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THE QUANTITATIVE ANALYSIS OF INORGANIC MATERIALS.

BY

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With 28 Illustrations.



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PREFACE.

THIS book has been written around a collection of analytical methods compiled for the use of Assistant Chemists formerly under my charge. In the course of a number of years the collection increased in volume and scope, and it was suggested to me that if the outlined methods were suitably amplified and classified, they might fill a gap in the literature of Chemical Analysis, voluminous though this is.

My aim has been to give none but sound, practical, and commercially accurate methods, treating the more important estimations in considerable detail, though it is hoped that in no case has any essential been omitted.

Text-books on Chemical Analysis are of many kinds, and indeed there is plenty of scope for variety both of matter and treatment between the limits of the elementary school text-book on the one hand, and, let us say, an original paper as published in the technical journals by a professional analyst or a research chemist on the other. In the present case the author has tried to cater primarily for the University Student who is reading for his final degree examination, but it is hoped that "The Quantitative Analysis of Inorganic Materials" may prove to be of value to that same student both at earlier and later stages of his career, so that selected methods will not be too "advanced" for the undergraduate on the one hand, nor will the complete book be too "elementary" for the "Honours man" on the other.

From my own experience I know that there is a tendency in some places to make Quantitative Analysis too academic; cumbrous traditional methods are used, and all sorts of unnecessary precautions are detailed; the gnat is strained out while the camel is often cheerfully swallowed, with the result that error may creep in through excessive manipulation. Strangely enough, in these same academic circles there is often a lack of appreciation of the theoretical considerations underlying processes and methods; the fact that there is no such thing as an "insoluble" substance, the effect of one reagent upon another, adsorption and kindred phenomena, the peculiar properties of colloids, and so on, are lost sight of in the Laboratory even when they may be familiar friends in the Lecture Room, and the results are occasionally disastrous. This fact has led me to emphasise the theoretical side of Analytical Chemistry on the one hand, and the ultra-practical aspect on the other. Theory

is necessary for the intelligent carrying out of analytical processes, and I can imagine nothing but good coming from the use of tried commercial methods, in University examinations at least, as in both cases the time factor is of vital importance.

As regards the scheme of things, the opening Section is devoted to a discussion of apparatus and its manipulation. Following this comes a section devoted to a brief sketch of Chemical Theory as it affects the Analyst in particular. Section III deals with the Estimation of the Metals considered in the order which is already familiar to the student, that of the Qualitative Groups. Section IV is the corresponding section for the Anions and Non-metals, and this is followed by a synopsis of Volumetric Analysis, with numerous data and factors. Sections VI and VII are of the greatest importance, dealing as they do with the separation of the metals and non-metals preparatory to their estimation by the methods described in Sections III and IV.

It is manifest that no writer could hope to detail a complete catalogue of methods for the analysis of such artificial mixtures as might be given for analysis in an examination, and this has not been attempted; instead, there is a section (VIII) dealing with the quantitative analysis of a variety of materials of industrial importance: Iron and Steel, the chief Non-ferrous Alloys, Refractories, Cement, a few Ores, Water, and the like, which it is hoped will give the student ample practice in the separation and estimation of metals in mixtures which are often very complex, while at the same time retaining a strong element of practical utility, and affording experience which cannot fail to be of use if the intention is to take up Analytical Chemistry as a profession. Useful Tables and Factors occupy the final section.

N. HACKNEY.

December, 1929.

It should be stated that the views expressed in this book are not to be taken as representing the official opinions of the Indian Railway Board.

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THE QUANTITATIVE ANALYSIS OF INORGANIC MATERIALS.

SECTION I.

APPARATUS, REAGENTS AND MANIPULATION.

APPARATUS and reagents are the tools with which the analyst works. It is well known that a skilful craftsman acquires a genuine affection for the tools that he is constantly handling, and if he should have the misfortune to break an old favourite he feels lost and strange in handling its successor.

Apart from the balance, and maybe also his washbottle, the chemist can hardly attain this degree of intimacy with his apparatus ; but, just as the craftsman derives confidence and much of his sureness of touch from the use of well-tried tools, so ought the budding analyst to know and trust his apparatus, for only by knowing and understanding the possibilities of each " tool " can he acquire that deftness in manipulation that the professional chemist possesses. This deftness is a real asset, and in some cases reaches a marvellous degree of perfection, as will be admitted by anyone who has seen an old hand swirl two almost full beakers, one in each hand, without spilling a drop, check the swirling liquids with a turn of his wrists, and reverse the rotation, all without seeming to pay the least attention to what he is doing.

The Balance.

The manipulation of the Balance is perhaps the most important point in all quantitative work ; certainly it is fundamentally important to be able to make an accurate weighing, and the more rapidly accurate weighings can be performed by the student, the better it is for his work in every respect.

The chief point about weighing is to have a system. A good " tip " is to make a neat white cardboard tray for your weights, with outlined places for each (Fig. 1), and place it inside the balance case with the weights set out in position when beginning work. This saves a great deal of carrying to and fro of the weights when a number of weighings are to be made, and the elusive " fractions " are always under the worker's eye, for they need never leave the balance-case until the end of the day. It also serves as a very handy check on the weighings made,

as the student can first add up the weights on the pan, and then check his result from the blank places on the "tray." It need hardly be mentioned that the worker should *never* allow himself to grow careless in weighing, or omit to check his weights ; the mistaking of one small fraction for another, an error which is very easy to make, unfortunately, will render a whole analysis useless, and though the student may have acquired valuable experience, the busy professional cannot afford the time to carry through constant "repeats" necessitated by his carelessness.

Know the *Sensitiveness* of your balance. An experienced chemist knows almost instinctively what weight to try from his observation of the speed with which the pointer swings, even if it goes clean across the scale and the pan hits the stop pad underneath. If, after trying one of the larger weights, the pointer does not fly swiftly across the scale when the beam is next freed, the man who knows his balance will not waste

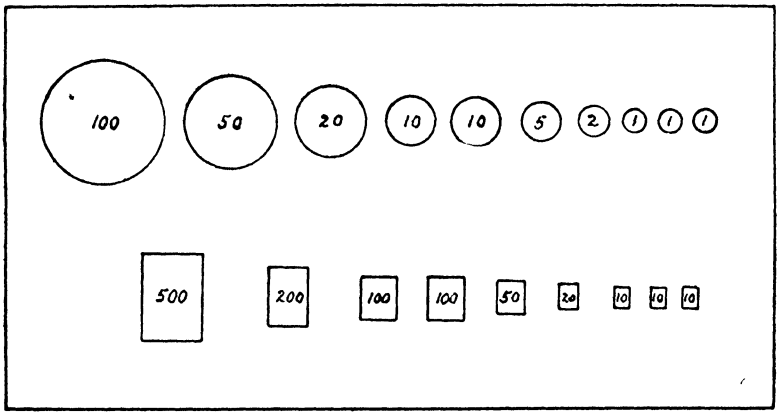


Fig. 1.—Cardboard Tray for Weights.

his time with trying 0·5 and 0·2 gm., so he goes straight to the 0·1 or the 0·05, or even to the 0·01 gm. without hesitation, and has finished his weighing minutes before the tyro. This intimacy with the balance, however, is more particularly to be seen in the manipulation of the rider after the weights have been adjusted to within 0·01 gm. Using his own balance, the student should always know to 1 mgm. where to put the rider, and from the first swing after placing it he should be able to tell to within 0·1 or 0·2 mgm. where its final position is to be ; certainly it is bad work if the rider has to be shifted more than two or three times.

Take the reading with the pointer swinging not less than 3 and not more than 7 or 8 divisions on either side of the zero, and do not rely on the first swing, as the slight disturbance of the air caused by closing the case will affect its accuracy to a small extent. With the beam gently oscillating and the pans steady, it should be possible to place the rider in its final adjustment without checking the pans, **but**: on no account risk jarring the beam by clumsy handling of the rider carrier! Rider

manipulation is a delicate business, and demands the worker's whole attention and care.

As regards speed attainable, the writer has seen a chemist weigh out accurately (*i.e.* to within 0·1 mgm.) 34 assays of steel drillings in 50 minutes, and steel drillings are not so easy to handle as a powder is.

In weighing, have a thin aluminium, or better, a glass or silica scoop on the left hand pan of the balance in order to hold the substance weighed. A similar scoop or a counterpoise of lead foil or wire is kept on the other pan as a tare. (Thick electric fuse wire is useful for this, as it is easily adjusted to balance exactly, and when weighed out, lies in a small flat coil that does not get in the way when the weights are being manipulated.) Note, however, that glass and silica have a tendency to adsorb moisture on their surface, but if the balance case is kept dry (as it should be) by the aid of a vessel containing $CaCl_2$ or H_2SO_4, this will not interfere.

The professional chemist, unless he is handling volatile or hygroscopic substances, rarely uses a weighing bottle, and he always, when possible, weighs out an integral number of grams (or an aliquot part of a gram) for his estimation. This for several reasons. Firstly, it eliminates calculation to a large extent, as the percentage can be read off directly from the final weighing. Secondly, it is easier weighing, as he soon learns to within a little what 1 gm. of his material looks like, so that he is able to take up almost exactly the correct amount with the first plunge of his spatula ; and thirdly, if he always uses the same weight of material, he quickly learns to make close estimates of percentages by looking at his precipitates or the colour of his solutions, so that he is never working quite in the dark.

Analyses should always be done in duplicate, and the same weight should not be taken for both assays. For example, weigh 1·0 gm. for one and 1·2 gms. for the other analysis if 1 gm. is a suitable quantity. This, while hardly complicating the final calculations, tends to eliminate the unconscious " cooking " of results in titrations where there is an end-point depending on " personal factor " especially. Where percentages greater than 3 or 4 are concerned, the two assays should agree to within 0·2 per cent., and the sum of the mean totals should check up to within 0·2 per cent. of the theoretical 100 per cent. In the case of constituents which are present in quantities less than about 1 per cent., an accuracy of about 0·03 per cent. should be expected, and in a few special cases, the accuracy should be even greater.

Glass Ware.

It is a mistake to have too great a variety of glass-ware. For ordinary analysis the following sizes of flasks and beakers are the most convenient.

Beakers: 1,000 cc. Wide, squat. Relatively rarely used.
Uses.—To evaporate down solutions and filtrates that by reason of many washings have become too dilute to be convenient for handling. Note, however, the practised chemist never allows his filtrates to become unduly bulky.

Beakers: 600 cc. Wide, squat.

Uses.—For receiving fairly bulky filtrates when evaporation or concentration is necessary. It is perhaps unnecessary to mention that evaporation proceeds more rapidly in a wide, squat beaker, because there is: (*a*) more surface in contact with the source of heat, (*b*) more surface from which evaporation can take place, and (*c*) less surface above the liquid on which condensation can take place.

400 cc. Wide, squat. For ordinary work.

600 cc. Tall, narrow.

Uses.—(*a*) For settling-out of precipitates preparatory to decantation. If a wide beaker containing a settled-out precipitate is tilted, it is obvious that the precipitate has further to "slide," and it is the more likely to swirl up and render the previously clear liquid turbid, thereby delaying filtration by prematurely clogging the paper. In a tall beaker this is minimised; the depth of clear liquid is greater, as is consequently the volume of liquid that can be decanted without interfering with the precipitate.

(*b*) The boiling of liquids or the prolonged digestion of precipitates at or near the boiling point when concentration is not desired.

(*c*) For titrations. The tall type enables the liquid to be swirled vigorously without danger of spilling, and the extra depth of solution enables the operator to gauge colour changes with greater accuracy.

The tall type also enables the operator to estimate with considerable accuracy the volume of his solution. This is extremely useful when it is necessary that the acidity (*e.g.*) should not exceed a definite amount, and also in maintaining a uniform volume for a series of assays. (This keeps the blanks uniform.)

400 cc. Tall, narrow. For ordinary work when the volume is not great enough to warrant using the 600 cc. size.

100 cc. Wide, squat. For electrolysis in particular. For general work when volumes and precipitates are small. For some titrations where stirring is necessary. (The narrow form is too easily upset.)

The lipped type of beaker is the more generally useful.

Flasks: 750 cc. A few, for certain special operations.

500 cc. Erlenmeyer conical. For certain special operations.

250 cc. Erlenmeyer conical. The most generally useful type of flask where a precipitate has to be handled. Every part of this form of flask can be reached with the wash-bottle jet. Conical flasks have the advantage of (1) Wide base; less easily upset, more heat can reach the contents. (2) Slow loss by evaporation. (3) Contents can be vigorously swirled or shaken without spilling.

500 cc. Round. A few only.

250 c.c Round. Used for heating in the naked flame as being less likely to crack than the conical form. (See estimation of antimony.)

General; Flasks and Beakers.—A few large flasks and beakers will be necessary. One or two 5,000 cc. and one or two 2,000 cc., both flasks and beakers, are useful in making up standard solutions where large quantities are to be handled; for storing special wash liquids (flasks), *e.g.* 5 per cent. H_2SO_4, 2 per cent. NH_4Cl, 5 per cent. HNO_3, 1·2 sp. gr. HNO_3, and the like.

Cover-Glasses.—These are essential pieces of apparatus. A cover should always be used: (1) During digestion, to prevent loss by evaporation. (2) To accelerate heating. (3) To exclude dirt and dust; this is essential in works' laboratories and in large cities.

Cover-glasses should be concave and overlap the edge of the beaker at least $\frac{1}{4}''$. A cover should never be left on a beaker which is on the hotplate when the volume of liquid is very small. The reason for this is that should the beaker happen to "go dry," the drop of condensate hanging from the middle of the cover-glass, will, when it falls, crack the beaker.

Funnels.—Ribbed funnels are an abomination for inorganic work. Use smooth ones, as near the standard 60° and with as long stems as possible. Cut the bevelled end off; it serves no useful purpose, and the ends must be square for pulp filtration (*q.v.*). At least 1 cm. free space should be left above the paper.

Stirring Rods.—Use a stout glass rod with about 1″ of soft rubber tubing slipped over one end, which end should be slightly rounded in the flame of a Bunsen burner to prevent cutting the rubber and scratching the bottom of beakers. The rubber is (1) To prevent breaking the beaker when stirring with the rod. (2) To "scrub" the beaker when removing an adherent precipitate. The other end of the rod is advantageously made into a miniature pestle by heating it to the softening point and then pressing it firmly down upon a flat surface. This is useful to break up crystals that are slow to dissolve, and in removing "protective coatings" from metallic surfaces, such as SiO_2 in the case of cast iron.

The stirring rod is also useful when pouring a liquid from a full

beaker, and in preventing drops from running down the outside when pouring.

Washbottle.—One of the noticeable external distinctions between the beginner and the professional chemist is in their washbottles. Nothing under 1,500 cc. is of any real use, and in commercial laboratories the washbottles are usually nearer 2,500 cc. than 1,500 cc. capacity. One's washbottle is an intimate personal tool, and should be carefully put together ; I do not like the " ready for use " kind, preferring to make my own to my own specification (see fig. 2).

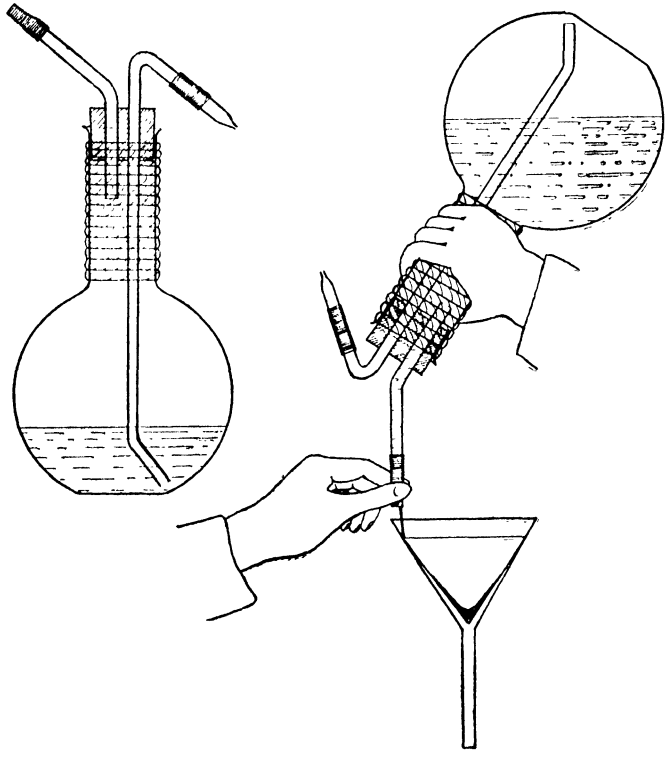


Fig. 2.—The Washbottle.

Obtain a 2,000-2,500 cc. flask of *resistant* glass (*not* an Erlenmeyer ; I have seen the bottom blown out of this type, and anyway, they have no convenient neck to wield them by), and carefully select a soft, two-holed rubber bung to fit. Make the glass tubes carefully ; it is worth a little trouble to get these just right. The " inlet " tube should be about 3·5 inches above the 135° bend, and both ends should be rounded in the flame. Insert the tube so that it projects not more than $\frac{1}{2}''$ below the bung, while the mouthpiece end is provided with a piece of new rubber tubing about 1″ long, put on so that it is half on and half off the glass tube. The " jet " tube should reach to within $\frac{1}{4}''$ of the bottom of the flask ; or, if preferred, it may be curved forward so that the end

comes to within $\frac{1}{4}''$ of the 'angle' of the flask. This arrangement enables the operator to use the last few drops of the wash-liquid, even though the bottle is tilted forward over the funnel.

The projecting end is bent down at 45° to the stem and a separate jet is attached by means of a stout piece of rubber tubing, stiff enough to hold the jet quite steady, but pliable enough to enable the operator to direct the jet of water with the tip of the forefinger of the hand that grips the bottle. Round the neck of the flask a handle of some heat-insulating material should be bound. The cork-like strips of birch-bark which come with Muncktell's Swedish filter papers are excellent for the purpose if they are properly treated. Remove the bark carefully from the package and make it into a compact roll. Bind this tightly with string and place it in a tall beaker full of water, which is then set on the corner of the hotplate for several hours. When the roll is quite soft and pliable, remove it, still keeping it tied up in its string, and let it dry naturally in air. As soon as it is perfectly dry the string may be removed, when it will be found that the bark has become a springy coil that will curl closely round the neck of the wash-bottle and remain in position without any further precaution. This bark handle is very comfortable to the grip, and is an excellent heat insulator.

Failing birch-bark, a good handle may be made of asbestos cloth bound round with string ; or thin asbestos board, softened in water and applied wet, works well. This latter sticks very close when dried on, but as a precaution, it should be bound with string. Use string, not wire ; wire gets hot.

The rubber mouthpiece is useful in two ways. First, it saves the operator's lungs and cheeks. When pressure is applied it will be found that after a short time the cheeks begin to hurt ; if, however, the rubber mouthpiece be gripped between the teeth, the bottle will continue to deliver a stream of water without it being necessary for the worker to apply any more pressure from his cheeks and lungs. Secondly, the rubber is convenient when many washings, as distinct from "washings-on" are to be performed, as the bottle may be inverted and a stream of water of any desired volume may be directed on to the paper by pinching the end of the rubber and partly closing it. This method is just as efficient as the ordinary method of washing, for most purposes, and is far less troublesome to the operator.

The student will find it convenient to have a smaller wash-bottle at hand (one of 750 cc. is convenient) in addition to the larger one. This serves to apply special wash liquids as occasion necessitates without it being necessary to "soil" the main bottle with such reagents as dilute nitric acid, dilute sulphuric acid, ammonium chloride, ammonia, sulphuretted hydrogen water, alcohol, and the like. The smaller bottle is also less wasteful.

Refractory Ware.

Crucibles and dishes are made of porcelain or fused silica. Both kinds are useful ; silica ware withstands sudden variations of temperature perfectly on account of its low coefficient of expansion, and apparatus made of this material rarely breaks except when dropped by accident, but it is obvious that basic precipitates cannot be ignited on

silica. It serves admirably for the ignition of such substances as $BaSO_4$, SiO_2, $Fe(OH)_3$ (there is no ferric silicate), but crucibles of this material are at once spoilt by alkalis, CaO, Al_2O_3, etc.

Porcelain serves for any ordinary precipitate, but is liable to be fractured by sudden temperature shocks. If, however, the heating is performed as gradually as possible, porcelain will last almost indefinitely.

Dishes are used for evaporations that have to end in the ignition or "baking" of the residue; in all cases it is preferable to use platinum for this purpose, *except* when the substance in solution is alkaline (caustic) or liable to generate chlorine or bromine. In such cases porcelain should be used.

Platinum.

Platinum is expensive, and unfortunately but few students are able to possess platinum apparatus of their own. Platinum is, however, essential in accurate commercial work. A minimum list of suitable apparatus is appended.

1. *Dish.*—200-250 cc. capacity and about 50 gms. weight. Used for evaporations and the attack of certain ores and alloys by acid mixtures such as acid + HF, or fused $KHSO_4$.

2. *Crucible(s).*—20-25 cc. capacity and 20 gms. weight. For fusions with Na_2CO_3, treatment of precipitates with HF, $KHSO_4$ fusions. Platinum-Gooch crucibles are also useful.

3. *Capsules.*—3 or 4 cc. capacity, 10 gms. weight, for the above operations on a smaller scale.

4. *Electrodes.*—See Electrolytic estimation of Copper.

5. *Wire.*—A piece of stout platinum wire should be in every chemist's drawer; its uses are many and various. A length of thinnest wire for suspending such articles as pyknometers, absorption bulbs and the like while weighing.

Hotplates.

Hotplates may be electrically or gas heated. My own experience leads me to prefer the gas-heated plate, though I do not doubt that an electrical plate could be made equally efficient; in practice, however, the gas plate has several obvious advantages, not the least of which is its simplicity and immunity from failure.

A long, smokeless burner is set upon a stone block or cast-iron plate and a sheet of $\frac{3}{8}''$ boiler-plate is supported over it on four stout iron legs. This arrangement permits of the most delicate gradation of heating power, ranging from the centre, where the temperature may reach 500°-600° C., to the outer edge, where it should not even bring alcohol to the boil. This gradation enables the analyst to drive his evaporations hard while the solutions are dilute, and to finish at a gentle heat by simply drawing the vessel back further and further from the centre. It enables him to heat up a cold solution quickly at the same time that he is gently "simmering" another assay; he can "bake" a dry residue at 500° C. in the centre, and dry precipitates on the edges without charring the paper.

It will be found convenient to have, besides the large main plate, a smaller one with a single rose burner under it, and it is an additional advantage if this can be placed in a separate fume chamber, so that

igesting precipitates shall not become contaminated by fumes arising om the evaporating beakers on the other plate. The small plate is seful for keeping washbottles hot, and for standing beakers on when ıere are a number of precipitates which have to be settled and coagu-ıted.

In this connection it may be well to mention that it is convenient) have a large smokeless gas-ring with a wire gauze to go over it. This :rves to heat up washbottles from the cold when time is precious, and)r rapidly boiling bulky solutions, etc.

If inflammable liquids, such as ether, petroleum "ether," carbon isulphide, benzene and the like have to be heated or evaporated, this ıould *on no account* be done in the open laboratory, as these substances ave heavy vapours which form explosive mixtures with air, making such perations dangerous in the vicinity of a naked flame. These liquids ıay well be distilled from a water-bath filled up with hot water brought ı afresh from the outside as the previous lot cools off, or a small carbon-lament electric lamp may be used as a heater. This device is quite ıfficient to drive a Soxhlet extractor, and there is no danger even if ıe flask breaks.

Drying Oven.

An electrically heated oven is to be preferred, as the heat is so easily :gulated; the heat source is also unaffected by draughts. The oven ill normally be maintained at 100° to 110° C. for drying purposes, ut it should be possible to attain 300°–350° C. if necessary. (See under ntimony.)

Muffle Furnace.

For ignitions and fusions a muffle furnace is much more convenient than gas burner. In the very great majority of cases it is not necessary) burn the paper apart from the precipitate. The preliminary drying, :ushing off, ignition of paper, and then ash plus precipitate is a routine hich is in most cases an entirely unnecessary complication, not to ıention a waste of time, and these are the two things the chemist should y at all costs to avoid. In this book, except where it is specially marked, it is expected that the routine will be as follows:—

1. Fold the wet paper plus precipitate into a compact parcel and ace it in the crucible.
2. Place crucible and its moist contents on the shelf in front of the uffle door until the paper begins to char. (The hotplate will serve r this if the muffle is congested.)
3. Gradually push the crucible forward until the paper catches fire ıd burns, leaving a carbonaceous ash.
4. Push the crucible further into the muffle mouth, so that the carbon ırns off.
5. Finish by introducing the crucible and contents completely into e muffle and holding them there until the desired amount and degree ignition have been attained.

This procedure may be followed even with such reducible compounds SnO_2, CuS, ZnS, etc. without the least danger of producing the etal. Note, however, that compounds of Ag, Pb, Sb and a few other

metals, are reduced by charred paper; special directions will be given in these cases. In all cases, the aim of the analyst should be speed and simplicity.

The advantages of the muffle are:

1. The heat is *controlled.* It is possible to know the temperature of any part of the furnace with considerable accuracy, and this is often of great importance, as some precipitates decompose or volatilise at elevated temperatures.

2. The substance undergoing ignition is not liable to be contaminated by the products of combustion, as no flame comes into contact with the crucible.

3. It is possible to "roast" a sulphide precipitate to oxide in a muffle; in a flame, the reducing gases that surround the crucible make this uncertain or impossible.

As regards the shape and design of the muffle, it should be:

1. Capacious (within reason), and should take two ordinary crucibles standing abreast.

2. Wide enough to take a 250 cc. dish.

3. High enough to enable the chemist to place a crucible at the back of the chamber without having to remove all the crucibles at the front.

4. It should have a large shelf of asbestos board or firebrick in front of the hot chamber. This serves, as explained, to support crucibles while drying wet paper and precipitate and to char the dry paper before ignition.

Either gas or electricity may be used for heating the muffle. The former works well, but the heat is not so much under control as when electricity is used; also the gas muffle, with its large burner and chimney, is very uncomfortable to work near. The electric muffle has the disadvantage that if and when the winding burns out, the furnace is out of commission until a new lining and winding can be fitted.

As a general rule, the temperature of the muffle should be kept at 900° C. or as near that temperature as possible. This will suffice for sodium carbonate fusions, and for all ordinary ignitions.

Reagents.

Very little need be said about reagents beyond remarking that it is as well to have a rough idea of the "strength" of the solutions in use, using the word in the sense of "concentration."

For the bench, the following are necessary:

Sulphuric Acid.	Conc. (Sp. Gr. 1·84) = practically 100 per cent. H_2SO_4.
	Dilute. 1 : 3 (by vol.).
Hydrochloric Acid.	Conc. (Sp. Gr. 1·20) = 39 per cent. HCl.
	Dilute. (*a*) Constant boiling-point acid, Sp. Gr. 1·102 = 20 per cent. HCl.
	(*b*) 1 : 4 (by vol.).

