will probably have crystallized out of the filtrate from the insoluble matter. Heat the liquid until it is clear, and then add to it 100 c. c. of 3 per cent hydrogen peroxide solution *

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* The hydrogen peroxide solution must be free from sulphate; this will be the case if it has been prepared by distillation.

followed by ammonia with stirring until the lead separates as a light brown precipitate of the hydrated peroxide. Allow to stand for an hour or two, then filter cold. Add more ammonia to the filtrate, and allow it to stand in case any further precipitate separates. Wash the precipitate with cold water and reserve the filtrate for the estimation of sulphate; dry and burn the filter paper separate from the precipitate, roasting the ash thoroughly to oxidize any reduced lead. Ignite the precipitate, weigh as PbO, and calculate the percentage of lead present.

(*b*) *Iron or Manganese, or both, are present.*

Obtain the precipitate with hydrogen peroxide and ammonia as above, and filter it as before. Remove the precipitate from the filter, and dissolve it in hydrochloric acid; then add 5 c. c. of concentrated sulphuric acid and proceed according to instructions on p. 60, Part I.

Estimate iron and manganese in the filtrate from the lead sulphate by the methods described under the analysis of zinc-blende, p. 112.

Estimation of Sulphur.—All the sulphur of the ore is present as sulphate in the ammoniacal filtrate from the lead. Evaporate the solution until it ceases to smell of ammonia, then add to it a few cubic centimetres of concentrated hydrochloric acid and again boil. Add boiling barium chloride solution and estimate sulphate in the usual way. From the weight of barium sulphate obtained calculate the percentage of sulphur in the ore.

5. ANALYSIS OF COPPER PYRITES

Copper pyrites is a sulphide of iron and copper having a composition represented approximately by the formula $CuFeS_2$. Insoluble siliceous matter is present, but very little else.

Procedure.—The chief analytical problem is the separation of copper and iron. For this two methods are available: (*a*) the copper can be precipitated from solution by hydrogen sulphide, and weighed as Cu_2S; whilst the iron in the filtrate after oxidation is precipitated by ammonia, and weighed as Fe_2O_3. (*b*) The copper can be precipitated as metal from solution of the mixed sulphates by metallic aluminium, whilst the iron, reduced by the aluminium to the ferrous state, is estimated volumetrically by titration with standard permanganate or dichromate solution. The sulphur is estimated separately in a portion of the ore which has been fused with sodium peroxide, or dissolved in nitric acid.

Estimation of Insoluble Matter.—Act upon about 1·25 gm. of the very finely powdered ore with fuming nitric acid (1·5 specific gravity) in a porcelain dish, keeping the dish covered with a clock glass while the reaction is proceeding. When no more oxidation takes place add 2 or 3 c. c. of concentrated sulphuric acid, and evaporate over a tiny flame until all the nitric acid has been vaporized* and dense fumes of sulphuric acid begin to appear, adding a little more sulphuric acid if necessary. Allow the solution to become cold, then pour it into about 50 c. c. of water in a beaker, being careful to obtain all the contents of the dish by rinsing the latter with water. Digest the liquid in the beaker so as to dissolve completely the metallic sulphates; filter and wash the residue with hot water; ignite the filter, weigh and calculate the percentage of insoluble matter.

Estimation of Copper and Iron.—Dilute the filtrate from the insoluble matter to 250 c. c., and take 100 c. c. for the estimation of copper and iron by each of the two following methods.

(*a*) *Precipitation of Copper as Sulphide and Iron as Ferric Hydroxide.*

To estimate the *copper*, heat to boiling the solution of cupric and ferric sulphates contained in a beaker and pass a stream of hydrogen sulphide through the hot liquid for about fifteen minutes. Then cover the beaker with a clock glass and let it stand on the water bath until the precipitate settles, leaving the supernatant liquid faintly green owing to the ferrous sulphate present. The liquid should then smell of hydrogen sulphide, proving that excess is present; otherwise pass the gas again. Filter the solution, keeping the filter as full of liquid as possible all the time, so as not to expose the precipitate to atmospheric oxidation; for if this occurs and copper enters the filtrate it is precipitated therefrom by hydrogen sulphide wash water in a colloidal state. A bent tube (p. 31, Part I) may be employed to hasten filtration. To wash the precipitate employ in your wash bottle a solution of hydrogen sulphide containing a little acetic acid, removing the last portions of the pre-

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* It is very necessary to get rid of all nitric acid for the estimation of copper by either of the methods which follow.

cipitate from the beaker by the aid of this liquid. Wash the precipitate until it is free from sulphate, but do not allow it to become exposed to the air until the last lot of wash water drains away from it. Set aside the filtrate for estimation of the iron and proceed to convert the precipitate into cuprous sulphide (Cu_2S) in the following way.

Dry the filter, remove as much as possible of the precipitate from it, and burn the paper in a Rose crucible. This is a porcelain crucible furnished with a perforated lid and tube by means of which a current of hydrogen can be led into the crucible to exclude air during the ignition; the hydrogen passes through a sulphuric acid wash bottle so that its rate of passage can be observed and regulated (see fig. 6). Burn the paper openly in the crucible; then add the precipitate and sprinkle upon it a little sulphur which has been proved to leave no residue on ignition. Regulate the flow of the hydrogen so that about four bubbles pass through the acid per second, then place the tube and lid in position over the crucible. Gently ignite the crucible and contents with a small flame until combustion of sulphur round the crucible ceases; then slightly increase the rate of flow of the hydrogen, and allow the crucible and contents to cool in the current of gas. Place the crucible in the desiccator and after fifteen minutes weigh it. By this procedure the copper is obtained in the form of pure Cu_2S, from the weight of which the percentage of copper in the ore can be calculated.

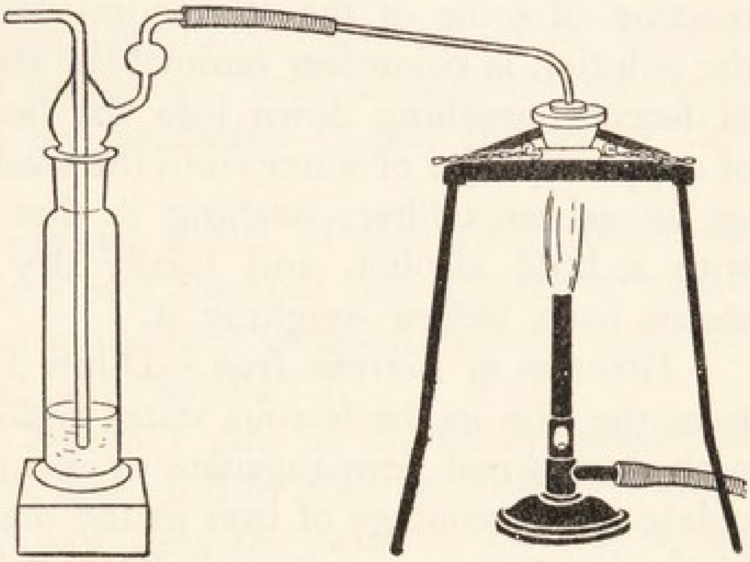

Fig. 6

To estimate the *iron* boil the filtrate from the copper to expel hydrogen sulphide, and add a little concentrated nitric acid to re-oxidize the iron, which will have been reduced to the ferrous state by the hydrogen sulphide. Then add ammonium chloride and ammonia in excess, and estimate the iron in the usual way (Part I, p. 56).

(*b*) *Precipitation of Copper by Aluminium and Titration of Ferrous Iron.*

Precipitation of Copper.—Procure some aluminium foil free from iron and cut it into strips 2 cm. by 1 cm. Bend these strips at an angle across the middle so that they may easily provide an edge to be laid hold of by forceps. Place in a beaker 100 c. c. of the solution of copper and ferric sulphates containing a little free sulphuric acid, drop in several pieces of aluminium foil, and heat the solution to boiling. Metallic copper will be precipitated whilst the solution loses colour and hydrogen gas is evolved owing to the reaction of some of the aluminium with the acid present. When the solution is colourless remove the strips of aluminium by means of forceps, washing down into the beaker any adhering particles of copper by a jet of water from the wash bottle. Collect the copper on an asbestos filter, washing it first with cold water and then with a little alcohol, and finally dry it for a short time in the steam oven before weighing it.

Titration of Ferrous Iron.—Dilute the filtrate, which now contains the iron in the ferrous state, to 250 c. c., and titrate 100 c. c. with decinormal permanganate or dichromate solution. Then calculate the percentage of iron in the ore, remembering what weight of the latter corresponds with 100 c. c. of the ferrous solution.

Estimation of Sulphur.—Fuse 1 gm. of the finely powdered ore with sodium peroxide, and proceed according to the process as described under the analysis of zinc-blende (p. 112).

ANALYSIS OF SILICATES

For analytical purposes natural silicates are divided into two classes: those which, being hydrated, are of a comparatively loose structure and decomposable by hydrochloric acid, and those which being produced anhydrous at high temperature are not attacked by hydrochloric acid but must be fused with a mixture of sodium and potassium carbonates before they can be treated analytically. The alkalis in these silicates cannot be estimated after the later process of fusion in which alkalis are employed; they are, however, estimated after the mineral has been decomposed by being heated with a mixture of calcium carbonate and ammonium chloride.

Serpentine is a good example of the former kind of silicate, *felspar* of the latter.

6. ANALYSIS OF SERPENTINE

Serpentine is essentially hydrated magnesium silicate; but in addition to water, silica, and magnesia the mineral may contain ferrous and ferric oxides and alumina, lime, and the alkalis.

Procedure.—The water is estimated by heating the mineral, and absorbing the evolved vapour in a weighed calcium chloride tube. Silica is estimated by decomposing the mineral with hydrochloric acid, evaporating, igniting, digesting with hydrochloric acid, and filtering off the silica. Iron, aluminium, calcium, magnesium, and the alkalis are estimated in the filtrate by the usual methods.

Estimation of Water.—Ignite 2 gm. of the finely powdered mineral in a porcelain or silica boat inserted into a piece of combustion tube, and collect the water in a weighed calcium chloride tube by the method described on p. 50, Part I.

Estimation of Silica.—Weigh 1 gm. of the finely powdered mineral, place it in a porcelain dish, add to it about 10 c. c. of concentrated hydrochloric acid, and heat the mixture on the water bath with constant stirring. If the mineral consists of hydrated silicate only, it will be quickly decomposed with the separation of gelatinous silica. Evaporate the mass to dryness on the water bath, taking care that none of the light powdery silica eventually produced is carried away by a draught. Then moisten the mass with concentrated hydrochloric acid, and let it stand for a few minutes so that all metallic chlorides may be dissolved. Add hot water and filter, washing the residue of silica on the filter until it is free from chloride.

A small proportion of silica, however, remains in solution, since in the finely divided state in which it has been obtained it is not quite insoluble in hydrochloric acid. Therefore return the filtrate to the dish, again evaporate to dryness, and leave the residue on the water bath for an hour or more after it appears to be dry. Again add hydrochloric acid and allow the mixture to stand for about ten minutes, after which add hot water, and filter the residue through a small filter. The amount of silica now remaining in solution is negligible. Ignite the two filters moist in, preferably, a platinum crucible, and weigh the silica, which should be white.

NOTE 1.—The hydrated silicate may contain anhydrous silica as, say, quartz, or an insoluble silicate such as felspar. These will remain unaffected by the hydrochloric acid and will be weighed with the originally combined silica. If it is desirable to differentiate between the combined silica and these other substances, this may be done by digesting the whole residue, after weighing, with moderately strong sodium carbonate solution on the water bath for an hour. Under this treatment the silica which was separated from chemical combination by the hydrochloric acid dissolves in the mild alkali, leaving the rest of the residue unaffected. The latter is then obtained by filtration, through washing, and ignition, and the weight of pure combined silica estimated by difference. Together with the insoluble residue will be the small amount of impurity with which the precipitated silica was contaminated (Note 2), but unless an analysis of this residue is attempted, this is immaterial.

NOTE 2.—Even if the impurities mentioned in Note 1 are absent the silica obtained by the above treatment is seldom quite pure; and its impurity can be tested and allowed for in the following way.

After being weighed in a platinum crucible the silica is moistened with water and then a few drops of concentrated sulphuric acid are added to it, followed by 2 or 3 c. c. of aqueous hydrofluoric acid which has been proved to leave no residue after evaporation. The hydrofluoric acid when heated with the silica converts it into gaseous silicon tetrafluoride which escapes, and the sulphuric acid, which becomes concentrated by evaporation, prevents the hydrolysis of the tetrafluoride with the regeneration of silica. Therefore this mixture, if the silica was pure, will leave no residue after being heated till all the sulphuric acid has been vaporized, and any residue will be impurity in the silica. Conduct the operation in a fume chamber, finally heating the crucible to dull redness. A slight dark coloured residue will probably be found. Subtract its weight from that of the impure silica to obtain the weight of pure silica. The residue consists chiefly of ferric oxide, and its weight should be added to that of this constituent found otherwise.

Estimation of Ferric Oxide, Alumina, Lime, and Magnesia.—These constituents of serpentine, present as chlorides in the filtrates from the silica, are estimated just as the similar constituents of dolomite are estimated (*vide* p. 100 *et seq.*).

Estimation of Alkalis.—Owing to the use of microcosmic salt to precipitate magnesia, the alkalis cannot be determined in the filtrate from the above operations; but this estimation is carried out as follows. Weigh 2 gm. of the finely powdered mineral, digest it with hydrochloric acid, and remove the silica by a double evaporation as before. To the filtrate add milk of lime till it is alkaline, so as to precipitate all the metals except those of the alkalis. Heat, filter, and wash the residue. To the filtrate add ammonium carbonate solution in excess, and a few drops of ammonium oxalate. Heat to boiling, and again filter and wash the residue. Thus the excess of added lime has been eliminated, and the filtrate contains only salts of the alkali metals, and ammonium. Acidify the solution with hydrochloric acid, and evaporate it to dryness in a porcelain, silica, or, preferably, a platinum dish. Then very carefully ignite* the residue over a tiny flame so as to volatilize ammonium chloride. The residue will probably be brown, and contain a small quantity of insoluble matter. Dissolve it in water, and filter, being very careful to lose none of the solution. Return the solution to the dish and again evaporate and gently ignite, cool, and weigh. The residue, which should be white, consists of sodium and potassium chlorides. Estimate the proportion of each chloride present, either by titration with decinormal silver nitrate (p. 56), or by precipitating the potassium as perchlorate (p. 92). Calculate the results to Na_2O and K_2O.

7. ANALYSIS OF FELSPAR

Felspar is an anhydrous alumino-silicate of the alkalis; potash predominates in *orthoclase*, soda in *albite*. Ferric oxide, lime, and magnesia are also usually present in small quantities.

Procedure. — Since felspar and similar anhydrous silicates are not attacked by hydrochloric acid, they must be decomposed by fusion with sodium carbonate, or preferably with " fusion mixture ", an intimate mixture of sodium and potassium carbonates in molecular proportions.†

By this means silica and alumina are converted into alkali silicate and aluminate, and the other metals into carbonates. After the

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* Potassium chloride is distinctly volatile at anything above a dull red heat.

† According to a well-known principle a mixture of solids melts at a lower temperature than the single solids.

melt has been extracted with water and decomposed with hydrochloric acid, the procedure is similar to that with a hydrated silicate, except for the estimation of the alkalis.

To estimate the alkalis the silicate is decomposed by being heated with a mixture of calcium carbonate and ammonium chloride, according to the method of Lawrence Smith. The mass does not fuse, but the alkalis, liberated from the alumina and silica, are converted into chlorides, whilst the silica becomes calcium silicate. After the mass has been extracted with water and lime eliminated, the alkalis are estimated in the usual way.

Fusion with Alkali Carbonates.—Obtain the felspar in an exceedingly fine state of subdivision, or the fusion will not be a success. Weigh about 1 gm. of the mineral and mix it with about 6 gm. of fusion mixture. If the platinum crucible available is a large one, the mixing can be done in the crucible itself after weighing the mineral therein. The fusion mixture is then added, little by little, and mixture effected by stirring with a rounded glass rod. The crucible must not, however, be more than half filled with the mixture, or the frothing which ensues during fusion is likely to carry the mass over the edge of the crucible. Instead of running such a risk it is better to fuse a portion of the mixture first, and gradually add the rest as there becomes room for it.

Carefully support the crucible and contents on a suitable triangle, and gradually apply heat. If fusion mixture is used the Bunsen flame with plentiful air-supply will probably be hot enough; if sodium carbonate only, the blow-pipe flame will be required. The mass will froth owing to the escape of carbon dioxide, and then gradually subside into a quiescent liquid state. When no more gas bubbles appear the reaction is at an end. To facilitate removal of the mass from the crucible, take hold of it whilst hot with a pair of clean crucible tongs—which should have their tips wound round with platinum wire, unless they are of iron—and stand it upright in cold distilled water in the dish in which the extraction of the melt is to be carried out. Cooling in this way will cause the mass, as it solidifies,* to shrink away from the sides of the crucible and so facilitate its removal. Then upset the crucible so that water enters it, and apply heat to the dish so that the mass gradually disin-

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* The solid mass may appear bluish-green; this is due to a trace of manganese which has formed manganate with the alkali. There will probably not be sufficient to be estimated.

tegrates and partially dissolves. Remove the crucible by means of tongs when the mass has dissolved away from it, and wash it out with a jet of water from the wash bottle so that no material may be lost. When the mass has disintegrated the insoluble matter should be flocculent. If any gritty particles remain the fusion was ineffectual and must be repeated. Now cover the dish with a clock glass and gradually add hydrochloric acid. There will be much effervescence owing to the decomposition of the remaining carbonates, so that great care must be taken to avoid loss. Remove the silica by two evaporations to dryness, closely following the directions given under the analysis of serpentine, and, having ignited the filters and weighed the silica, test its purity. (Note 2, p. 120.)

Estimation of Ferric Oxide, Alumina, Lime, and Magnesia.—For the estimation of these constituents follow the instructions given under the analysis of dolomite (p. 100 *et seq.*). Since the proportion of ferric oxide is very small this need not be separated from the alumina.

Estimation of Alkalis (Method of Lawrence Smith).—For this process a finger-shaped platinum crucible is desirable, though a crucible of the more ordinary shape may be employed. The ammonium chloride and calcium carbonate used must be free from alkalis. Consequently the ammonium chloride should be sublimed before use, and the calcium carbonate, unless known to be pure, should be dissolved in acid, reprecipitated by ammonium carbonate, filtered, washed, and dried.

Weigh about 0·5 gm. of the exceedingly finely powdered felspar, and an equal weight of sublimed ammonium chloride. Intimately mix these two substances by grinding them together in an agate mortar; then add 3 gm. of dry purified calcium carbonate and again mix thoroughly. Transfer this mixture to the platinum crucible, using a small square of glazed paper and a camel-hair brush for the purpose, and place another gram of the calcium carbonate on the top of the mixture in the crucible. Put the lid on the crucible, but take care that there is room for the escape of gases. Support the crucible obliquely so that it can be heated throughout its length with a flame. It may be convenient to cut a slit, a little narrower than the crucible, from a side to the centre of a square of asbestos millboard, and to place this on a tripod stand, while a retort stand ring is wrapped with asbestos string. The crucible can then be made to rest with its lower end against the end of the slit, and its upper end against the asbestos on the retort stand ring fixed suitably. A piece of asbestos paper can then be placed over the crucible to keep in the heat, and the crucible can be heated by a flame which passes through the slit.

Heat the crucible gently with a small flame until ammonia, which is first evolved, is no longer smelt, taking care to avoid the volatilization of ammonium chloride. Then heat the crucible to a dull red heat through three-quarters of its length, and maintain it at this temperature for about an hour. Remove the mass from the crucible and heat it with water in a porcelain dish until it is completely disintegrated, and what remains undissolved is in the condition of fine powder. The mass may come out of the crucible whole, but if it does not, place the crucible and contents in hot water, and digest the whole, until the crucible can be lifted out of the liquid in a clean condition; then if necessary use a glass rod with flattened end to break up lumps. Filter the turbid liquid, and thoroughly wash the residue until it is free from chloride. If decomposition was complete some of the residue will dissolve entirely in hydrochloric acid.

The solution contains calcium chloride, which must now be removed by precipitation. Heat the solution to boiling, add to it excess of ammonium carbonate, and keep the liquid hot until the precipitate becomes granular. Filter and wash the precipitate; then dissolve it in hydrochloric acid and reprecipitate calcium carbonate by adding ammonia and ammonium carbonate under the same conditions as before. This double precipitation is necessary to recover the small amount of alkali which is carried down with the first precipitate. Mix the two filtrates and evaporate them to dryness in a dish, preferably of platinum. When the residue is thoroughly dry gently ignite it by means of a small flame so as to volatilize ammonium salts. Dissolve the residue in a little water, place the solution in a beaker, add a few drops of ammonia, and heat to boiling. Drop into the boiling solution a single small crystal of ammonium oxalate; this is to precipitate the small amount of calcium which has remained in solution. If the liquid appears turbid after a few minutes, filter it and wash the residue with hot water containing a little ammonia. Receive the filtrate and washings in the platinum dish, and again evaporate to dryness, then gently ignite the residue. Finally moisten this residue with a few drops of dilute hydrochloric acid, and again evaporate and ignite. The residue will now consist of sodium and potassium chlorides only, and must be weighed.

Determine the proportion between the two chlorides as before by titration, or by converting the potassium salt into perchlorate.

8. ANALYSIS OF BASIC SLAG AND OTHER PHOSPHATIC MANURES

Basic slag is the slag obtained in the removal of phosphorus from cast iron during the manufacture of steel. It is used in a finely divided state as a phosphatic manure, and contains ferrous and ferric oxides, alumina, lime, magnesia, phosphoric oxide, carbon dioxide, and insoluble siliceous matter. Other phosphatic manures may contain water and organic matter. " Superphosphate of lime " contains also much sulphate, reckoned as SO_3, and most of its phosphate is soluble in water.

Procedure.—The composition of basic slag differs from that of dolomite by the presence in it of a larger proportion of iron, but chiefly on account of the phosphate it contains. As in qualitative analysis, so here, the presence of phosphate necessitates a modified procedure. The finely powdered mineral is dissolved in hydrochloric acid, and insoluble matter filtered off. From an aliquot portion of the solution ($FePO_4 + AlPO_4$) is precipitated by excess of phosphate in presence of acetic acid. The iron is estimated in another part of the solution; this is calculated to $FePO_4$, which is subtracted from the above to give $AlPO_4$. These are then calculated to Fe_2O_3 and Al_2O_3. The filtrate from ($FePO_4 + AlPO_4$) contains Ca, Mg, and PO_4 in presence of acetic acid. From this solution calcium is precipitated directly as oxalate by ammonium oxalate, a double precipitation being resorted to in order to free the precipitate from magnesium oxalate; and from the filtrate magnesium is precipitated in the usual way. Phosphate is precipitated from another part of the original solution as magnesium ammonium phosphate after addition of citric acid, which prevents the precipitation of ferric iron and calcium by ammonia. Carbonate is estimated in the usual way; and ferrous iron by dissolving a weighed portion of the basic slag in hydrochloric acid in an atmosphere of carbon dioxide, and titrating with decinormal dichromate solution after cooling.