Nitric Acid.	Fuming. (Sp. Gr. 1·52) = 100 per cent. HNO_3.
	Conc. (Sp. Gr. 1·42) = 70 per cent. HNO_3.
	Dilute. (Sp. Gr. 1·20) = 33 per cent. HNO_3.
Acetic Acid.	Glacial.
Ammonia.	Conc. (Sp. Gr. 0·880).
	Dilute. 1 : 3 (by vol.).
Caustic Soda.	A stock bottle containing saturated NaOH is useful.
Bromine.	Pure liquid.
	Saturated solution in water or in KBr.
Sulphur Dioxide.	Syphon of liquid gas. And/or:
	Solution made by passing SO_2 gas into 1 : 2 ammonia.
Ammonium Acetate.	Saturated solution of the crystals, or
	Neutralise 1 : 3 acetic acid with ammonia. No indicator will serve; the solution should not smell of NH_3.
Ammonium Chloride.	Saturated solution.
	2 per cent. solution.
Ammonium "Carbonate."	Saturated solution of the carbonate-carbamate lumps.
Mercuric Chloride.	Saturated solution.
Stannous Chloride.	Conc. solution, containing drillings of metallic tin and free HCl.
Ammonium Phosphate.	10 per cent., neutralised with NH_4OH using phenolphthalein as indicator. (See Indicators.)
Barium Chloride.	10 per cent. solution.
Ammonium Molybdate.	10 per cent. solution. Or special solution with NH_4NO_3 and HNO_3, for which, see under Phosphoric Acid.
Ammonium Oxalate.	Saturated solution. 1 cc. precipitates 0·01 gm. of CaO.

It is preferable to use Ammonium Chloride in the solid state, and ı a large laboratory this reagent is available in a capacious stone or ırthenware jar, in which a glass scoop or spatula is kept. This serves ı a rough measure when using ammonium chloride. Other reagents ıat are kept in the solid state are:

Sodium Carbonate.	Anhydrous powder. For alkaline fusions.
Sodium Peroxide.	In a wide-mouthed, close-stoppered bottle. For oxidising fusions.
Sodium Sulphide.	Crystals.
Caustic Soda and Potash.	
Ammonium Persulphate.	Crystals; the solution decomposes.
Oxalic Acid.	Crystals.
Sodium Bismuthate.	Powder.

It will be found useful to keep specially purified standardising reagents on a shelf in the balance room. The following is a fairly complete list:

1. Recrystallised Ferrous Ammonium Sulphate.
2. Recrystallised Nickel Ammonium Sulphate.
3. Recrystallised Sodium Oxalate.
4. Recrystallised and fused Potassium Dichromate.
5. Electrolytic Copper foil or wire.
6. Assay Silver foil or wire.
7. Assay Lead foil.
8. Pure Tin, granulated.
9. Pure Zinc foil.
10. Standard Steel, 0·10 per cent. Carbon.
11. ,, 0·30 per cent. Carbon.
12. ,, 0·50 per cent. Carbon.
13. ,, 0·05 per cent. Sulphur.
14. ,, 0·05 per cent. Phosphorus.
15. ,, 0·75 per cent. Manganese.
16. ,, 3·0 per cent. Nickel.
17. Armco Iron.

FILTRATION.

Filtration is the chief means of separating substances in analytical work, and as almost half of the analyst's manipulatory technique is concerned with filtration, the subject will be dealt with in some detail. There is no department of his work in which the chemist may more thoroughly waste precious time than by adopting faulty methods of filtration, and a little care exercised in this direction will well repay the trouble.

There are only two filtration media that are of practical importance; paper and asbestos. The latter is used in relatively few special cases, principally when dealing with liquids that attack paper, or, as has been already noted, when an easily reducible precipitate is to be ignited. Paper is of more general application, and as the chemist requires more than one type of filter paper for his work, the characteristics of each type will be briefly discussed.

Ashless paper is paper which has been treated with HCl and HF while in the state of pulp, and from which, in consequence, the mineral matter of the fibre has been practically entirely removed. This is the only kind of paper that can be used for quantitative work when the paper has to be ignited with the precipitate. It is best to have more than one size of paper, always choosing the *smallest* possible, and remembering that it is the volume of the precipitate and not that of the solution which determines the size of the filter. For ordinary purposes it will be best to keep to two sizes, viz., the 11 cm. and the 12·5 cm. papers, but it will be necessary to have a few sheets of 9 cm. and 15 cm. paper at hand for occasional use.

Ashless paper is made in several grades, with different degrees of "ashlessness" and porosity. As the speed of filtration depends on the size of the pores of the paper, it is of course correct always to use the coarsest grade that will hold the precipitate. To avoid the complication

of having a number of grades of paper available, it is preferable to keep to two only, a very "open" paper and one of moderately close grain; for if the preparation of the precipitates is properly attended to, there will be no need for a very close-grained variety. To give the student some idea of the type of paper that is meant, it may be remarked that Whatman's No. 41 is a good example of "open" paper and No. 40 is sufficiently "close" to hold any properly prepared precipitate. In subsequent pages all filtration processes will be referred to one or the other of these two types of papers.

Ordinary paper, *i.e.* non-ashless, is fairly close grained and is considerably stronger than ashless. This is used (1) when the paper is not to be burnt with the precipitate, *e.g.* when the precipitate is to be "washed back" for some further treatment. (2) When the paper is to be burnt, but the precipitate is not to be weighed without further treatment. (3) When a very acid or alkaline solution is being filtered, because this type of paper is so much tougher than ashless.

Ordinary paper is not so much used as ashless in quantitative work, and one size will be sufficient to stock in quantity. For general purposes 12·5 cm. paper is the most convenient, as this will comfortably hold even the bulkiest precipitates that are ordinarily handled; it is, however, an advantage to have a certain number of 9 cm. sheets available for occasional use.

Toughened paper is that which has been treated with acid so that it is partially "parchmentised" and its surface left very smooth and free from loose fibre. Such paper is used to filter precipitates that are to be brushed off; these are usually those that have a low "factor," *i.e.* are heavy when compared with the weight of the substance that is being determined, so that if a little remains on the paper its amount will be too small to affect the second decimal place per cent. of the result; this device is useful when dealing with precipitates that volatilise or decompose on heating. The smoothness of the paper makes brushing off a very easy matter, and the method may even be employed without any serious error in the case of precipitates such as $PbSO_4$, when great accuracy is not necessary. The objection to this type of paper is that the pores are very much closed by the toughening process and washing is consequently rather slow. This disadvantage is, however, more than counterbalanced by the fact that the paper is tough enough to bear the full pressure of the atmosphere even when wet, so that the filter-pump may be made full use of without danger of tearing. A small size (9 cms.) will be the only paper necessary; Whatman's No. 50 is typical.

The following table will give the student an idea of the relative quantities of the papers used in ordinary chemical analysis:

ASHLESS: "Open"	(No. 41).	9 cms.,	10 sheets
		11 cms.,	50 sheets
		12·5 cms.,	20 sheets
		15 cms.,	5 sheets
"Close"	(No. 40).	9 cms.,	10 sheets
		11 cms.,	20 sheets
		12·5 cms.,	5 sheets
		15 cms.,	2 sheets

ORDINARY:	9 cms.,	5 sheets
	12·5 cms.,	20 sheets
TOUGHENED: (No. 50).	9 cms.,	1 sheet

In fitting the filter-paper to the funnel, fold it, not as frequently explained in text-books, but as shown in fig. 3.

The paper is opened between the two folds of the *larger* side, so that when it is placed in the funnel it only touches the glass with its upper edge, which should be pressed into close contact with the funnel all round. The result of this way of fitting is that the paper hangs freely in the funnel and liquid can pass through at *all* points of its surface instead of only at the apex, as is the case if the paper is folded to the exact 60°

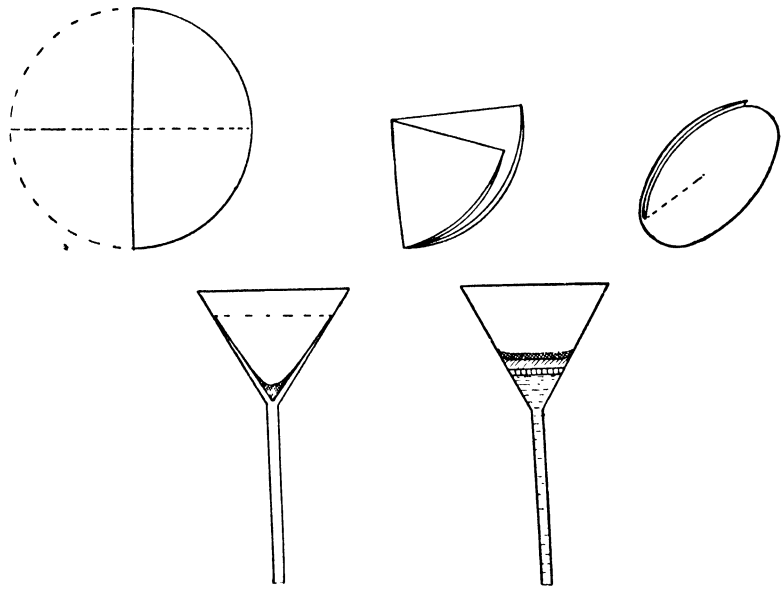


Fig. 3.—Preparation of Filter-paper.

cone. Care should be taken, however, not to make the widening too pronounced or the paper may collapse under the weight of the wash liquid which is poured on.

Washing the Precipitate.—This is another point which demands careful attention and a good realisation of the physics of the process. One is apt to think too much of the precipitate and not enough of the paper in spite of the fact that an 11 cm. ashless paper holds no less than 1·5 cc. of solution after complete draining. The best method of washing is as follows:

Having rinsed the precipitate on to the paper, it should be the aim of the first washings to remove and drive it off the sides into the apex of the paper as far as possible, stirring it up well with a vigorous jet of water. This washes the precipitate thoroughly. Continue by washing

carefully all round just *above* the top edge of the paper, paying special attention to the double fold and trying to manage the jet so that as much water goes down *behind* the paper as into it; this washes the paper. Continue to apply the jet until the filter is from half to three-quarters full, and then allow the liquid to drain *completely* before adding another drop of water. Each successive wash should be carried out in the same manner, *i.e.* by first stirring up the precipitate, rinsing it down into the apex of the paper, and secondly, washing round above the edge of the filter. Do not attempt to test the filtrate until after at least four washes.

The top edge is the part of the filter-paper that needs most attention, because the solution we are trying to eliminate will tend to creep up to the top by capillarity as the funnel drains.

An experiment which will prove this truth to the student is as follows:—Prepare a solution of about 1 gm. $FeCl_3$ dissolved in 30 cc. of water. Pour this through a filter and wash it until there is no more evidence of the yellow colour of the Fe^{+++} ion. Iron is now apparently entirely removed. Now wash round above the paper with a little hot 10 per cent. HCl, and, unless the first washing was very carefully carried out, it will be seen that quite a considerable amount of Fe remains, and it is all in the top edge.

Pulp Filtration.—In the majority of cases it is preferable to adopt this device in the place of a conventional folded filter-paper, and the student is recommended to filter on pulp in all cases unless specially instructed to use a folded paper.

Paper pulp is prepared as follows:—Ashless paper clippings are *torn* (not cut) into small fragments and placed in a large flask. A little hot water is added, sufficient to moisten the paper and to cause the pieces to ball up when the flask is shaken from side to side. Shaking is continued until the paper is thoroughly disintegrated and the individuality of the small pieces can no longer be distinguished. When this stage is reached, distilled water is added until the mixture has about the consistency of cream; it is then ready for use.

To prepare a filter:—Choose a smooth-sided funnel with a long stem that has had its tip cut off square at the end. (It is as well to perform this simple operation upon all the laboratory funnels so that all may be used for pulp filters.) The bevelled end serves no useful purpose at all; it does not even assist the last drop of liquid to fall, as the funnel should always touch the side of the beaker when filtering. It is *wrong* to allow drops of filtrate to fall directly upon the free surface of the liquid in the receiving beaker on account of the probability of losing solution by splashing; the stem of the funnel should, on all occasions, touch the side of the beaker, so that the solution flows down the beaker walls. Place a filter-disc in the funnel (its size depends on the bulk of the precipitate; use as small a disc as possible), close the bottom of the stem with the forefinger and pour in distilled water until the stem is full and the level of the liquid is above the disc. Dislodge any air-bubbles that may remain entrapped below the disc by tilting this with the finger; place the disc level and pour the paper-pulp into the funnel in sufficient quantity to leave a layer at least $\frac{1}{4}''$ thick covering the disc when the superfluous water has drained away. The actual amount of pulp to be added can only be learned by experience, but it is a general rule that for a large

precipitate it is best to have a rather thicker pulp, while for a small precipitate the merest film of paper will suffice.

When the excess water has drained off, carefully press the pulp down round the sides of the funnel with the tip of the forefinger in order to consolidate it and to prevent its being disturbed when the solution is poured on. The amount of pressure is varied according to the nature of the precipitate. For a coarse or flocculent precipitate such as ferric hydroxide or the ordinary acid sulphides, very little pressure is necessary and a very free-running filter is possible; for a fine precipitate such as barium sulphate or metastannic acid firmer pressure is desirable; the extra compression of the paper, of course, very considerably slows down the speed at which the solution filters. It will be found that this kind of filter will keep back all of the ordinary analytical precipitates if the density of the pulp is properly adjusted. It has, therefore, a great advantage in that it is unnecessary to keep both " open " and " close " filter-papers, as the pulp can be adjusted to suit any precipitate.

The solution is now poured into the funnel, taking care to prevent the stream of liquid from impinging directly upon the paper or the latter may be disturbed and lifted up from the disc; the funnel may be completely filled. Filtration carried out in this manner will take place much more rapidly than through a folded paper, as it is aided by the weight of the water in the stem of the funnel. Note, of course, that the stem should always be full of liquid; it is to secure this end that the tip of a pulp filter is cut off square. Washing is effected simply by inverting the wash-bottle and pouring from the mouthpiece.

To remove the precipitate and paper, proceed as follows:—Slip the tip of a platinum wire or a glass rod that has been drawn out to a fine point down one side of the pulp, gently raising one edge of it, without squeezing, until it turns over. Then slip the forefinger of the right hand under the turned-up edge and lift pulp and precipitate, carrying it on the finger-tip and steadying it with the wire until it can be dropped into the crucible, precipitate upwards. Take a small piece of ashless paper, about 1″ by ½″, fold it into a firm, flat roll, moisten it slightly, and then after wiping the soiled tip of the wire on it, place it along the forefinger of the right hand and wipe it over the inner surface of the funnel, commencing at the disc and gradually raising it in a spiral from centre to outer edge. This paper is then added to the pulp in the crucible and the whole is dried and ignited after charring off the paper in the mouth of the muffle.

Note 1.—This method is *not* suitable for very heavy precipitates nor for gelatinous ones such as silica, aluminium hydroxide, etc.

Note 2.—Do not try to transfer the pulp until it has completely drained. If it is attempted to do so, it will be found that on raising the pulp, some of the precipitate will be carried down into the stem of the funnel.

Asbestos Filtration.—Asbestos filters are prepared in the same way as paper pulp filters. A few notes on the preparation of asbestos for use will be given.

Fine, silky, first-grade asbestos is used. A suitable quantity is picked out and packed into a beaker, where it is covered with 10 per cent. HCl and digested for several hours on the edge of the hotplate. At the end of this period, the acid is poured off and the asbestos washed

with two or three successive lots of water; the pulpy mass is then removed, squeezed dry in the hands, and placed in a platinum or porcelain dish, which, after drying, is thrust into the hottest part of the muffle until the whole mass is red-hot. Having thus eliminated soluble and carbonaceous matter which might possibly be present, the glowing mass is removed and allowed to cool in a dust-free, closed space (*e.g.* a large desiccator). When cold, the ball is loosely broken up and the now pinkish asbestos transferred to a capacious wide-mouthed bottle. It is now ready for use, and only requires shaking up with water to obtain the necessary " pulp " for making filters.

Asbestos is used: 1. For filtering graphite before making a carbon determination (see Steels; Carbon). 2. For filtering solutions that are too acid for paper to bear (*e.g.* see under Arsenic; Separation from Antimony). 3. For filtering hot, powerfully oxidising solutions, which would attack paper (*e.g.* dichromates; see under Chromium in Steel). 4. For filtering off precipitates of reducible metals, such as $PbSO_4$. The fact that asbestos is non-reducing enables such precipitates to be ignited in a Gooch crucible without the analyst having to have recourse to the elaborate and troublesome technique of igniting paper and precipitate separately. (See under Silver and Lead, Antimony.)

Note 1.—Fresh asbestos is apt to be " stringy " and not very amenable to pulp making. If there are stringy pieces in the material at hand, make the coarse pieces the basis of the filter, picking them by hand if necessary, and then pour the finer suspended pulp over the whole. This will usually make a filter that will " hold," and a filter prepared in this way has the advantage of being extremely free-running.

Note 2.—Asbestos should be used over and over again. All the used filter-pads are placed in a large beaker when finished with, and periodically, when a sufficient amount has been collected, the asbestos is recovered as follows:—

Add water to make a fairly fluid pulp, then a few crystals of sodium sulphite (or ammonium bisulphite), followed by a little dilute HNO_3. Stir with a glass rod, and it will be found that the asbestos cleans very quickly. Transfer the clean mass to a large funnel in which a filter disc has been placed and allow it to drain completely, compressing it with a glass rod to squeeze out the excess of acid. Wash with hot water five or six times, then once with faintly pink $KMnO_4$ solution (it would be fatal to leave sulphites in the pulp!), and finally with water until the $KMnO_4$ is washed out. The mass is then squeezed into a ball and ignited in the muffle as already described in order to burn off any dust which may have fallen into the " Waste Asbestos " beaker while standing in the laboratory.

Gooch Crucibles are extremely useful in the many cases where the usual folded paper filters or paper pulps are not available on account of some special peculiarity of the precipitate that is being handled:—1. Paper-lined Gooches are used when a volatile precipitate is to be weighed, *e.g.* nickel dimethylglyoxime, ammonium phospho-molybdate, arsenic trisulphide, etc. 2. Asbestos-lined Gooches serve when the precipitate has to be ignited or when it contains a reducible metal.

The crucible is placed in its rubber collar on the pressure-flask and the water-pump is started. A very little fine paper or asbestos pulp

is then poured into the crucible and sucked dry. The crucible is then removed and, if the filter is paper, it is placed in the air oven at 110° C. until its weight is constant (about 1 hour); if asbestos, the crucible is set on the hotplate until dry, and then placed inside the muffle to be heated to redness. After filtering and washing as required, the crucible and its contents are dried or ignited before the final weighing, the final treatment being in all cases identically the same as that used before the preliminary weighing.

Scrubbing Out.—In transferring a precipitate to its filter it is usually necessary to " scrub out " the beaker in order to remove particles of precipitate which adhere to the sides of the glass vessel. Precipitates vary considerably in their tendency to stick to glass; some, such as AgCl, $PbSO_4$, $BaSO_4$, and the like, have a very slight tendency to adhere, and may usually be transferred completely by means of the washbottle jet; others, such as Group II sulphides, $MnO_2.H_2O$, and most hydroxides, can often be detached completely with a strong jet of water, but these stick very firmly if they should happen to get dry. Lastly, certain acidic oxides of a colloidal nature, notably WO_3, SnO_2, SiO_2, and the like,

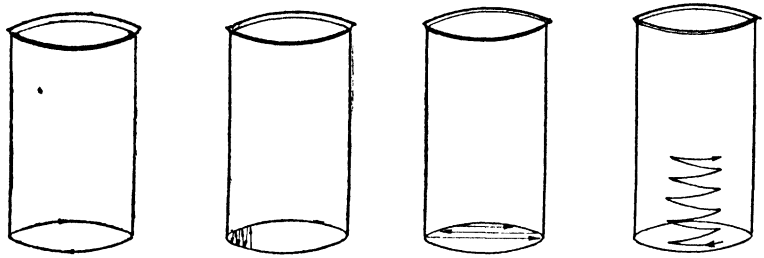


Fig. 4.—Scrubbing out Beaker with "Policeman."

appear to be partly ' gelled ' by the oppositely charged colloids in the glass, and their adhesion is very firm.

In order to remove such precipitates, a tool known as a " policeman " and consisting of a piece of soft rubber tubing slipped over the end of a rounded-off glass rod, is used. The piece of rubber should be about 1·5″ long, and it must fit tightly to the glass support; there is no great need to close the end, provided that it projects far enough beyond the glass to prevent the latter from scratching the bottom of the beaker; it is easy to remove any precipitate from the hollow end with the jet from the washbottle. In scrubbing out, a system is essential in order that no area of the glass vessel be overlooked during the operation. The writer uses the method shown in the diagram (fig. 4); briefly it is as follows:—

1. Place about 2 cc. of water in the rinsed-out beaker; this keeps the " policeman " wet.
2. Scrub right round the curved surface where sides meet bottom with the tip of the " policeman," completing the circle several times.
3. Scrub from side to side (" North to South ") of the bottom, using the tip.
4. Scrub from side to side at right angles to this (" East to West ").
5. Holding the beaker tilted towards you at 45°, scrub *up* the sides

with the side of the "policeman," rubbing him to and fro through an arc of about 30° and slowly raising the scrubber until the highest point reached by the precipitate is well covered. It is a good plan to start at the lip (or at the identification mark on the beaker) so that a datum point is established.

6. Turn the beaker through about one-tenth of a circle and repeat the process until a return to the starting point has been made. The series of arcs should overlap considerably.

7. Rinse the "policeman" with the jet, and remove him. Rinse down the sides of the beaker with the jet to collect the detached precipitate. Transfer it to the filter.

"Washing Back" and "Dissolving Off."—A very frequently recurring operation in analytical work is that of transferring a washed precipitate from its filter to a beaker or dish for further treatment. This operation is of the greatest possible importance, and the following notes are inserted in order to indicate the best method for its effective and rapid execution:—

Washing Back.—The precipitate is washed into the apex of the funnel, where it is allowed to drain completely. The beaker containing the filtrate is now replaced by the beaker or dish into which it is desired to transfer the precipitate. The paper is then carefully removed by pressing the tip of the forefinger against its trebly folded side, as being the strongest and least liable to tear, and sliding it upwards until it is clear of the rim of the funnel. The paper and precipitate are transferred to the crook of the thumb and first finger of the left hand, and, while still holding over the funnel in case of accident, the folds of the paper are gently opened out with the right hand, allowing the paper to drop back into the funnel.

As a rule the wet precipitate slides down into the apex of the funnel; if it does not, the gently applied washbottle jet will cause it to do so. Now, before rinsing the paper, direct a strong jet on to the precipitate in the apex, breaking it up and forcing it down the stem into the beaker placed to receive it. The paper is then systematically cleared of adhering precipitate, supporting the paper with the unoccupied hand if necessary (filter-paper is very flimsy when wet). It is rarely possible to remove all the precipitate in this way without completely breaking up the paper, and the next step is to dissolve off the adhering solids with that reagent in which the whole is subsequently to be dissolved or digested. This reagent is best applied from a small washbottle, or it is poured over the paper from a small beaker; after this application and a reasonable interval for draining, the paper is rinsed with water in order to wash out the secondary solution that will have been absorbed into its pores, then again with the reagent and pure water, applied alternately until all the solid is removed. The paper is then made into a ball and squeezed between the finger-tips over the funnel.

This is the only correct method. The writer has seen it recommended in text-books to punch a hole in the apex of the paper and so rinse the precipitate out without opening the paper. It cannot be too strongly emphasised that this method is very inefficient, and should be ruled out of serious consideration in quantitative analysis, if only because it

entirely fails to remove the precipitate that is invariably drawn up behind the folds of the paper by capillarity.

Dissolving Off.—This is the parallel operation for removing a precipitate from a pulp filter. Note, however, that it is only efficient where small amounts of easily soluble precipitates are concerned; others had better be filtered off on to paper as usual.

The filter having drained, the reagent is poured over the precipitate a little at a time, catching the runnings in a clean beaker or dish. As before, alternate washings with reagent and water are necessary. After the final washing the edge of the pulp is raised and the water in the stem is allowed to run out; the paper is then squeezed out, and the operation is complete.

This method is often very useful in separating the constituents of a mixed precipitate, one of which is soluble and the other insoluble in the reagent used. Thus, in the analysis of a lead-bearing metal, after the removal of the lead as $PbSO_4$ or $PbCl_2$, copper, antimony and tin may be precipitated as sulphides, which are filtered off from the iron, etc., through a small pulp. The washed sulphides may then be treated with several small doses of Na_2S solution, whereby SnS_2 and Sb_2S_3 are dissolved off, leaving CuS behind in a condition which permits of direct ignition to CuO. Note that in such a case, it is very important that the precipitate should be well "stirred up" with the reagent in the funnel each time.

SECTION II.

THEORETICAL CONSIDERATIONS.

LAW OF MASS ACTION.

CONSIDER the simple reaction $AX + BY = AY + BX$, where AX, BY, AY and BX are compounds which do not ionise in solution. In order that this reaction may take place it is necessary that molecules of AX and BY shall come into contact. It is not supposed that every contact results in reaction; but under similar conditions it is reasonably certain that the same proportion of the number of colliding molecules will react. The probability of contact obviously depends upon the number of molecules present, or rather, upon their *concentration*, which is defined as their number per unit volume. If, now, the concentration of AX is doubled, each molecule of BY has double its previous number of opportunities of encountering a molecule of AX, and the reaction might be expected to proceed with doubled velocity, other conditions remaining the same. Similarly, if the concentration of BY is now also doubled, the probability of contact between the two kinds of molecules will again be doubled, so that we conclude that the velocity of reaction between non-electrolytes is proportional to the product of the concentrations of the reacting molecules.

Denoting " concentration of " by square brackets, we may symbolise this result thus:

(1) Velocity of forward reaction $= [AX]\,[BY]\,K_1$, where K_1 is a constant.

The same argument, however, holds when considering the molecules AY and BX, which will tend to react so as to re-form AX and BY, so that we get:

(2) Velocity of reverse reaction $= [AY]\,[BX]\,K_2$, K_2 being another, and different, constant.

As the reaction between AX and BY proceeds, their concentrations diminish, and the velocity of (1) falls off, while that of (2) increases, a point ultimately being reached at which the two velocities are equal. At this, the equilibrium point, no further change of concentration takes place in the solution, and we have:

(3) $[AX]\,[BY]\,K_1 = [AY]\,[BX]\,K_2$, or

$$\frac{[AX]\,[BY]}{[AY]\,[BX]} = \frac{K_2}{K_1} = K,\ K \text{ being a new constant.}$$

The inorganic analyst, however, only very occasionally deals with non-electrolytes; his reactions are almost entirely those of *ions*. Fortun-

ately, however, the same Law of Mass Action applies (with, of course, suitable modifications) to ionic reactions, and the implications of this will be discussed after the Ionic Hypothesis has been outlined.

IONIC HYPOTHESIS.

The Ionic Hypothesis is, in outline, extremely simple to understand, and as a thorough grasp of its basic principles is of first rate importance to the student of chemical analysis, the following section should be carefully studied.