Estimation of Insoluble Matter and Preparation of Solution.—Weigh 5 gm. of the finely powdered material; digest it in an evaporating dish with concentrated hydrochloric acid and a very little nitric acid; evaporate the liquid to dryness in a fume chamber and gently ignite the residue. Add dilute hydrochloric acid, and heat with stirring to promote solution; decant through a filter, and digest residue with more hydrochloric acid until the solution running through the filter appears to be colourless. Transfer residue to filter, and wash thoroughly. Ignite the filter, moist, in a crucible and weigh the residue of insoluble matter. Dilute the filtrate to 500 c. c. and mix thoroughly.

Estimation of Ferric Oxide and Alumina as Phosphates.—Place in a 500-c. c. beaker 100 c. c. of the prepared solution, equivalent to 1 gm. of the material; heat the solution and add ammonia until it is alkaline, and a precipitate appears. If phosphate is in excess of the basic oxides the precipitate will be pale, otherwise it will be red because basic. The latter will probably be the case, and if so add a solution of ammonium phosphate with stirring until the precipitate becomes pale. Then add a few drops of phenolphthalein, which will cause a red colour owing to the alkalinity of the solution, followed by acetic acid until the red colour is discharged. Heat to boiling; filter and wash the precipitate. A second precipitation is necessary to obtain the phosphates of iron and aluminium pure; therefore dissolve the precipitate in as little dilute hydrochloric acid as possible, add to the solution a little more ammonium phosphate, and repeat the precipitation in the same manner. After filtering and washing the precipitate, ignite it moist, and weigh it as ($FePO_4 + AlPO_4$). Mix the two filtrates and reserve them for the estimation of lime and magnesia.

Estimation of Total Iron.—Estimate the iron in a fresh part of the solution by titrating it with decinormal dichromate solution after reduction with stannous chloride (p. 135, Part I). From the result calculate the weight of Fe_2O_3 and then of $FePO_4$ which must be present in the mixed phosphate precipitate obtained above; then by subtraction obtain the weight of $AlPO_4$, and thence of Al_2O_3 in the same precipitate. Thus the percentage of iron reckoned as Fe_2O_3 and of alumina in the original material is estimated. Much of the iron, however, is present in the ferrous condition, represented as FeO; hence the following estimation.

Estimation of Ferrous Iron.—Carry out this estimation as with spathic iron ore, p. 108, using, as in that case, 1 gm. of the material, and titrating one-fifth of the ferrous solution obtained.

Calculation of FeO and Fe_2O_3 present.—The total iron and ferrous iron have now been estimated, and may be obtained as percentages. The difference between them is the ferric iron. Calculate the ferrous iron as percentage of FeO, and the ferric iron as percentage of Fe_2O_3.

Estimation of Lime.—Calcium oxalate is practically insoluble in boiling dilute acetic acid solution, in which calcium phosphate, and magnesium phosphate and oxalate are soluble. Now the mixed filtrates from the ferric and aluminium phosphate precipitate contain calcium and magnesium and phosphate in presence of very little acetic acid. Add to this solution a few cubic centimetres of dilute acetic acid, heat to boiling, then add solid ammonium oxalate to precipitate the calcium. A double precipitation of calcium is necessary, as was shown under the separation of calcium and magnesium (p. 90). Weigh the calcium as carbonate or sulphate.

Estimation of Magnesia.—Precipitate the magnesium as magnesium ammonium phosphate, and weigh as pyrophosphate, according to directions on p. 90.

Estimation of Phosphoric Oxide.—The student is familiar with the estimation of phosphate by precipitating it as magnesium ammonium phosphate, using a process reciprocal to that employed in the estimation of magnesium (*vide* p. 62, Part I). This process, however, cannot ordinarily be employed in presence of metals that are precipitated with ammonia. It is well known, nevertheless, that certain organic hydroxyacids form complex salts with various metallic oxides, and therefore prevent their precipitation by ammonia. Citric acid can be employed for the purpose, for in presence of citrate phosphate in solution can be precipitated from an ammoniacal liquid as magnesium ammonium phosphate, uncontaminated with metallic oxides.

This furnishes one method of estimating phosphate in such material as basic slag. Another method is to precipitate phosphate from nitric acid solution as ammonium phosphomolybdate, the well-known yellow precipitate obtained in the qualitative test for phosphate. Formerly it was customary to dissolve this precipitate in ammonia solution, by which it is decomposed into phosphate and molybdate, and then to precipitate the phosphate from this solution by magnesia mixture. A more direct method, however, is to weigh the phosphomolybdic precipitate itself after ignition, for its composition is known. Ammonium phosphomolybdate, the yellow precipitate, is $(NH_4)_3PO_4$, $12MoO_3$, xH_2O, and this on gentle ignition loses water and ammonia and becomes phosphomolybdic anhydride, which is P_2O_5, $24MoO_3$. To obtain and weigh this compound is a second method of estimating phosphate.

(i) *As Magnesium Pyrophosphate.*

The original hydrochloric acid solution of the material may be employed, and 100 c. c. $\equiv$ 1 gm. may be taken, or two portions of 50 c. c. each may be used, and the estimation done in duplicate. To the solution add 10 gm. of citric acid dissolved in a little water, followed by excess of magnesia mixture. Then add ammonia until the liquid begins to smell of the gas, followed by 15 to 20 c. c. of the strongest ammonia solution. Stir the liquid, but do not touch the sides of the beaker with the glass rod. Allow the mixture to stand for 12 hours, then proceed as usual for the estimation of phosphate.

(ii) *As Phosphomolybdic Anhydride.*

Details of this process are given under the analysis of spathic iron ore on p. 108. Since the proportion of phosphoric oxide in the precipitate is small, not more than about 0·2 gm. of the material should be taken for each estimation. Therefore weigh 1 gm. of the finely powdered slag, and after having acted upon it with nitric acid according to the instructions given, dilute the solution to 250 c. c. and take 50 c. c. of this for an estimation. Carry out the operations previously described, and from the weight of phosphomolybdic anhydride obtained, calculate the percentage of P_2O_5 in the slag.

Estimation of Carbon Dioxide.—If carbonate is present in the basic slag, estimate it as in the case of dolomite (p. 102). The quantity of material to be used must be judged from the amount of effervescence shown with acid in a qualitative test.

ANALYSIS OF ALLOYS

Considered analytically, alloys are mixtures of metals, seldom containing non-metallic constituents; for the present purpose varieties of cast iron and steel, and such alloys as contain phosphorus, silicon, &c., are excluded.

Nitric acid is the solvent usually employed to dissolve an alloy, since it has a greater range of action than hydrochloric acid, and most metals form nitrates soluble in water. It must be remembered, however, that tin and antimony are converted into insoluble, hydrated oxides by nitric acid. Nevertheless, nitric acid may be used as an oxidizing agent in conjunction with hydrochloric acid, i.e. as aqua regia; e.g. type metal, an alloy of lead, tin, and antimony, can be dissolved in aqua regia without the separation of insoluble oxides.

When nitric acid has been used to dissolve an alloy, it is necessary to displace it by evaporation with sulphuric acid before metals are precipitated from solution by hydrogen sulphide. Much care must be taken to avoid passing hydrogen sulphide through a solution containing nitric acid in quantity.

A careful qualitative analysis must precede quantitative work, it being remembered that some metals may be present in an alloy in small quantities only.

9. ANALYSIS OF SILVER COIN

Silver coinage—excluding the recent debased coinage, which contained a large proportion of nickel—is an alloy of silver with less than 10 per cent of copper, which is added to harden the metal.

Procedure.—Since there are various methods of estimating both silver and copper, either gravimetric or volumetric, there is a choice of procedure; though in any case the coin is first to be dissolved in somewhat diluted nitric acid. The methods to be described here are:

Gravimetric Methods.—The silver is precipitated from solution as chloride, and the copper from the filtrate as hydroxide, which is subsequently converted into oxide by ignition.

Volumetric Methods.—The silver is titrated in acid solution by thiocyanate, and the copper in another portion of the same solution by thiosulphate after addition of potassium iodide, the presence of precipitated silver iodide in no way interfering with the titration.

Preparation of Solution.—Thoroughly clean with emery cloth a threepenny piece, remove any particles of dust from it by means of a clean handkerchief; then weigh it. Place the coin in a suitable beaker provided with a clock-glass cover; add a few cubic centimetres of water and then concentrated nitric acid little by little, until on warming the coin gradually dissolves; then boil the solution for a minute or two to expel nitrous fumes. Dilute the solution to 250 c. c.

Estimation of Silver gravimetrically.—Measure 50 c. c. of the solution; heat the liquid to boiling and precipitate the silver as chloride by adding a small excess of dilute hydrochloric acid. Filter through asbestos (p. 38, Part I), and reserve the filtrate for the estimation of copper.

Estimation of Copper gravimetrically.—Heat to boiling the filtrate from the silver chloride, add pure sodium hydroxide* drop by drop, till hydrated cupric oxide is precipitated; then proceed according to instructions on p. 52, Part I.

Estimation of Silver volumetrically.—Prepare and standardize a decinormal solution of ammonium thiocyanate, and with this solution titrate 25 c. c. of the nitric acid solution of the alloy, according to the method described on p. 59.

Estimation of Copper volumetrically.—Prepare and standardize a decinormal solution of sodium thiosulphate, and with this solution titrate, in presence of silver iodide, the iodine liberated by adding potassium iodide to 50 c. c. of the original solution, according to the method described on p. 46.

10. ANALYSIS OF GERMAN SILVER

German silver is an alloy of copper, zinc, and nickel containing, generally, a little iron.

Procedure.—The procedure consists in separating the copper by hydrogen sulphide from a solution of the alloy containing some dilute sulphuric acid, a double precipitation being necessary because a little zinc is at first precipitated with the copper. From

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* For accurate work it is well to prepare the sodium hydroxide solution as it is required by interaction between clean sodium and water in a silver or nickel dish.

the mixed filtrates iron is precipitated twice as basic acetate; and the zinc and nickel in the mixed filtrates from the iron are separated by one of the methods already described.

Preparation of Solution and Estimation of Copper.—Weigh about 1 gm. of the alloy in the form of clippings of foil or turnings; dissolve this in somewhat diluted nitric acid in a covered beaker or dish; add 10 c. c. of dilute sulphuric acid and evaporate the solution over a tiny flame until fumes of sulphuric acid begin to appear, nitric acid being in this way vaporized. Allow the liquid to cool; then dilute it with water to about 100 c. c., heat to boiling, and pass hydrogen sulphide gas through the hot solution. Filter according to directions given under the analysis of copper pyrites (p. 116); then dissolve the precipitate from the filter by means of hot dilute nitric acid, evaporate the solution with sulphuric acid, dilute, and precipitate the copper as before. Convert the precipitate into Cu_2S and weigh it as such.

Estimation of Iron.—Mix the filtrates from the copper sulphide, and heat them until hydrogen sulphide is eliminated; then add a few drops of concentrated nitric acid to the hot solution to oxidize the iron. Precipitate the iron by ammonia added after ammonium chloride and perform a double precipitation. Ignite and weigh the precipitate as Fe_2O_3. Mix the filtrates from the iron precipitate and evaporate them to about 100 c. c.

Separation of Zinc and Nickel.—Follow the instructions for separating zinc and nickel given on p. 87 adopting method I or II.

11. ANALYSIS OF SOLDER

Solder is a variable alloy of tin and lead; the finer the solder the larger is its proportion of tin.

Procedure.—A characteristic of tin alloys is that nitric acid converts their tin into insoluble metastannic acid. When, however, solder has been acted upon by nitric acid, a little of the lead is found in the insoluble residue as monoxide, though most of it enters into solution as nitrate. The amount of lead occurring with the tin is reduced to a minimum by having the nitric acid that acts upon the alloy as concentrated as possible. The metastannic acid, which is hydrated stannic oxide, is converted into the anhydrous oxide on ignition, in which condition it is weighed; whilst the lead in the filtrate is estimated as sulphate. It is necessary, however, to estimate the lead occurring as oxide with the stannic oxide. This is done by performing a "sulphur fusion" upon the weighed residue. Thus by fusing a mixture of SnO_2 and PbO with a mixture of sodium carbonate and sulphur the former is converted into sodium thiostannate, which can be extracted with water, whilst the latter is changed into PbS, which can be filtered off, and then converted into and weighed as sulphate.

Treatment of Alloy with Nitric Acid.—Weigh about 0·7 gm. of the alloy in the form of turnings or sheet; place it in a covered dish and add to it about 7 c. c. of concentrated nitric acid, and 2 or 3 c. c. of water to start the reaction. A violent reaction occurs when the water is added; it is best, therefore, to add the latter slowly by means of a pipette the tip of which passes through the gap between the lip of the dish and the clock glass. When the reaction appears to be nearly finished gently warm the dish, and when no more brown fumes are being evolved add about 25 c. c. of water, and boil gently for a few minutes so as to give opportunity for the lead nitrate to be dissolved.

Estimation of Tin.—Filter off the suspended matter obtained above, and wash it on the filter till it is free from acid. Dry the filter, ignite the paper apart from the residue in a porcelain or silica crucible, and thoroughly roast the ash so as to reconvert to oxides any reduced tin or lead. Add the residue and ignite till the weight is constant. After weighing, mix thoroughly with the residue in the crucible about six times its weight of a mixture of equal parts of anhydrous sodium carbonate and sulphur, which has been proved to leave no residue when vaporized or burnt; cover the crucible with the lid, and gently heat so as to fuse the mixture. Allow the escaping sulphur to burn round the lid, and continue heating till the flame disappears. Let the crucible and its contents get cold, then extract the melt with hot water, preferably by having the crucible in a beaker or large dish containing water which is gradually heated. If the fusion has been successfully performed, everything will dissolve except a very small quantity of black powder which is lead sulphide. Filter and wash the lead sulphide, first with water containing a little sodium sulphide, and then with hydrogen sulphide water. Dry and ignite the filter; then convert the lead compound present into sulphate by adding to it when cold a drop of concentrated sulphuric acid, and again cautiously igniting. From the weight of $PbSO_4$ obtained calculate the weight of PbO originally present in the stannic oxide residue. Subtract this weight from the weight of residue found, and from the weight of pure SnO_2 calculate the percentage of tin in the alloy.

Estimation of Lead.—The filtrate from the metastannic acid contains lead nitrate. Place this filtrate in a porcelain dish, evaporating it somewhat if the dish will not otherwise contain all the solution. Add to the solution 5 c. c. of concentrated sulphuric acid and proceed according to the instructions for estimating lead in Part I, p. 60. Add to the weight of lead sulphate obtained that produced from the lead oxide present in the stannic oxide, and from the total weight of lead sulphate calculate the percentage of lead in the alloy.

12. ANALYSIS OF BRASS OR BRONZE

Brass is an alloy consisting chiefly of copper and zinc; bronze consists chiefly of copper and tin; in addition to these metals lead and iron may also be present in small quantities. It is necessary, therefore, to describe the analysis of an alloy which may contain copper, tin, lead, iron, and zinc.

Procedure.—The alloy is acted upon by nitric acid, and a residue of stannic oxide obtained which also contains small quantities of the oxides of copper, lead, and iron. A sulphur fusion removes the stannic oxide as alkali thiostannate, whilst converting the oxides of the latter three metals into sulphides. These are then reconverted to oxides by roasting, and their combined weight is subtracted from the weight of impure stannic oxide. The mixed oxides are then dissolved in acid and their solution is added to the filtrate from the metastannic acid. This solution is then evaporated with sulphuric acid to eliminate the lead as sulphate, and from the filtrate copper is precipitated as sulphide, a double precipitation being necessary on account of the presence of zinc. The filtrates from the copper contain iron and zinc. Iron is separated from zinc by a double precipitation as basic acetate; and zinc is estimated in the filtrate from the iron by precipitation as zinc ammonium phosphate.

In the absence of any of these metals the process is correspondingly shortened.

Treatment of Alloy with Nitric Acid and Estimation of Tin.—Place about 0·7 gm. of the alloy in a covered porcelain dish, and act upon it with about 10 c. c. of concentrated nitric acid diluted with a little water. When the alloy is dissolved, except for any earthy residue, dilute the solution with 50 c. c. of water and boil for a few minutes. Filter off and wash the impure stannic oxide, and reserve the filtrate. Dry and ignite the residue apart from the filter, as described under the analysis of solder, and after weighing it submit it to sulphur fusion, and extract with water the alkali thiostannate produced. Again filter, and dry and ignite the residue, roasting it well to convert metallic sulphides into oxides. Subtract the weight of these oxides from that of the impure stannic oxide previously weighed, and from the net weight of stannic oxide calculate the percentage of tin in the alloy.

Dissolve the oxides in a few drops of concentrated nitric acid, using hydrochloric acid also if necessary, and add the solution to the filtrate containing the rest of the other metals.

Estimation of Lead.—Add to the mixed solution, containing all the metals of the alloy except tin, 5 c. c. of concentrated sulphuric acid, and estimate the lead as sulphate according to instructions in Part I, p. 60.

Estimation of Copper.—Estimate the copper as sulphide after a double precipitation, according to the method described under the analysis of German silver, p. 131.

Estimation of Iron.—Estimate the iron by precipitating it as basic acetate, using a double precipitation unless the quantity of iron is very small.

Estimation of Zinc.—Estimate the zinc by precipitating it as zinc ammonium phosphate according to the method described on p. 89.

INORGANIC PREPARATIONS

Foreword

Inorganic preparations have rightly been receiving increased attention during recent years. Formerly, practical inorganic chemistry, after the first-year course in which gases and a few simple compounds were prepared, consisted almost entirely of qualitative and quantitative analysis. It is true that nature's raw material must be analysed to discover its components for scientific purposes and with a view to their use, and that manufactured products must also be analysed to determine their composition and purity; but between these two processes of analysis occur all those operations of chemical transformation and synthesis with which the chemical manufacturer is so intimately concerned. It is these processes of which in former times scarcely a hint was given in the educational laboratory. They were lectured about, and the chemical reactions connected with them were illustrated experimentally on the lecture table. There, however, the matter ended; for when the student left the lecture room and entered the laboratory, it was only that he might get on with his analysis.

Meanwhile, in his study of organic chemistry, the student was more fortunate. In practical organic chemistry analysis did not take so prominent a place; but from the first organic preparations were regarded as important. The methods of formation as well as the reactions of the various types of organic compounds were studied systematically, and the student was encouraged to make a collection of his own products. Such a course of practical work was of the highest educational value, and the accumulation of a number of nicely labelled specimens became to the keen student a very attractive task.

Hence the question might well be asked: why should not an analogous course of inorganic preparations be developed? Ought it not to become a recognized part of the training of the scientific chemist?

Now whilst inorganic chemistry differs so widely from the organic branch of the science that courses of preparations in the two branches cannot follow parallel lines, it is a sufficient answer to this question to state that in some universities and colleges courses of preparation of inorganic compounds do actually form parts of the curricula.

In arranging a course of inorganic preparations at least two different purposes may be kept in view.

The first is to illustrate, as far as possible, the different types of compounds formed by non-metals and metals. For example, the modes of formation of non-metallic and metallic chlorides may be illustrated, as well as those of the different types of salts, viz. single salts, double salts, and complex salts.

The second is to illustrate the methods of treatment of mineral products in order to prepare pure compounds from them. By such a study some little light is thrown upon actual processes of chemical manufacture; though it is very important to realize that small-scale operations differ in many ways from operations on a manufacturing scale.

A further important purpose of a course of chemical preparations is to draw attention to principles of economy in chemical manufacture. If the operations by which a beginner in chemistry prepares a small quantity of some simple salt could be magnified to a manufacturing scale, the waste occurring would probably appear prodigious. Therefore it is of great value for a student to pay attention to the " yields " as well as the purity of his products, remembering that both quality and quantity are important for success in chemical manufacture.

In the inorganic preparations described in this section, a variety of salts, and other simple compounds, arranged more or less in order of difficulty, are included; these are followed by a set of preparations chosen to illustrate methods of manufacture of compounds from minerals; after these is a series of preparations involving more specialized treatment, chiefly distillation; and finally, on account of the great intrinsic interest of such compounds to the pure chemist, there is a short series of double and complex salts.

I—PREPARATION OF SALTS AND OTHER SIMPLE COMPOUNDS

1. Sodium Thiosulphate, $Na_2S_2O_3{\cdot}5H_2O$

Sodium thiosulphate, frequently known as sodium hyposulphite or " hypo ", is formed by the union of sodium sulphite and sulphur, thus:

$$Na_2SO_3 + S = Na_2S_2O_3.$$

This reaction takes place gradually when flowers of sulphur are heated with sodium sulphite solution; and the salt is prepared on the large scale by passing sulphur dioxide gas into sodium sulphide solution, when the following reactions occur:

$$\begin{aligned} Na_2S + H_2SO_3 &= Na_2SO_3 + H_2S \\ 2H_2S + SO_2 &= 2H_2O + 3S \\ Na_2SO_3 + S &= Na_2S_2O_3. \end{aligned}$$

The salt crystallizes in monoclinic prisms freely soluble in water.

Preparation.

Requirements: Crystallized sodium sulphite, 50 gm.
Flowers of sulphur, 6·4 gm.

Choose crystals of sodium sulphite which have been but little exposed to the air, and are as nearly as possible free from sulphate. Dissolve the salt in the minimum amount of hot water in a flask fitted with a reflux condenser, and add the flowers of sulphur. Keep the contents of the flask boiling gently for some hours. The sulphur will gradually dissolve, and when it does not seem possible to dissolve any more, filter the solution and evaporate it in a dish until a little of it, removed on a glass rod, crystallizes. Allow the solution to cool to atmospheric temperature, so that crystallization may take place; and when no more crystals separate filter them off through a Büchner funnel by means of suction, and dry them between filter paper, or on a porous plate. A further crop of crystals may be obtained by evaporating the mother liquor, or by cooling it in ice, but the salt is likely to be contaminated with unchanged sulphite or with sulphate. Weigh the salt, prove its identity by qualitative tests, and calculate the percentage yield of $Na_2S_2O_3{\cdot}5H_2O$

from 50 gm. of $Na_2SO_3 \cdot 7H_2O$; then determine the purity of the salt by preparing 100 c. c. of a decinormal solution, and titrating it into decinormal iodine.