Practically all inorganic compounds when in solution in water behave as though they were binary; that is, they split up primarily into two distinct parts, each of which appears to have a separate existence, and acts in many cases independently of the other part. These parts are called *ions*, and they carry electric charges, so that if charged electrodes are introduced into a solution containing ions, those ions that carry positive charges of electricity will migrate to the negative pole and *vice versa*, giving rise to the well-known phenomenon of electrolysis. Substances which are ionised in solution are called *electrolytes*, because they conduct the electric current.

Ions are not necessarily simple; often they consist of combinations of atoms, and many of these combinations are incapable of separate existence unless they are in the "ionic" state, *i.e.* still carrying their electric charges. When such ions as OH^-, $SO_4^=$, etc. are discharged by coming into contact with the positive pole of the electrolytic cell, we may imagine that for an instant of time they do exist as OH and SO_4, but as we never obtain any OH or SO_4 by electrolysis, but only (in these cases) free oxygen or oxygen and sulphuric acid, we conclude that these combinations of atoms at once react either with themselves or with water, thus:

$$2OH = H_2O + O \text{ and}$$
$$SO_4 + H_2O = H_2SO_4 + O.$$

Those ions which are attracted to the positive electrode of an electrolytic cell (*i.e.* that connected to the red terminal or carbon end of the battery) are called *Anions* and the positive electrode is known as the *Anode*, while the ions which travel in the reverse direction, finally reaching the *Kathode* or negative electrode (that connected to the zinc of the battery), are termed *Kations*. Thus, anions carry a negative electric charge and include the hydroxyl of bases and the acidic parts of salts, whilst kations carry a positive charge and include the hydrogen of acids and the basic or metallic parts of salts.

In solutions of ordinary concentrations, electrolytes are not completely split up into ions (*i.e.* "dissociated"); there are always at least three types of entities present in a solution of an electrolyte, viz:—

1. Some Kations,
2. An equivalent quantity of Anions, and
3. A number of *undissociated molecules* of the electrolyte.

The relative proportions of these depend on the concentration of the solution, and upon the temperature, the invariable rule being that as

the solution is diluted, more and more of the undissociated molecules split up into ions, so that at sufficiently great dilution all "good" electrolytes will be practically 100 per cent. dissociated. On the other hand, when the solution is concentrated, the ions tend to *associate*, though with good electrolytes, that is, "strong" acids and bases, and all * salts, this association never becomes complete. Rise of temperature promotes ionisation, and *vice versa*.

It is well to remember, then, that in general, there are many more sets of free ions in a solution of an electrolyte than there are un-ionised molecules.

Ionisation results not in a static but a dynamic equilibrium; that is to say, if we consider a compound A B that ionises into A^+ (Kation) and B^- (Anion), the two reactions: $A\,B = A^+ + B^-$ and $A^+ + B^- = A\,B$ must be imagined to be in constant progress, proceeding simultaneously and to exactly equal extents. This means that any one associated molecule A B has no more than a momentary existence, but dissociates again almost as soon as it is formed, its ions finding other partners as the reverse reaction comes into play, but the number of undissociated molecules is always the same (at the same temperature) at any instant. We may, therefore, write the process as a reversible reaction, thus:

$$A\,B \rightleftarrows A^+ + B^-$$

the left to right reaction tending to get the upper hand if we dilute, and the right to left if we concentrate the solution. At a certain dilution and at constant temperature, the two reactions exactly balance.

The reacting ions also appear to obey the Law of Mass Action. In the case of a compound giving two monovalent ions we have:

$$A\,B \rightleftarrows A^+ + B^-$$

and at equilibrium, applying the Law of Mass Action, we may write:

$$\frac{[A^+]\,[B^-]}{[A\,B]} = K \text{ (constant)}.$$

If the solution is of such concentration that one mole of A B is contained in V litres of water, and if, at this concentration, N represents the ratio of dissociated molecules to total molecules, then, in volume V:

$$[A^+] = [B^-] = \frac{N}{V}, \text{ and:}$$

$$[A\,B] = \frac{1 - N}{V}.$$

i.e.

$$\frac{[A^+]\,[B^-]}{[A\,B]} = K = \frac{\frac{N^2}{V^2}}{\frac{1 - N}{V}} = \frac{N^2}{(1 - N)\,V}.$$

* "All" is not quite true. There are a few inorganic salts which do not ionise to any great extent, *e.g.* mercuric cyanide, $Hg(CN)_2$, and some cadmium salts; also, of course, some complexes of cobalt, chromium, palladium, platinum, etc. are not electrolytes at any concentration.

This is *Ostwald's Dilution Law*, and from it the preceding rules connecting dissociation and dilution may be deduced. Similar expressions may be obtained for more complex compounds giving divalent, trivalent, etc. ions.

This Dilution Law is only rigidly true for compounds that are slightly ionised—that is, for weak acids and bases such as acetic acid and ammonium hydroxide—but it is a close approximation for all electrolytes at low concentrations. Results obtained by applying the Dilution Law to strong acids or bases such as hydrochloric acid or sodium hydroxide are not nearly so good. It is probable that this is due to the dissolved substance uniting with the solvent, so that in more concentrated solutions some of the solvent molecules unite with the ions and undissociated molecules of the solute, thereby ceasing to act as solvent. The constant K is known as the *Dissociation Constant*, and is a measure of the "*strength*" of an acid or base.

It should be noted that ions may themselves undergo further dissociation, and that a compound may ionise in more than one way, so that a solution containing only one electrolyte may contain more than two kinds of ions; this, however, does not affect the analyst as a rule, so that, though it is of importance in general theory, it will not be considered fully here. Examples may, however, be helpful in enabling the student to picture the nature of ionisation.

(*a*) If potassium cyanide solution is added to silver nitrate solution, a precipitate of silver cyanide, AgCN, is produced. When the potassium cyanide is in excess of the amount required for the reaction

$$KCN + AgNO_3 = KNO_3 + AgCN,$$

the excess combines with the precipitated silver cyanide thus:

$$KCN + AgCN = KAg(CN)_2,$$

and since the latter is a salt that is soluble in water, the precipitate re-dissolves. The double cyanide, $KAg(CN)_2$, ionises thus into K^+ (Kation) and $AgCN_2^-$ (Anion), but the anion further breaks up into Ag^+ (Kation) and $2CN^-$ (Anions). It will be noticed that no matter how far the secondary ionisation proceeds, there will always be an equivalent number of ions present, for the liberation of each Ag^+ kation sets free two CN^- anions.

(*b*) H_2SO_4 ionises thus: $H_2SO_4 \rightleftarrows H^+ + HSO_4^-$, and the latter further into $H^+ + SO_4^-$, so that there are three different ions present. It may be remarked that this secondary ionisation is characteristic of the polybasic acids (and polyacid bases). In every case, however, the secondary dissociation constants are very much smaller than the primary constants.

It has been mentioned in a preceding paragraph that the principles of the Law of Mass Action can be applied to ionic reactions as well as to reactions between non-electrolytes, the ions acting as though they were separate entities; to illustrate the manner of applying the principle to analytical problems and methods, one or two actual cases will now be discussed.

Example 1.—Consider the reaction $KNO_3 + NaCl \rightleftarrows KCl + NaNO_3$

from the ionic point of view. In the first place, this equation really conceals several equilibria:

$$KNO_3 \rightleftarrows K^+ + NO_3^-, \quad . \quad . \quad . \quad . \quad 1$$
$$NaCl \rightleftarrows Na^+ + Cl^-, \quad . \quad . \quad . \quad . \quad 2$$
$$KCl \rightleftarrows K^+ + Cl^-, \quad . \quad . \quad . \quad . \quad 3$$

and

$$NaNO_3 \rightleftarrows Na^+ + NO_3^-, \quad . \quad . \quad . \quad . \quad 4$$

There is also a fifth, viz.:

$$HOH \rightleftarrows H^+ + OH^-, \quad . \quad . \quad . \quad . \quad 5$$

which enters into many equilibria in a manner which is often of the highest importance. In analysis, however, such equilibria as the foregoing are of but little practical importance, as it is quite impossible to distinguish in any way between a mixture of solutions of $NaNO_3$ and KCl, and one of solutions of KNO_3 and NaCl, since they both yield the same ions.

The analyst requires reactions which are able to proceed to (virtual) completion, and this can only be brought about in two ways:

(*a*) By removing one of the products of reaction as fast as it is formed,

or

(*b*) By adding an overwhelming concentration of one of the reacting ions.

In case (*a*) the forward reaction completes itself because there can be no reverse reaction to compete with it, and in case (*b*), while the reaction can never proceed to theoretical completion, yet if the concentration of one of the reacting ions is made very great, the reaction is able to proceed so near to theoretical finality that the error made in assuming absolute completion becomes negligible.

Example 2.—If we mix solutions of silver nitrate and sodium chloride we again have four primary equilibria to consider, viz.:

$$AgNO_3 \rightleftarrows Ag^+ + NO_3^-, \quad . \quad . \quad . \quad 1$$
$$NaCl \rightleftarrows Na^+ + Cl^-, \quad . \quad . \quad . \quad . \quad 2$$
$$Ag^+ + Cl^- \rightleftarrows AgCl, \quad . \quad . \quad . \quad . \quad 3$$

and

$$Na^+ + NO_3^- \rightleftarrows NaNO_3, \quad . \quad . \quad . \quad . \quad 4$$

but there is an important difference from the preceding example. Silver chloride is a substance of which the solubility in water is exceedingly small, and if the amounts of Ag^+ and Cl^- present are appreciable, the solution will rapidly become saturated with respect to AgCl molecules, and precipitation will take place, removing the AgCl from the sphere of reaction. As soon as this saturation point is reached, every Ag^+ ion that encounters a Cl^- ion will pass out of the system as solid AgCl, and this process will continue until equilibrium is reached, which practically means until either the Ag^+ or the Cl^- is exhausted. In consequence of this there will be practically no reverse reaction in the case of equation

3, which will thus proceed from left to right to completion, and, in the process, either all the Ag^+ ions or all the Cl^- ions will have been removed, so that not only will equation 3 be completed from left to right, but equations 1 and/or 2 will also complete themselves in the same direction, owing to lack of Ag^+ and/or Cl^- ions respectively in the solution.

The reactions will not, however, be quite 100 per cent. complete, because AgCl is not completely insoluble in water; a few Ag^+ and Cl^- ions will remain in the system.

Example 3.—When hydrochloric acid and sodium carbonate solutions are mixed, the ionic equilibria are:

$$Na_2CO_3 \rightleftarrows 2Na^+ + CO_3^=, \quad . \quad . \quad . \quad . \quad 1$$
$$HCl \rightleftarrows H^+ + Cl^-, \quad . \quad . \quad . \quad . \quad . \quad 2$$
$$2H^+ + CO_3^= \rightleftarrows H_2CO_3, \quad . \quad . \quad . \quad . \quad 3$$
$$(H_2CO_3 = H_2O + CO_2), \quad . \quad . \quad . \quad . \quad 3a$$
$$Na^+ + Cl^- \rightleftarrows NaCl, \quad . \quad . \quad . \quad . \quad . \quad 4$$

In this case also, the reaction can proceed to theoretical completion, because H_2CO_3 is a compound which is only very slightly ionised in solution. This means that although there is no precipitation, nevertheless equation 3 will proceed from left to right almost to completion, owing to the fact that the ionisation of carbonic acid is so small (especially with other H^+ ions in the solution) that the right to left reaction is negligible, the same result being obtained as in example 2. This case differs slightly, however, in that reaction 3*a* is possible, and, on boiling the solution, or otherwise removing CO_2, reaction 3 does actually proceed from left to right to theoretical completion, the net result being:

$$Na_2CO_3 + 2HCl = 2NaCl + H_2O + CO_2,$$

no reverse reaction being possible owing to decomposition of the carbonic acid formed and elimination of the CO_2 as gas.

SATURATION, SOLUBILITY PRODUCT AND PRECIPITATION.

It is well known that the amount of any solid substance that can be dissolved in water is not unlimited; also that the amount depends chiefly upon temperature, and, as a rule, increases with rising temperature.

When a solution, at constant temperature, will dissolve no more of the solute, and equilibrium is attained, the solution is said to be *saturated* with respect to that solute. It is possible, however, for a solvent liquid to hold in solution more of a solute than is in accordance with equilibrium conditions; when this is the case the solution is said to be *supersaturated.* The latter is naturally an unstable condition, and may be terminated either spontaneously or by means of an external stimulus, such as the introduction of a particle of the solid solute or by agitation of the liquid. It is probable that every case of precipitation is preceded by a state of supersaturation.

Consider the equilibrium of a saturated solution of an electrolyte A B which contains some undissolved salt. It is obvious that at a definite temperature the concentration of the solution must be constant, for there is excess of the solid always in contact with the solvent; and since,

at constant temperature, the degree of ionisation is constant, it follows that [A B] in the solution is constant.*

Applying the Law of Mass Action to the equilibrium of the ions and the associated molecules, and assuming a saturated solution in contact with excess of solute, we have:

$$\frac{[A^+]\,[B^-]}{[A\,B]} = \text{constant},$$

and therefore,

$$[A^+]\,[B^-] = \text{constant};$$

or, in words: "In a solution saturated with respect to a compound, the product of the concentrations of the ions of this compound is a constant (whatever their individual values may be)."

This ionic product is called the *Solubility Product.*

The above, of course, is the simplest case. In case of a compound $A_x B_y$, having ions A^+ and B^-, the equilibrium will be represented thus: $A_x B_y = x\,A^+ + y\,B^-$; whence $\frac{[A]^x\,[B]^y}{[A_x B_y]} = \text{constant}$, and therefore, $[A]^x\,[B]^y$ is constant. When the product of the ionic concentrations has attained the value of the Solubility Product, the slightest excess of either ion brings about a state of supersaturation, and precipitation ensues, the solid substance being deposited from the solution until the product of its ions again equals the Solubility Product.

The converse is also true; for if by any means the concentration of either of the ions concerned is lowered, more of the solid will pass into solution.

The fact that the precipitation point depends upon the *product* of the ionic concentrations is very important from an analytical point of view, as it follows that if the concentration of either of the reacting ions is increased the concentration of the other ion in the solution must be diminished proportionately, and *vice versa.* The quantitative effect of an excess of (*e.g.*) the Cl^- ion on the solubility of AgCl may be worked out thus:

AgCl is soluble in pure water to the extent of 0·00134 gm. per litre at 18° C.

$$0{\cdot}00134 \text{ gm.} = \frac{0{\cdot}00134}{143} \text{ gram-molecule}$$
$$= 0{\cdot}00001 \text{ gm.-mol. (approx.).}$$

Now at this extreme dilution, and for rough calculation, we may reasonably assume that AgCl is completely ionised, so that:

$$\text{Solubility product} = [Ag^+]\,[Cl^-]$$
$$= 0{\cdot}00001 \times 0{\cdot}00001$$
$$= 1 \times 10^{-10} \text{ gm.-mol.}$$

* The statement that [A B] is constant rests upon two assumptions; firstly, that the concentration of the undissociated molecules remains constant when a second electrolyte is added, and secondly, that the Law of Mass Action applies to ions. These assumptions are not strictly justified, and the principle can only be applied rigidly to very dilute solutions. The analyst, however, does not, as a rule, wish to consider any equilibria except those of very slightly soluble precipitates, so that which follows may be considered to be true so far as practical analysis is concerned.

Suppose, now, that 0·1 gm. excess of NaCl is added to 1 litre of a saturated solution of AgCl; then, NaCl at this dilution being completely ionised, we shall have added 0·00171 gm. -ion of Cl^- ions, so that the total concentration of Cl^- is 0·00171 + 0·00001. But $[Ag^+]$ $[Cl^-]$ is a constant, $= 1 \times 10^{-10}$, whatever the individual concentrations of the ions, and $[Cl^-]$ is now 0·00172 gm. -ion per litre.

Therefore, $[Ag^+]$ will be $\dfrac{1 \times 10^{-10}}{1{\cdot}72 \times 10^{-3}}$ (approx.)

$= 0{\cdot}58 \times 10^{-7}$ gram-ion per litre.

In other words, $[Ag^+]$ is considerably reduced, and this involves, of course, a corresponding reduction of the amount of AgCl dissolved, so that on adding the NaCl solution a turbidity will be produced. (See under Titration of Silver with Sodium Chloride for further remarks on this case.)

The addition, therefore, of a " common ion " to the saturated solution of an electrolyte, reduces the solubility of that electrolyte. On the other hand, the addition of a " neutral " electrolyte (*i.e.* a substance containing no common ion) increases (relatively slightly) the solubility. This may easily be understood from the following:

Taking the case just considered:

$$Ag^+ + Cl^- \rightleftarrows AgCl \text{ (dissolved)} \rightleftarrows AgCl \text{ (solid)}.$$

If now a substance possessing no ion in common, *e.g.* KNO_3, is added, we have:

$$Ag^+ + Cl^- \rightleftarrows AgCl \text{ (dissolved)} \rightleftarrows AgCl \text{ (solid)},$$

and also $$K^+ + NO_3^- \rightleftarrows KNO_3$$

as primary equilibria. But some of the Ag^+ ions, instead of associating with and dissociating from Cl^- ions, can now unite with NO_3^- ions, and Cl^- can unite with K^+ ions, so that we have:

$$Ag^+ + NO_3^- \rightleftarrows AgNO_3,$$

and $$K^+ + Cl^- \rightleftarrows KCl.$$

The result is that more solid AgCl must dissolve to supply Ag^+ and Cl^- ions for the two new equilibria.

MECHANISM OF PRECIPITATION AND ADSORPTION.

Colloids are " solid " particles so small that they will remain indefinitely suspended in a medium unless they are made to coalesce by some external means. It seems probable that in all cases when a solid separates out from a solution, the first stage is the formation of a colloidal " solution " (suspension), and it is possible to obtain a series of solution-suspensions filling the whole range between a true solution, with the solute in the ionic or molecular state (particle diameter of the order of 0·1 to 1×10^{-6} mm.), through colloidal " solutions," in which the presence of solid particles is observable by optical methods,

and which are only called solutions in the sense of being unfilterable (particle diameter of the order 4 to 30 $\times$ 10^{-6} mm.) to genuine suspensions in which the particles are evident to the unaided eye (size about 2 $\times$ 10^{-4} mm.).

Note.—It is important to remember that a colloidal "solution" is not a solution in the true sense of the word. The particles are not in the molecular or ionic form; they are not electrolytes in the ordinary sense of the term, but they resemble true solutions in that they (1) show no visible particles (naked eye), (2) do not "settle out" on standing, and (3) the colloid cannot be separated by filtration.

The whole matter may, in one sense, be referred to the size of the particles. In a true solution, the solute is divided down to the ionic or molecular state, so that the particles consist at the most of a few molecules only; a colloid "solution" carries particles each consisting of, say, a few hundreds or thousands of molecules, while the particles of even the most finely divided suspension are very many times larger.

The two properties of colloidal matter that are important from the analyst's point of view are:

1. Colloid particles carry an electrical charge, either positive or negative, a fact which enables them to be coagulated by electrical means. Colloidal solutions behave somewhat as though they contain unusually large ions.

2. Colloid solutions can be coagulated and converted from *pseudo*-solutions ("**Sol**"—unfilterable) into true suspensions ("**Gel**"—filterable).

Coagulation may occur spontaneously, but the analyst usually accelerates the process, either by boiling the solution or by adding an electrolyte.

Note.—There is also, of course, the method of inserting a charged electrode into the colloidal solution. This, by discharging the electrified particles, causes their precipitation.

It will be instructive to attempt to picture what occurs when a precipitate is in the process of formation; the student must, however, remember that there is much in the domain of colloid chemistry which is still under debate, and must not accept the following sketch as beyond all criticism or modification.

Imagine a solution to which a reagent capable of producing a precipitate has just been added. At the instant when the solubility product for the precipitate is exceeded, a period of supersaturation ensues, the duration of which depends upon various factors, but principally upon the degree of "insolubility" of the precipitate; finally, however, we may imagine that solid single molecules of the substance separate (though it is not strictly accurate, of course, to speak of a single molecule of a substance isolated in a solvent as being "solid"), the number of these depending on the degree of supersaturation, the concentration of the precipitating substance, and the temperature. Those molecules act as "nuclei," and to them more of the separating solid attaches itself, so that the particles, originally of molecular dimensions (and so not different from those of a true solution), grow in size and mass, and a "colloidal solution" results. These aggregates behave as large "mole-

cules," and if the separating substance is crystalline, they are probably definitely oriented.

The surrounding solution and its contents (ions and associated molecules) now begin to act upon this extremely finely divided " suspension; " molecules of the same kind tend to attach themselves in a regular (crystalline) manner, and at the same time ions are split off, leaving the aggregates with an electrical charge, the sign of which depends on the nature of the ionisation. In addition to this, *adsorption* comes into play.

It is probable that adsorption is a purely physico-chemical phenomenon; certainly it is easily understandable in a qualitative way in the light of the Braggs' investigations into the nature of crystals. We know that the atoms of a crystalline solid are arranged in symmetrical layers (lattices), being held in position by chemical " affinity " (whatever this may be). Since these forces presumably balance in the interior layers of the crystal, it is obvious that there will be " affinity " to spare at the surface and edges. It is not to be wondered at, therefore, that suitably charged alien ions and molecules may be held fast by adsorption. The degree of adsorption will depend on the surface area available, so that it is manifestly advantageous to obtain the final precipitate in as compact a condition as possible.

Our growing aggregates, still too small to be either visible (naked eye) or filterable (paper), are, therefore, possessed of the following characteristics:

1. They carry an electrical charge, which may be positive or negative.
2. They have an adsorbed surface layer of " alien " ions and molecules.

In dilute solution, the bulk of the adsorbed layer must undoubtedly be water, because that compound predominates so greatly, but there will always be a certain amount of other substances derived from the solution; hence the method of keeping down (harmful) adsorption is to work in as dilute a solution as possible.

In pure solutions it is possible for the separated particles to remain for prolonged periods in the colloidal condition, but in most analytical processes this cannot persist, chiefly owing to the presence of electrolytes with their charged ions. The aggregates, therefore, continue to grow, firstly, by the deposition of their own kind of molecules upon their surfaces in relief of the supersaturation, and secondly by the coalescence of the particles. The latter process is very slow in pure and dilute solutions owing to the mutual repulsion of similarly charged particles, but in the presence of electrolytes, coagulation is rapid, probably owing to the neutralisation of the charges on the particles by encounter with oppositely charged ions in the solution. These processes are accelerated by heating the solution; the effect is partly mechanical, the internal movement of the medium being increased so that there are more and more violent collisions, and partly results from the increased dissociation of the electrolytes concerned.

The analyst, therefore, consciously or unconsciously, conducts his precipitation with an eye to the foregoing points. From his point of

view, the most satisfactory precipitates to handle are those which are crystalline, preferably coarsely crystalline, and for the following reasons:

1. They settle quickly.
2. They are easy to wash on the filter.
3. They are generally purer than gelatinous amorphous precipitates,
   (*a*) Because of their lesser surface area, and consequent lesser adsorption, and
   (*b*) Because there is less danger of impurities being enclosed by the precipitate.
4. They are less likely to pass back into colloidal solution on washing.

In order to obtain a precipitate in this condition, the following points must be attended to:

1. Precipitate *slowly*, adding the reagent by drops, stirring meanwhile in order to avoid local concentrations of the precipitant.
2. Use dilute solutions and reagents.
3. Avoid unnecessary excess of the precipitant, such avoidance making the precipitate more "soluble" and assisting in retarding the growth of the particles.
4. Precipitate *hot* for the same reason.
5. Avoid high concentrations of electrolytes, so that electrolytic coagulation may be retarded.

In general, it is important to retard the *initial* growth of the particles if the precipitate is to be obtained in the optimum condition for subsequent handling.

Amorphous precipitates have, however, to be dealt with in analysis. The essential difference between these and crystalline precipitates is that the former are produced almost entirely by ionic coagulation, and thus, by their very nature, they are bound to suffer from higher adsorption, apart from the fact that they invariably possess a much larger surface area over which adsorption can act. The ions which discharge the ultra-microscopic particles of the original sol and allow it to coagulate (gel) become attached by electrostatic forces to the surface of the coagulum, and they usually defy removal by washing with water. If, however, they *are* removed, the particles of the gel become re-charged by the loss of the neutralising ions, and there is now nothing to prevent the gel passing back into the sol state; or, as the analyst sometimes puts it: "the precipitate 'goes colloidal' and passes back through the filter."

This trouble may often be avoided by washing with an electrolyte, so that the attached ions may be replaced by others which will not prevent the obtaining of an ignited residue of correct composition. Many cases will occur to the student where precipitates are washed with a dilute electrolyte. Examples of such electrolytes are: NH_4NO_3, NH_4Cl, acid H_2S water, and mercurous nitrate; in every case it will

be noticed that it does not matter if the ions of the wash liquid are adsorbed, as they are all volatilised at low temperatures.

The other practical device for minimising the effects of adsorption is that of *double precipitation.* This device is most commonly employed in the separation of the metals of Analytical Group IV. from those of Group III.

For example, if the solution contain much Fe and some Ni, it is certain that the $Fe(OH)_3$ precipitate will contain considerable amounts of nickel salts, rendering the value obtained for the Fe too high (unless determined volumetrically), and that of the Ni correspondingly too low. Suppose, for argument, 0·5 gm. of Fe and 0·5 gm. Ni are to be separated, and that, under the original conditions of concentration, the $Fe(OH)_3$ precipitate adsorbs 1 per cent. of the nickel salt that cannot be washed out with hot water. On first precipitating with ammonia, 1 gm. (approx.) of $Fe(OH)_3$ will be formed, and this, by hypothesis, will hold 0·01 gm. of nickel salt or about 0·005 gm. of Ni, the remaining Ni being in the filtrate. If, now, the precipitate be dissolved in dilute acid and re-precipitated with ammonia, it is obvious that with the far lower concentration of Ni^{++} only a small fraction of the 0·005 gm. will be retained. This small quantity is of no importance analytically, and a reasonably complete separation is effected, in spite of adsorption.

It is interesting to note that the fibres of filter paper act as negative colloids, and are consequently able to coagulate and adsorb positive sols; conversely, they tend to 'peptise' (*i.e.* 'de-coagulate') negative gels, which will begin to pass back through the filter at an earlier stage of washing than would otherwise be the case.

ACIDS, BASES AND SALTS.

Acids owe their special properties to their H^+ ions. If the acid is relatively completely ionised, and therefore contains a high concentration of H^+ compared with that of associated molecules, it is said to be *strong*; while if it is but little dissociated, it is said to be *weak.*

Strong acids include the common mineral acids such as H_2SO_4, HCl, HNO_3, H_3PO_4, H_2SiF_6. Weak acids include the organic acids and most of the borderline acids; *e.g.* Acetic, oxalic and tartaric acids, H_2CO_3, HCN, H_2S, H_2SiO_3, H_3BO_3.

The strength of *bases* similarly depends upon their degree of dissociation in solution; they owe their special properties to their OH^- ions.

Strong bases include the hydroxides of the alkalies and alkaline earths. Weak bases include ammonia solution and solutions of the substituted ammonias or amines.

Salts.—Practically all salts are highly dissociated in aqueous solution, even those of weak acids and weak bases, and, as far as the analyst is concerned, he may assume that all salts are ionised to the extent of 70–100 per cent. at normal analytical concentrations.