2. Potassium Chlorate, $KClO_3$

Potassium chlorate is the final product of the action of chlorine on potassium hydroxide, in presence of water, according to the reactions:

$$\begin{aligned} 2KOH + Cl_2 &= KCl + KOCl + H_2O \text{ (in cold dilute solution)} \\ 3KOCl &= 2KCl + KClO_3 \text{ (in hot concentrated solution).} \end{aligned}$$

On the manufacturing scale, however, it is found convenient to pass chlorine into hot milk of lime so as to produce calcium chlorate, and then to decompose this salt with an equivalent of potassium chloride so that potassium chlorate may crystallize. In the modern electrolytic process, in which potassium chlorate is obtained from an aqueous solution of potassium chloride with an equivalent of hydrogen thus:

$$KCl + 3H_2O = KClO_3 + 3H_2,$$

hypochlorite no doubt intervenes between chloride and chlorate.

Preparation.

Requirements: Potassium hydroxide (sticks), 20 gm.
Chlorine gas, a sufficiency.

Having weighed the potassium hydroxide, place it in a suitable flask and dissolve it in about 50 c. c. of warm water. Pass chlorine gas into the solution until a drop of liquid removed on a glass rod ceases to show an alkaline reaction with litmus. Filter the solution and concentrate it by boiling in a dish, until on cooling crystallization occurs rapidly. Filter with suction the crystals of potassium chlorate obtained, washing them once with cold water. Then dry the crystals. Test your product for chloride, and if more than a trace of chloride is found, recrystallize the specimen from a little hot water.

State the percentage yield obtained, and prove the identity and purity of the product by ascertaining the loss which 1 gm. of it undergoes on ignition in a crucible or test-tube.

NOTE.—Sometimes the solution shows a pink colour during evaporation. This is due to potassium ferrate formed by oxidation of a little ferric iron occurring in the potash, thus:

$$2Fe(OH)_3 + 3O + 4KOH = 2K_2FeO_4 + 5H_2O.$$

3. Potassium Nitrate, KNO_3

Sodium nitrate is more plentiful in nature than the potassium salt, yet it is not so useful in the arts because it is somewhat deliquescent. Therefore the preparation of potassium nitrate from sodium nitrate is a useful operation. Moreover, it is of interest because of the chemical principle which it illustrates.

When sodium nitrate and potassium chloride are mixed together in dilute aqueous solution there is no obvious reaction between them. In that they differ from silver nitrate and sodium chloride, which when mixed cause an immediate precipitation of silver chloride because of the insolubility of this salt. Yet the difference is one of degree rather than of kind; for whenever two salts are mixed together in solution there is always a precipitation of the salt whose " solubility product " has the least value when the concentration is such that this value is exceeded.

Of the four salts that can exist when sodium nitrate and potassium chloride are mixed in aqueous solution thus:

$$NaNO_3 + KCl \rightleftharpoons NaCl + KNO_3,$$

sodium chloride is the salt which has the least solubility product; therefore when the mixed solution is concentrated enough sodium chloride will crystallize; i.e. it will be formed as a crystalline precipitate leaving potassium nitrate in solution. The separation of the two salts thus effected is not immediately perfect; but it is facilitated by the fact that whilst sodium chloride is almost equally soluble in hot and cold water, the solubility of potassium nitrate increases rapidly with rise of temperature.

Preparation.

Requirements: Sodium nitrate, 85 gm.
Potassium chloride, 74·5 gm.

Dissolve the sodium nitrate in 100 c. c. of boiling water in a porcelain dish, add the potassium chloride little by little, and boil the liquid gently with frequent stirring until most of the sodium chloride has separated from the solution as a crystalline powder. Filter rapidly through a hot-jacketed funnel (fig. 15, p. 132, Part I), and set aside the filtrate for some hours to cool and crystallize. When crystallization appears to be at an end filter off the potassium nitrate crystals by suction. Then add to the mother liquor the sodium chloride previously filtered off, and heat the mixture for a short time so as to extract from the sodium chloride any potassium nitrate it might contain. Again filter off the sodium chloride from the hot liquid; allow the filtrate to cool, and add to the main quantity of potassium nitrate any of the salt which crystallizes as the result of this extraction.

Recrystallize the potassium nitrate from the least quantity of boiling water, and obtain large prismatic crystals of the salt by slow cooling. State the percentage yield obtained.

The recrystallized potassium nitrate will be almost completely free from sodium chloride owing to the different gradients of solubility with temperature of the two salts. Test the salt for chloride, and if there is only an opalescence with silver nitrate further recrystallization is unnecessary.

4. Potassium Nitrite, KNO_2

Alkali nitrites can be obtained by heating strongly their nitrates, which lose oxygen, thus:

$$2K(Na)NO_3 = 2K(Na)NO_2 + O_2.$$

Other nitrites are unstable at high temperature, and other nitrates are therefore decomposed completely by strong heating, leaving a residue of oxide or metal.

It is difficult, however, to obtain potassium nitrite in quantity by heating the nitrate alone; it is better to provide a reducing agent to remove the necessary amount of oxygen. Metallic lead is usually employed for this purpose; it is converted thereby into monoxide thus:

$$KNO_3 + Pb = KNO_2 + PbO.$$

Preparation.

Requirements: Potassium nitrate, 50 gm.
Lead, as foil or granules, 102 gm.

Provide a large iron crucible, together with a piece of stout iron wire to serve as a stirrer. Heat the potassium nitrate in the crucible until it fuses, and then introduce the lead into the fused mass, little by little, with stirring, continuing the heating until all the lead has disappeared. Allow the mass to cool, and extract it with hot water. Pass carbon dioxide through the solution for a few minutes to convert into insoluble carbonate any lead that has passed into solution. Filter, and evaporate the solution to a small volume; then carefully add dilute nitric acid until the liquid is neutral, and allow crystallization of any potassium nitrate to take place. Filter and evaporate the solution to dryness and finally fuse the residue in a clean iron or nickel dish. Break up the mass while hot, and store it in a well-stoppered bottle. Estimate the percentage yield, and determine the purity of the specimen of potassium nitrite by titrating a solution of it into decinormal permanganate (p. 31).

5. Potassium Iodide, KI

A mixture of potassium iodate and iodide can be obtained from potassium hydroxide solution and iodine by the following reactions, which are analogous to those occurring between potassium hydroxide and chlorine:

$$\begin{aligned} 2KOH + I_2 &= KI + KOI + H_2O \\ 3KOI &= 2KI + KIO_3. \end{aligned}$$

If the resulting solution is then evaporated and the residue is ignited, the iodate loses oxygen and only iodide remains.

An alternative method of preparing iodide, which is more generally employed, consists in causing iodine to react with a metal to form an iodide which is then decomposed with potassium carbonate so that the metallic carbonate or hydroxide is precipitated and potassium iodide remains in solution.

In practice iron is employed as the metal, and after the formation of ferrous iodide, FeI_2, more iodine is added to produce a mixture of the composition $FeI_2, 2FeI_3$ ($\equiv Fe_3I_8$), since a ferrous precipitate is unsatisfactory to filter. From this mixture potassium carbonate precipitates hydrated Fe_3O_4, the corresponding carbonate being unstable. This is easily filtered, so that a clear, colourless solution of potassium iodide is obtained from which the pure salt crystallizes after evaporation.

Preparation.

Requirements: Pure iron (filings, wire, or small nails), 5 gm.
Iodine, 21 gm. and 7 gm.
Potassium carbonate,* 15·2 gm.

Place the iron in a flask with 50 c. c. of water, and gradually add 21 gm. of iodine. Combination will occur between the iron and the iodine with evolution of heat; it may be necessary, however, to warm the flask to start the reaction, and then to cool again if it becomes too vigorous. Allow the mixture to stand with occasional shaking until the supernatant liquid becomes green, showing that all the iodine has been converted into ferrous iodide; the mixture may stand overnight with advantage. Filter the liquid, and wash the remaining iron. Then add to the solution 7 gm. of iodine, so as to convert one-third of the FeI_2 into FeI_3. Heat if necessary to dissolve the iodine. Next dissolve 15·2 gm. of pure potassium carbonate in 50 c. c. of water, and heat the solution to boiling in a porcelain dish. To the boiling solution add the iodide of iron solution, little by little. There will be much evolution of carbon dioxide, and nearly black hydrated ferrosoferric oxide will be precipitated. Filter off the precipitate and wash it with hot water. Add to the filtrate potassium hydroxide solution, until any iron remaining in solution is precipitated. Filter again, and evaporate the filtrate until potassium iodide crystallizes. If any hydrated oxide of iron separates during evaporation, filter again, or else evaporate the filtrate to dryness and extract the dry mass with hot water, obtaining a solution from which pure potassium iodide can be crystallized. The salt should be quite white, and if it has been crystallized slowly it will be obtained in cubical crystals.

Calculate the percentage yield, according to the weight of iodine taken.

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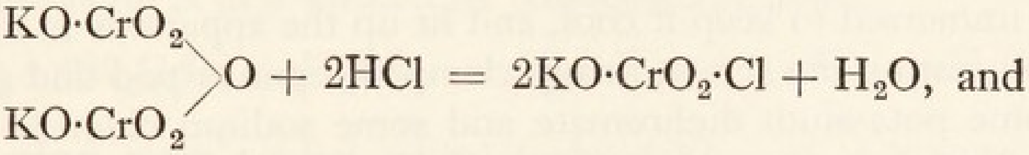
* Dry, and free from chloride and sulphate.

6. Potassium Chlorochromate, $KO{\cdot}CrO_2{\cdot}Cl$: Chromyl Chloride, $Cl{\cdot}CrO_2{\cdot}Cl$

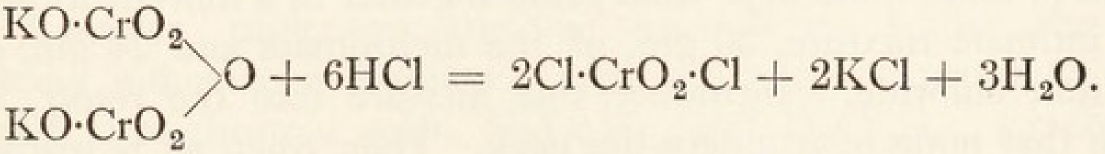
From a dibasic oxyacid the hydroxyl groups can be removed in two stages with the formation respectively of chloro-acid and acid chloride. Generally a chloride of phosphorus is used for this purpose, as in the preparation of chlorosulphonic acid and sulphuryl chloride, thus:

$$HO{\cdot}SO_2{\cdot}OH \xrightarrow{PCl_5} HO{\cdot}SO_2{\cdot}Cl \xrightarrow{PCl_5} Cl{\cdot}SO_2{\cdot}Cl.$$

In this case, however, hydrogen chloride effects the change, though to obtain chromyl chloride sulphuric acid must be present, not only to liberate the acids from the alkali chromate and chloride which are employed, but also to combine with the water liberated in the reaction. Thus the two reactions are:



$$\left.\begin{matrix}KO{\cdot}CrO_2\\KO{\cdot}CrO_2\end{matrix}\right>O + 2HCl = 2KO{\cdot}CrO_2{\cdot}Cl + H_2O, \text{ and}$$



$$\left.\begin{matrix}KO{\cdot}CrO_2\\KO{\cdot}CrO_2\end{matrix}\right>O + 6HCl = 2Cl{\cdot}CrO_2{\cdot}Cl + 2KCl + 3H_2O.$$

Preparation *of Potassium Chlorochromate.*

Requirements: Potassium dichromate, 50 gm.
Concentrated hydrochloric acid, 60 c. c.
Water, 40 c. c.

Dissolve with the aid of heat 50 gm. of potassium dichromate in a mixture of 60 c. c. of concentrated hydrochloric acid and 40 c. c. of water. Filter the solution, if necessary, and allow it to stand overnight for the chlorochromate to crystallize. Then filter and drain on a porous plate the crystals, which form large flat plates. Estimate the percentage yield, and prove the purity of the compound by quantitative analysis, as follows.

Potassium chlorochromate, $KO{\cdot}CrO_2{\cdot}Cl$, may be regarded for analytical purposes as a compound of CrO_3 and KCl. Therefore estimate its CrO_3 by dissolving a known weight in water and titrating some of this solution into a ferrous solution which has been previously titrated with decinormal dichromate solution; and its KCl by neutralizing some of the same solution with ammonia, and titrating it with decinormal silver nitrate, the chromate present serving as indicator.

Preparation *of Chromyl Chloride.*

Requirements: Potassium dichromate, 30 gm.
Sodium chloride, 24 gm.
Concentrated sulphuric acid, 30 c. c.

Chromyl chloride, like acid chlorides in general, is a liquid which is prepared by distillation.

Choose a stoppered retort of 250 c. c. or more capacity, and with as long a neck as possible; and fit to it a distilling flask to act as a receiver, making as good a joint as possible by means of asbestos paper. Attach to the side tube of the flask a small calcium chloride tube; then provide a trough to contain water in which the receiver may be immersed to keep it cool, and fit up the apparatus in a fume chamber, resting the retort, firmly clamped, upon tripod and gauze. Heat some potassium dichromate and some sodium chloride so as to have them quite dry; then grind together in a mortar, to produce an intimate mixture, 30 gm. of the dichromate and 24 gm. of the sodium chloride. Introduce this mixture into the retort, taking care that none of it enters the neck. Then when all is ready pour through a funnel into the retort 30 c. c. of concentrated sulphuric acid. Quickly fit the stopper into its place, and rotate the retort so that all the solid is wetted with the acid, otherwise there is risk of the retort being cracked when heat is applied. A dark red vapour at once arises from the mixture, and as it condenses in the neck of the retort and runs down into the receiver appears as an almost black liquid. This is chromyl chloride. Some hydrogen chloride gas will also probably be seen escaping from the end of the calcium chloride tube, and since the ingredients of the mixture were mixed in equivalent quantities, this means a reduction in the yield of chromyl chloride. Heat the retort gently, and continue the heating as long as chromyl chloride distils over. Then redistil the compound from a distilling flask having a long neck closed with a cork through which passes a thermometer. The thermometer bulb should be nearly at the lower end of the neck of the flask. Collect the distillate in another flask so fixed that the delivery tube of the distilling flask reaches into the body of the receiver which is cooled by water; and note the boiling-point of the compound, which should be 116°. Take scrupulous care that the chromyl chloride does not come in contact with any moisture, and preserve it in a boiling tube drawn out and sealed off in a flame. Chromyl chloride can be analysed by dissolving it in excess of dilute ammonia, neutralizing the solution with dilute nitric acid, and titrating the chloride with decinormal silver nitrate solution. The chromate in the same solution can be determined either by oxidizing ferrous iron by means of it, or by causing it to liberate iodine from acidified potassium iodide, and titrating the iodine with decinormal sodium thiosulphate solution.

7. Chromic Anhydride, CrO_3

When sulphuric acid is added to the solution of a chromate a dichromate is first formed by condensation, thus:

$$2K_2CrO_4 + H_2SO_4 = K_2Cr_2O_7 + K_2SO_4 + H_2O;$$

and when more acid is added dichromate acid is liberated. This acid, however, undergoes further condensation under the dehydrating influence of sulphuric acid. It may be supposed that tri- and tetra-chromic acids, $H_2Cr_3O_{10}$ and $H_2Cr_4O_{13}$, which are known to exist, are formed as intermediate products in solution, but the final result is complete dehydration with separation of the anhydride CrO_3 in deep red crystals. The ultimate reaction is thus expressed:

$$K_2Cr_2O_7 + 2H_2SO_4 = 2CrO_3 + 2KHSO_4 + H_2O.$$

Chromic anhydride, which is readily soluble in water with regeneration of chromic acid, is separated from the potassium hydrogen sulphate, formed at the same time, by the procedure outlined below.

Preparation.

Requirements: Potassium dichromate, 100 gm.
Sulphuric acid, concentrated, 200 c. c.
Water.

Dissolve 100 gm. of potassium dichromate in 260 c. c. of water by heating in a large porcelain dish. Add to the cooled solution 200 c. c. of concentrated sulphuric acid, in a thin stream, with stirring. Allow the solution to stand overnight in the dish, when crystals of potassium hydrogen sulphate will be found to have separated. Decant the solution from the crystals and evaporate it on the sand bath until chromic anhydride begins to separate in needles on the surface of the liquid. Place the solution in a beaker, cover it, and allow it to cool slowly. Filter off the crystals with suction, having a piece of ignited asbestos paper on the Büchner funnel, and evaporate the mother liquor to obtain a further crop.

Wash the crystals with concentrated nitric acid until the wash liquid is free from sulphate; then place them in a piece of dry combustion tube, and pass dry air through the tube whilst it is heated very gently. Preserve the product in a sealed or well-corked tube.

Chromic anhydride is a deliquescent and corrosive substance; it is a powerful oxidizing agent, being easily reduced by loss of oxygen to chromic oxide, Cr_2O_3.

8. Magnesium Chloride, $MgCl_2$

Magnesium chloride crystallizes from aqueous solution as the hexahydrate, $MgCl_2 \cdot 6H_2O$. This salt, however, is prone to hydrolysis, which may be prevented by the presence of hydrochloric acid. Moreover, the salt is very soluble in water, and during the evaporation of its aqueous solution is liable to precipitate the basic salt $Mg(OH)Cl$ by loss of hydrochloric acid. Similarly the crystallo-hydrate itself decomposes when heated, so that it cannot give up its water and leave the normal anhydrous salt.

Connected with this imperfection as a salt is the power which magnesium chloride possesses to combine with alkali chlorides, forming stable double salts which are not hydrolyzed when heated with water. Thus if ammonium chloride is added to magnesium chloride in solution in proportion sufficient to form the double or complex salt NH_4MgCl_3, this solution may be evaporated to dryness, and the double salt obtained free from any basic salt. If this double salt is then ignited in absence of water, it loses ammonium chloride, and leaves a residue of pure, anhydrous magnesium chloride which can be fused and volatilized without decomposition.

Preparation.

Requirements: Pure calcined magnesia, 4 gm.
Hydrochloric acid.
Ammonium chloride, 5·35 gm.

Grind the magnesia with water in a porcelain mortar, and place most of the " milk of magnesia " so made in a large porcelain basin, keeping back a little to neutralize any excess of hydrochloric acid that may be employed. To this mixture carefully add concentrated hydrochloric acid, with constant stirring, and when most of the solid has disappeared, heat the liquid in the dish. Finish the process of solution with dilute hydrochloric acid, using also the reserve of magnesia, so as to obtain a solution containing no excess of hydrochloric acid. Add to this liquid a solution of 5·35 gm. of ammonium chloride in the smallest quantity of warm water, filter the mixed solution, and carefully evaporate it to dryness in the dish. Heat the solid residue very carefully so as to drive off all the water without volatilizing any ammonium chloride. Then remove the mass from the dish, grind it in the porcelain mortar, and again heat it to remove the last trace of water. When this has been done test the product in the following way.

Place a little of it in the bottom of a dry test-tube and gently apply heat. No water should condense in the top of the tube, but when all the ammonium chloride has been vaporized, the residue should fuse to a clear liquid which sets to a solid, crystalline mass on cooling. This is pure anhydrous magnesium chloride.

When this test has proved satisfactory, powder the whole mass, introduce it into a large platinum crucible, and heat it similarly, excluding air as much as possible to avoid the formation of basic chloride.

After obtaining the magnesium chloride in a fused condition, allow the mass to solidify, break it up while warm, and store it in a well-stoppered bottle or sealed tube; ascertaining what percentage yield has been obtained.

9. The Calcium Phosphates

Phosphoric acid, being a tribasic acid, forms with a metal three salts, exemplified in the case of calcium by:

$Ca_3(PO_4)_2$: Tribasic calcium phosphate; $Ca_2H_2(PO_4)_2$ or $CaHPO_4$: Dibasic calcium phosphate; $CaH_4(PO_4)_2$: Monobasic calcium phosphate.

It is difficult to obtain these salts pure in presence of water only, because they are prone to hydrolysis. Thus $Ca_3(PO_4)_2$ is slightly hydrolyzed by pure water into a basic salt, $Ca(OH)_2 \cdot nCa_3(PO_4)_2$, which remains insoluble, and an acid salt or free phosphoric acid which enters solution; $CaHPO_4$ is also hydrolyzed into $Ca_3(PO_4)_2$ and free phosphoric acid; and $CaH_4(PO_4)_2$, whilst soluble in cold water, is hydrolyzed on heating with water with the formation of $CaHPO_4$ and free phosphoric acid. These three salts may, however, be obtained in a fair state of purity by the methods given below.

Tribasic Calcium Phosphate, $Ca_3(PO_4)_2$.

Preparation.

Requirements: Calcium chloride, anhydrous, 10 gm.
Sodium phosphate, crystallized, 20 gm.
Ammonia.

Dissolve 10 gm. of pure anhydrous calcium chloride in about 100 c. c. of water, add a little ammonia, and filter if necessary. Also dissolve 20 gm. of ordinary sodium phosphate, $Na_2HPO_4 \cdot 12H_2O$, separately in water. Heat the solutions and mix them with stirring as the precipitate forms. Keep the liquid hot for a time to allow the precipitate to become granular and settle. Then filter through a Büchner funnel, washing once by decantation and then on the filter with hot water. Dry the precipitate in the steam oven, and determine the percentage yield of $Ca_3(PO_4)_2$.

The phosphate content of the salt may be estimated gravimetrically by the molybdate method (p. 108), or the calcium by precipitation as oxalate from acetic acid solution made by dissolving the salt in dilute hydrochloric acid, and adding ammonia in excess, followed by acetic acid in excess.

Dibasic Calcium Phosphate.

When cold solutions of calcium chloride and ordinary sodium phosphate are mixed, dibasic calcium phosphate is precipitated in hydrated form thus:

$$Na_2HPO_4 + CaCl_2 = CaHPO_4 + 2NaCl.$$

The precipitate dissolves easily in dilute acetic acid, but on heating the solution to boiling much of the salt separates again as the crystalline hydrate $2CaHPO_4 \cdot H_2O$ or $Ca_2H_2(PO_4)_2 \cdot H_2O$.

Preparation.

Requirements: Calcium chloride, anhydrous, 5 gm.
Sodium phosphate: an equivalent quantity.
Acetic acid, dilute.

Dissolve 5 gm. of anhydrous calcium chloride in 100 c. c. of water and filter if necessary; dissolve separately in water an equivalent amount of sodium phosphate, $Na_2HPO_4 \cdot 12H_2O$, and mix the solutions cold. A bulky precipitate is formed. Now, with constant stirring, add dilute acetic acid until the precipitate is just dissolved; but be very careful not to add the acid in excess. Heat the solution to boiling, and keep it hot until the crystalline precipitate which separates has settled leaving a clear, supernatant liquor. Filter off the precipitate through a Büchner funnel, wash it with warm water containing a very little acetic acid until the wash water is almost or quite free from chloride, and dry it in the air. Estimate the percentage yield, and the purity of the product.

Monobasic Calcium Phosphate, $CaH_4(PO_4)_2$.

This salt is easily prepared by the combination of the tribasic salt with phosphoric acid, thus:

$$Ca_3(PO_4)_2 + 4H_3PO_4 = 3CaH_4(PO_4)_2.$$

Prepare some precipitate of $Ca_3(PO_4)_2$ as before, suspend it in water in a beaker, heat the mixture, then add to it sufficient solution of phosphoric acid to obtain a liquid which remains clear when boiled. Evaporate this solution first at high temperature and then in a vacuum desiccator over sulphuric acid until crystals of the monabasic salt separate.

Estimate the yield and phosphate content of the crystals, and show that they are decomposed by hot water with separation of the dibasic salt.

10. Barium Dithionate, $BaS_2O_6 \cdot 2H_2O$

Dithionic acid results from the partial oxidation of sulphurous acid thus:

$$2H_2SO_3 + O = H_2S_2O_6 + H_2O.$$

Equivalent oxidation occurs when ferric sulphite, formed by passing sulphur dioxide gas into ferric hydroxide suspended in water undergoes self-oxidation and reduction to ferrous dithionate and sulphite thus:

$$Fe_2(SO_3)_3 = FeS_2O_6 + FeSO_3.$$

Manganese dithionate is formed when sulphur dioxide is passed through manganese dioxide suspended in water, the reaction being often represented as simply:

$$MnO_2 + 2SO_2 = MnS_2O_6.$$

Probably, however, manganic sulphite is first produced, and then undergoes self-oxidation and reduction thus:

$$\begin{aligned} 2MnO_2 + 4SO_2 + H_2O &= Mn_2(SO_3)_3 + H_2SO_4 \\ Mn_2(SO_3)_3 &= MnS_2O_6 + MnSO_3. \end{aligned}$$

From the manganous dithionate the barium salt can be obtained crystalline by the addition of baryta solution and concentration of the filtrate after removal of manganous hydroxide.

Dithionic acid itself is liberated in solution when the barium salt is decomposed by dilute sulphuric acid, but on concentration the solution decomposes thus:

$$H_2S_2O_6 = H_2SO_4 + SO_2.$$

Dithionic acid is the first of a series of thionic acids, and is the only one which does not yield sulphur among its decomposition products.

Preparation.

Requirements: Crystallized manganese sulphate, 100 gm.
Sodium peroxide.
Sulphur dioxide.
Barium hydroxide.

The manganese dioxide employed for this reaction may be pyrolusite reduced to a very fine state of division by trituration with water, but artificially prepared manganese dioxide is more reactive and is to be preferred. To prepare the manganese dioxide dissolve the sulphate in about 250 c. c. of warm water in a large beaker, add to the solution sodium peroxide little by little until precipitation is complete and the liquid remains alkaline. Then heat to boiling, filter through a Büchner funnel, and wash the precipitated manganese dioxide until it is free from alkali. Suspend the washed precipitate in 500 c. c. of cold water in a litre flask and stand the flask in a trough containing crushed ice. This is necessary to prevent any considerable rise of temperature owing to the heat evolved by the reaction between the manganese dioxide and the sulphur dioxide. Then pass into the mixture sulphur dioxide gas from a siphon of the liquid. The manganese dioxide will gradually dissolve, leaving eventually a colourless liquid. If lumps form, saturate the liquid with sulphur dioxide, and then break them up. Place the liquid in a large evaporation dish, heat gently, and then add with stirring solid barium hydroxide until all the manganese is precipitated as hydroxide and the liquid reacts alkaline. Pass carbon dioxide through the turbid liquid until it becomes neutral to litmus paper; this will be when the excess of baryta in solution has been precipitated as carbonate. Filter the liquid cold, through a Büchner funnel; then evaporate the filtrate on the water bath, filtering again if more barium carbonate separates on evaporation. Barium dithionate, $BaS_2O_6 \cdot 2H_2O$, will crystallize from the solution. Estimate the yield and determine the purity of the salt by dehydrating it at 100°, and converting it into $BaSO_4$ by ignition.

11. Cuprous Chloride, CuCl

Cuprous chloride is obtained by the combination of cupric chloride with copper in presence of hydrochloric acid, with which both chlorides combine chemically; or else by the reduction of cupric chloride, generally by means of sulphur dioxide gas, according to the reaction:

$$2CuCl_2 + SO_2 + 2H_2O = 2CuCl + 2HCl + H_2SO_4.$$

Instead of cupric chloride it is usual to employ for this reaction an equimolecular mixture of cupric sulphate and sodium chloride. The first method serves to prepare cuprous chloride in quantity in the form of powder. By the second method the compound is obtained in a distinctly crystalline condition.

I. Preparation *from Cupric Chloride and Copper.*

Requirements: Crystallized cupric chloride, 20 gm.
Copper, turnings or powder, 15 gm.
Hydrochloric acid.

Place the copper chloride and metallic copper together in a 500-c. c. flask provided with a funnel, and add to them 100 c. c. of concentrated hydrochloric acid and 50 c. c. of water. Heat the mixture until it boils gently, and notice that the cupric chloride dissolving in the acid produces a dark greenish brown liquid. This contains a compound of cupric chloride and hydrogen chloride. As the reaction proceeds, however, the colour of the mixture becomes paler, because the compound of cuprous chloride with hydrogen chloride is colourless.

When the solution has become nearly colourless, showing that most or all of the cupric chloride has been converted into cuprous chloride, decant the hot solution in a slow stream into water contained in a tall cylinder leaving the residue of copper in the flask. A white precipitate of cuprous chloride will be formed immediately, leaving as it settles a supernatant solution which will be pale blue if much cupric chloride remained, but which will be nearly or quite colourless if the reaction approached completion.

Allow the precipitate to settle, then pour off the clear liquid, and transfer the precipitate to a Büchner funnel, filtering it by suction, and washing it, first with alcohol, and then with a little ether. Dry the product in a vacuum desiccator over sulphuric acid, and preserve the white dry powder in a closely stoppered bottle. Estimate the percentage yield on the basis of $CuCl_2 \cdot 2H_2O$ taken.

II. Preparation *by Reduction of Cupric Chloride by Sulphur Dioxide.*

Requirements: Cupric sulphate, 10 gm.
Sodium chloride, 5 gm.
Hydrochloric acid; sulphur dioxide.

Dissolve the two salts together in sufficient water to yield a concentrated solution when cold, and add to this solution one-third its volume of concentrated hydrochloric acid. Pour the solution into a gas wash bottle, and pass into it for thirty minutes a slow stream of sulphur dioxide gas. Then allow the liquid to stand for a few hours. At the end of this time cuprous chloride will have separated in distinct crystals, some of which adhere to the glass. Pour off the liquid, then filter, wash, and dry the crystals as before.

On exposure to the air cuprous chloride absorbs oxygen, and turns pale green, being converted into the basic cupric chloride Cu_2OCl_2. A hydrochloric acid solution of this substance is brown because it contains cupric chloride, and a similar solution of cuprous chloride, colourless at first, quickly turns brown by oxidation.

12. Lead Peroxide, PbO_2

Lead peroxide does not result from heating lead monoxide alone in the air, red lead, Pb_3O_4, or $2PbO \cdot PbO_2$ being the highest oxide produced in this way. If, however, the lead monoxide is mixed with a base with which PbO_2, being acidic, can combine to form a stable salt, this salt results. Thus calcium plumbate is formed when lead monoxide is heated with chalk in a current of air:

$$CaCO_3 + PbO + O \rightarrow CaPbO_3 + CO_2.$$

Lead peroxide is also produced from the monoxide or its salts by oxidation in solution. Thus it is formed at the anode by the electrolysis of lead salts in acid or alkaline solution, and is easily obtained by the action of chlorine on alkali plumbite solution thus:

$$HPbOONa + Cl_2 = PbO_2 + HCl + NaCl.$$

It is noteworthy that whilst hydrated PbO dissolves in alkali, forming plumbite, PbO_2 is precipitated when formed even in presence of excess of alkali, although it may be supposed to be more acidic than PbO.

Preparation.

Requirements: Lead acetate, $Pb(C_2H_3O_2)_2 \cdot 3H_2O$, 25 gm.
Sodium hydroxide, 25 gm.
Chlorine gas.

Dissolve the lead acetate in 100 c. c. of cold water in a 1-litre flask, and filter if necessary; turbidity due to incipient hydrolysis of the salt is, however, of no consequence. Dissolve the sodium hydroxide in 100 c. c. of water, add this solution to the lead acetate, and heat the mixture until the white precipitate which first forms is redissolved. Pass chlorine gas into the hot solution until no further precipitation takes place. Then pour out into a large evaporating dish the liquid which now contains the precipitated lead peroxide in suspension; heat it nearly to boiling, and after stirring well allow the precipitate to settle. Decant the liquid through a Büchner funnel, and wash the precipitate by decantation and on the filter until it is free from alkali. Place the moist product on a clock glass, and dry it in the air oven at a temperature of 120° to 130°, breaking up any lumps that form until a fine dry chocolate-coloured powder is produced. The reason it is necessary to heat the product above 100° is that some of the water is present in a combined state, probably in the form of metaplumbic acid, H_2PbO_3.

Estimate the percentage yield of PbO_2; and determine the purity of the product by igniting a weighed quantity of it in a porcelain * crucible at as low a temperature as possible. The loss of weight is due to conversion of PbO_2 into PbO.

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* A silica crucible must not be used, since lead monoxide combines readily with silica, forming a fusible glass, in consequence of which a hole might appear in the crucible.

13. Iodic Acid, HIO_3: Iodic Anhydride, I_2O_5

Iodic Acid.

Iodine alone among the halogens is oxidized by nitric acid, the product of oxidation being iodic acid, HIO_3, to which there corresponds the anhydride, I_2O_5. Nitrous fumes are produced by the reduction of the nitric acid, and these would reduce iodic acid again to iodine; it is therefore necessary to remove or oxidize them by driving a current of air or oxygen through the acid during the action.

Preparation.

Requirements: Iodine, finely powdered, 16 gm.
Fuming nitric acid, 1·5 specific gravity, 60 to 70 c. c.
Oxygen gas.

Choose a 500-c. c. flask with a neck as long as possible, so that vapour from the boiling acid may be condensed on the neck and run back again into the flask. Support the flask on a piece of asbestos cardboard, with a circular hole in the centre about 3 in. in diameter, and resting on a tripod stand. The purpose of the asbestos is to shield the sides of the flask from the heat of the flame so as to keep the surface of the glass as cool as possible for the condensation of the nitric acid. Fix a glass tube connected with an oxygen cylinder in such a way that a brisk current of oxygen can be driven continuously through the acid.

Place 60 c. c. of the fuming acid in the flask, heat it and drive oxygen through it till it is colourless; then introduce into the flask powdered iodine a little at a time, keeping the acid boiling by a small flame beneath, but not touching the flask. The iodine will gradually dissolve, and brown fumes liberated from the acid will be oxidized or carried away by the oxygen. If any iodine appears as a sublimate in the upper parts of the flask return it to the acid. Also add a few cubic centimetres of acid from time to time to replace that lost by evaporation. Gradually a white powder will begin to accumulate beneath the acid liquid. This is iodic acid; and when, after about eight hours, all the iodine appears to have been converted into this substance, allow the flask and its contents to get quite cold; then filter off the solid through an asbestos filter in a small Büchner funnel; also evaporate nearly to dryness in a porcelain dish the acid filtrate and drain the crystals that separate. Dissolve the iodic acid so obtained in a little hot water, and filter if necessary. Add to the solution half its volume of colourless concentrated nitric acid and set the liquid aside to crystallize in a beaker. Thoroughly drain the crystals, place them on a piece of porous plate, and dry them over sulphuric acid in a vacuum desiccator.

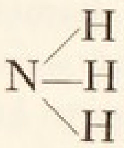
Estimate the yield of iodic acid; and study the reactions of this substance by reference to your Qualitative Analysis.

Iodic Anhydride, I_2O_5.

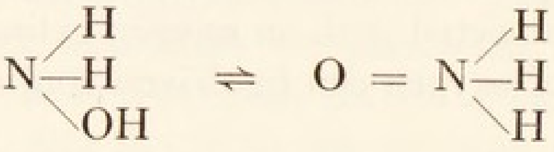
Gently ignite a little of the iodic acid in a dry test-tube, so that it gives off water, but does not decompose evolving iodine. The product is iodic anhydride.

14. Hydroxylamine Sulphate, $NH_2OH \cdot H_2SO_4$

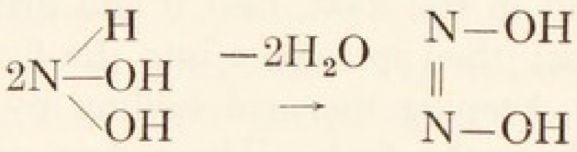
The following series of nitrogen compounds may be formulated, starting with ammonia:



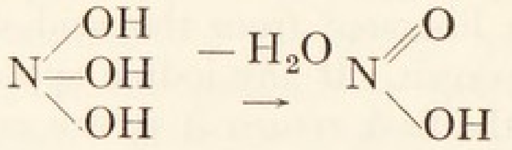
Ammonia.



Hydroxylamine (oxyammonia).



Hyponitrous acid.



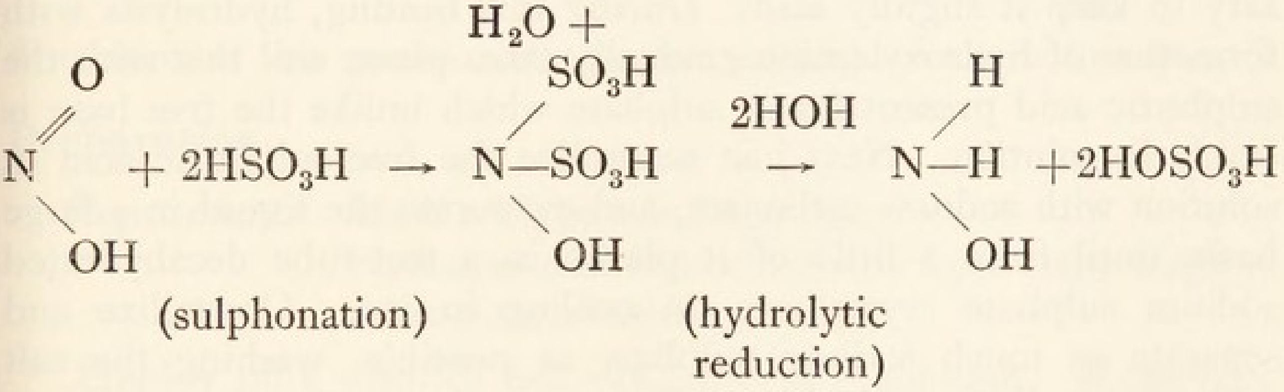
Nitrous acid.

From this it appears that hydroxylamine can be regarded as an oxidation product of ammonia, as well as a reduction product of nitrous or hyponitrous acid.

Hydroxylamine is obtained, however, not by the oxidation of ammonia, but by the reduction of nitric or nitrous acid, or else by the combination of nitric oxide and nascent hydrogen:

$$NO + 3H \rightarrow NH_2OH,$$

as, for example, when nitric oxide is passed through hydrochloric acid in which tin is being dissolved with displacement of hydrogen. In the well-recognized method of preparing hydroxylamine which will be employed here, nitrous acid is reduced indirectly by a process which may be described as sulphonation followed by hydrolytic reduction of the sulphonated product. Sulphonation of nitrous acid consists in its condensation with sulphurous acid; and the advantage of this condensation is that the sulphurous residue in the condensed molecule, being susceptible of oxidation to sulphuric acid in the process of hydrolysis by means of acid, provides just that degree of reducing power by which nitrous acid can be converted into hydroxylamine. This will be clear from the following scheme:



$$O{=}N{-}OH + 2HSO_3H \xrightarrow[\text{(sulphonation)}]{} N(SO_3H)_2OH \xrightarrow[\text{(hydrolytic reduction)}]{H_2O + 2HOH} N(H)_2OH + 2HOSO_3H$$

The process is carried out by passing sulphur dioxide gas through a mixture of sodium nitrite and sodium carbonate in solution at low temperature, so that sodium hydroxylaminedisulphonate, $N(OH)(SO_3Na)_2$ is formed; and then boiling the solution, slightly acidified with sulphuric acid, the result of which is hydrolytic reduction with formation of hydroxylamine sulphate, which can be crystallized by evaporating the solution.

Preparation.

Requirements: Commercial sodium nitrite, 73 gm.
Anhydrous sodium carbonate, 106 gm.
Sulphur dioxide gas.

Select a round-bottom flask of about 1500 c. c. capacity; fit it with a mechanical stirrer, and provide a thermometer. Dissolve the sodium nitrite and carbonate separately in water; thoroughly cool and mix the solutions, and dilute the mixed solution to 1 litre. Surround with a freezing mixture the flask containing the solution, and fix the thermometer so that the bulb is just immersed in the liquid, but in no danger of being struck by the stirrer. Stir the solution, and when the temperature has fallen to $-5°$, pass sulphur dioxide gas into the liquid. Pass the gas for an hour or more, until the liquid becomes just acid, the sign of acidity being the appearance of brown fumes owing to the decomposition of remaining nitrite. Take care, however, that the temperature of the liquid does not rise above 0° during the passage of the gas, or the yield of hydroxylamine will be reduced; therefore, if necessary, renew the freezing mixture.

At this stage sodium hydroxylamine disulphonate has been formed in solution. Now heat the liquid in the flask on the water bath for two days, adding a little dilute sulphuric acid if necessary to keep it slightly acid. During this heating, hydrolysis with formation of hydroxylamine gradually takes place, and this with the sulphuric acid present forms sulphate which unlike the free base is stable in solution. Next just neutralize the free sulphuric acid in solution with sodium carbonate, and evaporate the liquid in a large basin until from a little of it placed in a test-tube decahydrated sodium sulphate crystallizes on cooling in ice. Crystallize and separate as much sodium sulphate as possible, washing the salt with a very little cold water. Evaporate the mother liquor, separating more sodium sulphate if necessary at a later stage. Lastly, evaporate the mother liquor to dryness, extract the hydroxylamine sulphate with alcohol, and after filtering, crystallize the salt from that solvent.

Prove the identity of your product by showing that it reduces Fehling's solution, and estimate its purity by means of ferric iron and decinormal permanganate solution (p. 33).

15. Ammonium Perborate, $2NH_4BO_3 \cdot H_2O$

Numerous peracids and their salts have been prepared, either by the aid of hydrogen peroxide or a basic peroxide, or else by electrolysis of normal acids or their salts, resulting in anodic oxidation or condensation of acidic radicles.

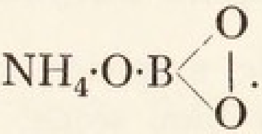
The formation of blue perchromic acid by the action of hydrogen peroxide on chromic acid is a well-known example of the first kind of reaction, and the formation of perdisulphates by the union of two SO_4'' radicles at the anode to form the S_2O_8'' radicle a prominent example of the second.

Ammonium perborate is obtained by the use of hydrogen peroxide, and is formed by dissolving boric acid in 2·5 per cent hydrogen peroxide solution and adding ammonia, and then alcohol. The product is a precipitate of the salt $NH_4BO_3{\cdot}3H_2O$; and this when kept in a desiccator over sulphuric acid for twenty-four hours loses five-sixths of its water, becoming $2NH_4BO_3{\cdot}H_2O$.

The reaction may be represented empirically thus:

$$H_3BO_3 + NH_3 + H_2O_2 = NH_4BO_3 + 2H_2O;$$

but this leaves undecided the question of the constitution of the perborate—whether it is $NH{\cdot}_4O{\cdot}O{\cdot}B{:}O$ or $NH_4{\cdot}O{\cdot}B\left\langle\begin{smallmatrix}O\\|\\O\end{smallmatrix}\right.$. For a discussion of this question the student is referred to the literature.*



Preparation.

Requirements: Boric acid, powdered, 5 gm.
Hydrogen peroxide solution, 2·5 per cent, 250 c. c.
Ammonia; alcohol.

Employ pure distilled hydrogen peroxide solution. If the concentrated solution is available it may be of 30 or more per cent strength. Therefore dilute a small measured volume of it, acidify the solution with dilute sulphuric acid, and titrate it with decinormal permanganate solution to determine its strength (see Part I, p. 122). Then prepare 250 c. c. of a solution containing 2·5 gm. H_2O_2 per 100 c. c.

Place this solution in a flask or stoppered bottle, and without heating shake it with 5 gm. of powdered boric acid until no more solid will dissolve. Filter, and add to the filtrate 10 c. c. of concentrated ammonia solution followed by alcohol until a crystalline precipitate begins to form. Allow the mixture to stand until precipitation is complete. Filter off the crystals with suction, wash

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[*] *Vide Per-Acids and the Salts*, by T. Slater Price, Longmans' "Monographs on Inorganic and Physical Chemistry", 1912.

them with a little alcohol, and dry them in a desiccator over sulphuric acid for twenty-four hours. Preserve the salt in a well corked tube.

The percentage of available oxygen in ammonium perborate may be determined by dissolving a weighed quantity of the salt in water, acidifying the solution with dilute sulphuric acid, and titrating it with decinormal permanganate solution. Other methods of estimation may be found in the literature. From the percentage of available oxygen found, calculate the percentage of $2NH_4BO_3 \cdot H_2O$ in your preparation.

II—PREPARATION OF SALTS FROM IMPURE PRODUCTS AND MINERALS

16. Cupric Sulphate, $CuSO_4 \cdot 5H_2O$, from the crude salt

Cupric sulphate, otherwise known as copper sulphate, blue vitriol, or blue stone, is prepared commercially either from scrap copper or a copper ore such as copper pyrites, $CuFeS_2$. When the salt is prepared from this ore the ore is roasted in such a way as to convert the copper into sulphate, whilst the iron is oxidized to ferric oxide. Nevertheless, crude copper sulphate, obtained in this way, is liable to contain ferrous sulphate as an impurity, and specimens of the salt such as are used in agriculture are sometimes greenish blue from this cause.

Copper sulphate cannot be freed from ferrous sulphate by recrystallization, since the two salts crystallize together, but if the ferrous salt is first converted into the ferric condition, the cupric sulphate may be obtained crystallized free from iron, since ferric sulphate does not readily crystallize from solution.

Preparation.