Water.—Water is ionised to a slight extent into H^+ and OH^-, there being about 1 mole (*i.e.* 18 gms.) dissociated in every 11,000,000 litres. Minute as this amount may seem, it is nevertheless of the highest importance in analysis. (See Hydrolysis.)

HYDROLYSIS.

In aqueous solution, a salt, A B (for example), if an electrolyte, is subject to the following equilibria:

1. $A\,B \rightleftarrows A^+ + B^-$.
2. $H_2O \rightleftarrows H^+ + OH^-$.
3. $A^+ + OH^- \rightleftarrows A\,.\,OH$.
4. $B^- + H^+ \rightleftarrows HB$,

or, we may write:

$$A\,B + H\,.\,OH \rightleftarrows A\,.\,OH + H\,B\ ;$$

in other words, there is a tendency for the salt to react with water, the reaction producing greater or less quantities of the acid and base which by their combination produced the salt originally. The extent to which this action proceeds will obviously depend upon the degree of ionisation of the base and acid produced from the salt relative to the ionisation of water.

This phenomenon is termed *hydrolysis*, and is of the very greatest importance in analysis. For a proper understanding of its effects upon analytical processes, we must consider four possible cases:

(a) *The Salt is formed from a Strong Base and a Strong Acid.*

In all cases under this heading, equilibria Nos. 1 and 2 will be unaffected, No. 1 because all salts are practically completely ionised in dilute solution, (*Note*: There are exceptions, *e.g.* mercuric cyanide, and some cadmium salts, but these are relatively unimportant), and No. 2 is the ordinary water equilibrium. In case (*a*), equilibria 3 and 4 will proceed from right to left, equally, and practically to completion, for, by hypothesis, both acid and base are "strong." The net result is that OH^- and H^+ will be present in equivalent amounts, and the solution will react neutral.

(b) *The Salt is formed from Strong Acid and Weak Base.*

In this case, equilibrium 4 will proceed almost to completion from right to left, while in equilibrium 3 the left to right reaction will predominate. The result is that H^+ begins to accumulate in the solution, while more and more A^+ becomes attached to OH^-, passing into the un-ionised state. Well known examples of this type are the salts of aluminium and ferric iron. Considering, for example, a solution of pure $AlCl_3$, the solution will react acid, and, as is well known, a deposit of hydroxide (basic chloride) is gradually thrown down from the theoretically neutral solution.

(c) *Salt formed from a Weak Acid and a Strong Base.*

This is the converse of case (*b*). In this case there will be very little ionisation in equilibrium 4, and considerable (nearly 100 per cent.)

in equilibrium 3. The result will be that H^+ ions will disappear from the solution, being taken into un-ionised combination by the "weak" anions, and a corresponding increase in the concentration of OH^- will produce an alkaline reaction.

This case is more frequently met with. Examples are: Na_2CO_3, KCN, the alkali borates, and alkali salts of organic acids.

(d) *Salt formed from Weak Acid and Weak Base.*

These salts are also considerably ionised in solution, and whether the final reaction is acid or alkaline depends upon the relative strengths of the acid and base in question. In any case, the amount of hydrolysis will be very great, as the ionisation of both acid and base are by hypothesis very small, so that the reactions 3 and 4 can proceed almost entirely from left to right. In most cases, of course, this leads to the precipitation of the base (most hydroxides have very small solubility products), and the salt is completely decomposed by the water. An example is aluminium sulphide, which, when placed in water, breaks up into $Al(OH)_3$ and H_2S.

Special Cases of Hydrolysis.

Ferric chloride furnishes an example of the hydrolysis of a salt formed from a weak base and a strong acid, which is of considerable practical interest in the separation of iron from Group IV. In this case, the base is insoluble, and numerous complications are possible for this reason.

When first prepared, ferric chloride forms a clear solution, with, as explained, a pronounced acid reaction, and we may imagine a sort of equilibrium between $FeCl_3$, HCl and $Fe(OH)_3$ being attained. On standing, however, two things happen ; the solution grows dark in colour, and at the same time the acidity increases. The latter can only mean one thing, viz., that the reaction:

$$HOH = H^+ + OH^-$$

is proceeding to an increasing extent, for the only possible source of H^+ is the ionising water. We know, of course, that the dissociation constant of water is, normally, very small, and consequently we are forced to conclude that the OH^- ions are being progressively removed.

It is almost certain that what is actually happening is that the undissociated molecules of $Fe(OH)_3$ are "collecting" similar molcules and forming complexes, or "polymers" of a sort, which grow in size in spite of the fact that the acidity of the solution is increasing with the "separation" of every molecule. In time, a "colloidal solution" is formed, and as the solubility product $[Fe^{+++}]\,[OH^-]^3$ appears to *decrease* with the increasing size of the colloid particles, the solubility product is finally attained and the base is precipitated.

As is usual with precipitated colloids, this precipitate becomes less "soluble" in acid as it "ages." The precipitate is usually spoken of as the "basic chloride," but it is essentially hydroxide (combined with chloride, possibly). It can, of course, contain other negative radicles besides OH^- on account of the $Fe(OH)_3$ complexes still throwing off OH^- ions [$Fe(OH)_3$ being a positive colloid]. These may be, and

frequently are, replaced by Cl^- ions, so that the precipitate may perfectly legitimately be termed a "basic chloride," though this title rather obscures the mechanism of the process of precipitation. Similar remarks apply to $AlCl_3$.

A further discussion of the practical effects of hydrolysis may be found under the metals Iron and Aluminium. In particular, refer to the separation of Group III from Group IV metals (Basic Acetate Separation).

SOLUBILITY OF SALTS IN ACIDS.

With "insoluble" salts of strong acids, the addition of moderate amounts of another strong acid has very little effect upon the solubility. The possible actions, in the case of the addition of HCl to $BaSO_4$, are symbolised:

1. $BaSO_4 \rightleftarrows Ba^{++} + SO_4^{=}$.
2. $HCl \rightleftarrows H^+ + Cl^-$.
3. $BaCl_2 \rightleftarrows Ba^{++} + 2Cl^-$.
4. $H_2SO_4 \rightleftarrows H^+ + HSO_4^-$.
5. $HSO_4^- \rightleftarrows H^+ + SO_4^{=}$.

In dilute solutions, the left to right reactions predominate greatly, as all the possible compounds are good electrolytes. The result of adding the HCl is, therefore, to increase the solubility of the $BaSO_4$ to a slight extent, owing to some Ba^{++} being requisitioned to form $BaCl_2$ and some $SO_4^{=}$ to form HSO_4^- and H_2SO_4. The effect is, however, small, and is of the same nature as the increased solubility produced by adding an electrolyte possessing no common ion to a precipitate in contact with its saturated solution (*vide ante*).

In the case of salts of weak acids, however, conditions are different. Consider, for example, the addition of HCl to a precipitate of $Ni(CN)_2$. The equilibrium conditions are:

1. $Ni(CN)_2 \rightleftarrows Ni^{++} + 2CN^-$.
2. $HCl \rightleftarrows H^+ + Cl^-$.
3. $NiCl_2 \rightleftarrows Ni^{++} + 2Cl^-$.
4. $HCN \rightleftarrows H^+ + CN^-$.

$Ni(CN)_2$, HCl and $NiCl_2$ are all good electrolytes, ionising almost completely in solution, but HCN is so weak an acid (D.C. $= 1{\cdot}3 \times 10^{-9}$) that once a CN^- ion has encountered a H^+ ion it may be considered "withdrawn from circulation" for all practical purposes. Since, hypothesis, there is considerable free HCl present, the CN^- ions from the $Ni(CN)_2$ are constantly being used up, with the result that more $Ni(CN)_2$ is able to pass into solution. The precipitate, therefore, dissolves.

THEORY OF INDICATORS.

According to Hantzsch, an indicator is a weakly acidic or basic compound which can exist in two differently coloured tautomeric forms, one being neutral (un-ionised) and the other giving, in solution,

either H^+ or OH^- ions and an ion of the same colour as itself. In symbols (taking litmus as an example):

$$\underset{\text{(neutral; un-ionised)}}{\text{Red compound}} \overset{\text{tautomeric change}}{\rightleftarrows} \underset{\text{(acid; ionisable)}}{\text{Blue compound}} \rightleftarrows (\text{Blue ion})^- + H^+.$$

[With a basic indicator the ionisation will obviously be Base $\rightleftarrows$ (Coloured ion)$^-$ + OH^-]. On adding an acid, the $[H^+]$ (read: "*the concentration of the hydrion*") will be increased, thereby throwing the equilibrium over from right to left, forming the red compound. If, on the other hand, an alkali be added, the OH^- will unite with the H^+ of the ionised acid, forming water and lowering the $[H^+]$. The consequence is that the reaction will take place from left to right, and more blue ion will be produced.

Properties of a Good Indicator.

1. The colour should be intense,
   (*a*) So that the change may be easily observed.
   (*b*) So that very little of the indicator may suffice. It is obvious that the indicator will always account for a small proportion of the H^+ (or OH^-) of the substance employed for titration, and if much indicator has to be used, results will be inaccurate.
2. The tautomeric change must be rapid.
3. We have: $[H^+]\,[\text{Blue ion}^-] = K\,[\text{Blue acid}]$
   and: $[\text{Blue acid}] = K'\,[\text{Red tautomer}]$.
   Therefore: $[H^+]\,[\text{Blue ion}^-] = K\,K'\,[\text{Red tautomer}]$.

   That is, the "apparent dissociation constant" depends upon the product $K\,K'$, and since the colour change reaction depends entirely upon the concentration of the H^+ ions (OH^- ions in the case of a basic indicator), it is evident that the sensitiveness of an indicator is a function of this product $K\,K'$, which, in a good indicator, should be *small*, so that the slightest excess of H^+ (or OH^-) ions will suffice to produce the colour change.

   Furthermore, since the sensitiveness depends upon a product, it is evident that if K' be very small, K may be reasonably large; or, in other words, the indicator may be a moderately strong acid (or base).

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r as an Acid-Base.

Water ionises thus:

$$H_2O \rightleftarrows H^+ + OH^-$$

so that in pure water both H^+ and OH^- ions are present, and in equivalent amounts. Expressing this as a mass action equation, we have:

$$[H^+]\,[OH^-] = K[H_2O],$$

but in water or dilute aqueous solution $[H_2O]$ is constant, and, therefore,

$$[H^+]\,[OH^-] = \text{Constant} = K_w.$$

K_w is the "ionic product" of water and is equal to $1{\cdot}7 \times 10^{-15}$ gm. Water, considered as an acid, is Normal (N) when it contains 1 gm. of H^+ per litre. In pure water, however, the ionisation is small, and it cannot approach normality. At 20° C. 1 litre of water contains only 0·0000001 gm. of H^+, so that water is a 10^{-7} N acid (or base, since there is an equal amount of OH^- also present). Thus:

$$\left.\begin{aligned}[H^+] &= 1 \times 10^{-7} \text{ gm.} \\ [OH^-] &= 17 \times 10^{-7} \text{ gm.}\end{aligned}\right\} \text{ in water at } 20° \text{ C.}$$

therefore: $[H^+]\,[OH^-] = 1{\cdot}7 \times 10^{-15} = K_w = \textit{Ionic Product.}$

The *Dissociation Constant* is $\frac{[H^+]\,[OH^-]}{[H_2O]}$, and since $[H_2O]$ in 1,000 cc. of water $= \frac{1{,}000}{18} = 55{\cdot}5$ gram-molecules, the Dissociation Constant is equal to the Ionic Product $\times$ 55·5.

In titrating acid against base, the end-point (colour-change) does not really represent neutrality in the sense of $[H^+]$ being equal to $[OH^-]$. What actually happens is that the H^+ (or OH^-) has been reduced to a certain definitely known *small* concentration, the actual value of which depends upon the "strength" of the indicator, considered as an acid (or base); *i.e.* upon the Dissociation Constant (D.C.) of the indicator.

The titratability of an acid or base depends upon the value of its D.C. in (dilute) solution. These D.C.'s vary very considerably; the so-called "strong" acids and bases are as a rule about 100 per cent. dissociated in $\frac{N}{10}$ solution, but some acids and bases are only ionised to a very small extent even in dilute solution. For an acid or base to be titratable, its D.C. should be considerably greater than that of the indicator which it is proposed to use; in order, therefore, that the chemist may see at a glance what indicator to use for any given titration, a list of D.C.'s at $\frac{N}{10}$ dilution is appended.

It may be taken as a good working rule that the D.C. of the acid or base should be at least ten times that of the indicator.

Substance.	Equilibrium Ratio.	Dissociation Constant at $\frac{N}{10}$ dilution and 25° C.
Hydrochloric Acid, .	$\frac{[H^+]\,[Cl^-]}{[HCl]}$	"strong"
Nitric Acid, . .	$\frac{[H^+]\,[NO_3^-]}{[HNO_3]}$	"strong"
Sulphuric Acid (1st H^+),	$\frac{[H^+]\,[HSO_4^-]}{[H_2SO_4]}$	"strong"
Oxalic Acid (1st H^+), .	$\frac{[H^+]\,[HC_2O_4^-]}{[H_2C_2O_4]}$	$3{\cdot}8 \times 10^{-2}$

Substance.	Equilibrium Ratio.	Dissociation Constant at $\frac{N}{10}$ dilution and 25° C.
Sulphuric Acid (2nd H^+),	$\frac{[H^+]\,[SO_4^=]}{[HSO_4^-]}$	3×10^{-2}
Phosphoric Acid (1st H^+),	$\frac{[H^+]\,[H_2PO_4^-]}{[H_3PO_4]}$	1×10^{-2}
Methyl Orange, . .	$\frac{[H^+]\,[\text{Red ion}^-]}{[\text{Methyl Orange}]}$	4×10^{-4}
Oxalic Acid (2nd H^+), .	$\frac{[H^+]\,[C_2O_4^=]}{[HC_2O_4^-]}$	3×10^{-5}
Acetic Acid, . .	$\frac{[H^+]\,[CH_3COO^-]}{[CH_3COOH]}$	$1{\cdot}9 \times 10^{-5}$
Litmus, . . .	$\frac{[H^+]\,[\text{Blue ion}^-]}{[\text{Litmus}]}$	1×10^{-6}
Carbonic Acid (1st H^+),	$\frac{[H^+]\,[HCO_3^-]}{[H_2CO_3]}$	3×10^{-7}
Phosphoric Acid (2nd H^+),	$\frac{[H^+]\,[HPO_4^=]}{[H_2PO_4^-]}$	2×10^{-7}
Hydrogen Sulphide (1st H),	$\frac{[H^+]\,[HS^-]}{[H_2S]}$	9×10^{-8}
Hydrocyanic Acid, .	$\frac{[H^+]\,[CN^-]}{[HCN]}$	$1{\cdot}3 \times 10^{-9}$
Phenolphthalein, . .	$\frac{[H^+]\,[\text{Colourless ion}^-]}{[\text{Phenolphthalein}]}$	2×10^{-10}
Boric Acid (1st H), .	$\frac{[H^+]\,[H_2BO_3^-]}{[H_3BO_3]}$	$6{\cdot}5 \times 10^{-10}$
Carbonic Acid (2nd H^+),	$\frac{[H^+]\,[CO_3^=]}{[HCO_3^-]}$	6×10^{-11}
Phosphoric Acid (3rd H^+),	$\frac{[H^+]\,[PO_4^{\equiv}]}{[H\,PO_4^=]}$	$3{\cdot}6 \times 10^{-13}$
Hydrogen Sulphide (2nd H), .	$\frac{[H^+]\,[S^=]}{[HS^-]}$	1×10^{-15}
Water, . . .	$\frac{[H^+]\,[OH^-]}{[H_2O]}$	2×10^{-16}
Potassium Hydroxide, .	$\frac{[K^+]\,[OH^-]}{[KOH]}$	"strong"
Sodium Hydroxide, .	$\frac{[Na^+]\,[OH^-]}{[NaOH]}$	"strong"

Substance.	Equilibrium Ratio.	Dissociation Constant at $\frac{N}{10}$ dilution and 25° C.
Barium Hydroxide,	$\frac{[Ba^{++}]\,[OH^-]^2}{[Ba(OH)_2]}$	about 3×10^{-2}
Calcium Hydroxide,	(presumably as for $Ba(OH)_2$, but the solubility is such that $\frac{N}{10}$ concentration is unattainable).	
Cyanin (indicator),	.. .. ..	$4{\cdot}2 \times 10^{-5}$
*Ammonium Hydroxide,	$\frac{[NH_4^+]\,[OH^-]}{[NH_4OH] + [NH_3]}$	$1{\cdot}8 \times 10^{-5}$
*Methylamine,	$\frac{[CH_3NH_3^+]\,[OH^-]}{[CH_3NH_3OH] + [CH_3NH_2]}$	5×10^{-7}
*Pyridine,	.. .. ..	$2{\cdot}3 \times 10^{-9}$
Zinc Hydroxide (2nd OH^-),	$\frac{[Zn^{++}]\,[OH^-]}{[ZnOH^-]}$	$1{\cdot}5 \times 10^{-9}$
*Aniline,	.. .. ..	$4{\cdot}6 \times 10^{-10}$
Dimethylamino-azo-benzene (indicator),	.. .. ..	1×10^{-11}

Note.—The substances marked with an asterisk (*) do not dissociate "normally." For a discussion of this point a text-book on Physical Chemistry must be consulted.

The above gives the key to what titrations are possible. There are four possible cases:

1. Strong acid against strong base: Any indicator will do.
2. Weak acid against strong base: Any indicator whose D.C. is less than one-tenth of that of the acid; *e.g.* Methyl Orange can be used for all acids down to and including the first H^+ of phosphoric acid, while Phenolphthalein serves to titrate as far as H_2S. Phenolphthalein is affected by Boric, Hydrocyanic Acid, etc., but the results are not accurate.

This also explains why the salts of weak acid/strong base can be titrated with an acid just as though the base were present alone. An

excellent example is the titration of Na_2CO_3. Carbonic acid (1st H^+) has a D.C. of 3×10^{-7}, while the 2nd H^+ has a D.C. of 7×10^{-11}. This being so, if methyl orange be used (D.C. $= 4 \times 10^{-4}$), the *whole* of the base can be titrated, since neither HCO_3^- nor $CO_3^=$ affects the indicator. Using phenolphthalein, however, (D.C. $= 8 \times 10^{-10}$), it will be seen that only *half* of the base can be titrated, as the D.C. of phenolphthalein comes between the D.C.'s of the two hydrogen ions of carbonic acid. Litmus is sufficiently close to carbonic acid to be affected, but the titration can be carried out if the HCO_3^- be decomposed and the CO_2 removed by boiling.

The case of phosphoric acid is similar. With this acid, the 1st H^+ is "strong" to all indicators; both 1st and 2nd are "strong" to phenolphthalein. In the case of the 3rd, the ionisation is so feeble that no indicator will serve to titrate it, though some are affected (trinitrobenzene).

3. Strong acid against weak base. . . . Similar to the preceding case, but a weakly *basic* indicator should be used. Thus, diaminobenzene serves for all bases from pyridine upwards. Cyanin can only be used for strong bases.

4. Weak acid against weak base. . . . No titration is possible.

HYDROGEN -ION CONCENTRATION (*p*H VALUE).

It may be advisable to state briefly what is meant by "*p*H value." *p*H is a measure of H^+ concentration, and is equal to

$$\text{Log } \frac{1}{[H^+]} = -\log [H^+].$$

In pure water, which is theoretically neutral, $[H^+]$ is (see foregoing) equal to 1×10^{-7}; whence $\log_{10} [H^+] = -7$ and $-\log_{10} [H^+] = 7$. This is the *p*H value for water. All values of *p*H which are greater than 7, therefore, represent *alkaline* solutions, while *acid solutions* have *p*H values *below* 7.

SECTION III.

ESTIMATION OF THE METALS.

The methods used in practical Quantitative analysis are, in general, based upon those set out in the well-known Group Tables for Qualitative analysis. That is to say, if we are analysing a mixture, or have to separate the substance we wish to estimate from its impurities, we usually proceed according to the Group Table, though it is true that very frequently short cuts are possible, and in many cases qualitative methods are unsuited for quantitative work.

The methods of analysing mixtures will be considered briefly after the reactions and methods of estimating the metals have been dealt with. In this book, consideration will be confined to the commoner substances, in fact only to those that might possibly be met with in an ordinary examination ; the methods are all severely practical, in the sense of being as rapid and convenient to conduct as possible while still retaining all necessary accuracy.

GROUP I.

This group consists of the three metals *Silver*, *Lead* and *Mercury* (*-ous*). The group reagent is *Hydrochloric Acid.*

SILVER.

It is unlikely that an alloy of silver will ever be given for analysis in an ordinary examination, especially as in the assaying of silver bullion, jewellery and plate it is usual to employ the dry methods of scorification and cupellation, for which a text-book on assaying must be consulted. Nevertheless, for the sake of completeness, a wet method will be given here. A silver compound might, however, be set for estimation, and, in any case, the advanced student must be conversant with the wet methods for the assay of silver owing to the fact that the halogens, *e.g.* are best estimated as silver salts in organic analysis (Method of Carius).

Estimation of Silver.

A. **Gravimetric.**—The solution containing the silver (not more than about 0·5 gm. of the metal) is made slightly acid with HNO_3 and dilute HCl is added cautiously, with constant stirring or shaking. This causes the precipitated AgCl to coalesce into large flakes, which settle very rapidly. After each addition of the acid, the precipitate is allowed to settle until the upper layer of the liquid is clear, and another drop of HCl is then added ; if further precipitation is noticed, more of the

reagent must be added, and the upper, clear liquid again tested, after stirring, until the additional drop of acid no longer produces cloudiness. The liquid is then thoroughly agitated and set aside to settle out completely.

Note 1.—The solubility of AgCl in water is reduced by a slight excess of HCl ; if, however, too great an excess is added, the solubility increases, and with quite a moderate concentration of acid the amount of unprecipitated silver becomes considerable. According to Whitby:

Water		at 20° C.	dissolves	0·0015 gm. AgCl	per 1,000 cc.
1 per cent. HCl		,,	,,	0·0002 gm. AgCl	,,
5	,,	,,	,,	0·0005 gm. AgCl	,,
10	,,	,,	,,	0·0555 gm. AgCl	,,

Note 2.—Government Mint practice is to conduct the precipitation of AgCl in special, conical, stoppered flasks. These are not stirred, but shaken, and left to settle in an inverted position. The precipitate, prepared in this way, comes out in a compact mass on the filter, and the bulk of the mother liquor can be poured away without the necessity of filtration.

Since AgCl is readily reduced to the metal by glowing carbon, we are not able to filter on paper and ignite directly as we should if it were not so reducible. Any of the following courses of procedure may be followed:

1. Weigh a Gooch crucible (paper pulp) that has been dried at 130°–140° C. in the air oven. Pour the solution carefully through this, and finally transfer the precipitate to the crucible, washing, under moderate suction, with five or six crucible-fulls of warm water. After the fifth wash, test the wash water with a drop of $AgNO_3$ reagent. When free from Cl^-, the crucible with precipitate is placed in the air oven and dried at 130°–140° C. to constant weight. The increase in weight represents AgCl.

2. If preferred, a Gooch crucible with asbestos pulp may be used. In this case there is no need to dry to constant weight in the oven, as the crucible and precipitate may be placed just inside the muffle (temp. 300°–400° C.) before weighing. This method is naturally quicker, as one weighing before and one after filtration suffice. The danger is that the precipitate may be overheated and caused to fuse and run through the filter-pad. (M. pt. of AgCl = 450° C.)

Note.—The prepared crucible, both before the original weighing and after the filtration, must not be placed in a hot part of the muffle before it has had time to dry, or spluttering is bound to occur. In the former case the asbestos pad is loosened and made too easy-running for efficient filtration, and in the second case there is danger of some of the precipitate being lost. The wet crucible should be sucked dry on the pump and given a preliminary drying on the hot plate or on the platform in front of the muffle.

3. If it is not desirable to use a Gooch crucible, the AgCl may be filtered off in the ordinary way on an open-textured paper (No. 41) and washed as above until free from Cl^-. The paper is then opened out on an old spot-reaction tile and placed on or under the hotplate until quite dry, when the precipitate may be separated easily and completely

from the paper. The precipitate is transferred to a piece of glazed paper (black, preferably), and the paper brushed over gently with a soft brush, after which it is folded up loosely and placed in a weighed porcelain crucible. This is set in the mouth of the muffle until the paper chars, then pushed further in until the paper is reduced to ash. It is then removed and allowed to cool; 1 drop of conc. HNO_3 is dropped upon the dark residue and the whole gently warmed on the hotplate for a few minutes. When sufficient time has elapsed to permit of any reduced silver being completely converted to nitrate, one drop of HCl is added on the tip of a glass rod and the crucible heated on the hotplate until it is quite dry. The main bulk of the precipitate is then transferred to the crucible and the whole heated just inside the muffle until the precipitate just begins to melt. It is then transferred to a desiccator and allowed to cool before weighing.

Note 1.—This method is troublesome to perform, and though there is no difficulty if care be taken, there are too many possibilities of accident to make it a good method from a practical point of view. The commercial analyst's practice is to use an asbestos Gooch in all such cases, thus saving not only time but minimising failures.

Note 2.—To remove adhering AgCl (fused): Fill the crucible with dilute HCl and add a piece of granulated zinc. The hydrogen reduces the AgCl to spongy silver, which is very easy to remove.

B. **Volumetric.**—If silver only is to be estimated (*i.e.* if the filtrate is not required for the estimation of other metals and acids), the volumetric process may be preferred on the grounds of time economy.

There are two volumetric processes in use, namely, titration with a standard solution of NaCl and titration with standard KCNS (or NH_4CNS). For the best results the approximate amount of Ag present should be known in order that the standard and the assay may be arranged to use equal volumes of the titration liquid.

(1) **Standard Sodium Chloride Titration**—*Standard NaCl.*—Weigh out exactly 2·7000 gms. of pure NaCl and dissolve in 1,000 cc. of water. This is the concentrated solution. Now dilute 100 cc. of this to 1,000 cc.; this is the dilute solution.

Note.—The weight of NaCl theoretically equivalent to 5 gms. of Ag is 2·7095 gms. The lesser weight is advised deliberately.

Standard $AgNO_3$.—Weigh out accurately 0·5 gm. of assay silver foil and dissolve it in 8–10 cc. of HNO_3 (dens. 1·2) in a small beaker, taking precautions against spurting and spraying. When dissolved, evaporate cautiously until crystals form, and take up in 25 cc. of water.

Standardisation of the NaCl Solution. Run exactly 100 cc. of the conc. NaCl solution (from an accurate pipette) into the $AgNO_3$ solution and stir until the precipitate coagulates. Now add from a burette the dilute NaCl in small amounts (0·2 cc. at a time) until no further turbidity is produced in the clear solution remaining above the precipitate after stirring for a moment and allowing to settle.

Suppose, neglecting the final 0·2 cc. added, that 2·4 cc. of dilute NaCl are necessary; the total volume of NaCl is, then, 100·24 cc. (in terms of conc. NaCl), and the strength of the titration liquid in terms of pure Ag is easily calculated.

Method of Estimating Silver in an 'Unknown' Solution or Solid.