Weigh 20 gm. of commercial blue vitriol,* powder it and dissolve it in a small quantity of hot water in a beaker. To the hot solution add about one or two cubic centimetres of concentrated nitric acid. If there was an appreciable quantity of iron to be oxidized, brown fumes will appear owing to the reduction of the nitric acid.

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* If copper sulphate containing ferrous sulphate as an impurity is not available, some artificial mixture of the two salts may be made for the sake of this exercise.

Cool the solution to about 60° C., adding more warm water, if necessary, to prevent rapid crystallization, and filter. Allow the clear, deep blue filtrate to stand for some hours in a cool place so that a maximum quantity of large, well-formed crystals may separate. Filter off the crystals and dry them in the air. A further crop of crystals may be obtained from the mother liquor by cooling it in ice, or by evaporating it further.

Crystals of cupric sulphate, $CuSO_4 \cdot 5H_2O$, consist of triclinic prisms. There is evidence that the water molecules in the salt are arranged thus: $[Cu(4H_2O)]SO_4 \cdot H_2O$, the cupric ion being tetrahydrated. The salt loses $4H_2O$ at 100°, and nearly all the remaining water at 220° to 260°. At a higher temperature it begins to lose sulphur trioxide, forming an insoluble basic salt. A green basic salt also separates from a boiling dilute aqueous solution.

17. Barium Chloride, $BaCl_2 \cdot 2H_2O$, from Witherite and Heavy Spar

The chief mineral sources of barium compounds are witherite, which is barium carbonate, and heavy spar or barytes, which is barium sulphate. From both of these minerals barium chloride can be prepared without difficulty.

Preparation from Witherite.

Procedure.—Witherite contains, besides barium carbonate and siliceous matter, carbonates of other metals in small quantities such as those of ferrous iron and calcium. When the mineral is dissolved in hydrochloric acid the chlorides of these other metals occur in solution with barium chloride. If, however, the iron is oxidized to the ferric state, its hydroxide, together with the hydroxides or carbonates of any heavy metals present, is precipitated when the solution is neutralized with barium carbonate itself. Therefore all that is necessary to obtain a solution of barium chloride containing only calcium chloride as an impurity is to allow the solution to stand for some time in contact with excess of the finely powdered mineral. Barium chloride is then easily obtained from the filtrate after evaporation, and by one recrystallization is freed from calcium chloride.

Requirements: Powdered witherite, 60 gm.
Hydrochloric acid, a sufficiency.

By means of its density ascertain the strength of some concentrated hydrochloric acid, and measure a volume sufficient to neutralize 50 gm. of barium carbonate. Dilute the acid with water to about 500 c. c. in a large porcelain dish, and add to it with stirring 50 gm. of powdered witherite. When all the mineral has been added, heat the liquid to complete the process of solution and drive out carbon dioxide. Then add to the solution about 25 c. c. of chlorine water, followed by 5 gm. of very finely powdered witherite, and leave the liquid on the water bath for a few hours, adding more witherite if that added dissolves completely. Allow the solution to stand overnight in contact with the excess of witherite, and in the morning test a few drops of the solution for ferric iron by means of sulphocyanide. If the liquid is free from ferric iron, filter it; if not, allow it to stand until it is. Evaporate the filtered solution until barium chloride crystallizes from it on cooling. If ferric hydroxide, having been present in the state of colloidal hydrosol, separates during evaporation, filter this off before crystallizing the barium chloride. Concentrate the mother liquor, and obtain a second crop of crystals. Then dissolve all the crystals in water containing a few drops of dilute hydrochloric acid, filter if necessary, and recrystallize. Estimate the yield of $BaCl_2 \cdot 2H_2O$, and test whether the salt is free from calcium chloride.

Preparation from Heavy Spar.

Procedure.—Barium sulphate is readily reduced to sulphide when it is heated with carbon out of contact with air, thus:

$$BaSO_4 + 4C = BaS + 4CO.$$

The barium sulphide produced can then be dissolved in hydrochloric acid, and barium chloride crystallized from the solution.

Requirements: Powdered heavy spar, 25 gm.
Powdered and sifted charcoal, about 8 gm.
Hydrochloric acid, concentrated, 30 c. c.

Intimately mix the powdered heavy spar with 6 gm. of sifted charcoal, and introduce the mixture into a graphite crucible provided with a lid, and of such a size that it is about three-quarters full of the mixture; cover the mixture with a layer of charcoal, and place the lid on the crucible. Heat the crucible and contents in a muffle furnace to a bright red heat for about two hours. When the crucible has been allowed to cool it will be found to contain a grey porous mass. Break up this mass with the pointed end of a file or other suitable tool, and introduce the fragments a little at a time into 30 c. c. of concentrated hydrochloric acid diluted with 100 c. c. of water, and contained in a large porcelain dish. Perform this experiment in a fume chamber on account of the hydrogen sulphide gas which will be evolved during the solution of the barium sulphide. Boil and filter the solution; then evaporate it until barium chloride readily crystallizes. Filter off the crystals; obtain a further crop of crystals from the mother liquor, and recrystallize the whole. If the salt obtained before recrystallization is found to be contaminated with iron, allow its solution to stand for some time in contact with a little pure precipitated barium carbonate, before recrystallizing. Estimate the percentage yield of $BaCl_2 \cdot 2H_2O$.

18. Aluminium Sulphate, $Al_2(SO_4)_3 \cdot 18H_2O$, from Bauxite

Potassium Alum from Aluminium and Potassium Sulphates.

Bauxite is hydrated oxide of aluminium containing ferric oxide, titanium oxide, and silica; and it is disintegrated by hot, somewhat diluted sulphuric acid, with the formation of aluminium sulphate and ferric sulphate in solution.

It is difficult, however, to crystallize aluminium sulphate from this solution free from iron, and therefore a better way to treat the mineral is to fuse it with sodium carbonate so as to produce sodium aluminate, which will dissolve in water leaving ferric oxide undissolved.

Carbon dioxide gas passed through the aluminate solution precipitates hydrated alumina, and this after being washed free from alkali can be dissolved in dilute sulphuric acid, forming a solution from which pure aluminium sulphate, $Al_2(SO_4)_3 \cdot 18H_2O$, will crystallize.

Preparation.

Requirements: Bauxite, 50 gm.
Anhydrous sodium carbonate, say 60 gm.*
Carbon dioxide gas; sulphuric acid.

Reduce the bauxite to fine powder; mix it intimately with the sodium carbonate, place the mixture in a Hessian crucible provided with a lid, and heat it for several hours at a bright red heat in a muffle or other furnace. Allow the crucible and its contents to cool, and lixiviate the mass with water, breaking up the lumps after transferring them to a large, porcelain dish, so that all soluble matter may be extracted; 500 c. c. or more of water may be used, and the liquid should be boiled to promote solution.

Filter the solution and wash the residue; if the solution is green, manganate is present. Place the filtrate in a large beaker or flask, heat it to about 70°, and pass through it a brisk stream of carbon dioxide until the precipitation of hydrated alumina is completed. Filter off and wash the precipitate; if it is quite white it may be at once dissolved in dilute sulphuric acid as directed below, but if not, dissolve it in sodium hydroxide solution, filter off the residue consisting of hydrated manganese dioxide, and again pass carbon dioxide through the filtrate to reprecipitate the alumina. Filter off and wash the precipitate, which should now be pure white; then dissolve it in the minimum quantity of hot dilute sulphuric acid, and evaporate the solution until aluminium sulphate crystallizes. As this salt, however, is exceedingly soluble in water, and crystallizes with difficulty, a little alcohol may be added to its cold, concentrated solution. It will then separate readily in snow-white crystalline plates. The salt is somewhat hydrolyzed when dissolved in water, yielding an acid solution.

Potassium Alum,

$K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$ or $K[Al(SO_4)_2] \cdot 12H_2O$.

Take half of the aluminium sulphate obtained and weigh it; then calculate and weigh an equivalent quantity of potassium sulphate, K_2SO_4. Dissolve the two salts separately in water, making

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* The amount of sodium carbonate required depends on the composition of the bauxite, which is variable. The amount stated is suitable for a bauxite containing 50 per cent of alumina and 25 per cent of silica.

concentrated solutions, and mix the solutions. Alum will crystallize, and by slow crystallization can be obtained in regular octahedra.

19. Ferric Alum from Spathic Iron Ore

Spathic iron ore is essentially ferrous carbonate with small amounts of the isomorphous carbonates of manganese, calcium, and magnesium, and also a little ferric oxide and insoluble matter. It thus contains about 50 per cent of ferrous oxide.

The finely powdered ore dissolves gradually in hot dilute sulphuric acid with evolution of carbon dioxide. The ferrous sulphate can then be oxidized by nitric acid, and the excess of this acid got rid of by evaporation. If then to the filtered solution of ferric sulphate containing free sulphuric acid ammonium sulphate is added in sufficient quantity, the solution on evaporation yields lilac coloured crystals of ammonium ferric alum, $(NH_4)_2SO_4 \cdot Fe_2(SO_4)_3 \cdot 24H_2O$ or $NH_4[Fe(SO_4)_2] \cdot 12H_2O$. The sulphates of manganese, calcium, and magnesium do not crystallize with the alum, but the alum may nevertheless be contaminated with small amounts of these salts, in which case it may be recrystallized.

Preparation.

Requirements: Spathic iron ore (finely powdered), 20 gm.
Dilute sulphuric acid, a sufficiency.
Concentrated nitric acid.
Ammonium sulphate, 10 gm.

Place the powdered ore in a 500-c. c. flask, and add to it 120 c. c. of dilute sulphuric acid (2N) and 30 c. c. of water. Heat the mixture until the evolution of carbon dioxide is vigorous; then place the flask on the water bath and allow the reaction to proceed gently until no more gas is evolved. Filter the solution, place it in a 6-in. basin, raise it to the boiling-point, and add a few cubic centimetres of concentrated nitric acid to convert the ferrous iron into the ferric state. Now evaporate the solution until its volume measures about 100 c. c. Add 10 gm. of crystallized ammonium sulphate, and stir until the salt is dissolved. If the solution is brown in colour, add concentrated sulphuric acid, a few drops at a time and with stirring, until the liquid becomes pale yellow. Put aside the dish and its contents in a cool place for a few days, protecting the liquid from dust. At the end of this time a crop of lilac coloured octahedra of ferric alum will be found to have separated. Filter them off, and dry them in the air.

It is not advisable to attempt to obtain a further crop of crystals from the mother liquor, since these are likely to be contaminated with calcium sulphate.

Estimate the yield of ferric alum; also dissolve a crystal of the salt in water and test for manganese by the production of permanganate. If manganese is found the salt may be recrystallized from water containing sulphuric acid.

Ferric alum is sometimes almost colourless instead of having a rich lilac colour *. This is due to the presence of a little ferric hydroxide — probably colloidal — separated by hydrolysis, which is prevented by sufficient acid.

It will be observed that pure ferric alum when dissolved in water gives a brown solution. This is due to hydrolysis and the formation of basic ferric sulphate; a little dilute sulphuric acid counteracts hydrolysis, and makes the solution almost colourless.

20. Manganous Sulphate from Pyrolusite

The mineral pyrolusite contains, in addition to manganese dioxide, siliceous matter and oxide of iron. When the mineral is heated with concentrated sulphuric acid manganous sulphate, $MnSO_4$, is formed, with evolution of oxygen, thus:

$$2MnO_2 + 2H_2SO_4 = 2MnSO_4 + 2H_2O + O_2.$$

Ferrous sulphate is also formed, but when the mass is heated at a high temperature this is decomposed and oxidized to ferric oxide, whilst manganous sulphate, being the salt of a more powerfully basic oxide, remains undecomposed. When, therefore, the mass is extracted with water after ignition, manganous sulphate dissolves, together with any ferrous sulphate which has escaped decomposition. This ferrous sulphate is eliminated by precipitating manganous carbonate from a small quantity of the solution by sodium carbonate, and then bringing the precipitate, after it has

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* Bonnell and Perman, *Trans. Chem. Soc.*, 1921, **119**, 1994.

been washed, into the main body of the solution. Any ferrous sulphate present then interacts with the manganous carbonate to give ferrous carbonate and manganous sulphate, and thus the solution is freed from iron. After filtration the solution of manganous sulphate can be evaporated and crystallized. This salt crystallizes with different molecular proportions of water according to temperature. These are: below 8° $7H_2O$, between 8° and 27° $5H_2O$, at about 30° $4H_2O$, above this temperature H_2O.

Preparation.

Requirements: Pyrolusite (powdered), 200 gm.
Sulphuric acid (concentrated), 140 c. c.

Place the pyrolusite in a shallow crucible or fire-clay saucer, and gradually mix the sulphuric acid with it so as to form a thick paste. Put the crucible with its contents in a muffle furnace, and gradually raise the temperature whilst stirring the mixture with an iron rod. The mass will become solid as the action proceeds, and the excess of sulphuric acid is vaporized. Continue the heating for an hour after the furnace has become red hot. Then allow the crucible to cool; remove the mass, crush it, and heat it with boiling water in a dish. Filter, and wash the residue, adding the washings to the filtrate; the total volume may conveniently be 200 to 300 c. c. Take about 25 c. c. of this solution, and add to it sodium carbonate solution as long as precipitation of impure manganous carbonate continues. Rapidly filter and wash the precipitate, then add this to the rest of the solution and stir well whilst heating the liquid to boiling. Filter, and boil the solution so as to evaporate it until its volume is about 150 c. c.; again filter if any hydrated ferric oxide has separated; then place the solution—which should have a pale pink colour—in a crystallizing basin over sulphuric acid in a desiccator. A pink crystalline mass of pentahydrated manganous sulphate, $MnSO_4{\cdot}5H_2O$, will form. When crystallization seems complete, break up and drain the crystals; then rapidly dry them between folds of filter paper, or on a piece of porous plate, and preserve them in a stoppered bottle or well-corked tube. The crystals are efflorescent triclinic prisms, resembling in form those of copper sulphate, $CuSO_4{\cdot}5H_2O$.

21. Potassium Permanganate from Pyrolusite

When a manganese compound is heated with alkali in presence of an oxidizing agent deep green manganate is formed; thus with manganese dioxide:

$$MnO_2 + O + 2KOH = K_2MnO_4 + H_2O.$$

When manganate is dissolved in water it tends to hydrolyze, and liberate manganic acid, which is unstable and undergoes self-oxidation and reduction thus:

$$\begin{aligned} 3K_2MnO_4 + 6H_2O &\rightleftharpoons 3H_2MnO_4 + 6KOH \\ 3H_2MnO_4 &\rightarrow 2HMnO_4 + MnO_2 + 2H_2O, \end{aligned}$$

or, adding and showing permanganic acid neutralized:

$$3K_2MnO_4 + 2H_2O = 2KMnO_4 + MnO_2 + 4KOH.$$

This reaction is promoted by an acid, and may be carried to completion by passing carbon dioxide gas through an aqueous solution of a manganate thus:

$$3K_2MnO_4 + 2CO_2 = 2KMnO_4 + MnO_2 + 2K_2CO_3.$$

The process is carried out by fusing powdered pyrolusite with potassium hydroxide mixed with potassium chlorate as an oxidizing agent, cooling and extracting the mass with water, passing carbon dioxide through the solution and crystallizing the permanganate after filtering off hydrated manganese dioxide and other insoluble matter.

Preparation.

Requirements: Potassium hydroxide, 40 gm.
Potassium chlorate, 20 gm.
Pyrolusite, finely powdered and ignited, 40 gm.

Choose an iron or nickel crucible of suitable size, and an old file or thick iron wire to act as stirrer.

Melt together the potassium hydroxide and chlorate, and to the melt add the pyrolusite a little at a time with stirring. Then heat the mass strongly, stirring as long as possible while it stiffens and dries up. Steam is evolved, and a dark green or brown mass of potassium manganate results. Heat this at a red heat for a few minutes; then allow it to cool. Remove the hard mass from the crucible by means of a sharp tool, powder it and boil it with 750 c. c. of water in a large beaker. While the liquid is boiling pass through it a rapid stream of carbon dioxide, first to carbonate the excess of potash, and then to liberate manganic acid, which in the free state undergoes the spontaneous change indicated in the equations above.

Allow the hydrated manganese dioxide which separates to settle, and when the supernatant solution shows the deep crimson colour characteristic of permanganate, decant it through an asbestos filter on a Büchner funnel, boil the residue with a little water, transfer it to the filter and drain it thoroughly, finally washing it on the filter with a little hot water.

Place the solution and washings in a large porcelain evaporating dish and by boiling rapidly concentrate the liquid to about half its original volume; by this time more manganese dioxide will have separated which must be filtered off through asbestos. Then further concentrate the solution until signs of crystallization appear on its surface. Allow the liquid to cool and crystallize. Drain the crystals rapidly by suction, and dry them over sulphuric acid in a desiccator. A further crop of crystals may be obtained after evaporating the mother liquor, but they are liable to be contaminated with potassium chloride.

22. Potassium Dichromate from Chrome Ironstone

Chrome ironstone, chrome iron ore, or chromite is a compound of chromic oxide and ferrous oxide, which may be regarded as ferrous chromite, $FeO{\cdot}Cr_2O_3$ or $FeCr_2O_4$. Oxidation of this substance alone affects only the ferrous oxide, for Cr_2O_3 is not oxidized in the air; but, if the mineral is first mixed with alkali, Cr_2O_3 can undergo atmospheric oxidation, with formation of alkali chromate, thus:

$$2Cr_2O_3 + 3O_2 + 4K_2CO_3 = 4K_2CrO_4 + 4CO_2.$$

Since, however, this mixture is fusible, oxidation will be incomplete for lack of air within it; therefore lime is added in excess to the mixture. Some of this lime forms calcium chromate, $CaCrO_4$, whilst the rest of it remains in the solid, uncombined state, and by preventing complete fusion keeps the mass porous, and so assists aeration and consequent oxidation, when the mixture is kept at a red heat in presence of air.

When the resulting mass is extracted with water a mixture of potassium and calcium chromates is obtained in solution together with some calcium hydroxide. Potassium sulphate is consequently added to precipitate the calcium as sulphate, and obtain all the chromate in solution as potassium chromate. Since, however, this salt is very soluble in water, sulphuric acid is added to convert it into dichromate, which is readily crystallized.

Preparation.

Requirements: Chrome ironstone (powdered), 100 gm.
Potassium carbonate, 50 gm.
Lime, 150 gm.
Potassium sulphate, about 16 gm.

Slake the lime, and dissolve the potassium carbonate in about 50 c. c. of water. Make a uniform mixture of the solution with the slaked lime in a 6-in. porcelain dish, and evaporate off the water, stirring well; then heat the dish on the sand bath until the residue is thoroughly dry. Transfer this residue whilst hot to a porcelain mortar, and mix with it intimately the powdered chrome ironstone. Then return the mixture to the dish and apply heat by means of a powerful ring gas-burner, heating gently at first so as not to crack the dish.* Do not allow the flame to envelope the dish, but stir the mixture well with an iron rod so as to effect aeration. Continue this heating for an hour or more, until a little of the solid removed from the dish, cooled, and shaken with water, gives, so far as it dissolves, a bright yellow solution. Then allow the whole mass to cool, break it up into coarse powder, and extract it with successive quantities of hot water with filtering, until the extract is nearly colourless.

Evaporate the yellow solution until it shows signs of crystallizing; then add to it a hot concentrated solution of potassium sulphate, as long as calcium sulphate appears to be precipitated.

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* If a sufficiently high temperature is not obtainable by this means, the mixture may be placed in a fire-clay dish and heated in a muffle furnace; but in this case a good draught must be maintained through the muffle so as to aerate the mixture.

Filter hot, and to the filtrate add dilute sulphuric acid so as to convert potassium chromate into dichromate, a change made manifest by the change of colour from yellow to orange-red; then evaporate if necessary, and crystallize. Filter off the crystals, using a Büchner funnel, and evaporate the mother liquor to obtain a further crop. If, however, these appear to be contaminated with potassium sulphate, reject them.

Recrystallize from water the whole of the potassium dichromate obtained; filter and drain the crystals; and dry them, first on a porous plate, and then in the steam oven.

III—PREPARATIONS GENERALLY INVOLVING DISTILLATION

23. Aluminium Chloride, $AlCl_3$ (Anhydrous)

Metallic aluminium and its hydroxide, $Al(OH)_3$, dissolve both in hydrochloric acid and sodium hydroxide solution, producing respectively chloride and aluminate. Thus the oxide of aluminium is amphoteric, being both basic and acidic; and its chloride will be expected to possess properties in harmony with those of the oxide. Such is the case; for aluminium chloride can be prepared, not only by the action of hydrogen chloride as gas or in solution on the element or its hydroxide, but also by the action of chlorine on the heated element in such a way as to obtain the chloride as a condensible vapour, according to a common method of obtaining non-metallic chlorides. Moreover, aluminium chloride itself shares other properties both of a non-metallic and a metallic chloride; for it is hydrolyzed by much water, but nevertheless can be obtained as the crystallohydrate, $AlCl_3{\cdot}6H_2O$, by the crystallization of its aqueous solution in presence of excess of hydrochloric acid.

Preparation.

Requirements: Aluminium turnings or clippings, 10 gm.
Chlorine gas.

As stated above, aluminium chloride can be obtained by either of the reactions:

$$2Al + 3Cl_2 = 2AlCl_3, \text{ or}$$
$$2Al + 6HCl = 2AlCl_3 + 3H_2.$$

Chlorine is more often employed than hydrogen chloride for small-scale experiments, and is said to yield a purer product.

Select a piece of combustion tubing 1·5 to 2·0 cm. in internal diameter, and 35 to 40 cm. long. Close one end with a well-fitting cork through which passes a delivery tube to be connected with a chlorine generating apparatus. Pass the other end of the tube through a large cork fitting into a wide-necked bottle, having a capacity of 250 c. c. or more. Through a second hole in this cork pass a length of narrow tubing bent conveniently so as to lead away the uncombined chlorine. Thoroughly cleanse and dry the whole apparatus; also wash the aluminium turnings with ether to remove any oil or grease upon them, afterwards drying them in the steam oven for a short time. Then place them in the tube, keeping them in position at either end by loose plugs of asbestos. The aluminium should not more than half-fill the tube, and there must be a free space in the tube above the metal.

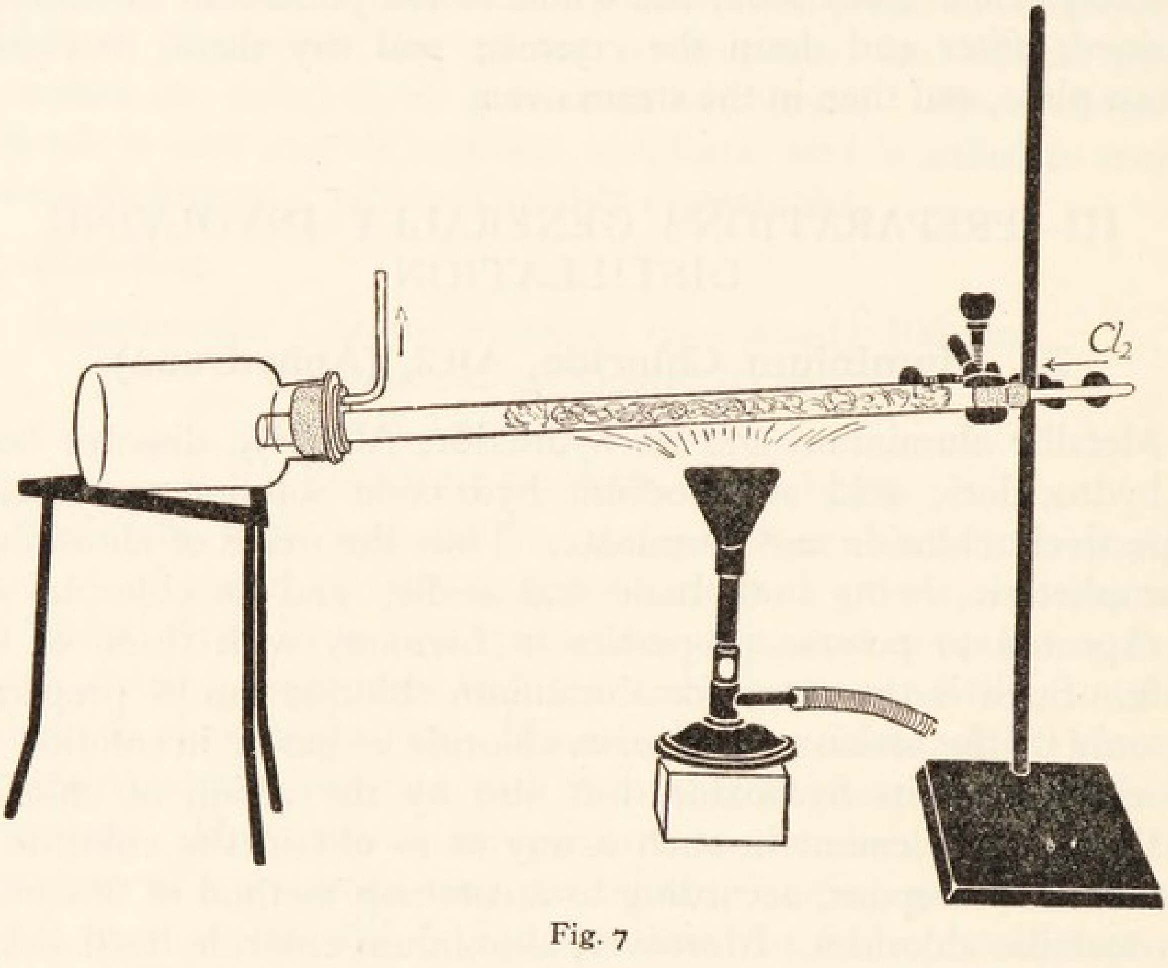

Fig. 7

Fix up the apparatus, either in a fume chamber, or in such a way that the chlorine can be led away so as to be harmless. It is convenient to prepare the chlorine in a Kipp by the action of hydrochloric acid on bleaching powder cubes or by dropping the acid on potassium permanganate; but it must be passed first through a wash bottle containing water to remove hydrogen chloride, then through a second wash bottle containing concentrated sulphuric acid to dry it.

Expel all air from the apparatus by chlorine before heating the aluminium. A single powerful burner, which can be moved about under the tube, or one giving a flat flame, will be sufficient for the heating. Begin to heat at the point nearest where the chlorine enters, and remove the burner for a time when the reaction becomes vigorous. The aluminium chloride, produced as a vapour, will collect in the cooler part of the tube, and in the bottle.

When the mass ceases to glow and the reaction is at an end, allow the tube to cool in an atmosphere of chlorine, and if convenient displace the chlorine by a current of air which has also been dried by passing through concentrated sulphuric acid. Then disconnect the parts of the apparatus, and as quickly as possible transfer the aluminium chloride to a dry boiling tube, and seal the tube, either by drawing it out in a flame, or by closing it with a cork which is then covered with paraffin wax. Estimate the percentage yield.

Aluminium chloride when pure is white as well as crystalline. It generally, however, appears yellow owing to the presence of a little ferric chloride derived from iron in the metal. It fumes in moist air, giving off hydrochloric acid owing to hydrolysis, and after a time deliquesces.

It dissolves in water with a hissing noise, producing a solution containing free hydrochloric acid and a basic salt. When a solution of the chloride is evaporated hydrated alumina separates.

24. Antimony Trichloride, $SbCl_3$

The chloride of an intense metal, e.g. sodium chloride, is not easily volatile, and is soluble in water but is not hydrolyzed by it; whilst the chloride of an intense non-metal, e.g. phosphorus trichloride, is easily volatile, being a liquid, and at once reacts with water, being completely hydrolyzed by it.

Bismuth trichloride, being the chloride of a metalloid, is intermediate in properties between these extremes; it is a fusible and volatile solid, hydrolyzed by water to the oxychloride BiOCl; and antimony trichloride, being the chloride of an element rather less metallic than bismuth, is also fusible and volatile, and hydrolyzable by water, first to the oxychloride SbOCl, and then the hydrated sesquioxide.

A metallic chloride can be obtained by the displacement of hydrogen in hydrogen chloride by the metal; a non-metal does not displace hydrogen from hydrogen chloride, so that its chloride is prepared by the action upon it of chlorine itself, either directly or indirectly. It is well known that powdered antimony catches fire in chlorine gas, forming the chloride. Antimony does not displace hydrogen from hydrogen chloride, but antimony sulphide reacts with hydrogen chloride thus:

$$Sb_2S_3 + 6HCl = 2SbCl_3 + 3H_2S.$$

Pure hydrogen sulphide can be obtained by this reaction, but unless this gas is needed, the solution of the sulphide can be expedited by the help of a little potassium chlorate, which causes the separation of sulphur instead. After solution has been effected the liquid on distillation yields first aqueous hydrochloric acid, then a stronger acid containing some antimony chloride in solution, and finally a distillate which solidifies to a white crystalline mass. This is anhydrous antimony trichloride.

Preparation.

Requirements: Powdered stibnite (Sb_2S_3), 50 gm.
Concentrated hydrochloric acid, 250 c. c.
Potassium chlorate, about 2 gm.

Place the stibnite in a suitable flask, pour upon it the hydrochloric acid, and heat the mixture in a fume chamber. To the hot liquid add the potassium chlorate a little at a time, and continue the heating until all black particles have disappeared. Filter off the sulphur and siliceous matter through glass wool or asbestos; place the solution in a distilling flask; insert a cork carrying a thermometer in the neck of the flask, and provide a condenser to condense the hydrochloric acid. Distil the solution, and when the thermometer reaches 200° C. and solid begins to appear in the distillate, remove the condenser and substitute for it a small flask in which the anhydrous antimony trichloride may collect. Arrange the heating so that the liquid chloride drops from the side tube of the distilling flask and solidifies in the receiver. Preserve the product in a bottle or tube so that atmospheric moisture does not reach it. Antimony trichloride is soluble in benzene and carbon disulphide—in which truly metallic chlorides are quite insoluble—and separates from these solvents in shining rhombic crystals. Because it is soft this compound is sometimes called butter of antimony; it melts at 73° C. and boils at 223° C.

25. Stannic Chloride, $SnCl_4$: Ammonium Stannichloride, $(NH_4)_2SnCl_6$

Stannic Chloride.

Tin forms two chlorides, $SnCl_2$ and $SnCl_4$. The dichloride is produced in solution when the metal is dissolved in hydrochloric acid; the tetrachloride similarly when *aqua regia* is employed, i.e. when enough nitric acid is present to liberate chlorine from hydrochloric acid, so that the metal may be fully chlorinated, but not enough to convert the tin into metastannic acid. Anhydrous stannic chloride is obtained, however, by the direct action of chlorine on the element. It is a liquid, as becomes the higher chloride of a metalloid, and it can be freed from dissolved chlorine by being distilled in contact with tin-foil. Evidently, then, quadrivalent tin is not easily reducible to the bivalent state; and, conversely, bivalent tin is a powerful reducing agent, being easily oxidized to the quadrivalent state.

Preparation.

Requirements: Granulated tin, 20 gm.
Tin-foil.
Chlorine gas.

Select a piece of wide combustion tubing about 75 cm. long, or employ the inner tube of a condenser. Pass one end of this tube through a bored cork, which fits tightly into the neck of a suction flask, and attach to the side tube of this flask a small calcium chloride tube to exclude atmospheric moisture. See that tube and flask are quite dry; also dry the granulated tin in the air oven. Then place the tin in the tube, keeping it in position at both ends with loose plugs of asbestos; and close the upper end of the tube with a cork carrying a tube for the entrance of chlorine. Fix the tube in an oblique position so that the stannic chloride which is formed may run down into the flask.

Prepare chlorine; pass it through wash bottles containing water and concentrated sulphuric acid to wash and then dry the gas before leading it over the tin. Gently warm at its upper end the tube containing the tin, and when the reaction starts allow it to continue without further heating. The stannic chloride, coloured yellow by dissolved chlorine, will collect in the receiver, while the tin disappears from the tube.

When all the tin has been converted into stannic chloride which has thus been collected in the flask, drop in some pellets of tin-foil, and after tightly corking the flask, allow the liquid to stand in contact with the tin overnight, so that all the free chlorine may be absorbed and converted into stannic chloride. If after this time the tin has all disappeared, add more until excess of tin remains after long standing. Then transfer the stannic chloride to a distilling flask provided with a fractionating column, leading to a water condenser, and collect the liquid boiling between 112° C. and 114° C.

Transfer most of the distillate to a dry boiling tube; then draw out and seal the tube. With the remainder perform the following experiments:

(i) Mix a little stannic chloride with an equal volume of water, and stir. A crystalline solid is formed which consists of one or more of several existing crystallohydrates, e.g. $SnCl_4 \cdot 5H_2O$.

(ii) Add a few drops of stannic chloride to excess of water. A clear solution is formed, which, however, is acid in reaction; on boiling the solution hydrolysis is shown by the separation of a precipitate of α-metastannic acid.

Ammonium Stannichloride.

A solution of tin in aqua regia contains hexachlorostannic acid, just as a solution of platinum in the same solvent contains hexachloroplatinic acid. Moreover, there is marked resemblance not only between these two acids, but also between their alkali salts. Consequently ammonium hexachlorostannate, or stannichloride, is obtained by adding the necessary quantity of ammonium chloride to a solution of tin in aqua regia, and causing crystallization to take place.

Preparation.

Requirements: Granulated tin, 10 gm.
Ammonium chloride, 9 gm.
Concentrated hydrochloric and nitric acids.

Place the tin in a flask and warm it with concentrated hydrochloric acid until the metal begins to dissolve, displacing hydrogen. Then add nitric acid in sufficient quantity to oxidize the tin to the stannic state. When the metal has dissolved, test a few drops of the solution with mercuric chloride. If a white precipitate forms stannous tin is present, and a little more nitric acid must be added to oxidize it. Filter the stannic solution, then dissolve the ammonium chloride in a small quantity of hot water; mix the solutions and evaporate until on cooling ammonium stannichloride crystallizes from the liquid. Filter the crystalline powder with suction, wash it with a little concentrated hydrochloric acid, and dry it on a piece of porous plate over sulphuric acid in a desiccator. Ammonium stannichloride is readily soluble in cold water, but is hydrolyzed in boiling dilute solution. This compound was formerly used by dyers under the name of *pink salt* as a mordant for madder-red colours.

26. Sulphur Chloride, S_2Cl_2

Sulphur forms one stable chloride, which can be distilled, and from its vapour density is proved to be S_2Cl_2. Other chlorides, SCl_2 and SCl_4, are unstable. SCl_4 existing only at low temperature. S_2Br_2 exists, but no iodide is known. Fluorine forms, in addition to S_2F_2 and SF_4, the gaseous hexafluoride SF_6; this is one example of the great chemical difference between fluorine and chlorine, which modern theories are now explaining.

Preparation.

Requirements: Sulphur, coarsely powdered, 25 gm.
Chlorine gas.

Place in a suitable retort 25 gm. of coarsely powdered sulphur, and close the tubulure of the retort with a well-fitting cork through which passes a bent tube to lead chlorine on to the surface of the molten sulphur.

Attach to the neck of the retort a globular receiver which can be cooled by water. A convenient way to employ the water is to fix above the receiver a glass tube, connected by rubber tubing with the tap, and beneath it a funnel by which the water is led away through a rubber tube to the sink. An alternative way of condensing the sulphur chloride vapour is to employ a water-cooled condenser leading to a receiving flask. In either case arrange a tube to lead away the excess of chlorine. Fix the retort on a sand bath or gauze, and gradually apply heat to melt the sulphur. Lead a current of dry chlorine beneath the surface of the sulphur kept molten, and thoroughly cool the receiver to condense the distillate. When all the sulphur has been converted into chloride, add a few grams of flowers of sulphur to the liquid, which may combine with any free chlorine present; then redistil the product, using a fractionating column, but taking great care that all the apparatus is dry. Sulphur chloride boils at 138° to 140° C.; it is a pale yellow liquid with a pungent odour, and is decomposed by water thus:

$$2S_2Cl_2 + 3H_2O = H_2SO_3 + 4HCl + 3S.$$

Thus S_2Cl_2 yields the acid corresponding to SCl_4, with liberation of the excess of sulphur. To preserve your specimen seal it up in a boiling tube.

27. Hydrobromic Acid

Hydrogen bromide cannot be obtained pure by the action of sulphuric acid on a bromide because when liberated it is oxidized, more or less, by the sulphuric acid to bromine and water. It can be obtained free from bromine by the substitution of phosphoric for sulphuric acid, and may also be prepared by direct synthesis from its elements; but the usual method of preparation is by dropping bromine on to a mixture of red phosphorus and water, when phosphorus tribromide is formed and hydrolyzed thus:

$$\left.\begin{aligned} 2P + 3Br_2 &= 2PBr_3 \\ 2PBr_3 + 6H_2O &= 2H_3PO_3 + 6HBr \end{aligned}\right\}.$$

The hydrogen bromide gas, freed from accompanying bromine vapour by passage through moist red phosphorus, is then conveyed into water, in which it very readily dissolves, forming a colourless solution of hydrobromic acid. According to Scott,* however, the acid thus obtained is liable to contain traces of arsenic compounds derived from this element present in the phosphorus, so that it is better to prepare hydrobromic acid by the interaction of bromine, sulphur dioxide, and water, thus:

$$Br_2 + SO_2 + 2H_2O = 2HBr + H_2SO_4,$$

the hydrobromic acid being subsequently separated from the sulphuric acid by distillation. Both methods will be described here.

Preparation *from Bromine, Red Phosphorus, and Water.*

Requirements: Red phosphorus, 5 gm., and some in U-tube.
Bromine, 40 gm.
Water; sand.

Fit up the apparatus shown in fig. 8. This consists of a 250-c. c. distilling flask provided with a tap funnel of about 100 c. c. capacity, which passes through a cork fitting tightly into the neck of the flask. The delivery tube of the flask, bent vertically downwards at its end, is connected with a U-tube furnished with well-fitting corks. The U-tube is to contain glass beads mixed with red phosphorus and moistened with water. From the U-tube there passes a bent glass tube connected with a bulb tube which may be a 20-c. c. pipette, as shown; the bulb is to prevent liquid being drawn back from the receiving flask into the U-tube, and the lower end of the bulb tube is made just to touch the surface of 50 c. c. of water in the receiving flask.

When all is ready, place a little sand in the distilling flask, and the red phosphorus, and shake the two solids together. Then add to the mixture 10 c. c. of water, and fit the cork carrying the tap funnel into the neck of the flask. Measure 13 c. c. of bromine,†

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* *Trans. Chem. Soc.*, 1900, **77**, 648.

† The density of liquid bromine at atmospheric temperature is about 3·1. Take care in measuring this dangerous liquid not to let any of it come into contact with the hands, nor to allow the vapour to come near the eyes. The whole experiment, including the measuring of the bromine, must be done in a fume chamber with the window shut down as low as possible, and the measuring-glass, and funnel if one was used, washed at once after use.

and pour it into the tap funnel. Surround the U-tube with a freezing mixture contained in a beaker, and stand the receiving flask in ice-water.

Add the bromine carefully, drop by drop, to the mixture in the distilling flask. A vigorous reaction occurs, and torrents of hydrogen bromide gas are evolved, accompanied by bromine. The colour of the bromine disappears, however, as the vapour passes through the U-tube containing the red phosphorus, so that colourless hydrogen bromide passes forward and dissolves in the water in the receiver. The reaction, vigorous at first, may be regulated, either by cooling the flask in water, or by applying gentle heat. When the reaction is at an end, transfer the hydrobromic acid solution to a distilling flask and distil it. Observe that the temperature rises to 125°–126° C. at a pressure of 760 mm., and remains constant whilst the remainder of the liquid distils. Collect this constant boiling fraction, and take its density. This should be 1·47 at 15° C., corresponding with a solution containing 47 to 48 per cent of hydrogen bromide. Test the solution to find if it contains a trace of arsenic.

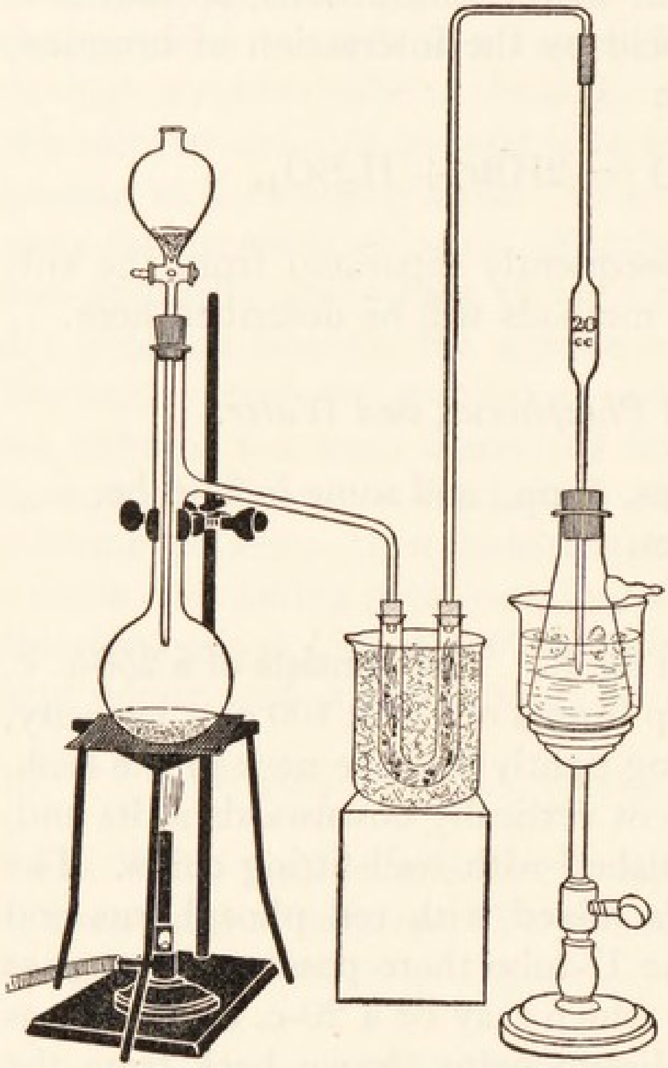

Fig. 8

Preparation *from Bromine, Sulphur Dioxide, and Water.*

Pass a glass tube, bent at right angles, through a cork that fits the neck of a 500-c. c. distilling flask, so that the tube reaches nearly to the bottom of the flask. Connect the flask with a condenser, and place in it 35 gm. of bromine and 200 c. c. of water. Lead sulphur dioxide from a siphon into the water in the flask having the end of the delivery tube about 1 cm. above the surface of the bromine. Pass the gas till all the bromine has disappeared, and a pale yellow liquid results. Do not allow the liquid to become colourless or it will contain sulphurous acid. If, however, too much gas has been passed, add bromine or bromine water, until a permanent yellow colour appears.

Now remove the cork and delivery tube, and replace them by a cork carrying a thermometer whose bulb hangs low in the neck of the flask. Fix at the end of the condenser a receiver; place a few pieces of broken porous plate in the liquid to prevent bumping, and distil, collecting the constant boiling fraction as before. Test the liquid for sulphate, and if this is found add a little barium hydroxide and redistil.

SPECIFIC GRAVITIES AND CONCENTRATIONS OF HYDROBROMIC ACID SOLUTIONS AT 15° C.

Specific Gravity.	Percentage HBr.	Specific Gravity.	Percentage HBr.
1·080	10·4	1·385	40·8
1·190	23·5	1·475	48·5
1·248	30·0	1·515	49·8

28. Phosphonium Iodide, PH_4I

Phosphonium iodide, PH_4I, and ammonium iodide, NH_4I, are plainly analogous compounds, but their chemical relationships are not close. Ammonia is decidedly basic, and forms with acids salts which are very slightly hydrolyzed by water; phosphine is scarcely at all basic, and its salts cannot be formed or exist in presence of water, which hydrolyzes them. Phosphonium iodide seems to be the only phosphonium salt which is formed at atmospheric pressure, and it is prepared by a complex reaction between phosphorus, iodine, and water, which is represented thus:

$$9P + 5I + 16H_2O = 5PH_4I + 4H_3PO_4.$$

The reaction is carried out by dissolving white phosphorus and iodine together in carbon disulphide, the proportion of phosphorus being rather in excess of that indicated by the equation, evaporating off the solvent so as to leave the elements together in a finely divided state, and then slowly dropping on to the mixture rather less than the indicated amount of water. Air must be excluded by carbon dioxide; and phosphonium iodide distils and condenses as a crystalline sublimate in the cooler part of the apparatus.

Preparation.

Requirements: White phosphorus, 25 gm.
Carbon disulphide, 20 gm.
Iodine, resublimed, 43 gm.
Water, 21 c. c.
Carbon dioxide.