(i.) *Preliminary.*—Weigh, if a solid, or measure, if a liquid, such a quantity of the material for assay as shall contain as nearly as possible 0·5 gm. of Ag. Transfer it to a tall beaker (400 cc.), and, if a solid, dissolve it in 10 cc. HNO_3 (dens. 1·2) and boil off nitrous fumes. If a liquid, add 7–8 cc. HNO_3 (dens. 1·2), and in either case dilute to about 30 cc.

Titrate with the conc. NaCl solution, adding it from a burette as follows: 5 cc. at a time for the first 40 cc., 2 cc. at a time for the next 20 cc., 1 cc. at a time for the next 20 cc. and finishing by additions of 0·5 cc. until no further turbidity occurs.

Suppose 90 cc. are used. We then know that the *true* volume of the NaCl is between 89·5 cc. and 90 cc.

(ii.) *Final Assay.*—Guided by the preliminary assay, weigh out (or measure) as before, a quantity of the substance for assay that shall contain 0·5 gm. of Ag.

Note.—This is calculated as follows:

Suppose W gms. (or W cc.) were used for the preliminary assay, which requires between 89·5 and 90 cc. of the conc. NaCl.

$$100{\cdot}24 \text{ cc. NaCl (conc.)} \equiv 0{\cdot}5 \text{ gm. Ag.}$$

$$90 \quad \text{,,} \quad \text{,,} \quad \equiv \frac{0{\cdot}5 \times 90}{100{\cdot}24} \text{ gm. Ag.}$$

Therefore W gms. (or cc.) contain (slightly more than)

$$\frac{0{\cdot}5 \times 90}{100{\cdot}24} = 0{\cdot}4490 \text{ gm. Ag.}$$

i.e. 0·4490 gm. Ag is contained in W gms. (or cc.) of the assay substance.

Hence 0·5000 gm. Ag is contained in $\frac{W \times 0{\cdot}5}{0{\cdot}4490}$ gms. of the assay substance = W′ (say).

That is, take W′ gms. for the final assay.

This amount, W′ gms., will contain a little more than 0·5 gm. of Ag, and the 100 cc. of conc. NaCl may be added with confidence. As in the standardisation, finish with dilute NaCl and calculate the result of the assay from the Ag equivalent of the NaCl found in the standardisation experiment.

(2) **Standard Potassium or Ammonium Thiocyanate Titration**—*Volhard's Method.*—This is very similar to the foregoing except that the titration liquid is a standard solution of potassium or ammonium thiocyanate, and an indicator is used.

Standard $AgNO_3$.—The commercial analyst generally employs volumetric solutions of such 'strength' that 1 cc. is equivalent to an aliquot part of a gram of the metal or acid to be estimated. This is for purposes of convenience and rapidity of calculation, not only in working out the results of an assay, but also in deciding how much of a substance for assay should be taken in order that a reasonable amount of titration liquid

may be required. For the sake of completeness, however, it is necessary to consider ' Normal ' solutions in analysis, and in the following method the use of $\frac{N}{10}$ solutions will be described. Needless to say, $\frac{N}{10}$ solutions could be quite well employed in the foregoing method, just as ' aliquot ' solutions might be used here.

Weigh accurately 10·788 gms. of assay silver into a tall 200 cc. beaker and dissolve in 30 cc. HNO_3 (dens. 1·2). Boil until free from nitrous fumes and dilute to 1,000 cc. after cooling. This will yield a solution of $\frac{N}{10}$ strength.

Standard KCNS (or NH_4CNS).—Weigh, roughly, 10 gms. of KCNS (or 9 gms. NH_4CNS) and dissolve in 1,000 cc. of water. Exact weighing is impossible, since both these thio-salts are hygroscopic.

Fe^{+++} Indicator.—Make a saturated solution of ferric alum, adding sufficient HNO_3 to discharge the brown colour of Fe^{+++}. This reagent gives a red colour [due to $Fe(CNS)_3$] when an excess of CNS^- has been added.

Standardisation.—25 cc. of the standard $AgNO_3$ are transferred by means of an accurate pipette to a tall 400 cc. beaker and diluted to 100 cc.: 1–2 cc. of the indicator are then added from a small pipette, and KCNS is added from a burette with constant stirring, until a permanent red coloration is obtained. The Ag equivalent for the thiocyanate is then worked out and expressed as " gms. of Ag per 1 cc. of thiocyanate."

Determination of ' Unknown ' Silver.

A quantity of the material for assay is chosen such that 20–40 cc. of the thiocyanate will be required for the titration. This is dissolved in dilute HNO_3 and diluted to 100 cc. in exactly the same way as was described for the standardisation. The titration is then carried out, using the same amount of the indicator as before.

Note.—This method cannot be used when the solution is so coloured that the end-point cannot be observed, nor can it be used in the presence of mercury, owing to the insolubility of $Hg(CNS)_2$. The presence of much copper also interferes, apart from the question of colour.

LEAD.

Lead is precipitated as $PbCl_2$ in a mass of shining, needle-like crystals, by the addition of HCl to its solutions, if not too dilute. $PbCl_2$ is not sufficiently ' insoluble ' in water to render it a suitable compound for the estimation of lead, but, in American practice especially, the insolubility of this compound in dilute alcohol is utilised in its separation from the metals of Group II.

Lead is one of the commonest of metals, and its accurate estimation is of the highest importance commercially. It may be estimated gravimetrically as sulphate or molybdate, volumetrically by titration with standard molybdate solution, and even colorimetrically when present in very small amounts by matching the depth of tint produced in a

plumbiferous solution by the passage of H_2S gas against that similarly produced in a standard of known concentration. The most general method of estimation is by conversion to $PbSO_4$ and weighing as such; this method is to be preferred since it involves no addition of an 'alien' metal to the solution under analysis, and an excellent separation is very easily effected from practically all metals, certainly all metals likely to be met with in an ordinary alloy.

Estimation of Lead.

A. **Gravimetric Method**—(i.) *As Lead Sulphate.*—Sufficient H_2SO_4 is added to the solution, contained in a wide beaker, to combine with all the lead and leave an excess of 5 to 10 cc. The solution is then placed on the hotplate and evaporated, at first rapidly, but as the solids separate, more cautiously; it is very necessary to watch the assay closely towards the end of the evaporation, as violent spitting is liable to take place if the heating is too strong. When the bulk is very low, and all the water has been expelled, the beaker is placed in the centre of the hotplate until the acid boils freely, and plenty of 'fumes' are given off; then it is removed to the bench, being set on a piece of asbestos (metal or stone would probably crack the beaker; a wet surface would certainly crack it, and the beaker will char wood) until cool enough to permit of the bare hand touching the bottom.

Note.—The signs of the complete expulsion of the water are: (1) absence of 'bumping'; (2) small oily droplets of condensed H_2SO_4 are to be noticed on the sides of the beaker, just above the level of the liquid; and (3) the lower part of the beaker fills with slowly swirling wisps of SO_3 vapour, having a choking effect on the lungs if accidentally inhaled.

Note.—The cooling may be accelerated if desired by blowing into the hot beaker and by swirling the hot liquid round the bottom and up the sides of the vessel.

When cool enough to handle, the solution is diluted to about 100 cc. (or 100 cc. per 5 cc. of H_2SO_4 used in excess), and set aside to cool completely. The addition of cold water to the hot acid demands much care and caution, not only on account of the danger to the operator's eyes, but on account of the possibility of spoiling the assay, either by spitting or by the fracture of the beaker; on the other hand it is unnecessary to wait until the acid is quite cold before diluting. There are two safe methods; either add the water boldly and rapidly in bulk, while swirling the beaker, or add it, a few drops at a time, from the wash-bottle jet directed upon the sides of the beaker, stopping the addition the moment the spitting becomes violent, and mixing water and acid completely by swirling before making further additions. After one or two small additions the rest of the water may be poured in quite boldly.

When the $PbSO_4$ has settled out completely, and the liquid is perfectly cold, it is ready for filtration.

Note 1.—The addition of alcohol, so frequently advised, is quite unnecessary. The weight of $PbSO_4$ dissolved in 1,000 cc. of 5 per cent. H_2SO_4 is only a few mgms.

Note 2.—All other metals in the original solution will be present as anhydrous sulphates, and some of these, especially those of copper, iron, aluminium and zinc, are very reluctant to dissolve in water. If there is any doubt as to whether they are properly dissolved or not, boil the solution after dilution until reasonably certain that complete solution has taken place. All these sulphates are white, or almost so, but $PbSO_4$ differs from them in its greater density, its greater 'whiteness,' and its absence of pronounced crystalline form. It may, therefore, be detected and recognised by swirling the solution and holding the beaker over the head in order to look up through the rotating liquid. $PbSO_4$ settles very rapidly and collects in the centre of the beaker in a small white cone ; any other sulphates (except $BaSO_4$, of course) show up unmistakably round the edges of this cone.

If, on evaporation, anything like a 'cake' of crystalline sulphates is formed on the bottom of the beaker, preventing the proper 'fuming' of the acid, it may be necessary to add more H_2SO_4 to keep the contents 'wet' and so avoid cracking. If more acid is added, the dilution must be greater in order to achieve the necessary 5 per cent. concentration of the acid before filtration. Any concentration much less or much greater than this will lead to the loss of some lead by solution in the mother liquor.

The $PbSO_4$ is filtered through a weighed Gooch crucible fitted with an ignited asbestos pad, and washed with seven or eight crucible-fulls of 5 per cent. H_2SO_4, sucking nearly dry on the water-pump before adding the next wash. Finally, the crucible is sucked as dry as possible on the pump and set on a piece of clean asbestos on the hotplate to dry completely. When dry, it is placed in the mouth of the muffle until no more fumes of H_2SO_4 can be detected, then introduced further and further into the hot chamber until the bottom of the crucible is red. It is then removed and transferred to a desiccator to cool before weighing. (*Note.*—$PbSO_4$ fuses at 930° C.)

It is perhaps needless to add that the ignition can be performed in an ordinary crucible if the paper is burnt separately as described under Silver. In this case, however, the acid treatment is: first HNO_3 to dissolve any reduced lead, and secondly H_2SO_4 to re-form $PbSO_4$. But this is waste of time so long as Gooch crucibles are available.

(ii.) *As Lead Molybdate.*—This method possesses one important advantage over the sulphate method; the precipitate plus paper can be ignited directly in the crucible, to be brushed out and weighed at the end of the assay, thus saving a weighing and also the necessity of preparing a Gooch crucible. Its great disadvantage has already been pointed out, viz. the precipitant is a salt containing another metal, the introduction of which renders the subsequent analysis of a mixture unnecessarily complicated, especially as molybdenum is a metal which requires considerable time and skill for its complete removal. Also, the molybdate precipitation is of very little use as a means of separating lead from other metals, since the molybdates of most of the heavy metals are insoluble in acetic acid and will be precipitated with the lead. It is interesting to note that $PbMoO_4$ is the *only* molybdate which has a simple, normal composition, MoO_3 having a strong tendency to form polyacid compounds.

Method.—The solution should contain no metals except lead and those of the alkali group. Carefully neutralise the solution, if acid, with ammonia, and then make it *just* acid with acetic acid. Boil, and add freshly filtered * ammonium molybdate solution until no further precipitation can be observed. The completion of the precipitation is easily observed, as in a hot solution the precipitate coagulates and settles well.

Filter off on to an ordinary paper pulp and wash with hot water containing a little ammonium acetate ; when washed, allow the paper and precipitate to drain as completely as possible, transfer them to an ordinary porcelain crucible and place in the mouth of the muffle. When the paper is dry and charred, push the whole well into the muffle and leave until all the paper has been completely burnt off and the precipitate is clean and white. Remove to the desiccator to cool ; weigh as $PbMoO_4$.

An alternative method is as follows: To the solution, which should contain free HCl up to 10 per cent. by volume, a considerable excess of ammonium molybdate solution is added (at least 10 cc. of 10 per cent. solution). The solution is then brought to the boil and two or three drops of methyl orange are added, followed by a strong solution of ammonium acetate (neutral), sufficient to bring the colour of the indicator back to yellow (ammonium acetate " neutralises " the free HCl by immobilising the H^+ ions, causing them to unite with the CH_3COO^- ions to form the very slightly ionised acetic acid). The boiling is continued for a few minutes (beaker covered), and the beaker then set aside to allow the precipitate to settle. The solution is filtered, and the precipitate washed, dried, ignited and weighed as before.

Copper, zinc and nickel do not yield precipitates with ammonium molybdate under the foregoing conditions, and consequently do not interfere, but if tin, antimony or arsenic be present, as for example, in the analysis of a bearing metal, they will be co-precipitated to some extent. In this case, the sulphate method is to be preferred, or the molybdate may be purified by a double precipitation, as follows:—

Dissolve the precipitate in a little HCl, assisted by a few drops of HNO_3, add a few cc. of the molybdate reagent in order to furnish a suitable excess, and re-precipitate with ammonium acetate as above, first adding a little NH_4OH if necessary, *i.e.* if the solution is unduly acid. It is advisable to perform this re-precipitation on every occasion if the bulk of the precipitate is greater than usual, as there is some tendency for it to carry MoO_3 down. As a rule there is no need to filter before re-precipitation ; the precipitate is allowed to settle completely and the clear solution is decanted carefully through a filter, stopping at the instant any precipitate passes. The precipitate left behind in the beaker is then dissolved in HCl without further treatment, and the second precipitation carried out after dilution and boiling.

If desired, the two gravimetric processes may be combined, using the sulphate method as a means of separation, and the molybdate method as the final means of estimation, thereby retaining all the advantages of the two processes. The $PbSO_4$, after one or two washings,

* This reagent is liable to become cloudy with deposited MoO_3 ; if it is clear, no filtration is of course necessary.

is transferred, pulp and all, to the precipitation beaker and 10 cc. of conc. ammonium acetate solution are added. The beaker is covered and the precipitate is digested for ten minutes on the hotplate ; the solution is then poured through a small pulp, washing with hot dil. ammonium acetate solution ; 10 cc. of acetic acid are added to the filtrate, followed by excess of molybdate solution. In this case, unless there is a very heavy precipitate, there is no need to perform a double precipitation, but the $PbMoO_4$ is ignited as soon as it is completely washed.

B. Electrolytic Method.

When solutions of lead compounds which contain considerable oxygen, or which contain free HNO_3, are electrolysed, PbO_2 is deposited on the anode as a dark brown, almost black deposit. This is so loosely adherent that when it exceeds about 0·03 gm. in weight it is apt to flake off an ordinary electrolytic anode, especially during washing. As a consequence of this, the electrolytic method should not be chosen when there is more than about 0·02 gm. of lead to be estimated. The method is not generally to be recommended for the ordinary analysis of mixtures, as the sulphate method is always preferable, but in the analysis of certain alloys, especially brasses and bronzes, to which 1 or 2 per cent. of lead is frequently added, the electrolytic method is invaluable, as it saves much time (the copper is invariably estimated electrolytically, and if the lead can be deposited simultaneously, it is obvious that considerable time will be saved). Besides this, there is some difficulty in handling small quantities of $PbSO_4$; furthermore, it is very valuable to have a means of knowing positively whether or not any lead is present, as if it is absent, much time may be wasted in carrying out the evaporation with H_2SO_4 in order to test for it ; the electrolytic method shows at once whether lead is present or absent. No special precautions are necessary ; the electrolysis is conducted exactly as described under Copper, *q.v.*, and the method is only mentioned here for the sake of completeness. It should be carefully borne in mind that the method is only useful in the analysis of alloys.

Note 1.—With traces of lead, *i.e.* less than 0·001 gm., the deposit appears as an iridescent golden-brown film ; with more lead, say, 0·005 gm. it is dark brown, and with 0·01 gm. it is almost black. Above 0·02 gm. of lead the oxide is somewhat like loosely adherent soot, and is very liable to be rubbed off the electrode.

Note 2.—To remove the deposit, dip the electrode in dil. HNO_3 containing a little SO_2; a few crystals of sulphite or thiosulphate dropped into the acid serve very well. HNO_3 containing ' nitrous fumes ' also dissolves the peroxide, but not so rapidly ; nevertheless, the acid used to remove the copper after an electrolytic copper assay is quite efficient in removing the lead compound. HCl must *not* be used because of the reaction: $PbO_2 + 4HCl = PbCl_2 + Cl_2$, the chlorine attacking platinum.

Note 3.—If manganese is present, MnO_2 is liable to be deposited with the PbO_2.

Note 4.—The theoretical factor for Pb in PbO_2 is 0·866, but, in practice, a factor of 0·862 is found to give more accurate results. This

is probably due to the inclusion of a certain amount of water. A convenient method for overcoming this discrepancy, and obtaining entirely accurate results, is to hold the electrode with the deposit inside the muffle until it is quite red-hot. This converts the PbO_2 to PbO, so that all the deposit will now be weighable as the lower oxide. For all practical purposes, however, this refinement is unnecessary, as the maximum error possible, when using either 0·866 or 0·862, is only about 0·01 per cent. of Pb on 1 gm. of alloy.

C. Volumetric Method.

An old-established method was to titrate a boiling ammonium acetate solution of $PbSO_4$ with standard ammonium molybdate solution, using tannic acid as an outside indicator. This method is nowadays considered to be unreliable, and only a brief description will be given:

Method.—Separate the lead as $PbSO_4$; filter on paper pulp and wash with dil. H_2SO_4 as already described. Transfer precipitate and pulp bodily to a tall 400 cc. beaker and add 20 cc. of conc. ammonium acetate solution. Cover, and boil gently for 10 minutes; add 30 cc. of water and again boil. Remove 10 cc. of the solution to a small covered beaker and set it aside on the hotplate.

Now titrate the main bulk of the lead solution (hot) with a solution of ammonium molybdate containing 4 gms. per 1,000 cc., adding the molybdate from a burette in 2 cc. quantities, stirring vigorously after each addition, and testing the solution for excess of molybdate by withdrawing a drop on a glass rod to a drop of 2 per cent. tannic acid solution on a spot-plate. When the spot turns bright golden yellow, quickly add the reserved portion of the lead solution and again test on the spot-plate. If the result is negative, continue adding the molybdate, but in smaller quantities (1 or 2 drops at a time), until the colour again turns.

Molybdate always contains polymolybdates, and the reagent cannot be weighed as a standard, but must be titrated against a known quantity of pure $PbSO_4$ in exactly the same way as is described above. If pure $PbSO_4$ is not available, weigh out a strip of assay lead and convert this into sulphate by heating to fumes with conc. H_2SO_4. It is necessary to use approximately equal weights of $PbSO_4$ for the standardisation and for the assay.

MERCURY (-OUS).

Mercury is an unlikely metal for even an advanced student to be required to estimate, in an examination at least. For the sake of completeness, however, a short account of this metal from the analytical point of view is appended, together with a "universal" method for its estimation.

Mercurous mercury is precipitated by HCl as a "ropey," white chloride, somewhat resembling AgCl when first thrown down. HgCl is insoluble in ammonia (separation from silver), but is decomposed by that reagent into metallic mercury and a black mixture of mercury and $Hg(NH_2)Cl$.

Mercuric mercury is a member of Group II, being precipitated as

HgS by H_2S. HgS is black, but when the H_2S is first passed into a mercuric solution the precipitate comes down almost white, the colour then passing through orange-yellow and brown to the final condition. Mercuric sulphide is insoluble in ammonium sulphide, but is dissolved by Na_2S and K_2S. Dilute (dens. 1·2) HNO_3 has no effect upon it (distinction from CuS, PbS, CdS and Bi_2S_3).

Estimation of Mercury.

Method 1.—Mercury compounds, when mixed with such substances as CaO, ZnO, Na_2CO_3, and the mixture heated, are decomposed,

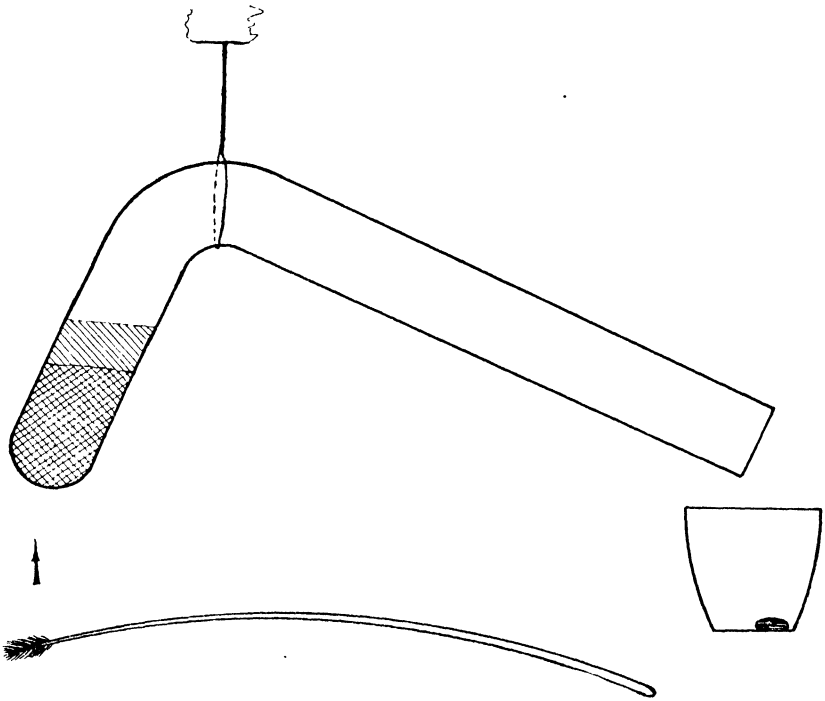


Fig. 5.—Apparatus for Estimation of Mercury as Metal.

metallic mercury being set free and volatilised. For sulphides (*note* that the only mercury ore is cinnabar, a sulphide) it is best to use fine iron filings, or a mixture of these and CaO.

The mercury compound, preferably the sulphide, is intimately mixed with fine iron filings in the proportion of 5 gms. of filings to each 0·1 gm. of mercury ; the mixture is introduced into a small silica retort (see fig. 5) made out of a silica ware test-tube bent over at right angles some 4 cms. from the closed end, and a layer of fresh filings is added as a guard against loss of mercury. The retort is supported in a suitable manner so that the open branch is inclined slightly downwards ; a

weighed porcelain crucible is placed under the open end and heat is then gently applied by means of a small Bunsen burner. By manipulation of the flame, held in the hand, the expelled mercury is driven up into the open branch of the tube, and if an appreciable amount is present, condensed droplets coalesce and run down into the crucible receiver. When no more mercury is evolved the flame is removed and the retort cooled. (*Note.*—Silica ware has so low a coefficient of expansion that the retort may even be held under the tap to cool without fear of fracture.) When the tube is cold, the condensed mercury is removed by gently brushing down the inside of the tube with a stiff feather,

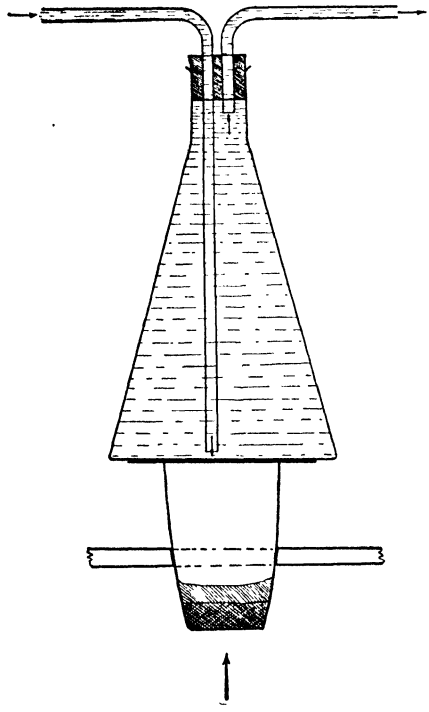


Fig. 6.—Apparatus for Determination of Mercury as Metal (Small Quantities).

clipped until only a small tuft remains at the tip ; the mercury will be found to coalesce readily, and it is a simple matter to transfer all the small droplets to the receiver, which is then weighed.

Note.—If silica ware is not available, a closed tube of combustion glass will serve, though there is some risk of fracture if the mercury condenses low down in the tube and has to be driven towards the mouth by the flame. It is also necessary to remember that if CaO is used as the flux, silica ware cannot be used, owing to the probable formation of calcium silicates if the heat is excessive. However, iron filings can always be used, if, in the case of a chloride or nitrate of mercury, the metal is first precipitated as sulphide by passing H_2S. The

sulphide is dried in the oven (steam) and then mixed with the flux as described.

For small quantities of mercury, the following method is useful; the principle is, of course, the same:

The substance for assay is weighed into a 25–30 cc. platinum crucible

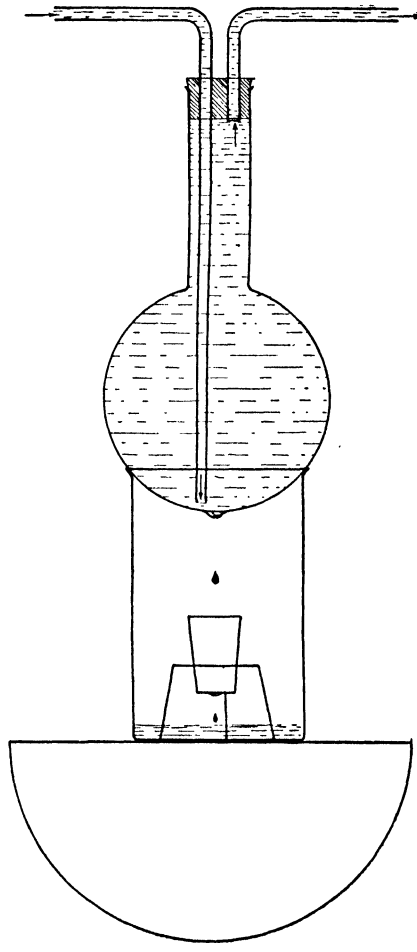


Fig. 7.—Apparatus for Mercury as Sulphide.

(see fig. 6), mixed with iron filings (or, of course, lime), as already described, and the crucible covered closely with a weighed disc of assay silver. The crucible is supported by being inserted into a closely fitting hole in a piece of (soft) asbestos sheet, and when the silver disc is in place, a condenser, consisting of a small flat-bottomed flask, fitted with inlet and outlet tubes for water, is set on the top. The cooling water is first

set flowing ; the bottom of the crucible may then be gently heated with a small flame, taking care not to let the flame come over the edge of the asbestos. The liberated mercury condenses upon and amalgamates with the silver, which is removed and weighed when the assay is complete.

Method 2.—Mercury may also be estimated as HgS. It is precipitated as HgS from its solution and the sulphide filtered off on a Gooch crucible. After washing with hot water the crucible is placed inside a tall beaker, being supported inside the latter on a small triangle which has its legs bent downwards at right angles. On the mouth of the beaker is placed a round-bottomed flask (see fig. 7) filled with cold water to serve as a condenser, and a small quantity of CS_2 is poured into the beaker ($\frac{1}{4}''$ depth will serve). The whole is then placed on the water-bath and heated until the CS_2 boils and the condensed drops fall back into the crucible. This CS_2 wash dissolves out the sulphur which is invariably found in precipitated HgS. After about a quarter of an hour of this washing, the crucible is removed, sucked quite dry on the pump and placed in the air oven at 110° C. to expel the last traces of water and CS_2. It is then cooled and weighed.