Assemble the apparatus shown in the figure, and have in addition a dry condenser which can be attached to the neck of the retort. Close the tubulure of the retort by a doubly bored cork, through one hole of which passes a tap funnel for the delivery of water, and through the other a glass tube bent at right angles by which dry carbon dioxide gas can be passed into the body of the retort. Also have ready an unbored cork which fits the retort exactly. Prepare

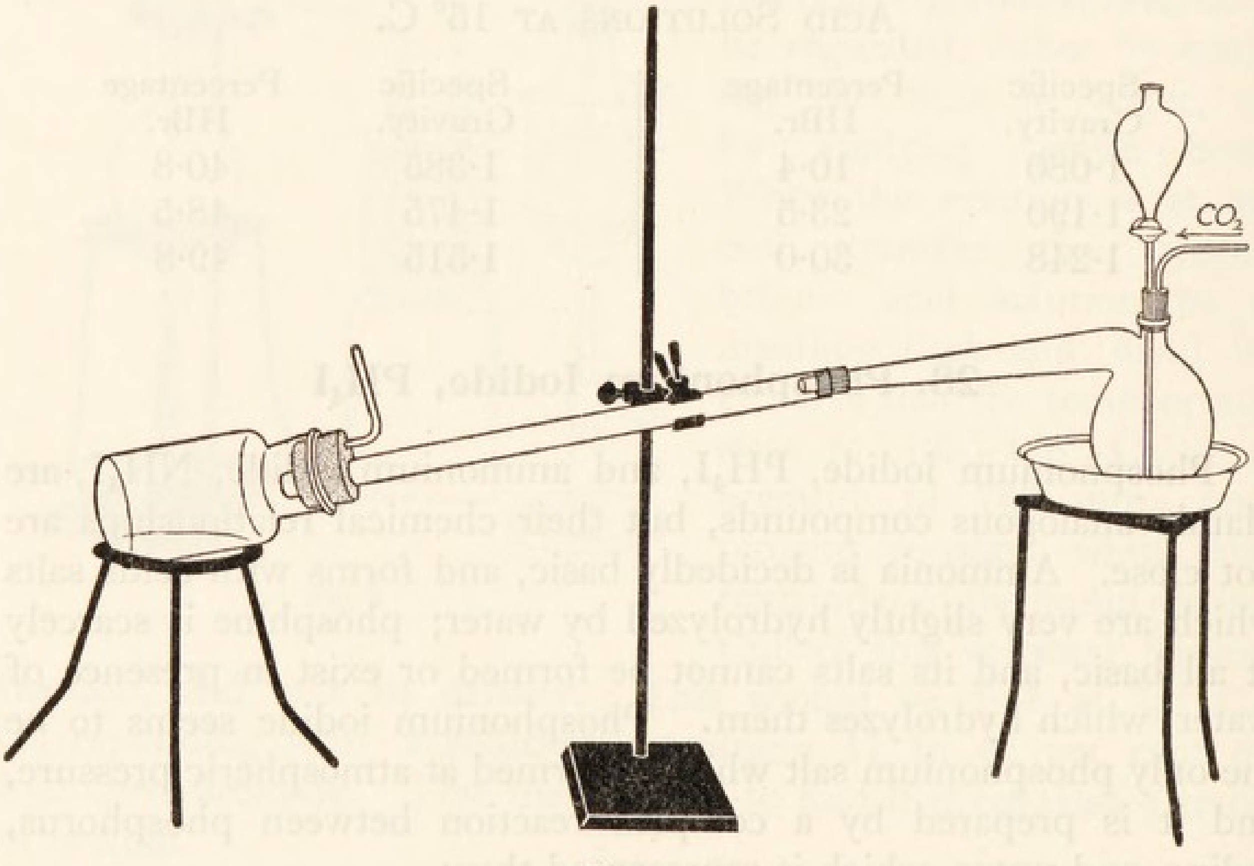

Fig. 9

a piece of glass tubing, from 30 to 40 cm. long, and a little wider than the end of the retort neck; fit a bored cork at one end of this tube, through which the neck of the retort can pass, and lead the other end through a cork which closes a wide-necked bottle; also pass through a second hole in this cork a tube to lead away carbon dioxide, and any escaping hydriodic acid produced by the decomposition of some of the phosphonium iodide.

Cut up the phosphorus under water; take hold of each piece with tongs, dry it on filter paper, and carefully drop it into the retort; then add the carbon disulphide, followed by the iodine. Close the tubulure of the retort with the unbored cork, fix on the water condenser, with a suitable receiver, and distil off the carbon disulphide (B.P. 46° C.) by immersing the retort in a dish of hot water. Be very careful not to have a flame near the carbon disulphide, which is very inflammable. When the carbon disulphide has been removed, leaving a dry finely divided mass, exchange the solid cork for the cork carrying the tap funnel (empty) and the tube for delivering carbon dioxide. As quickly as possible pass in the carbon dioxide, previously dried by passage through concentrated sulphuric acid in a wash bottle. Fit on the tube and bottle for condensing the phosphonium iodide, put the water in the dropping funnel, and add it very slowly, a drop at a time, to the mass in the retort. A vigorous reaction occurs, and phosphonium iodide vaporizes and begins to condense in the tube and bottle. If the reaction becomes sluggish towards the end, heat may be applied by immersing the retort in hot water.

To preserve the phosphonium iodide, transfer it to a bottle with a closely fitting stopper. Good crystals may, however, have formed on the walls of the tube. If so, it is well not to remove them, but to preserve them *in situ* by drawing out the tube and sealing it at each end. Phosphonium iodide crystallizes in brilliant quadratic prisms; thus it is not isomorphous with ammonium iodide. It is quickly decomposed by water into phosphine and hydriodic acid.

IV—DOUBLE AND COMPLEX SALTS

Introduction.

It has been customary to represent the structure of a salt such as ferrous sulphate, $FeSO_4$, in a quite definite way by means of bonds, standing for units of valency. When, however, it is considered that seven molecules of water are united chemically with this salt in green vitriol, there is a difficulty in representing structure, and in realizing the nature of the chemical forces of union between the salt and water. The assumption of the quadrivalency of oxygen, or of the existence of residual affinity has been made; these assumptions are not of much intrinsic value, but the modern electronic theory of valency is giving definiteness to our ideas, and is likely in time to furnish a clear mental picture of the structure of saline compounds.

The salt $FeSO_4{\cdot}7H_2O$ is, however, related to the double salt $FeSO_4{\cdot}(NH_4)_2SO_4{\cdot}6H_2O$, since, as Graham showed, one molecule of water in the heptahydrate is differently united from the other six, and is replaceable by a molecule of alkali sulphate thus:

$$FeSO_4{\cdot}H_2O{\cdot}6H_2O; \quad FeSO_4{\cdot}(NH_4)_2SO_4{\cdot}6H_2O.$$

Ammonium ferrous sulphate, or potassium ferrous sulphate, is said to be a double salt, whilst potassium ferrous cyanide is called potassium ferrocyanide, and regarded as a complex salt thus:

$$Fe(CN)_2 + 4KCN \rightarrow K_4[Fe(CN)_6].$$

It is useful, therefore, to ask why potassium ferrous sulphate is not called potassium ferrosulphate, and similarly formulated:

$$FeSO_4 + K_2SO_4 \rightarrow K_2[Fe(SO_4)_2].$$

The answer is that potassium ferrous sulphate behaves in solution as a mixture of potassium sulphate and ferrous sulphate, whilst potassium ferrocyanide behaves quite differently from potassium cyanide and ferrous cyanide. The behaviour of the latter salt shows that in its case the two single salts have entered permanently into a compact union with the production of a stable complex ion, the ferrocyanide ion.

Now concerning solid potassium ferrous sulphate, since it is recognized that ions of the compound parts of a salt exist in the solid state, it is impossible to say that the formula

$$K_2SO_4 \cdot FeSO_4 \cdot 6H_2O$$

is truer than the formula

$$K_2[Fe(SO_4)_2] \cdot 6H_2O.$$

Indeed the fact that the double ferrous sulphates are of a paler green than ferrous sulphate itself, and that the colour is the same whatever alkali metal is present, is some evidence to show that a common complex ion exists in all these salts. There is evidence, even, of the existence of complex ions in solution in the case of the so-called double salts, so that the difference between double and complex salts appears to be one of degree rather than kind.

In the case of complex salts the complex ions predominate to such an extent that they alone ordinarily show evidence of their existence; whilst in the case of double salts dissociation of the existing complex ions is very extensive, and becomes complete in the course of a chemical analysis; so that there is ordinarily no evidence of the existence of these ions.

Another fact, which is generally regarded as distinguishing complex from double salts, is that during the formation of a complex salt the less soluble of the two component salts is dissolved by the addition of the more soluble salt to a much larger extent than it is dissolved by water alone. Thus silver cyanide, $AgCN$, which is soluble in water to a minute extent only, is quickly dissolved by a solution of potassium cyanide, KCN, owing to the formation of the salt $KAg(CN)_2$ containing the complex anion $[Ag(CN)_2]''$. This again is a difference in degree rather than in kind, for cupric sulphate is more soluble in a solution of potassium sulphate previous to the crystallization of the double salt than it is in water.

Whilst molecules of water of crystallization are exchangeable for molecules of alkali salts in the formation of certain double salts, these same molecules are also exchangeable for molecules of ammonia in the formation of ammoniates which are thus analogous to hydrates.

Examples are:

$$CuSO_4 \cdot H_2O \cdot 4H_2O \text{ and } CuSO_4 \cdot H_2O \cdot 4NH_3.$$

There is, however, another class of ammoniacal compounds, which are formed by cobalt and other metals in or in the vicinity of the eighth group of the periodic system, in which the ammonia molecules, although exchangeable for water molecules, seem to be more intimately associated with the metal in a complex ion than is the case in the so-called ammoniates. These compounds are called ammines, and examples of them are:

$[Co(NH_3)_6]Cl_3$	and	$[Co(NH_3)_5H_2O]Cl_3$.
Hexammine cobaltic chloride		Aquopentammine cobaltic chloride

Moreover, other complex salts related to these are:

$[Co(CN)_6]K_3$ and $[Co(NO_2)_6]K_3$.

Concerning the relationships between these salts, however, the theoretical textbooks must be consulted.

The double and complex salts which follow are chosen to illustrate the principles of which the above is a brief outline.

29. Potassium Cupric Sulphate

$K_2SO_4 \cdot CuSO_4 \cdot 6H_2O$ or $K_2[Cu(SO_4)_2] \cdot 6H_2O$

Potassium cupric sulphate is easily prepared by mixing together the two component salts in aqueous solution, and crystallizing the product.

The question arises whether it is necessary to have the two salts present in equivalent proportions, or whether, if these proportions are much departed from, there is danger of obtaining a crystalline product which is a mixture of the double salt with that one of the two component salts which was present in the larger proportion.

The answer is that over a very wide range of proportion between the two salts nothing but the double salt crystallizes, either by cooling a concentrated solution, or by the evaporation at constant temperature of a more dilute solution. At 25°, for example, the double salt crystallizes from all solutions between the limits 7 : 1 and 1 : 8 for the ratios of cupric to potassium sulphate.

It is true that by isothermal evaporation of a solution in which a great disparity exists between the two component salts, one of the salts must necessarily crystallize when the solution, by the formation of double salt, is nearly exhausted of the other salt; this contingency, however, does not arise in ordinary cases of crystallization in which the process is intercepted when equilibrium at atmospheric temperature has been reached without evaporation necessarily taking place. Nevertheless, since it is easy to use equivalent proportions of the two component salts, it is as well in this case to do so.

Preparation.

Requirements: Cupric sulphate, $CuSO_4{\cdot}5H_2O$, 24 gm.
Potassium sulphate, K_2SO_4, 17·5 gm.

Dissolve the two salts separately in the smallest necessary quantities of hot water, mix the solutions, and crystallize either rapidly or slowly according to the size of the crystals desired. Filter the crystals with suction, and dry them on a porous plate or filter paper in the air.

It is noteworthy that crystals of $K_2SO_4{\cdot}Cu_2SO_4{\cdot}6H_2O$ contain a larger proportion of water than those of $CuSO_4{\cdot}5H_2O$; they may therefore be supposed to be derived from heptahydrated cupric sulphate, $CuSO_4{\cdot}H_2O{\cdot}6H_2O$, by the replacement of one molecule of water by K_2SO_4.

The crystals are lighter in colour than those of $CuSO_4{\cdot}5H_2O$, just as crystals of $K_2SO_4{\cdot}FeSO_4{\cdot}6H_2O$ are lighter in colour than those of $FeSO_4{\cdot}7H_2O$. The colour is a turquoise blue, reminiscent of the colour of glacier ice.

It is an interesting experiment to heat the crystals in an ignition tube or crucible. When the water has been driven off, the salt fuses but remains blue. Now anhydrous $CuSO_4$ is white, so that the blue colour is that of the anhydrous double salt, $K_2SO_4{\cdot}CuSO_4$, which has thus maintained its individuality during dehydration. Thence it is concluded that the six molecules of water in the hydrated salt surround $K_2SO_4{\cdot}Cu_2SO_4$ as a nucleus; and moreover the colour possessed by this nucleus when the surrounding water molecules are dispersed seems to justify the view that this substance is a complex salt, $K_2[Cu(SO_4)_2]$, the anion $[Cu(SO_4)_2]''$ being blue.

30. Microcosmic Salt, $NaNH_4HPO_4{\cdot}4H_2O$

Microcosmic salt is not generally thought of as a double salt, yet it may be regarded as such since it can be prepared by the combination of disodium hydrogen phosphate and diammonium hydrogen phosphate thus:

$$Na_2HPO_4 + (NH_4)_2HPO_4 + 8H_2O = 2[NaNH_4HPO_4{\cdot}4H_2O].$$

This method of preparation is to be preferred to the more usual one of bringing about interaction between disodium hydrogen phosphate and ammonium chloride thus:

$$Na_2HPO_4 + NH_4Cl = NaNH_4HPO_4 + NaCl,$$

since it introduces no extraneous matter, and there is no by-product.

Preparation.

Requirements: Crystallized sodium phosphate, $Na_2HPO_4{\cdot}12H_2O$, 36 gm.
Ammonium phosphate, $(NH_4)_2HPO_4$, 13 gm.

Dissolve the salts separately in the least quantities of boiling water necessary. Filter the solutions if they require it; then mix them, cool, and crystallize. Filter off the crystals by suction and dry them on a porous plate in the air. A further crop of crystals may be obtained by evaporating the mother liquor.

The purity of the product can be proved by igniting a weighed quantity of the dried salt in a crucible and estimating the loss of weight, the residue being sodium trimetaphosphate, $(NaPO_3)_3$.

31. Potassium Mercuric Iodide, $K_2HgI_4{\cdot}2H_2O$

The formation of potassium mercuric iodide as a complex salt is shown by the following simple and well-known experiment.

To a solution of mercuric chloride add potassium iodide solution little by little. Mercuric iodide is formed first as a yellow precipitate, which quickly becomes pale red. The red colour deepens as more potassium iodide is added, until after a certain point the precipitate grows less in bulk, and finally dissolves completely, forming a very pale yellow solution. As in other cases, the change in solubility of the mercuric iodide at a certain point marks the beginning of a complex salt formation. Moreover, the stability of the complex salt formed in this case is shown by the fact that alkali does not precipitate mercuric oxide from its solution but converts this into Nessler's reagent for detecting minute quantities of ammonia.

Preparation.

Requirements: Mercuric chloride, 6·8 gm.
Potassium iodide, 8·3 + 7·8 gm.

There are two complex mercuric iodides, $KHgI_3$ and K_2HgI_4. The preparation of the latter compound may be carried out in the following way.

Dissolve 6·8 gm. of mercuric chloride and 8·3 gm. of potassium iodide separately in water, and mix the solutions; scarlet mercuric iodide is precipitated. Filter off this precipitate and wash it with hot water so as to remove potassium chloride. Now dissolve 7·8 gm. of potassium iodide in about 10 c. c. of water, and heat the precipitate with the solution so as to dissolve all but a little of the mercuric iodide. Filter the pale yellow solution; receive it in a crystallizing dish, and place this in a desiccator over sulphuric acid. As the water evaporates, lemon-yellow prismatic crystals of the double salt will make their appearance. Allow evaporation and crystallization to proceed until only a little mother liquor remains. Then filter off the crystals, and, without washing, dry them on a porous plate and preserve them.

Potassium mercuric iodide or mercuri-iodide, $K_2HgI_4 \cdot 2H_2O$, is decomposed by water with separation of red mercuric iodide, i.e. the mercuri-iodide ion $(HgI_4)''$ is stable only in presence of iodide ions.

32. Potassium Cobaltinitrite, $K_3[Co(NO_2)_6]$
(Fischer's Yellow)

Potassium cobaltinitrite is evidently related in type to potassium ferricyanide, $K_3[Fe(CN)_6]$, to which also potassium cobalticyanide, $K_3[Co(CN)_6]$, formed in solution in the qualitative separation of cobalt from nickel, is closely related. This salt is thus a cobaltic compound, a derivative of trivalent cobalt. Now although cobalt does not readily form simple salts in which it is trivalent, i.e. in which the trivalent cobalt ion exists alone, it forms many compounds in which cobalt in this state is part of a complex ion, and in which the metal is united to either basic or acidic groups. Prominent among the complex compounds containing basic groups are the celebrated cobaltammines, of which luteocobaltic chloride, $[\mathrm{Co}^{\cdots}(\mathrm{NH_3})_6\mathrm{Cl_3}]$, is the simplest example. The compounds $[\mathrm{Co}^{\cdots}(\mathrm{NH_3})_6]\mathrm{Cl_3}$ and $\mathrm{K_3}[\mathrm{Co}^{\cdots}(\mathrm{NO_2})_6]$ are two extreme members of a series containing intermediate members in which the complex group containing the metal passes from basic through neutral to acidic properties.

Potassium cobaltinitrite is obtained as a yellow precipitate when potassium nitrite is added to a solution of cobaltous chloride in presence of acetic acid. Nitrous acid oxidizes cobalt from the cobaltous to the cobaltic state, being thereby reduced to nitric oxide, and the cobaltic nitrite thus resulting unites with potassium nitrite to form the sparingly soluble complex salt, thus:

$$\begin{aligned}
&\mathrm{CoCl_2} + 2\mathrm{KNO_2} \rightleftharpoons \mathrm{Co(NO_2)_2} + 2\mathrm{KCl}\\
&\mathrm{Co(NO_2)_2} + 2\mathrm{HNO_2} \rightleftharpoons \mathrm{Co(NO_2)_3} + \mathrm{H_2O} + \mathrm{NO}.\\
&\mathrm{Co(NO_2)_3} + 3\mathrm{KNO_2} \rightarrow \mathrm{K_3Co(NO_2)_6}.
\end{aligned}$$

Preparation.

Requirements: Crystallized cobaltous chloride, 12 gm.
Potassium nitrite, 26 gm.
Dilute acetic acid (2N).

Dissolve the cobalt chloride in 25 c. c. of water, and the potassium nitrite in 10 c. c. If the solutions are not quite clear, filter them. Place the cobalt chloride solution in a suitable beaker, and acidify it with 85 c. c. of dilute acetic acid (2N). To this solution add the nitrite solution with stirring. The solution will gradually change in colour from pink to orange, and become turbid as the complex salt begins to separate from the liquid. Cover the beaker with a clock glass and set it aside in a cool place for some hours. When the separation of the yellow crystalline precipitate appears to be complete, filter it with suction; wash first with a solution of potassium acetate, then with 80 per cent alcohol, and dry it on a porous plate in the air.

The salt, which is dark yellow in colour, may contain from 1 to 4 molecules of water of crystallization, according to the concentration of the solution from which it has crystallized.

33. Cuprammonium Sulphate, $CuSO_4 \cdot H_2O \cdot 4NH_3$ or $[Cu(NH_3)_4]SO_4 \cdot H_2O$

It is well known that when ammonia is added to a solution of upric sulphate, there is formed first a greenish blue precipitate, nd then as this precipitate dissolves in excess of the ammonia a eep blue solution. The addition of alcohol to this solution causes he separation of a deep blue crystalline solid which has the composition $CuSO_4 \cdot H_2O \cdot 4NH_3$, in which it appears that four molecules f ammonia take the place of four of water. The blue solution has een shown, however, to contain the cation $[Cu(NH_3)_4]^{\cdot\cdot}$ in which our molecules of ammonia are intimately associated with the metal. he compound is therefore known as cuprammonium sulphate, and formulated thus:

$$[Cu(NH_3)_4]SO_4 \cdot H_2O.$$

reparation.

Requirements: Cupric sulphate, $CuSO_4 \cdot 5H_2O$, 10 gm.
Concentrated ammonia solution.
Alcohol.

Dissolve the copper sulphate in 60 c. c. of hot water, and cool he solution to atmospheric temperature, filtering it if necessary. dd to the solution contained in a beaker strongest ammonia, drop y drop, until the precipitate at first formed dissolves in the excess f ammonia, giving a deep blue solution. Then add another cubic entimetre of ammonia, followed by alcohol, until a permanent lue precipitate begins to form. Warm the solution on the water ath, adding more alcohol, if this can be done without causing recipitation; then allow the clear, deep blue solution to cool, and o stand at atmospheric temperature as long as crystallization connues. Cuprammonium sulphate separates in fine, deep blue prisms. rain the solution from the crystals; then dry the crystals on a orous plate or filter paper in the air. Do not, however, leave them xposed longer than necessary, since they easily lose ammonia. reserve the crystals in a closely stoppered bottle or a sealed glass ube. The salt can be analysed by decomposing it with alkali and bsorbing the ammonia in excess of standard acid.

34. Hexammine-nickelous Bromide, $[Ni(NH_3)_6]Br_2$

When concentrated ammonia is added to a strong solution of nickelous bromide at low temperature, a pale violet crystalline precipitate of hexammine-nickelous bromide falls.

The formation of this ammine serves to separate nickel from cobalt, which does not form an insoluble ammine of this kind. It may be observed that this compound differs from the well-known cobaltammines, inasmuch as the complex containing the metal is dibasic, i.e. it is a nickelous compound in contradistinction from the cobaltammines which are cobaltic compounds, e.g. $[Co(NH_3)_6]Cl_3$.

Preparation.

Requirements: Crystallized nickel sulphate, 28 gm.
Sodium hydroxide, 8 gm.
Hydrobromic acid: a solution containing 16 gm. HBr.
Ammonia, ·880 specific gravity.

Since nickelous bromide is not generally available it must first be prepared. Dissolve the nickel sulphate and sodium hydroxide separately, each in about 400 c. c. of water. Heat the solutions and mix them hot in a large beaker. Stir the mixture well, and allow it to stand on the water bath till the light green precipitate has subsided. Siphon or decant off most of the supernatant clear liquid, add 1 litre of hot water, again stir, and allow to settle. Again remove most of the supernatant wash water; stir the precipitate with more hot water, and filter it off through a Büchner funnel. Then wash the precipitate on the filter till it is almost or completely free from alkali.

Ascertain the density of some hydrobromic acid—that obtained in preparation No. 27 will serve—and having found its strength from tables measure a volume of the solution containing 16 gm. of hydrogen bromide. Dissolve the nickelous hydroxide in this acid, filter the solution, and evaporate it to dryness on the water bath. Dissolve the residue in a little water, and again filter if necessary. Have the solution in a small beaker, and cool it in a freezing mixture. Then add to the cold solution concentrated ammonia with stirring. The ammine is precipitated at once, and when precipitation is complete filter off the product with suction, and wash it with a little concentrated ammonia which has been cooled in ice.

Dry the product in a desiccator over quicklime. It is well to add a little ammonium chloride to the quicklime to produce an atmosphere containing dry ammonia, as this ammine, like that of copper sulphate, but unlike the cobaltammines, is liable to give off ammonia into an ammonia-free atmosphere. Such rather unstable ammines are sometimes called ammoniates.

Weigh the product and calculate the percentage yield.

This compound is soluble in hot, moderately concentrated ammonia solution, but separates from the solution again on cooling. When heated gently it evolves ammonia.

35. Chloropentammine-cobaltic Chloride (Purpureo-cobaltic Chloride), $[Co(NH_3)_5Cl]Cl_2$

When a current of air is passed through a mixture of cobaltous chloride solution with ammonia, the basic chloride which has been precipitated by the ammonia dissolves, forming a brown solution which contains aquopentammine-cobaltic chloride (roseo-cobaltic chloride), $[Co(NH_3)_5{\cdot}H_2O]Cl_3$.

If ammonium chloride also is present, a molecule of ammonia takes the place of the molecule of water, hexammine-cobaltic chloride (luteo-cobaltic chloride), $[Co(NH_3)_6]Cl_3$, being formed.

These compounds, however, appear to be stable in solution only at atmospheric temperature. On heating, an ammonia or water molecule is displaced from the basic complex by an atom of chlorine with the production of chloropentammine-cobaltic chloride, $[Co(NH_3)_5Cl]Cl_2$.

This compound, which forms purplish red rhombic crystals, and is therefore known as purpureo-cobaltic chloride, is so formulated because only two-thirds of the chlorine present is precipitated from cold aqueous solution by silver nitrate, the remaining one-third being present in a non-ionized condition in the basic complex containing the cobalt atom.

In the following preparation, which is due to Sörensen,* the

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* *Zeitsch. anorg. Chem.*, 1894, **5**, 369.

presence of ammonium carbonate causes the formation of some carbonatotetrammine-cobaltic chloride $[Co(NH_3)_4CO_3]Cl$; but this compound disappears in the subsequent treatment, so that the pentammine compound is readily obtained pure.

Preparation.

Requirements: Crystallized cobaltous chloride, 20 gm.
Concentrated ammonia solution, 125 c. c.
Ammonium carbonate, 25 gm.
Ammonium chloride, 75 gm.
Concentrated hydrochloric acid.

Dissolve the cobalt chloride in a sufficiency of cold water, filter the solution if necessary, then add to it a solution of 125 c. c. concentrated ammonia (specfic gravity 0·880) and 25 gm. of ammonium carbonate in 125 c. c. of water. Now pass through the liquid a brisk current of air for about two hours, to oxidize the cobalt, and bring it into solution as an ammine. At the end of this time place the product in a porcelain dish, dissolve in it 75 gm. of ammonium chloride, and heat on the water bath for several hours. Then add dilute hydrochloric acid to decompose the carbonate still present, and make the solution faintly acid, followed by ammonia till the liquid again becomes alkaline. Stir well, and heat on the water bath for another hour; then add 150 c. c. of concentrated hydrochloric acid and continue heating for another half-hour. Allow the solution to cool, when the pentammine salt will crystallize. Filter off the product, and after draining, recrystallize some of it by dissolving it in sufficient 2 per cent solution of ammonia without heating.* Filter if necessary, and add excess of concentrated hydrochloric acid to reprecipitate the ammine. Filter with suction, wash with concentrated hydrochloric acid, and dry over sulphuric acid in a desiccator.

Estimate the percentage yield.

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* If the ammine is heated with ammonia a change occurs, the solution becomes redder, and the product is not precipitated by hydrochloric acid.

36. Sodium Nitroprusside, $Na_2[Fe(CN)_5NO]\cdot 2H_2O$

Sodium nitroprusside must be regarded as a derivative of sodium ferricyanide.

According to the principles underlying the chemistry of ammines and related compounds, the valency of a basic complex is reduced from its maximum by a number equal to that of the acidic radicles taking the place of basic groups within the complex.

Thus $[Co^{\cdots}(NH_3)_6]Cl_3$ gives rise to $[Co^{\cdots}(NH_3)_5Cl]Cl_2$.

Also the reciprocal relation holds good that the valency of an acidic complex is reduced by a number equal to that of the basic groups which have displaced acidic radicles in that complex.

Thus $[Fe^{\cdots}(CN)_6]Na_3$ gives rise to $[Fe^{\cdots}(CN)_5NH_3]Na_2$.

If NH_3 in the latter compound is exchanged for NO, sodium nitroprusside, $[Fe^{\cdots}(CN)_5NO]Na_2$, results; thus it appears that the group NO functions in this compound as basic group.

Sodium nitroprusside is obtained from sodium ferrocyanide by first oxidizing it to ferricyanide, and then causing NaCN to be exchanged for NO. This is effected by the action of moderately concentrated nitric acid on the salt; the reaction, however, is complex, for not only are hydrogen cyanide and cyanogen evolved, but also carbon dioxide and nitrogen, by the oxidation of cyanogen.

In practice it is convenient to make potassium ferrocyanide the starting-point in the preparation of this compound; to add sodium carbonate to produce sodium nitroprusside which is less soluble than the potassium salt, and to separate this by fractional crystallization from sodium and potassium nitrates which are also formed.

Preparation.

Requirements: Potassium ferrocyanide (finely powdered), 20 gm.
Concentrated nitric acid (1·42 specific gravity), 40 gm. (28 c. c.).
Sodium carbonate, anhydrous.

Dilute the acid with an equal volume of water in a suitable flask, and add the potassium ferrocyanide a little at a time with shaking. Conduct this operation in a fume chamber with a good draught, because the gases evolved are poisonous.

After adding all the ferrocyanide, heat the flask and contents on the water bath until a few drops of the liquid give no precipitate with a drop of ferric chloride solution. Leave the flask to stand overnight, then filter off through glass wool the potassium nitrate crystals which will have separated. Next neutralize the solution with sodium carbonate, added solid in small portions at a time, heating the liquid when it is near the neutral point so as to drive off carbon dioxide gas and hasten the action. Take care that the sodium carbonate is added only just in excess; then filter off if necessary, and evaporate the dark red filtrate on the water bath until crystals of sodium nitroprusside separate. Filter hot from these crystals which are the main crop, evaporate the filtrate to a small volume and set it aside to crystallize slowly. From the mixture of red crystals of sodium nitroprusside and colourless crystals of sodium and potassium nitrates pick out the nitroprusside with forceps, and add them to the main quantity of this salt. Then dissolve the whole in a little hot water, filter, and receive the filtrate in a dish or crystallizing basin. Allow this solution to stand over sulphuric acid in a desiccator, so as to promote the growth of fine separate crystals of the salt. Protect the compound from the light as much as possible during its preparation, since its solution is easily decomposed thereby.

Sodium nitroprusside is used as a test for alkaline sulphide, though not for hydrogen sulphide. Add one drop of yellow ammonium sulphide to some water in a test-tube, and then a few drops of dilute nitroprusside solution: a beautiful purple colour will gradually develop.

APPENDIX

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

Temperature, Deg. Centigrade.	Pressure in Mm. Hg.	Temperature, Deg. Centigrade.	Pressure in Mm. Hg.	Temperature, 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	—	—

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	—	—

Sulphuric Acid

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

Specific Gravity at 15°/4° in Vacuo.	Percentage H_2SO_4.	Specific Gravity at 15°/4° in Vacuo.	Percentage H_2SO_4.	Specific Gravity at 15°/4° in Vacuo.	Percentage H_2SO_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

SULPHURIC ACID—*Continued*

Specific Gravity at 15°/4° in Vacuo.	Percentage H_2SO_4.	Specific Gravity at 15°/4° in Vacuo.	Percentage H_2SO_4.	Specific Gravity at 15°/4° in Vacuo.	Percentage H_3SO_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	—	—

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						4	9	13	17	21	26	30	34	38
						0212	0253	0294	0334	0374	4	8	12	16	20	24	28	32	37
11	0414	0453	0492	0531	0569						4	8	12	15	19	23	27	31	35
						0607	0645	0682	0719	0755	4	7	11	15	19	22	26	30	33
12	0792	0828	0864	0899	0934	0969					3	7	11	14	18	21	25	28	32
							1004	1038	1072	1106	3	7	10	14	17	20	24	27	31
13	1139	1173	1206	1239	1271						3	7	10	13	16	20	23	26	30
						1303	1335	1367	1399	1430	3	7	10	12	16	19	22	25	29
14	1461	1492	1523	1553							3	6	9	12	15	18	21	24	28
					1584	1614	1644	1673	1703	1732	3	6	9	12	15	17	20	23	26
15	1761	1790	1818	1847	1875	1903					3	6	9	11	14	17	20	23	26
							1931	1959	1987	2014	3	5	8	11	14	16	19	22	25
16	2041	2068	2095	2122	2148						3	5	8	11	14	16	19	22	24
						2175	2201	2227	2253	2279	3	5	8	10	13	15	18	21	23
17	2304	2330	2355	2380	2405	2430					3	5	8	10	13	15	18	20	23
							2455	2480	2504	2529	2	5	7	10	12	15	17	19	22
18	2553	2577	2601	2625	2648						2	5	7	9	12	14	16	19	21
						2672	2695	2718	2742	2765	2	5	7	9	11	14	16	18	21
19	2788	2810	2833	2856	2878						2	4	7	9	11	13	16	18	20
						2900	2923	2945	2967	2989	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	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	3	4

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	2	2	2	2
·05	1122	1125	1127	1130	1132	1135	1138	1140	1143	1146	0	1	1	1	1	2	2	2	2
·06	1148	1151	1153	1156	1159	1161	1164	1167	1169	1172	0	1	1	1	1	2	2	2	2
·07	1175	1178	1180	1183	1186	1189	1191	1194	1197	1199	0	1	1	1	1	2	2	2	2
·08	1202	1205	1208	1211	1213	1216	1219	1222	1225	1227	0	1	1	1	1	2	2	2	3
·09	1230	1233	1236	1239	1242	1245	1247	1250	1253	1256	0	1	1	1	1	2	2	2	3
·10	1259	1262	1265	1268	1271	1274	1276	1279	1282	1285	0	1	1	1	1	2	2	2	3
·11	1288	1291	1294	1297	1300	1303	1306	1309	1312	1315	0	1	1	1	2	2	2	2	3
·12	1318	1321	1324	1327	1330	1334	1337	1340	1343	1346	0	1	1	1	2	2	2	2	3
·13	1349	1352	1355	1358	1361	1365	1368	1371	1374	1377	0	1	1	1	2	2	2	3	3
·14	1380	1384	1387	1390	1393	1396	1400	1403	1406	1409	0	1	1	1	2	2	2	3	3
·15	1413	1416	1419	1422	1426	1429	1432	1435	1439	1442	0	1	1	1	2	2	2	3	3
·16	1445	1449	1452	1455	1459	1462	1466	1469	1472	1476	0	1	1	1	2	2	2	3	3
·17	1479	1483	1486	1489	1493	1496	1500	1503	1507	1510	0	1	1	1	2	2	2	3	3
·18	1514	1517	1521	1524	1528	1531	1535	1538	1542	1545	0	1	1	1	2	2	2	3	3
·19	1549	1552	1556	1560	1563	1567	1570	1574	1578	1581	0	1	1	1	2	2	3	3	3
·20	1585	1589	1592	1596	1600	1603	1607	1611	1614	1618	0	1	1	1	2	2	3	3	3
·21	1622	1626	1629	1633	1637	1641	1644	1648	1652	1656	0	1	1	2	2	2	3	3	3
·22	1660	1663	1667	1671	1675	1679	1683	1687	1690	1694	0	1	1	2	2	2	3	3	3
·23	1698	1702	1706	1710	1714	1718	1722	1726	1730	1734	0	1	1	2	2	2	3	3	4
·24	1738	1742	1746	1750	1754	1758	1762	1766	1770	1774	0	1	1	2	2	2	3	3	4
·25	1778	1782	1786	1791	1795	1799	1803	1807	1811	1816	0	1	1	2	2	2	3	3	4
·26	1820	1824	1828	1832	1837	1841	1845	1849	1854	1858	0	1	1	2	2	3	3	3	4
·27	1862	1866	1871	1875	1879	1884	1888	1892	1897	1901	0	1	1	2	2	3	3	3	4
·28	1905	1910	1914	1919	1923	1928	1932	1936	1941	1945	0	1	1	2	2	3	3	4	4
·29	1950	1954	1959	1963	1968	1972	1977	1982	1986	1991	0	1	1	2	2	3	3	4	4
·30	1995	2000	2004	2009	2014	2018	2023	2028	2032	2037	0	1	1	2	2	3	3	4	4
·31	2042	2046	2051	2056	2061	2065	2070	2075	2080	2084	0	1	1	2	2	3	3	4	4
·32	2089	2094	2099	2104	2109	2113	2118	2123	2128	2133	0	1	1	2	2	3	3	4	4
·33	2138	2143	2148	2153	2158	2163	2168	2173	2178	2183	0	1	1	2	2	3	3	4	4
·34	2188	2193	2198	2203	2208	2213	2218	2223	2228	2234	1	1	2	2	3	3	4	4	5
·35	2239	2244	2249	2254	2259	2265	2270	2275	2280	2286	1	1	2	2	3	3	4	4	5
·36	2291	2296	2301	2307	2312	2317	2323	2328	2333	2339	1	1	2	2	3	3	4	4	5
·37	2344	2350	2355	2360	2366	2371	2377	2382	2388	2393	1	1	2	2	3	3	4	4	5
·38	2399	2404	2410	2415	2421	2427	2432	2438	2443	2449	1	1	2	2	3	3	4	4	5
·39	2455	2460	2466	2472	2477	2483	2489	2495	2500	2506	1	1	2	2	3	3	4	5	5
·40	2512	2518	2523	2529	2535	2541	2547	2553	2559	2564	1	1	2	2	3	4	4	5	5
·41	2570	2576	2582	2588	2594	2600	2606	2612	2618	2624	1	1	2	2	3	4	4	5	5
·42	2630	2636	2642	2649	2655	2661	2667	2673	2679	2685	1	1	2	2	3	4	4	5	6
·43	2692	2698	2704	2710	2716	2723	2729	2735	2742	2748	1	1	2	3	3	4	4	5	6
·44	2754	2761	2767	2773	2780	2786	2793	2799	2805	2812	1	1	2	3	3	4	4	5	6
·45	2818	2825	2831	2838	2844	2851	2858	2864	2871	2877	1	1	2	3	3	4	5	5	6
·46	2884	2891	2897	2904	2911	2917	2924	2931	2938	2944	1	1	2	3	3	4	5	5	6
·47	2951	2958	2965	2972	2979	2985	2992	2999	3006	3013	1	1	2	3	3	4	5	5	6
·48	3020	3027	3034	3041	3048	3055	3062	3069	3076	3083	1	1	2	3	4	4	5	6	6
·49	3090	3097	3105	3112	3119	3126	3133	3141	3148	3155	1	1	2	3	4	4	5	6	6

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	5	6	7
·53	3388	3396	3404	3412	3420	3428	3436	3443	3451	3459	1	2	2	3	4	5	6	6	7
·54	3467	3475	3483	3491	3499	3508	3516	3524	3532	3540	1	2	2	3	4	5	6	6	7
·55	3548	3556	3565	3573	3581	3589	3597	3606	3614	3622	1	2	2	3	4	5	6	7	7
·56	3631	3639	3648	3656	3664	3673	3681	3690	3698	3707	1	2	3	3	4	5	6	7	8
·57	3715	3724	3733	3741	3750	3758	3767	3776	3784	3793	1	2	3	3	4	5	6	7	8
·58	3802	3811	3819	3828	3837	3846	3855	3864	3873	3882	1	2	3	4	4	5	6	7	8
·59	3890	3899	3908	3917	3926	3936	3945	3954	3963	3972	1	2	3	4	5	5	6	7	8
·60	3981	3990	3999	4009	4018	4027	4036	4046	4055	4064	1	2	3	4	5	6	6	7	8
·61	4074	4083	4093	4102	4111	4121	4130	4140	4150	4159	1	2	3	4	5	6	7	8	9
·62	4169	4178	4188	4198	4207	4217	4227	4236	4246	4256	1	2	3	4	5	6	7	8	9
·63	4266	4276	4285	4295	4305	4315	4325	4335	4345	4355	1	2	3	4	5	6	7	8	9
·64	4365	4375	4385	4395	4406	4416	4426	4436	4446	4457	1	2	3	4	5	6	7	8	9
·65	4467	4477	4487	4498	4508	4519	4529	4539	4550	4560	1	2	3	4	5	6	7	8	9
·66	4571	4581	4592	4603	4613	4624	4634	4645	4656	4667	1	2	3	4	5	6	7	9	10
·67	4677	4688	4699	4710	4721	4732	4742	4753	4764	4775	1	2	3	4	5	7	8	9	10
·68	4786	4797	4808	4819	4831	4842	4853	4864	4875	4887	1	2	3	4	6	7	8	9	10
·69	4898	4909	4920	4932	4943	4955	4966	4977	4989	5000	1	2	3	5	6	7	8	9	10
·70	5012	5023	5035	5047	5058	5070	5082	5093	5105	5117	1	2	4	5	6	7	8	9	11
·71	5129	5140	5152	5164	5176	5188	5200	5212	5224	5236	1	2	4	5	6	7	8	10	11
·72	5248	5260	5272	5284	5297	5309	5321	5333	5346	5358	1	2	4	5	6	7	9	10	11
·73	5370	5383	5395	5408	5420	5433	5445	5458	5470	5483	1	3	4	5	6	8	9	10	11
·74	5495	5508	5521	5534	5546	5559	5572	5585	5598	5610	1	3	4	5	6	8	9	10	12
·75	5623	5636	5649	5662	5675	5689	5702	5715	5728	5741	1	3	4	5	7	8	9	10	12
·76	5754	5768	5781	5794	5808	5821	5834	5848	5861	5875	1	3	4	5	7	8	9	11	12
·77	5888	5902	5916	5929	5943	5957	5970	5984	5998	6012	1	3	4	5	7	8	10	11	12
·78	6026	6039	6053	6067	6081	6095	6109	6124	6138	6152	1	3	4	6	7	8	10	11	13
·79	6166	6180	6194	6209	6223	6237	6252	6266	6281	6295	1	3	4	6	7	9	10	11	13
·80	6310	6324	6339	6353	6368	6383	6397	6412	6427	6442	1	3	4	6	7	9	10	12	13
·81	6457	6471	6486	6501	6516	6531	6546	6561	6577	6592	2	3	5	6	8	9	11	12	14
·82	6607	6622	6637	6653	6668	6683	6699	6714	6730	6745	2	3	5	6	8	9	11	12	14
·83	6761	6776	6792	6808	6823	6839	6855	6871	6887	6902	2	3	5	6	8	9	11	13	14
·84	6918	6934	6950	6966	6982	6998	7015	7031	7047	7063	2	3	5	6	8	10	11	13	15
·85	7079	7096	7112	7129	7145	7161	7178	7194	7211	7228	2	3	5	7	8	10	12	13	15
·86	7244	7261	7278	7295	7311	7328	7345	7362	7379	7396	2	3	5	7	8	10	12	13	15
·87	7413	7430	7447	7464	7482	7499	7516	7534	7551	7568	2	3	5	7	9	10	12	14	16
·88	7586	7603	7621	7638	7656	7674	7691	7709	7727	7745	2	4	5	7	9	11	12	14	16
·89	7762	7780	7798	7816	7834	7852	7870	7889	7907	7925	2	4	5	7	9	11	13	14	16
·90	7943	7962	7980	7998	8017	8035	8054	8072	8091	8110	2	4	6	7	9	11	13	15	17
·91	8128	8147	8166	8185	8204	8222	8241	8260	8279	8299	2	4	6	8	9	11	13	15	17
·92	8318	8337	8356	8375	8395	8414	8433	8453	8472	8492	2	4	6	8	10	12	14	15	17
·93	8511	8531	8551	8570	8590	8610	8630	8650	8670	8690	2	4	6	8	10	12	14	16	18
·94	8710	8730	8750	8770	8790	8810	8831	8851	8872	8892	2	4	6	8	10	12	14	16	18
·95	8913	8933	8954	8974	8995	9016	9036	9057	9078	9099	2	4	6	8	10	12	15	17	19
·96	9120	9141	9162	9183	9204	9226	9247	9268	9290	9311	2	4	6	8	11	13	15	17	19
·97	9333	9354	9376	9397	9419	9441	9462	9484	9506	9528	2	4	7	9	11	13	15	17	20
·98	9550	9572	9594	9616	9638	9661	9683	9705	9727	9750	2	4	7	9	11	13	16	18	20
·99	9772	9795	9817	9840	9863	9886	9908	9931	9954	9977	2	5	7	9	11	14	16	18	20

ATOMIC WEIGHTS

(1934)

Aluminium,	Al	26·97
Antimony,	Sb	121·76
Arsenic,	As	74·91
Barium,	Ba	137·36
Bismuth,	Bi	209·00
Boron,	B	10·82
Bromine,	Br	79·916
Cadmium,	Cd	112·41
Calcium,	Ca	40·08
Carbon,	C	12·00
Chlorine,	Cl	35·457
Chromium,	Cr	52·01
Cobalt,	Co	58·94
Copper,	Cu	63·57
Fluorine,	F	19·00
Hydrogen,	H	1·0078
Iodine,	I	126·92
Iron,	Fe	55·84
Lead,	Pb	207·22
Magnesium,	Mg	24·32
Manganese,	Mn	54·93
Mercury,	Hg	200·61
Molybdenum,	Mo	96·0
Nickel,	Ni	58·69
Nitrogen,	N	14·008
Oxygen,	O	**16·0000**
Phosphorus,	P	31·02
Potassium,	K	39·096
Silicon,	Si	28·06
Silver,	Ag	107·880
Sodium,	Na	22·997
Strontium,	Sr	87·63
Sulphur,	S	32·06
Tin,	Sn	118·70
Uranium,	U	238·14
Zinc,	Zn	65·38

NOTE.—The atomic weights given in the above table are those published by the International Union of Chemistry, 1934. 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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