Note.—Instead of the contrivance described, a Soxhlet apparatus may be used. This is naturally rather an improvement, as the extraction is more rapid and the evil-smelling reagent does not escape to anything like the same extent. It is, however, hardly worth the time to set up extractor and condenser when the simpler device is quite as effective ; if, however, ready set-up Soxhlets are available in the laboratory, it is worth while to use one.

GROUP II.

The chief metals of this group are:

IIa. Mercury, Copper, Bismuth, Cadmium (Lead). IIb.—Antimony, Arsenic, Tin.

Gold, Platinum and *Molybdenum*, among the semi-rare metals, also belong to this group.

The group reagent is *Sulphuretted Hydrogen* passed into *dilute acid solution.*

The Sulphide Groups: General.

All the common metals, with the exception of the alkali metals, the alkaline earth metals, and the weakly basic metals, ferric iron, aluminium and chromium, are precipitated as sulphides by H_2S. These sulphides form what is really an uninterrupted series from Ag_2S and HgS at one end to MnS and CoS at the other, but analytically they are always considered in two groups, viz.: Ag, Pb, Hg, Cu, Bi, Cd, Sb, As and Sn, on the one hand, and Fe^{++}, Ni, Co, Zn and Mn, on the other. The former are usually precipitated from *acid* solutions and the latter from *alkaline* solutions ; the difference is, however, merely one of degree, for there is no distinct difference in behaviour between the two groups, which meet at the point Cd, (Pb), Zn.

Considering a divalent metal M^{++}, it can be shown that the dissociation constant, K, of its sulphide is equal to $\frac{[M^{++}]\,[H_2S]}{[H^+]^2}$,* *i.e.* the concentration of the sulphide in solution (100 per cent. ionised and in equilibrium with the precipitate) is proportional to the square of the hydrogen-ion concentration and inversely proportional to the concentration of the H_2S in the solution. The case of a divalent metal is considered because almost all the Group II metals are divalent ; in the case of monovalent and trivalent metals the values of K are, respectively: $\frac{[M^+]^2\,[H_2S]}{[H^+]^2}$ and $\frac{[M^{+++}]^2\,[H_2S]^3}{[H^+]^6}$. The proofs of these formulæ are similar to that given for the divalent metal. (See note.)

In view of the extremely low value of $\frac{[H^+]\,[S^=]}{[H\,S^-]}$, and the exceptionally small $[S^=]$ in acid solution,† it is probable that the precipitation of sulphides takes place almost entirely by means of the HS^- ions, thus:

$$M^{++} + 2HS^- = M(HS)_2$$
$$= MS + H_2S,$$

a process comparable to:

$$M^{++} + 2OH^- = M(OH)_2 = MO + H_2O.$$

e.g., $Cu^{++} + 2OH^- = Cu(OH)_2 = CuO + H_2O.$
(from KOH)

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* Formal proof of the equation $K = \frac{[M^{++}]\,[H_2S]}{[H^+]^2}$:

The equilibria are :

$$M\,S \rightleftarrows M^{++} + S^=$$
$$H_2S \rightleftarrows H^+ + H\,S^-$$
$$H\,S^- \rightleftarrows H^+ + S^=,$$

which yield mass action equations :

$$K^{i}\,[M\,S] = [M^{++}]\,[S^=], \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$
$$K^{ii}\,[H_2S] = [H^+]\,[H\,S^-], \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$
$$K^{iii}\,[H\,S^-] = [H^+]\,[S^=], \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Multiplying (2) by (3), we obtain :

$$K^{ii}\,K^{iii}\,[H_2S]\,[H\,S^-] = [H^+]^2\,[H\,S^-]\,[S^=].$$

Dividing both sides by $[H^+]^2\,[H\,S^-]$, and multiplying by $[M^{++}]$, we obtain

$$K^{ii}\,K^{iii}\frac{[H_2S]\,[M^{++}]}{[H^+]^2} = [S^=]\,[M^{++}] = K^{i}\,[M\,S],$$

whence, dividing by $K^{ii}\,K^{iii}$,

$$\frac{[H_2S]\,[M^{++}]}{[H^+]^2} = \frac{K^{i}}{K^{ii}\,K^{iii}}[M\,S] = K$$

because $[M\,S]$ is constant if solid $M\,S$ is present.

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† G. M. Smith in the *J. Amer. Chem. Soc.* states :

5 cc. of 0·2 N HCl, saturated with H_2S (giving 0·24 N H_2S), will contain :

3×10^{20} non-ionised molecules of H_2S,
15×10^{13} $H\,S^-$ ions, and
only one $S^=$ ion.

Bruner gives the following figures for the *solubility products of the sulphides*:

Bi_2S_3,	$3{\cdot}2 \times 10^{-91}$
Ag_2S,	$4{\cdot}8 \times 10^{-53}$
HgS,	$7{\cdot}7 \times 10^{-48}$
CuS,	$5{\cdot}9 \times 10^{-42}$
CdS,	$7{\cdot}1 \times 10^{-28}$
PbS,	$3{\cdot}4 \times 10^{-28}$
ZnS,	$8{\cdot}0 \times 10^{-24}$ (from acid solution)
	$1{\cdot}1 \times 10^{-24}$ (from alkaline solution)
FeS,	$3{\cdot}7 \times 10^{-19}$
MnS,	$7{\cdot}0 \times 10^{-16}$

It is obvious from the foregoing (and footnotes) that unless a sulphide has an extremely low solubility product, it will not be precipitated from acid solutions owing to the low concentration of $S^=$ in the presence of H^+, because added acid drives back the reaction $H_2S \rightleftarrows 2H^+ + S^=$ according to the usual mass action laws. The limit lies about 1×10^{-27}, and this is the dividing line between the so-called 'acid' sulphides and the 'alkaline' sulphides. In alkaline solution, the concentration of $S^=$ and SH^- may be quite high on account of the removal of H^+ by the OH^- of the alkali to form water. SH^- (and $S^=$ probably) will, therefore, go on accumulating so long as H_2S and NH_4OH are present.

General Notes on the H_2S Precipitations.

1. There is a well-marked tendency for sulphide precipitates to become less reactive on 'ageing.' This fact is the cause of the well-known phenomenon that many sulphides, when precipitated, will not dissolve in a concentration of H^+ ions which would be quite high enough to prevent the precipitate from forming.

2. Sulphides, especially those precipitated from alkaline solutions, show a marked tendency to pass through the paper and 'go colloidal.' This passing through is partly attributable to oxidation, to which the sulphides are rather prone, and partly to the peptization of the colloids consequent upon the removal of electrolytes by washing. As noted in the section on Colloids, the removal of the coagulating electrolytes and their charged ions removes the neutralising charges which originally caused the coagulation of the colloid *sol*. The particles of the *gel* become recharged, and the *gel* passes back into the *sol* state. This may be noticed in detail when, *e.g.*, the precipitate left insoluble after extracting stannic polysulphide (during the purification of SnO_2, described under Tin) is washed with pure water. At first the filtrate comes through a clear golden yellow, which is characteristic of polysulphide ions. When, however, the electrolytes are washed down to a very low concentration in the paper, the sulphides (especially the FeS) of the precipitate pass through as a clear, greenish 'colloidal' solution which floats upon the denser polysulphide layer. Each layer is perfectly clear and free from visible suspended particles, but at the plane of junction a black precipitate

of re-coagulated FeS will be seen. This has of course been *re-gelled* by the electrolytes in the lower layer of filtrate.

To avoid this passing through of sulphide precipitates they are usually washed with H_2S water. This prevents oxidation also, and is to be recommended in the case of, *e.g.* CuS, but H_2S *per se* has very little power of preventing colloid formation on account of its very small ionisation. Any good electrolyte will serve the purpose, and it has been recommended to use NH_4NO_3 ; it would appear, however, that if oxidation is to be feared, and especially if the precipitate is to be weighed as sulphide, a nitrate is not a good wash liquid, because of: $NH_4NO_3 = N_2O + H_2O$, on heating, N_2O being a powerful oxidising agent. A more suitable combination is H_2S-water acidified with HCl or H_2SO_4. The acid keeps the sulphide from ' going colloidal ' and the H_2S prevents oxidation.

3. H_2S is very prone to atmospheric oxidation:

$$H_2S + O = H_2O + S$$

so that sulphur is almost invariably present in sulphide precipitates. This is the reason for washing sulphides which have to be weighed as such (*e.g.* Sb_2S_3), with CS_2, or igniting in hydrogen (*e.g.* Cu_2S).

4. The order of 'sensitiveness' of sulphides to acids (see p. 240) is: As, Ag, Cu, Bi, Hg, Sb, Sn, Cd, Pb, Zn, Fe^{++}, Ni, Co, Mn; the As being the least soluble and the Mn the most soluble. (See pp. 239, 240 for notes on separation of the metals of Group II by taking advantage of the different solubilities of their sulphides in HCl.)

5. A further point, which is sometimes lost sight of, is that when H_2S is passed through a solution containing such compounds as ferric salts, and most per-salts such as permanganates, perborates, percarbonates, an appreciable amount of H_2S may be oxidised to H_2SO_4, ($S^=$ to $SO_4^=$). If this occurs, barium may be precipitated with the metals of Group II.

GROUP IIa.

Mercury (-ic), Copper, Lead, Bismuth, Cadmium.

Group reagent : *Sulphuretted Hydrogen gas*, passed through a *weakly acid* (HCl) solution.

To precipitate Group II metals, the solution should be just acid with HCl ; 3 per cent. by volume of conc. reagent serves very well for a standard acidity, and a brisk stream of pure H_2S gas should be passed through the liquid until no further precipitation takes place and the precipitate settles in large flakes at the bottom of the reaction vessel, leaving a perfectly clear solution.

Note.—CdS may even under the foregoing conditions be imperfectly precipitated. A common fault is to work with solutions that are too acid to permit of CdS and PbS being completely thrown down. In the analysis of a mixture, this will cause trouble in Group III, the soluble lead being precipitated as a gelatinous, white compound and the cadmium as a bulky white precipitate soluble in excess of ammonia, which may result in its passing over into Group IV.

Group II*a*. is distinguished from Group II*b*. by the fact that its sulphides are insoluble, on digestion, in alkalis and alkali sulphides. The best and most usual separating agent is '*yellow ammonium sulphide*,' *i.e.* NH_4HS that has been allowed to stand until polysulphides are formed, but other agents are Na_2S and NaOH. Aqueous ammonia is also useful, not as a means of separation of the two sub-groups, because ammonia attacks CuS, but as a ' non-messy ' non-metalliferous reagent for bringing the sulphides of antimony, tin and arsenic into solution if required.

It is well to remember that H_2S is a gas with a limited solubility in water (100 cc. water at 0° C. dissolve 437 cc. H_2S at 760 mm.), so that at its maximum concentration it is only about 0.25 N ; also it is a very weak acid, being only very little dissociated even in pure water, while in acid solutions its dissociation is considerably less.

Physical Appearance of the Sulphides.

HgS.—First white, becoming orange-yellow, then brown, and finally black.

CuS.—Very dark brown to black. Sometimes has a greenish lustre superficially.

Cu_2S.—Similar.

Bi_2S_3.—Very dark brown to black.

PbS.—Black.

CdS.—Lemon yellow to nearly orange. The colour depends upon the acidity, temperature and concentration of the solution.

MERCURY (-ic) AND LEAD.

The determination of mercuric mercury has already been discussed under Mercurous Mercury in Group I (p. 50).

Lead falls more naturally into Group II than Group I from a quantitative point of view, but as its chloride is precipitated by the reagent of Group I when there is any appreciable amount of lead present, it has been discussed under that heading.

COPPER.

There are a very large number of possible methods for the estimation of copper, the choice of which must depend upon the nature of the material under analysis and the quantity of metal present.

Estimation of Copper.

A. Gravimetric Methods—(i.) *As Thiocyanate.*—The solution, which must contain no oxidising agent and a minimum of free acid, is saturated with SO_2 in the cold. The SO_2 may be supplied either by bubbling the gas through the solution from a syphon of the liquid gas (best), or by adding a concentrated solution of a sulphite. Suitable sulphites are NH_4HSO_3, prepared by bubbling SO_2 through dil. NH_4OH until the smell of the latter disappears, Na_2SO_3 crystals, or a metabisulphite.

When saturation is complete, add a concentrated solution of KCNS or NH_4CNS with constant stirring until no further precipitation of CuCNS is observed ; then set the beaker aside for at least 2 hours to settle the precipitate.

The original precipitate is usually of a dirty white colour on account of the co-precipitation of some $Cu(CNS)_2$, but this is reduced to the pure white CuCNS on standing. The precipitate may then be treated in various ways:

(*a*) *Weighing CuCNS Direct.*—Pour the liquid off through a weighed Gooch crucible (paper pulp or asbestos). Wash once or twice by decantation with cold water, transfer the precipitate to the crucible and continue washing until the filtrate gives no more than a very faint coloration when tested for CNS^- with a ferric salt. Suck the precipitate as dry as possible on the pump and dry at 130–160° C. in the air oven.

Note 1.—CuCNS begins to decompose at about 180° C.

Note 2.—The results are usually slightly low, but with care the error should not be more than 0·05 per cent., an error which is negligible in practice, at least when several per cent. of copper is to be estimated.

Note 3.—The precipitate is apt to creep and may give trouble when washing out of the precipitation vessel ; great care is necessary when washing the precipitate in the crucible to keep the level of the wash water well below the top of the Gooch.

(*b*) The precipitation may be used as a separation only, and the copper, thus isolated, may be estimated as follows:

Filter on to a close textured paper (No. 40) and wash as above. Open out the paper and rinse the precipitate into the original beaker. (*Note.*—If this is done, there is no need to rinse every particle of the precipitate into the filter in the first case.) Dissolve the adherent precipitate from the filter paper with a little hot dil. HNO_3 and wash several times with water. When the precipitate has dissolved, add 10 to 15 cc. of H_2SO_4 to the solution and evaporate to 'fumes' (see under Lead) ; the copper may then be estimated as Cu_2S, or iodometrically (*see p.* 63).

Or, transfer to a large porcelain crucible and gently incinerate paper and precipitate. Dissolve the residue in conc. HNO_3, add 5 cc. of H_2SO_4 and evaporate to fumes. Dilute, and estimate the copper as Cu_2S, or iodometrically.

Note 1.—" The solution must be free from oxidising agents and must only contain small quantities of free (' strong ') acids." If the solution is too acid, or if, *e.g.* HNO_3 has been used to effect solution of the substance for assay, add 10 cc. of H_2SO_4 and ' take to fumes.' Dilute when cold, and add a saturated solution of Na_2CO_3 until a slight permanent precipitate is obtained. Clear this with a few drops of dil. H_2SO_4, and the solution is ready for the KCNS precipitation.

Evaporation to fumes with sulphuric acid is almost a panacea for trouble in analysis. Sulphuric acid is a very harmless substance from the analytical point of view ; it is neutral in the sense of being neither oxidising nor reducing, there are very few ' insoluble ' sulphates, and the process is certain, comparatively rapid, and simple to carry out. This being so, whenever the analyst finds himself embarrassed by the presence of unknown or unwieldy amounts of other acids, whenever he has HNO_3 in his solution and wishes to use a reducing agent, when-

ever HCl is present and he has to apply an oxidant such as $KMnO_4$, these embarrassments may be removed by the simple evaporation with H_2SO_4. This acid has such a high boiling point that by the time it begins to boil and show the white fumes which are evidence of its decomposition, the operator may be certain that any substance with a boiling point below, say, 200° C., will have been completely evaporated away. Many cases of its use will be found in the following pages, and the student should learn to look upon the process of 'taking to fumes' as one of the most useful devices at his disposal. It should be noted, however, that the method is of no avail in getting rid of phosphoric acid, which has a boiling point higher than that of sulphuric acid.

Note 2.—The thiocyanate method separates copper completely from Cd, As, Sb, Sn, Fe, Zn and Ni. Lead and mercury interfere, but lead is conveniently removed as $PbSO_4$ before the copper is precipitated, and it is very unlikely that the student will meet with mercury in an analytical mixture for quantitative separation from copper.

Note 3.—If arsenic is present in large quantities, as in the analysis of the speisses produced in copper smelting, the only free acid permissible is HCl. On the other hand, it is usually necessary to attack these these substances with an oxidising mixture, usually *aqua regia*, in order to prevent loss of arsenic. The use of H_2SO_4 being precluded, the analyst must evaporate nearly to dryness, and then, after adding 20–30 cc. of HCl, evaporate once or twice more in order to decompose the HNO_3 remaining.

(ii.) *As Oxide.*—The solution, which must not contain ammonium salts, is boiled in an *old* refractory glass beaker, or in a large porcelain dish. Pure KOH solution (by alcohol) is then added, drop by drop, until the test solution reacts alkaline to litmus. The solution is boiled for ten minutes longer and put aside to settle. The dark precipitate is rinsed on to an open textured paper (No. 41) and washed copiously with boiling water. The paper and precipitate are transferred to a porcelain crucible, the latter dried in the mouth of the muffle and the precipitate finally roasted at full redness.

The results are invariably a little high, owing to the impossibility of washing out the last traces of adsorbed alkali. It is obviously a disadvantage moreover, to add K^+ to the solution if other metals are to be estimated in the filtrate, partly because it means that another metal has to be washed out at each filtration, but chiefly because K^+ is notoriously prone to be adsorbed. The method is not to be recommended, and the author has never heard of its being used in a commercial laboratory.

CuS, if roasted in air, is converted into CuO, the sulphur burning off as SO_2. In the case of a crushed ore, it is possible to reduce the sulphur content to 3 or 4 per cent. on a commercial scale, or even less, if the roasted lumps are crushed and re-roasted. (This, of course, is not a paying procedure commercially, nor is it desirable to remove all the sulphur.) In the laboratory, however, we are able to roast the sulphide almost completely to oxide by adopting the following method:

The CuS, wet, and in its filter paper, is transferred to a porcelain crucible and dried at the mouth of the muffle. When the paper commences to char, the crucible is pushed just inside the muffle, where

the combustion is allowed to proceed as far as possible with an ample supply of air. The half-roasted compound is then placed in the heart of the muffle and heated to redness (700° C.) for a few minutes, after which it is taken out and allowed to cool somewhat, not necessarily in the desiccator. The still hot crucible is gripped with a pair of tongs, and with the flattened end of a piece of glass rod the hard lumps are gently crushed to powder. The contents of the crucible are again roasted to redness for 15 minutes or so. It will then be found that only a very little sulphur remains ; so little, in fact, that for percentages of copper less than about three, no serious error is committed by weighing the oxide and assuming its purity. This is often very useful when small amounts of copper are concerned. Similar methods may be applied to the roasting of most other sulphides ; analytically, NiS, CoS and ZnS are often treated in this way for the estimation of small amounts of their metals.

In the case of larger amounts of copper, the sulphide may be roasted as a preliminary to obtaining a solution containing only copper, *e.g.* for a thiosulphate titration. The roasted precipitate is dissolved in HNO_3 *in the crucible if desired, but it is better to brush it out into* a beaker and attack it there. The roasting obviates the separation of free sulphur during the acid attack.

(iii.) *As* Cu_2S.—*A.* Add 10 cc. of H_2SO_4 to the HNO_3 solution containing the copper and evaporate to copious fumes. Dilute so that the acid represents about 5 per cent. of the bulk of the solution, and boil. Now pass in a rapid stream of purified H_2S gas, which under the conditions described will throw down the copper as a rapidly settling precipitate of CuS. Filter off on an open paper (41) and wash thoroughly with H_2S water containing a little acetic acid. Spread the paper out on a glazed tile and set it to dry under or on the hotplate. When dry, brush the precipitate off the paper into a Rose crucible and ignite the paper separately in a clean crucible. Add the paper ash to the main precipitate in the Rose crucible and sprinkle the surface with a little powdered sulphur.

Pass hydrogen from a cylinder into the crucible through the perforated lid, *via* a wash bottle containing a little H_2SO_4 to serve as a means of observing the rate of flow of the gas. Now heat the crucible over a small flame, the hydrogen passing at about 2 or 3 bubbles per second. Slowly increase the heat until the bottom of the crucible is at dull redness, when the flame may be removed and the rate of flow of the hydrogen slightly accelerated. Maintain the current of hydrogen until the crucible is quite cold, when the precipitate may be brushed out and weighed as Cu_2S.

Note 1.—A neat method for preparing H_2S wash-water is given in Treadwell's Quantitative Analysis. The jet of the operator's wash-bottle is connected to the delivery pipe of the Kipp's apparatus, and the gas bubbled through the water for a minute or two. After disconnecting the gas supply the bottle is vigorously shaken in order to dissolve the gas.

Note 2.—The wash with H_2S water is necessary to prevent the CuS from oxidising on the filter and passing through as sulphate.

B. A better method of conducting the precipitation if copper only is to be estimated in the solution, *e.g.* in the case of a simple assay of copper,

or if copper has already been separated by the KCNS or other method, is to precipitate directly as Cu_2S with $Na_2S_2O_3$. To do this, reduce the acidity by dilution to about 2 per cent. (H_2SO_4 only), and add to the boiling solution, in small quantities at a time, a saturated solution containing 5 gms. of sodium thiosulphate. At first only sulphur separates, but on continuing the addition, black cuprous sulphide comes down in large flocks which settle remarkably rapidly and filter very well. This precipitate may be washed with hot water only, as it shows no tendency to oxidise, and the sulphur with which it is mixed does no harm as it is removed during the subsequent heating in the Rose crucible. Since the precipitate is Cu_2S in the first place there is no need for a very prolonged heating, in fact the only necessity for heating at all is to drive off the sulphur.

B. Electrolytic Method.

Copper is most easily and usefully estimated electrolytically. This method has two important advantages over all others, apart from its inherent accuracy ; these are, firstly, it requires no manipulation or attention, and secondly, it removes copper (and lead) without the addition of any reagent or increase in bulk of the solution.

Electrolysis may be carried out either in HNO_3 or H_2SO_4 solution, but it appears to be desirable to have some HNO_3 always present for rapid deposition.

Procedure.—The solution, measuring 100 to 150 cc. in bulk and containing HNO_3 up to 5 per cent. or 10 per cent. by volume, is placed in a small, wide beaker and electrolysed using a revolving kathode at 2-3 volts pressure and using up to 3 amps. current. One gram of copper is deposited in about 45 minutes under these conditions, but the safe working rule is to continue electrolysis for 20 minutes after the disappearance of the blue colour of the Cu^{++} ion.

The beaker should stand upon a wooden block ; on completion of the electrolysis the block is removed and the beaker supported in the left hand while the right manipulates the wash-bottle. The beaker is slowly lowered (current still passing) and with the kathode rotating very slowly while a stream of water is directed upon the deposited copper. When the electrode is clear of the exhausted electrolyte the current is switched off and the anode rinsed down. The kathode is rotated rapidly for a few moments in order to throw off the excess water, then stopped, and a small beaker containing alcohol (methylated spirit) is raised to surround the electrodes. This is followed by a beaker containing ether. (*Note.*—Be certain that the current is *off*, as if there is a trace of acid water in the ether there will probably be arcing and an ether fire.) After these washes, the electrodes dry very rapidly if placed on a piece of filter paper on the top of the steam oven, and the deposit may be weighed immediately. The increase in weight of the kathode represents copper ; that of the anode represents PbO_2 (*q.v.*).

Note 1.—Traces of silver, arsenic, antimony and bismuth may be deposited with the copper, but they will not total more than a few thousandths of 1 per cent., and may be ignored. In fact, the official method of assaying copper (*Brit. Engrg. Std. Specns.*), whether for electrical

or engineering purposes, is this electrolytic method, and it is laid down that all the deposit is to be reckoned as copper. If arsenic is deposited in serious quantities, the copper will show greyish specks ; in case of doubt the deposit may be redissolved in HNO_3, the solution boiled for a few minutes, and then re-electrolysed.

Note 2.—If rotating electrodes are not available the process is much slower, and there is often much doubt as to whether the deposition is complete or not. The safest and most convenient method is to use a very low current density, 0·75 amp. per sq. dm. is advised, and allow the electrolysis to continue over night. In this case, it is well to withdraw a small portion of the electrolyte with a pipette and test it for copper by adding excess of NH_4OH in a test-tube.

Note 3.—In a complete quantitative analysis, *e.g.* of an alloy, there should be no need to test the electrolyte if the foregoing instructions are carefully observed. If, however, some copper remain undeposited, it will reveal itself when ammonia is added to precipitate the iron, etc. As there should be no more than a few mgms. of copper remaining, it is not worth while to reacidify and continue the electrolysis ; the following method is quicker and more convenient. Filter off and estimate the iron, aluminium, etc. as usual ; reacidify the filtrate with a few drops of HCl and saturate with H_2S. Filter off the CuS and estimate it either colorimetrically or by titration with KCN, or even, if it is very little, by roasting it to CuO in the muffle. The solution may then be made ammoniacal again and the separation of zinc, nickel, etc. proceeded with.

This method saves much time, as only one treatment with H_2S is necessary. The alternative is to pass H_2S through the solution before removing the iron, after reacidifying. If this is done, the operator will have to boil off the H_2S before adding ammonia, and then pass H_2S again after filtering off the Group III precipitate.

Note 4.—*It is of course essential to remember that nascent chlorine attacks platinum, and if HCl has been used in the process of bringing the substance under analysis into solution, the assay MUST be evaporated to copious fumes with* H_2SO_4 *before electrolysing. In this case,* 5 *cc. of* HNO_3 *should be added before electrolysing.*

C. Volumetric Methods.

(i.) *By Iodine Titration.*—This method is the most generally applicable and is a very accurate means of estimating copper. It depends upon the reaction:

$$2CuSO_4 + 4KI = 2CuI + 2K_2SO_4 + I_2,$$

the liberated iodine being titrated with sodium thiosulphate:

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

Solutions. (*a*) *Standard Sodium Thiosulphate.*—34 gms. of the moist crystals are dissolved in 1,000 cc. of water. This concentration bears no simple relation to the N reagent. It is designed to use about 90 cc. of thiosulphate for 0·8 gm. of copper, the reason being that the analyst prefers to use as large an amount of titration solution as is reasonably

possible in order to obtain the utmost possible accuracy. At this concentration 1 drop (= 0·05 cc. approx.) is equivalent to about 0·0005 gm. of copper, so that, taking 1 gm. for the assay, results are correct to 0·05 per cent. If the strength of the thiosulphate were doubled, 1 drop would represent 0·1 per cent., which is hardly accurate enough ; if on the other hand, it were halved, the solution would become too dilute to obtain a sharp end-point.

(*b*) *Standard Copper Solution.*—0·8 gm. of the finest electrolytic copper is exactly weighed out and dissolved in 2 cc. of HNO_3 in a small beaker. When this is dissolved, 1 cc. of conc. H_2SO_4 is added and the solution evaporated to fumes, cooled, and diluted to 30 cc., transferred to a beaker-flask similar to those used for the assays and a saturated solution of Na_2CO_3 added from a burette or dropping funnel until a slight permanent precipitate remains. This is cleared with a few drops of dil. acetic acid, (1 : 2 of the ' glacial ' acid).

(*c*) *Potassium Iodide Solution.*—About 2 gms. of KI are required for each titration. If only one or two assays are to be made it is quickest to weigh (roughly) one 2 gm. quantity and judge the others, using the original weighed quantity for comparison. These weights of solid KI are then added directly to the assays before titration. If, however, several assays are to be made, it is better to weigh out just sufficient KI for the whole work, *i.e.* (No. of assays × 2) grams, and dissolve in a number of ccs. of water which shall be an even multiple of the weight of KI taken, taking care always to use the minimum amount of water in order to minimise dilution of the assay solution. The proper volume of this solution is then pipetted out and added to each assay just before titration ; it should not be added until ready to commence titration, or some iodine may be lost by evaporation.

(*d*) *Starch Solution.*—Boil 100 cc. of water in a small, lipped beaker. Shake up about 1 gm. of starch powder with a few cc. of cold water in a test tube and pour the suspension quickly into the boiling water. Boil for 30 seconds longer and cool to room temperature. It is necessary to prepare fresh starch for each batch of assays, as the sensitiveness rapidly falls off on keeping.

Method of Assay.—The copper solution is, if necessary, freed from HNO_3 or other oxidising agents by evaporation to fumes with 1 cc. of H_2SO_4. It is then transferred to a tall 400 cc. beaker, beaker-flask or Phillips' flask (bulk of solution not more than 30 cc.) and carefully neutralised with saturated Na_2CO_3 solution added from a burette or tap-funnel. When a slight permanent precipitate remains, dil. acetic acid is added until clear, scrupulously avoiding excess, as the assay must not be too acid ; the warm mixture is cooled finally under the tap.

When quite ready to titrate, add the KI, or KI solution, and mix well by swirling the liquid. White CuI is at once precipitated, and the solution is coloured brown by the liberated iodine. Now run in the thiosulphate from a 100 cc. burette, constantly rotating the flask, but not too violently, until the brown colour is almost discharged, and the contents of the beaker look somewhat like cream. At this point add about 2 cc. of the starch indicator, when the colour will change to a deep blue. Continue adding the thiosulphate cautiously until the blue colour is completely discharged.

The end-point is very sharp, but the titration is one which requires care and experience, as it is very easy to overshoot the end-point. The best method of finishing is to keep the solution slowly rotating, adding the thiosulphate one drop at a time at a point about midway between the centre and the circumference of the surface circle. If the reaction is incomplete, a white circular streak will be observed on the surface of the liquid, showing up well by contrast with the rest of the liquid ; when the end-point is reached, however, the only result of the addition of a drop of thiosulphate as described is to produce a clear, watery streak.

Note 1.—Work with a small volume, certainly not exceeding 50 cc. at the commencement of the titration. It is important that all the assays of one batch should be of the same bulk, the standard included.

Note 2.—The solution must be cold, or iodine will be lost.

Note 3.—Do not add the starch until the reaction is nearly completed. This makes for increased sensitiveness. It is bad working if more than 2 cc. of thiosulphate have to be added after the starch.

Note 4.—As^{+++}, Sb, and Fe^{+++} interfere by liberating iodine from KI, with the result that high results are obtained. Bi, Pb, Hg and Ag have insoluble or coloured iodides, and interfere by making the end-point difficult to observe. It should be remembered, however, that, in practice, lead is the only one of these three metals which is commonly present in important amounts in commercial alloys ; if, however, the assay has been taken to fumes with H_2SO_4 in the preliminary stages, the lead will be converted to sulphate and will then be unable to give trouble. In the case of a stanniferous alloy that has to be attacked with HNO_3, the solution will contain a suspension of metastannic acid. This will not interfere with the titration, and will not generally be the cause of error during the neutralisation of the solution, as the white tin compound should not be mistaken for the blue carbonate which is precipitated.

Note 5.—No free ' strong ' acid must be present, or there will be no definite or permanent end-point.

The method is very generally applicable to the estimation of copper. The strength of thiosulphate given is the best when amounts of copper varying between 0·5 and 1·0 gm. have to be estimated. With smaller amounts the thiosulphate may be used at half or quarter strength. The weight of KI should be adjusted to the amount of copper present ; 2 gms. of KI to each 1 gm. of copper is a safe proportion. Unnecessary excess of KI is wasteful, and this is an expensive salt.

(ii.) *Titration with Potassium Cyanide.*—This method is very useful when small amounts of copper have to be estimated. With a dilute solution of KCN it may be used for weights of copper up to 0·05 or 0·06 gm., but with a stronger cyanide solution it may be employed for larger amounts of copper.

Potassium Cyanide Solution.—15 gms. per litre.

Standard Copper Solution.—0·1 gm. of pure electrolytic copper foil is carefully weighed out into a tall 300 cc. beaker or Phillips' flask and dissolved in a few cc. of HNO_3. The solution is evaporated to a syrupy consistency on the hotplate (beware of spitting), and 50 cc. of water are added, followed by 5 cc. of bromine water. The solution is boiled until free from the excess of bromine and cooled, when 10 cc. of ammonia

(dens. 0·90) are added. The solution is then ready for titration. It is necessary to titrate a standard with each batch of assays, as not only does the cyanide solution lose strength on keeping, but the end-point depends very greatly upon the exact conditions of the solution as regards temperature, volume, alkalinity, etc.

It saves much time, if many assays are to be made, if, instead of weighing out 0·1 gm. of copper every time for the standard, a large quantity of standard copper solution is made up at once. For this purpose weigh out 1 gm. of pure copper and dissolve it in the minimum amount of HNO_3. Evaporate to syrup as described, dilute to 100 cc. and treat with bromine as before; boil free from excess bromine and cool, dilute to 500 cc. (exactly), and use a suitable volume of this solution for each standardisation, choosing the volume that shall contain a weight of copper as nearly as can be judged equal to that in the solution for assay. In every case make the volume up to the standard (50 cc.).

The reliability of the method depends so largely upon the conditions that special precautions must be taken to ensure uniformity. The following will be found to be the simplest and safest method to follow:

Precipitate the copper as CuS; filter and wash (see under Copper, Gravimetric). Dry the precipitate and paper, ignite and roast the sulphide as far as possible to CuO. Brush the oxide from the crucible and transfer it to the titration beaker, add a few cc. of HNO_3, warm until all the copper is dissolved and evaporate to syrup. Dilute and treat with bromine, ignoring any globules of sulphur that may be left unattacked; cool, add the ammonia, and the solution is ready for titration.

Titration.—Set the beaker upon a white tile in a good light, but not in direct sunlight, and add the cyanide solution rapidly, with constant swirling, until the colour begins to pale. Now add the cyanide more cautiously; the colour changes to purple, then lavender (almost rose) and finally the solution becomes water-white. Great caution is necessary when the end-point approaches, as the discharge of colour is apt to come very suddenly and unexpectedly. Some analysts do not take the titration to the complete water-white stage, but stop while the solution is still of a pale lavender colour. In any case it is a good plan to have a standard assay standing close beside the assay that is being titrated, for the purpose of matching the colour. The author proceeds as follows: *Two* standards are pipetted out from the stock standard copper solution, and one is titrated until, in the operator's opinion, the end-point is reached. This solution is then placed on the white tile on the left of the burette while the first of the batch of assays is titrated, the end-point being judged by comparison of the colour of the assay with that of the standard. The whole batch is handled in the same manner, and the second standard is titrated last; all titrations are carefully matched with the initial solution, which remains on the tile close to the beaker which is actually being titrated. The two standards should not differ by more than 0·1 cc. The advantage of titrating a standard first is that should the end-point be overshot, another standard may be prepared for titration without great loss of time or trouble, whereas the loss of an assay would entail the repetition of a considerable amount of manipulation, even if the solution were replaceable.

D. Colorimetric Method.

Small amounts of copper are very conveniently estimated by colorimetric methods, advantage being taken of the intense colour of the cuprammonium ion.

Procedure.—The copper is separated, preferably as CuS, which is dissolved in a few drops of HNO_3 ; one or two drops of ammonia are then added until the deep blue colour of the cuprammonium ion is fully developed, and the colour is compared with that of a standard prepared by dissolving 1 gram of copper in the least possible amount of HNO_3 and diluting to a litre ; each cc. of this solution contains 0·001 gm. of copper.

There are two ways of making a colorimetric estimation. In the first, the assay solution is diluted with water until it matches the standard in colour when viewed transversely, *i.e.* by having the two solutions in tubes of equal diameter and looking through them at right angles to their axes. In the second, a copper solution is added to the standard until the colour, viewed axially, is equal to that of the assay. In the former method it is obvious that when the colours match, the concentration of copper *per cc.* is the same in the two tubes, and the total amount of copper present is proportional to the volume of the solution ; in the latter method, the total *amounts* of copper in the two tubes are equal.

Method 1.—The standard copper solution should be in a burette or graduated pipette. From this burette, a volume of the standard solution representing an aliquot part of 1 gm. approximating to the amount of copper in the assay should be run into one of the graduated comparison tubes, and a few drops of ammonia are added so that the deep blue colour is developed. The tube containing the standard is then marked in some way so that it may not be confused with the assay tube, and the solution is diluted to a convenient bulk, depending upon the depth of colour. It is convenient to select a bulk such that the concentration of the copper is a simple fraction of unity ; this will simplify calculation. The solution in which the copper is to be estimated is then rinsed into the other tube and distilled water from a tap-funnel is added in small quantities until the colours of the two solutions almost match when held side by side and viewed transversely. When the colours are nearly equal in depth, after each addition of water and well mixing by inverting the tubes several times, the colours should be viewed with first one tube on the left and then the other. It will usually be found that the eyes are unequal in their power of estimating depth of colour, and when the true 'match' is attained, the colours will rarely match actually, as viewed by the operator. The way to finish the matching process is, therefore, to proceed until, *e.g.* the tube on the left appears slightly darker than the other, but on reversing the tubes the other appears the darker, and to the same degree. Of course, it may be the right eye that is the more sensitive to colour, but the point is that the transposition of the tubes should also transpose the order of the colour intensities.

The volume of the assay solution is read off on the scale, and the amount of copper present is then calculated. To make the above perfectly clear, an example will be taken:

Suppose that the sample for estimation contains about 0·003 gm.

of copper. The standard should contain the same amount (approximately), so that operator runs out exactly 3 cc. of the standard solution, and, after adding ammonia, the bulk is made up to, say, 30 cc., though any multiple of 3 will do. In the 'standard' tube we have, therefore, a solution containing 0·0001 gm. of copper per cc. When the colours match it is obvious that the concentration of the copper in the assay tube is the same, *i.e.* 0·0001 gm. per cc. The volume being known, *e.g.*, 27·6 cc., the total weight of copper in solution in the assay tube follows, being 27·6 × 0·0001 gm. = 0·00276 gm.

To compare the colours it is necessary to have good illumination, but not direct sunlight. An excellent device is to wet a large filter paper and stick it to a window with a north light, viewing the tubes side by side against this bright matt background.

Method 2.—Two Nessler tubes are selected, 50 or 100 cc. capacity. Into one the assay solution is rinsed and made up to the mark with water,

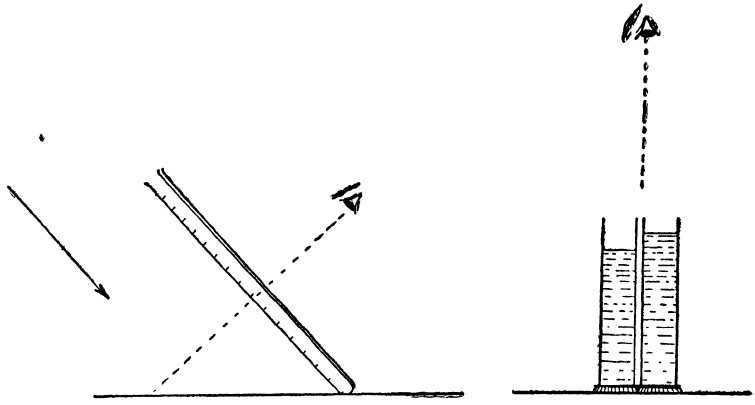


Fig. 8.—Colorimetric Estimation of Copper.

while the other is about half filled with water, to which a few drops of ammonia are added. Standard copper solution from a burette is run into the second tube in small quantities at a time, stirring after each addition with a thin glass rod. After each addition the two Nesslers are placed on a white tile in a good light and the colours compared while looking down into the cylinders, axially. As already explained, the tubes must be transposed after each addition when the colours nearly match.

When the colours are equal, it is obvious that the two tubes contain the same *amounts* of copper, and, knowing the amount of copper added to the standard tube, the amount of copper in the assay solution follows.

Notes.—For Method 1 use two 50 cc. Eggerz carbon tubes graduated in ccs. and tenths, and fitted with ground-in glass stoppers for convenience in mixing. The comparison is made as in the diagrams.

In Method 2 the exact volumes of the two solutions do not matter greatly, but they should be within a few cc. of one another.

BISMUTH.

Bismuth is not a very satisfactory metal to have to estimate analytically, at least when it is mixed with other metals, as it is not easy to effect a good separation from its co-members of Group II., especially lead. Separation, however, will be considered in Section V. of this book, and for the present we assume that the element bismuth has been separated, and is present as a pure solution, usually either the chloride or the nitrate.

Estimation of Bismuth.

A. Gravimetric Methods—(i.) *From Chloride Solutions as Oxychloride.*—The solution, which should be fairly concentrated, say, 70 to 100 cc., is heated to about 50°–60° C. and the excess acid carefully neutralised with ammonia. At first the reagent is added in concentrated solution, until the precipitate which forms (bismuth hydroxide), dissolves with difficulty on shaking and swirling the solution. At this point dilute ammonia (1 : 3) is used and added by drops until traces of the hydroxide remain undissolved. The solution is then diluted to about 300–350 cc., and, if necessary, a drop or two more of ammonia is added, the object being to produce a faint opalescence. Three cc. of 1 : 3 HCl are now added, and the mixture is well stirred. A white, crystalline precipitate is formed, which is allowed to settle out completely by placing the beaker, covered, on the corner of the hotplate.

The solution is then filtered hot, decanting the clear liquid off through a Gooch crucible (asbestos or paper pad). The precipitate is washed well with hot water, by decantation as far as possible, and then until the filtrate no longer gives a reaction with $AgNO_3$. The precipitate is dried at 100° C. and weighed as BiOCl.

(ii.) *As Bi_2S_3 from Sulphuric or Hydrochloric Acid Solution.*—The solution, which must not be too acid (10 cc. conc. HCl per 100 cc. of solution will be safe), is placed in a stout glass flask ; a 500 cc. suction filter flask serves well. The side tube should carry a piece of stout rubber tube about 2 inches long, and a screw clamp (open) is kept in readiness loosely on the free end. The solution is diluted to 250 cc. and H_2S gas passed to saturation in the cold. A rubber bung is inserted into the mouth of the flask and tied firmly into place with string or wire ; the clamp is screwed up and the whole arrangement placed into a cold water-bath, so that the level of the water outside comes nearly up to the neck of the pressure flask. Heat is applied to the water-bath and it is kept hot, but not boiling, for half an hour. This treatment ensures the complete precipitation of the bismuth sulphide, and at the same time brings it down in a compact form which filters well.

The sulphide is filtered off through a weighed Gooch crucible (asbestos or paper) and washed well with H_2S water. When free from other metals, two or three crucible-fulls of alcohol are poured in to remove the water, sucking quite dry each time, and then the precipitate is extracted with CS_2 as explained under Mercury, in order to remove any sulphur that may contaminate the precipitate.

Note.—There is always some sulphur, as H_2S oxidises in the air. Note also, that if the precipitation is performed in a *pure* bismuth solution

there will be no need for much washing. See under Mercury (p. 54), and fig. 7.

(iii.) *From Nitrate Solutions.*—There is a method for the estimation of bismuth which consists in its precipitation as basic nitrate. This method is, however, rather lengthy, as it involves several evaporations in order to convert the whole of the nitrate into the basic salt before igniting to oxide. It will be better, and usually easier, to convert the nitrate to chloride or sulphate by evaporation with hydrochloric or sulphuric acid, and then to conduct the estimation by one of the foregoing methods.

Other methods are: *Precipitation as Carbonate and ignition to Oxide; precipitation as Hydroxide and ignition to Oxide; estimation as Metal, by reducing the Oxide with fused Potassium Cyanide; a Volumetric Method by titration of the Oxalate with Permanganate.* There is also an *Electrolytic Method.* These methods are not to be recommended, though, of course, almost any method will serve provided the bismuth solution contains bismuth *only*, that it gives a product of definite composition, and that the precipitation is complete.

B. Colorimetric Method.—This is very useful for the estimation of the small amounts of bismuth met with in, *e.g.* lead ores, copper concentrates, mattes, alloys, commercial lead, and the like. The estimation of bismuth is of special importance in copper and copper alloys, since this metal has a very bad effect upon the tenacity of such alloys, even in traces of the order of 0·05 per cent.

Standard Bismuth Solution.—Dissolve 1 gm. of pure bismuth in HNO_3. Dilute to 1,000 cc., adding more HNO_3 if a precipitate of basic nitrate is formed. Take 100 cc. of this solution and dilute to 1,000 cc. This is the standard solution of bismuth, and 1 cc. = 0·0001 gm. metal.

Procedure.—The solution, containing not more than 0·0005 gm. of bismuth, is treated with a few drops of ammonia and ammonium carbonate solution, and filtered. The precipitate will contain the bismuth and any lead that may be present, copper passing into the filtrate. The precipitate is dissolved in a few drops of dil. H_2SO_4 and the liquid evaporated to fumes; the solution is poured off into an Eggerz carbon tube, decanting it from any $PbSO_4$ that may be present. (*Note.*—It is particularly necessary to eliminate all traces of lead, as PbI_2 is yellow.) Then add, first, a crystal of sodium sulphite to reduce Fe^{+++} to Fe^{++}, [Fe^{+++} liberates iodine (yellow) from KI], and then a crystal (small) of KI. If bismuth is present, a vivid yellow coloration will be produced, and the metal may be estimated by comparing the depth of colour with that of a known amount of the standard bismuth solution, treated similarly as regards sulphite and KI. For details of the colorimetric method of estimation, see under Copper (p. 67), and fig. 8.

CADMIUM.

Cadmium is not a metal which may be expected in a practical examination. In nature, cadmium occurs in ores associated with zinc, and, in consequence, in the metal zinc and its alloys as an impurity, which rarely amounts to more than a few tenths per cent. Commercially, therefore, the estimation of cadmium is more or less confined to the

estimation of small quantities of the metal, and generally involves the separation of these small amounts from large excesses of zinc and/or other metals. There are, however, a few alloys of cadmium, notably cadmium solder and a cadmium-copper alloy used for electric cables, and, of course, for examination purposes it is conceivable that a pure cadmium salt might be given as an ingredient of a mixture for analysis.

Cadmium is invariably separated from other metals as its sulphide ; this salt, however, is not suited for direct estimation, and the general procedure is to convert the sulphide to the sulphate and weigh the metal in that form.

Estimation of Cadmium.

A. Gravimetric Method.—Precipitate the separated cadmium as sulphide by passing a stream of H_2S through the weakly acid solution (hydrochloric or sulphuric) until the yellow sulphide settles completely. Filter off on a paper pulp filter and wash with water once or twice. Dissolve the sulphide off the filter by pouring a few cc. of hot 1 : 3 HCl upon it, catching the runnings in a weighed porcelain or silica dish ; following this wash with a little hot water and again with the hot acid and sufficient water to rinse all the cadmium through the filter. Then evaporate the chloride solution cautiously to fumes with not more than 5 cc. of conc. sulphuric acid (less, if possible), the amount of sulphuric acid depending, of course, upon the quantity of cadmium present. This may be roughly judged from the bulk of the sulphide precipitate. When all the water is expelled, gradually push the crucible towards the centre of the hotplate, finishing up in the very hottest part, where the excess of acid is finally driven off. Then remove the dish to the mouth of the muffle, place it upon a small piece of asbestos sheeting, and when the last traces of acid fumes have disappeared the dish may be cautiously introduced into the muffle, still keeping it upon its piece of asbestos. Heat the dish to a dull redness (no more), and finally transfer it to the desiccator to cool before weighing. Weigh as $CdSO_4$.

Note.—If the quantity of cadmium is not great, say, less than 0·05 gm., the evaporation may be conducted in a porcelain crucible. It is very important to keep the sulphate from overheating, or SO_3 may be lost. The small pad of asbestos, as described, is usually sufficient to prevent this, but if desired, the following device may be adopted.

Make a hole in a piece of asbestos sheet, slightly smaller than the upper rim of the crucible. Push the crucible containing the sulphate, after expelling the last traces of acid, through the hole, and insert it into a larger crucible so that no part of the weighed crucible comes into contact with the latter. The larger crucible is then heated boldly to redness in the muffle, though even now the heating must not be too strong, or too prolonged.

B. Volumetric Method.—This method is the converse of a well-known method for the estimation of small quantities of sulphur (sulphide), and for further details this should be consulted ; see under Sulphur.

The method is not suitable for more than very small quantities of cadmium, say, for not more than 0·005 gm.

Procedure.—The cadmium is precipitated as sulphide, filtered off on a small pulp filter, and the precipitate washed with water. The

precipitate and pulp are transferred to a tall beaker or conical flask, and about 25 cc. of conc. HCl added, diluted with 100 cc. of water. The precipitate dissolves easily in the acid and the solution is then titrated with dilute iodine solution. When the yellow colour of the iodine disappears but slowly, add a few drops of starch solution and titrate to a full blue colour.

An alternative method, which is perhaps preferable, owing to the possibility of losing H_2S when the solution is acidified, is to add immediately a fair excess of the iodine from a burette and then titrate back with standard thiosulphate solution.

The iodine is standardised by titrating it against a solution containing a known amount of cadmium. This may be prepared by either of the following methods: (1) Weigh out 1·855 gms. of $CdSO_4$ (the anhydrous salt) and dissolve it in a litre of water. One cc. of this solution contains 0·001 gm. of Cd. Pipette out, say, 5 cc. of this solution and, after diluting to 100 cc. pass in H_2S until the cadmium is all precipitated. Filter and wash until free from H_2S as in the case of the estimation. Then dissolve the precipitate in dilute HCl and titrate the solution with the iodine as described above. Knowing the weight of cadmium in the solution the "*cadmium value*" of the iodine may be calculated.

(2) It is perhaps preferable to weigh out 1 gm. of pure cadmium metal in the form of drillings from a rod. Dissolve these in dilute HCl, taking precautions against the loss of cadmium by spraying or spitting; a close cover-glass will serve, but this must be rinsed into the beaker before making up the solution. When dissolved, dilute to a litre, and standardise the iodine as above.

This titration depends upon the reactions:

1. $CdS + 2HCl = CdCl_2 + H_2S$ (which dissolves in the water).
2. $H_2S + I_2 = 2HI + S$.

i.e. 254 gms. $I_2 \equiv$ 112·4 gms. Cd.
1 cc. 0·1 N iodine solution $\equiv$ 0·00562 gm. Cd.

C. Electrolytic Method.—Cadmium may also be estimated by the electrolysis of its double cyanide with KCN. The cadmium is present as sulphate; the acid is neutralised with NaOH, and conc. KCN solution is added until the precipitate just dissolves. The solution is diluted to about 150 cc. and electrolysed, using about 0·5 amp. at 5 volts. It is said that this method gives very accurate results.

GROUP IIb.

Antimony, Tin, Arsenic.

The metals of this group are precipitated as sulphides on passing H_2S gas through the acid solution of their compounds. They are separated from the metals of Group IIa by digesting the precipitated sulphides with a solution of one of the following: *Potassium hydroxide, sodium hydroxide, sodium sulphide, yellow ammonium sulphide, (ammonia, ammonium carbonate)*. Yellow ammonium sulphide, $(NH_4)_2S_x$, is the most generally

applicable reagent, but this polysulphide tends to dissolve some CuS, and if copper is present its use is to be avoided, if possible. The caustic alkalies and sodium sulphide have the great advantage of not being " messy " to handle in the sense that their use does not entail complicating the analytical processes with large quantities of precipitated sulphur if the solution is acidified, but these reagents have their own disadvantages ; the alkali metals are notorious for their tendency to be adsorbed by precipitates, from which they cannot be removed by washing, but the most serious objection to their use is that they dissolve HgS to an extent which cannot be ignored. On the other hand, they do not dissolve CuS, and as copper is far more frequently met with analytically than mercury, the student is advised to use a 10 per cent. solution of NaOH containing a little Na_2S for separating the two sub-groups. This reagent may be prepared by passing H_2S through the NaOH solution for a few minutes before using it.

ANTIMONY.

A. Gravimetric Method—1. *As* Sb_2O_4.—Antimony may be estimated as Sb_2O_4 by following exactly the same procedure as detailed under Tin for its estimation as SnO_2. HNO_3 oxidises antimony to Sb_2O_5, which is left as a white residue on concentrating the acid ; the residue is essentially antimonic acid, but the amount of combined water depends upon the conditions of the attack. Unfortunately, this oxide is very easily reduced by glowing carbon (unlike SnO_2), and the method is not to be recommended. If it is necessary to adopt this method of estimation, the paper with the precipitate should be dried in the air oven, the precipitate brushed off and the paper ignited separately, (for details, see under Silver and Lead), any reduced antimony being reoxidised by adding a drop or two of HNO_3 to the ash in the crucible and heating on the hotplate until dry. The main precipitate is then added and the whole roasted to Sb_2O_4 by heating in the muffle to 750°–800° C., *not higher*, or Sb_2O_3, which is volatile, may be formed. This method is not recommended, as all the objections which apply to the estimation of tin as SnO_2 apply here also.

An excellent method for small amounts of antimony is, however, as follows: The separated antimony is precipitated from HCl solution as Sb_2S_3 by passing H_2S through the hot liquid ; or, as sometimes happens, depending on the method adopted for the separation of the metals, by acidifying a solution of the thio-salt with HCl. The Sb_2S_3 is filtered off on to a small pulp and well washed. A weighed porcelain crucible is then placed under the stem of the filter and a few drops of concentrated ammonium sulphide poured through the pulp and precipitate. The filter is washed with a few drops of water, and a second and even third wash with ammonium sulphide is made, each time following with a rinse of water. The crucible is then placed on the corner of the hotplate where it cannot actually boil, and the contents are evaporated down to dryness. The pulp is given a final wash with water (if necessary) and the washings added to the crucible, which is again taken dry. The sides of the crucible are then carefully treated with

conc. HNO_3, which is applied drop by drop and the crucible tilted and rotated until all the dried residue has been in contact with the acid. The acid is now evaporated off on the hotplate and the treatment repeated. Usually a globule of fused sulphur forms, but the heat in the centre of the plate should be sufficient to volatilise this. The crucible is then roasted at 750° C. and the Sb_2O_4 weighed.

2. *As Sb_2S_3.*—This is the standard gravimetric method for antimony, and is applicable to large or small quantities of the metal. Antimony is not completely precipitated from HCl solutions containing more than about 15 per cent. of HCl by volume, and with concentrations only slightly less, the oxychloride, SbOCl, is thrown down. The solution of the difficulty, therefore, lies in commencing the precipitation with H_2S from the hot, rather concentrated solution, and finishing in a cold, dilute solution after the bulk of the sulphide has been precipitated.

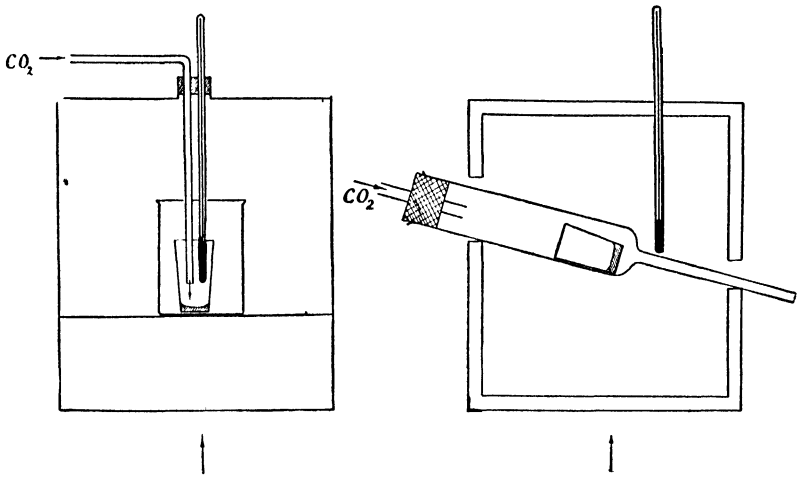


Fig. 9.—Ignition of Sb_2S_3 Precipitate in Antimony Estimation.

Also, if -ic antimony is present, some Sb_2S_5 will be thrown down from a cold solution, especially with a rapid stream of gas.

Procedure.—The solution may contain either -ous or -ic antimony, or both. The acidity is adjusted to 20 per cent. of the conc. acid by volume and the solution then saturated with H_2S in the cold, subsequently diluted with an equal volume of boiling water with the gas still passing, and the whole raised to the boiling point for 10–15 minutes, admitting the H_2S in a steady stream the whole time. After boiling, the solution is allowed to cool on the bench to ordinary temperatures, still passing the gas. By this method all the antimony is precipitated as rather dark coloured Sb_2S_3, which settles well. The sulphide is filtered off cold through a tared asbestos Gooch, washed by decantation and then on the filter with hot dilute acetic acid that has been saturated with H_2S, ceasing the washing at the first sign of the precipitate " peptising " and passing through the filter. The crucible is placed in an electric oven and the precipitate heated to 300° C. in an atmosphere of CO_2 to prevent

oxidation. This temperature is necessary, firstly to decompose any Sb_2S_5 that has been precipitated, and secondly, to volatilise the sulphur which invariably contaminates the precipitate. This sulphur is derived from the oxidation of the H_2S by the air and by -ic antimony. The crucible is cooled in CO_2 and weighed when cold.

The apparatus is set up in as the diagram, fig. 9.

B. Volumetric Methods—1. *By Potassium Permanganate.*—This method is an excellent one for the estimation of antimony in alloys where there is not much iron present. It is very rapid, almost foolproof, and accurate. The method depends on the fact that alloys are attacked by hot conc. H_2SO_4 with the formation of sulphates, while at the same time the acid is decomposed and SO_2 is formed, which reduces -ic antimony to -ous antimony. The SO_2 is expelled by boiling, and the diluted solution titrated with permanganate.

Procedure.—Weigh 0·5 gm. of the alloy, in the form of sawings, fine drillings, or (best) granulations, and place in a dry 250 cc. conical flask. Add 25 cc. of conc. H_2SO_4 and gently heat over a naked Bunsen flame. For a time the action is very slight, but as the temperature rises, a sudden reaction sets in and the alloy passes into solution in a few seconds. If the alloy contains lead, there will be an insoluble residue of $PbSO_4$, which may be ignored. Occasionally the residue has a dirty grey tinge ; this is due to sulphides, as the acid decomposes into H_2S among other compounds ; on continuing the heating, however, these are converted into sulphates. The heating of the acid is continued until it boils, and oily drops condense on the sides of the flask, which fills with SO_3 fumes. Gradually the ring of condensed droplets is driven further and further up the sides of the flask, carrying before it a scum of liberated sulphur, and when, finally, the flask is full of clear acid vapour, and the ring of condensate has reached to the neck, it is removed from the flame and set aside on an asbestos pad to cool.

When the flask is cool enough to bear touching (on the bottom), 100 cc. of cold water are *suddenly and quickly* poured in ; the jet from the mouthpiece of the washbottle is convenient for this. The operator must not flinch from the clouds of steam produced by the violent reaction, but add the water *boldly*, and no harm will be done; timid dilution results in violent spurting, which may be dangerous.

Having added the water, 5 cc. of conc. HCl are immediately added, and the flask at once cooled under the tap. When quite cold, the solution is titrated with standard permanganate (the 'iron' solution ; see Volumetric Reagents). The end-point is taken at the point at which the pink colour completely fills the solution. In the presence of HCl the pink will fade almost immediately when the permanganate is in excess.

Note 1.—The flask should be held in a pair of crucible tongs, the points of which are shaped semicircularly to fit the neck of the flask. Wooden grippers are of no use as the boiling point of sulphuric acid is sufficiently high to char wood. The flask must be kept in rapid rotation at the commencement of the reaction or it will probably crack ; when the acid is boiling freely, however, there is no need to rotate the solution.

Note 2.—The dilution, cooling and titration should be performed as rapidly as possible, as the antimony tends to reoxidise on standing.

Note 3.—The addition of HCl is to keep basic antimony compounds in solution. If this precaution is omitted, a white precipitate of the basic -ous sulphate is slowly deposited, especially if there is much antimony present. With small quantities, however, *e.g.* 0·05 gm., which is equivalent to 10 per cent. antimony on the 0·5 gm. sample, the danger of the antimony precipitating is slight. In presence of HCl the solution must be *cold* (below 20° C.) before titration, or chlorine will be formed and the assay spoiled. If, instead of remaining clear, the solution goes yellow or brown and throws down a brownish precipitate, the assay should be rejected and a fresh sample weighed out. In this case, it is usually possible to detect the odour of chlorine by smelling at the neck of the flask. This form of failure also occurs if too strong a solution of $KMnO_4$ is used for the titration.

Note 4.—Tin does not interfere ; nor does the presence of $PbSO_4$ in the flask. Arsenic does interfere. Iron is reduced to the ferrous state by the attack with H_2SO_4, and the results in the presence of iron are high by the equivalent of this metal. In a complete analysis of an alloy, when iron is determined later, its equivalent in permanganate may be deducted from the antimony figure. As a rule, however, there is practically no iron present in antimony alloys such as Babbitt metal, hard lead, pewter and the like, and this correction may be ignored without serious error.

Note 5.—The method depends on there being something present that will decompose the H_2SO_4 and yield an -ous compound for titration. The metal of an alloy meets this condition admirably, but the method is not adapted for the analysis of most antimony salts, for example. A modification is used for some ores, but as a rule in these cases it is best to separate the antimony first and then estimate it by the titration with iodine, or with potassium bromate, since these are effective in HCl solution ; or it can be estimated gravimetrically as sulphide.

2. *Titration with Potassium Bromate* (Györy's method).—The method depends on the reaction:

$$3SbCl_3 + KBrO_3 + 6HCl = 3SbCl_5 + KBr + 3H_2O.$$

When all the antimony has been oxidised, the first drop of excess bromate liberates free bromine which bleaches the methyl orange that is added as an indicator. The titration should be performed hot and the indicator should not be added until the reaction is nearly complete.

Procedure.—The sample of the alloy, 1 gm. (see Method 1), is placed in a tall beaker and dissolved in 100 cc. of conc. HCl to which a few drops of bromine have been added. Antimony is normally almost insoluble in HCl, but in the presence of Br_2 the finely divided metal passes into solution quite rapidly. When all is dissolved, the solution is boiled down to about two-thirds of its bulk to expel the excess of bromine and two or three crystals of Na_2SO_3 are added to reduce pentavalent antimony and arsenic to the trivalent compounds respectively. The solution is then further concentrated to about 20 cc. by vigorous boiling; this has the effect of removing the arsenic as the volatile $AsCl_3$, (B. Pt. 119° C., but volatilises rapidly at temperatures below this; the HCl boils at about 110° C.), and also the excess of SO_2. The

solution is then diluted to about 50 cc. with conc. HCl and heated to boiling.

The solution is now titrated rapidly with the bromate solution, 5 drops of methyl orange being added when within about 3 cc. of the end-point. On the addition of the first drop of excess of bromate the red colour fades suddenly, being bleached by liberated bromine.

Note 1.—*Bromate Solution.*—Weigh 2·82 gms. of $KBrO_3$ and dissolve in a litre of water. One cc. of this is equivalent approximately to 0·006 gm. Sb. It is impossible to make the solution of standard strength by weighing, as the bromate always contains bromide. The solution is standardised against a solution of $SbCl_3$ prepared from the pure metal by following the foregoing directions ; a suitable weight of antimony, which must be finely powdered, is 0·2 or 0·3 gm. These amounts require about 33 and 50 cc. of bromate solution respectively.

Note 2.—The methyl orange, if added at the commencement of the titration, begins to fade at once, and if more is added as the colour vanishes, the results will be too high. To obtain correct results, therefore, it is necessary to make a trial titration on a separate weight of sample, adding methyl orange as necessary. For the assay, the bromate is run in to within 3 cc. of the end-point found in the trial before adding the dye. It is necessary to add the same amount, viz., 5 drops, for each titration, as the bleaching uses a definite amount of the reagent. Any easily oxidisible dye will serve as indicator ; methyl orange is chosen because it is a regular laboratory reagent.

3. *Titration with Iodine.*—This is the standard volumetric method. The sample, if a metal or alloy, is brought into solution by the HCl and Br_2 attack detailed under the bromate titration. As described there, the excess of Br_2 is first expelled and then the antimony is reduced by boiling with a sulphite. The solution is then evaporated down to quite low bulk, which has the effect of expelling arsenic as $AsCl_3$ and at the same time driving off the excess SO_2. Note, however, that $SbCl_3$ boils at 223° C. and is perceptibly volatile at 190° C. ; the evaporation to low bulk must not, therefore, be carried to extremes or antimony will be lost. There is no danger of loss if the final bulk is not less than 15 cc. with a 1 gm. sample, especially if the evaporation is conducted in a conical flask or tall beaker. About 5 gms. of tartaric acid or Rochelle salt are then added in the form of a saturated solution in order to prevent the precipitation of antimony, and the solution is carefully neutralised with Na_2CO_3 added from a burette as a saturated solution. The solution is then made just acid with HCl and 3 or 4 gms. of solid $NaHCO_3$ are quickly added. One cc. of fresh starch solution is then added as indicator and the antimony titrated immediately with standard iodine solution. To avoid making up more than one strong iodine solution, it is usual to titrate antimony (and arsenic) with the same iodine as is used for tin. (See Volumetric Solutions.)

If the sample is a mixture of salts, or a solution, the antimony is separated as sulphide (see Separation of Antimony) and filtered off. The sulphide is then washed back into the precipitation beaker and dissolved in a little conc. HCl, from which point the preparation of the solution is continued as detailed above.

There is at least one other method for the estimation of antimony

means of iodine. This depends on the liberation of an equivalent ıount of iodine from a solution of KI when the latter is added to a ution of $SbCl_5$, prepared by attacking the metal with HCl and $KClO_3$. few cc. of CCl_4 are added after the excess of chlorine has been boiled ', followed by excess of KI. Iodine is liberated, and is dissolved by ; heavy CCl_4. The iodine is then titrated with a standard solution thiosulphate, the solution being well shaken after each addition of ; reagent. When all the iodine is oxidised, the CCl_4 is colourless.

stillation Method for Estimation of Antimony.

Antimony may be separated by taking advantage of the volatility its (-ous) chloride. The procedure is exactly like that given for the ıilar method of estimating Arsenic, except that higher temperatures ; required, $SbCl_3$ boiling at 223° C., whereas $AsCl_3$ boils at 130° C. ıe chlorides are, however, actively volatile at temperatures much low their boiling points, arsenic being freely distilled from Const. Pt. HCl (110° C.), and it is usually found that all the arsenic is evolved the time the temperature of the liquid reaches 115° C. (provided there plenty of HCl, and the conditions of the distillation are otherwise ictly observed). Antimonous chloride begins to come over at this nperature, is freely volatile at 180° C., and may be reckoned to be npletely distilled at 220° C. The boiling point of the solution is sed by the addition of 5 gms. of $ZnCl_2$ (ferrous and calcium chlorides ; sometimes advised, but they have no advantage over zinc chloride, ile the latter possesses one great advantage, namely that it fuses quietly hout bumping at the end of the distillation).

Procedure.—The solution, metal or alloy is treated exactly as described der Arsenic (p. 84), except that in addition to the other directions, ms. of $ZnCl_2$ are added to the contents of the flask, and a thermometer, ding to 250° C., is fixed so that its bulb dips *into the solution* in the flask e fig. 10).

Distillation over a small flame is now commenced and the bulk of contents come over at slightly over 110° C., which is the boiling nt of the HCl-water mixture. The flask is still heated, until the rmometer shows 115° C., when the receiver is changed (but see note Arsenic, p. 87), and the flame turned up somewhat. Antimonous oride now begins to distil, and the heating is maintained until the ıperature reaches 220° C. or slightly higher. The second receiver ıtains all the antimony. The solution is diluted somewhat, but not ficiently to cause the precipitation of the basic chloride, and is titrated h iodine as directed under volumetric methods. This method, since nvolves a separation from all other metals, is often of very great value the analysis of alloys, especially when there are large amounts of oup II metals present.

Note 1.—If any doubts are felt as to the completeness of the separation the antimony and arsenic, as for instance, if their amounts are large, one of them is in considerable excess, the following method may be value. Distil completely into one receiver, so that the chlorides are h together in the distillate. Now treat with a rapid stream of H_2S the cold, *without* diluting. At this concentration of HCl no antimony

will be precipitated, and the precipitate will consist of pure arsenious sulphide. Filter this off through a tared asbestos Gooch crucible and estimate it gravimetrically (see under Arsenic). Dilute the filtrate considerably (at least four times), and precipitate the antimony as sulphide as described under Gravimetric methods.

Note 2.—If the amounts of antimony and arsenic are at all considerable, and especially if the antimony is present in quantities exceeding a

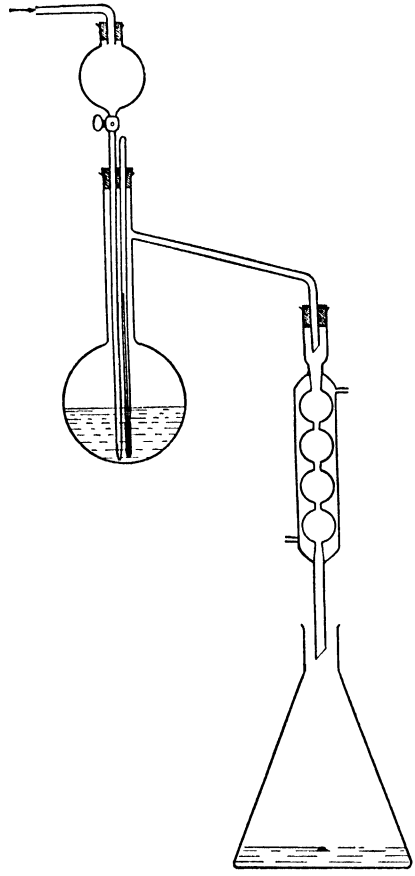


Fig. 10.—Apparatus for Estimation of Antimony by Distillation Method.

few milligrams, it is best to make a slight alteration in the apparatus, for whereas arsenious chloride is completely carried over with the distilling HCl and water, by the time the antimony is ready to distil there will be very little HCl or water left, and the antimony may be lost as a condensate in the upper parts of the flask. A gas that will flush the flask and condenser out is required, and HCl gas is the best. The flask is accordingly fitted with a two-holed bung, one hole carrying a bent glass tube reaching below the surface of the solution and terminating

in a drawn out point, while the other carries the thermometer, as before. HCl is generated outside the flask by dropping conc. H_2SO_4 from a tap-funnel into conc. HCl solution in a small flask. The gas comes off in a steady stream, which may be regulated by adjusting the flow of the H_2SO_4, and is passed into the boiling solution as soon as the temperature indicated by the thermometer shows a rise above 110° C., continuing the stream of gas until the end of the distillation. As this extra apparatus is so simple to set up and attach, it is perhaps advisable to use it in all cases where antimony is to be separated by this method.

Alternatively (but not quite so good) is the following: Instead of the delivery tube and the stream of HCl gas, a dropping funnel may be used to deliver conc. HCl, drop by drop, on to the surface of the hot solution. This has much the same effect, *i.e.* while the *solution* can heat up sufficiently to distil the antimony, there is still a stream of gas rising up in the flask to carry with it the traces of volatile chloride that are present.

A very complete separation can therefore be attained, even with considerable amounts of both metals, as follows (in outline): With the thermometer bulb opposite the side-tube, distil until the temperature rises above 110° C. Remove the flame and cool below 100° C. Add 50 cc. of HCl and again distil until the temperature reaches 110° C. Change the receiver and connect up the HCl delivery tube, (or, open the tap of the dropping funnel, which may be already attached), lower the thermometer so that the bulb dips into the solution, and continue distilling until the temperature reaches 225° C. The first receiver contains all the arsenic, the second all the antimony.

ARSENIC.

Arsenic is one of the elements that lie on the borderline between metal and non-metal ; that is to say, it forms compounds which may be classed with the metallic salts, *e.g.* $AsCl_3$, As_2S_3, and also well-defined acids which yield salts with bases. The non-metallic character predominates, but the element is always regarded as a metal analytically, because it is precipitated as sulphide with the metals of Group II even though the arsenic in the compound or mixture under investigation is originally in the anion.

Arsenic may be either tri- or penta-valent, and in its chemical properties it resembles phosphorus on the one hand and antimony on the other.

Estimation of Arsenic.

A. Gravimetric Methods—1. *As Arsenious Sulphide.*—The solution for analysis should contain the arsenic as chloride, or should be the HCl solution of an arsenate or arsenite. If the element is combined in any other way, a chloride solution may be obtained by separating the arsenic as sulphide and dissolving this in HCl + $KClO_3$, and boiling off excess of Cl_2 and ClO_2 before proceeding as follows:

The arsenic should be entirely in the trivalent state ; if there is any doubt about the condition of the metal in the solution, or if the HCl + $KClO_3$ treatment has been followed, the solution should be gassed with

SO_2 until the mixture smells strongly of the gas ; the excess is then removed by bubbling CO_2 in a rapid stream through the *cold* solution until no suspicion of SO_2 can be detected when the nose is applied close to the solution. The arsenic solution is then made *strongly* acid (50 per cent. by volume conc. HCl) and a rapid stream of H_2S is passed through the liquid for at least an hour. At the end of this time the yellow precipitate should have settled out well ; it is filtered off through a tared Gooch crucible (paper or asbestos) which has been dried at 110° C. The sulphide is washed with cold 50 per cent. HCl that has been saturated with H_2S, then once with a little cold water, followed by two or three washes with a little pure alcohol. When the HCl is almost entirely removed, the crucible is dried to constant weight at 110° C., the increase being As_2S_3.

Note 1.—Arsenious solutions containing Cl^- must *never* be boiled ; nor may they be gassed at any temperature above that of the laboratory. The reason for this is that though $AsCl_3$ boils at 130° C., it is volatile at temperatures considerably below this and the metal may be lost during such treatment.

Note 2.—As_2S_3 is practically insoluble in conc. HCl (and H_2SO_4), though the other sulphides of this group are entirely soluble in quite moderate concentrations of acid. This fact is extremely useful, therefore, as providing a means of *separating* arsenic from the metals Cu, Pb, Bi, Cd, Sb, and Sn ; particularly the last two. If this fact is taken advantage of, it is, in fact, unnecessary to separate other metals from the arsenic before passing H_2S, though it is generally wiser to do so. It is this ' separation ' that lies at the root of the instruction to wash with 50 per cent. HCl, the idea being to prevent any other metals coming down in the Gooch after the strong acid of the precipitation beaker has been filtered off.

Note 3.—Reduction with SO_2 is necessary chiefly to convert pentavalent arsenic into trivalent arsenic, but partly, also, to reduce compounds of hexavalent chromium or ferric iron (etc.) which may be in the solution and the reduction of which by H_2S would liberate sulphur to contaminate the final precipitate. For the same reason the excess of SO_2 must be removed, on account of the reaction:

$$SO_2 + 2H_2S = 2H_2O + 3S.$$

Note 4.—As_2S_3 exhibits a tendency to " go colloidal " if washed with pure water, which removes the electrolytes that are necessary to cause the sol to gel. Also, the precipitate is rather slow in forming. It is sometimes an advantage, therefore, to precipitate As_2S_3 in a pressure flask. The method is as follows: The arsenious solution is placed in a stout conical flask and saturated in the cold with H_2S. The tube that admits the gas is then withdrawn and a well-fitting rubber bung is pushed into the neck of the flask and tied or wired securely into place. The flask is then immersed in a water-bath or a large beaker or saucepan full of water, and the whole heated to near boiling-point on the hot-plate. The expansion of the H_2S in the flask and the additional pressure due to the lesser solubility of the gas in hot water produce a fairly high pressure inside the flask, which has the effect of making the precipitate

settle out more completely and rapidly than would otherwise be the case.

Note 5.—Arsenic may also be estimated as As_2S_5 in a similar manner, except, of course, that all the arsenic must be in the -ic condition before precipitating. The -ic sulphide is precipitated by passing a rapid stream of H_2S through the cold solution, which should contain two-thirds of its volume of conc. HCl.

2. *As Magnesium Pyroarsenate.*—The arsenic must be in the pentavalent condition (arsenate). With a solution of pure arsenic acid, or that of an alkali arsenate, 5–10 cc. of HCl are added and the precipitation proceeded with immediately, as below. If, however, as is more usual, the mixture contains metals of Groups I–V, the arsenic is first separated as sulphide. It does not matter here in what state of oxidation the arsenic is ; the solution is made strongly acid with HCl by adding a volume of the conc. acid equal to that of the solution, and the mixture is saturated with H_2S in the cold, preferably in a " pressure flask " as explained in Method 1. The sulphide is filtered off, washed with 25 per cent. HCl containing H_2S in solution, and rinsed back into a beaker, covered with a few cc. of conc. HCl, and a crystal or two of $KClO_3$ added. If any precipitate adheres to the filter paper it is removed by pouring a few drops of saturated $KClO_3$ solution over the opened paper, followed by a wash with hot 1 : 1 HCl and rinsing with cold water until the arsenic is all transferred. The acid in the beaker is heated until the sulphide is dissolved and the sulphur that is liberated, if any, is coagulated. The solution is brought to the boil to expel Cl_2 and ClO_2 and diluted so that it has a bulk of not more than 100 cc. for every decigram of arsenic present.

Ten cc. of magnesia mixture are now added for each decigram of arsenic (minimum 10 cc.), and the solution carefully neutralised with dilute ammonia, added drop by drop from a tap funnel, until just alkaline to phenolphthalein, stirring continually during the process. When the precipitation is complete, one-third of its bulk of 0·90 sp. gr. ammonia is added to the solution, and it is stood aside in a warm place for several hours, preferably overnight.

The precipitate is filtered off through a weighed asbestos Gooch that has been ignited at full redness, and washed with 2·5 per cent. ammonia until free from chlorides. The crucible is sucked quite dry and placed on the hotplate until no more steam is driven off. It is then transferred to the mouth of the muffle and gradually worked back until it is at a full red heat (800° C., at least). It is then cooled, and the $Mg_2As_2O_7$ weighed.

Note 1.—Since the sulphides are to be dissolved in an oxidising mixture it does not matter what the state of oxidation of the arsenic is originally. H_2S precipitates As_2S_3 from -ous solutions and As_2S_5 from -ic solutions, so that all the arsenic will be thrown down from any arsenic compound or mixture.

Note 2.—$AsCl_5$ is not volatile at the boiling point of HCl, so it does not matter if the solution is boiled.

Note 3.—The precipitate that comes down first is white and flocculent. On standing and stirring, especially in hot solution, it gradually changes to a crystalline variety, which filters and washes well. The precipitate

is $MgNH_4AsO_4$, $6H_2O$; this loses nearly all its combined water at 100° C., and the remainder is expelled at a somewhat higher temperature. If the precipitate is heated rashly the evolved water is apt to cause spattering: hence the need for caution in the heating. The final ignition expels the ammonia and water and leaves the pyroarsenate, which is analogous in every way to the pyrophosphate. The arsenate precipitates are rather more soluble in water than the corresponding phosphates ; the washing should, therefore, be conducted with discretion, using small and many washes. The use of dilute ammonia is absolutely essential, as the arsenate is quite soluble in pure water.

Note 4.—The precipitation is conducted on lines similar to those detailed for phosphates. The student is advised to refer to the section on Phosphate precipitations and the theory that accompanies it.

B. Volumetric Methods.—Arsenic is best determined volumetrically ; in most cases this involves separation from other metals.

Oxidation with Iodine.—This is the best method for the estimation of arsenic in the very great majority of cases. Often there is no need to undertake any further manipulation after separating the arsenic, *e.g.* in the estimation of arsenic in alloys, and in many estimations there is no manipulation at all, except in the case of arsenates, which have first to be reduced.

" White arsenic " (As_4O_6) is dissolved directly in NaOH or Na_2CO_3 (conc. solution), just acidified with HCl (to phenolphthalein) and a few grams of solid $NaHCO_3$ added. The solution is then ready for titration. An arsenite is dissolved in dil. HCl, neutralised with carbonate, just acidified, and the usual addition of bicarbonate made before titration. Arsenates must be reduced first; the material is dissolved in dil. HCl and saturated with SO_2 ; the excess of this is then removed in the cold by bubbling CO_2 through the solution in a rapid stream ; the usual neutralisation is performed and the solution titrated at once.

The titration depends on the reaction:

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

but as the reaction is reversible, it is necessary to remove the HI as it is formed in order that complete reaction shall occur. This is the reason for the addition of the solid bicarbonate ; the normal carbonate or caustic soda cannot be employed because they react with iodine.

The solution is cooled, if necessary, and titrated with standard iodine until the yellow colour fades but slowly. Two or three ccs. of fresh starch solution are then added and the titration continued to the point at which the solution takes a full blue colour. The end-point is sudden and sharply defined.

The iodine solution is standardised directly against arsenic by weighing exactly 1 gm. of pure, resublimed arsenious oxide into a tall 400 cc. beaker. The oxide is dissolved in a few cc. of conc. NaOH or Na_2CO_3 solution and the solution diluted somewhat ; a drop of phenolphthalein is added and then HCl until the red colour is discharged. The solution is then diluted to a convenient bulk for the titration and 2 or 3 gms. of solid sodium bicarbonate are added (this does not affect phenolphthalein). The titration with the iodine solution is carried out, and, taking the

arsenious oxide as standard, the strength of the iodine solution is calculated (see Volumetric reagents).

The same method can be followed for arsenious chloride solutions, such as are obtained after separating arsenic by the Evolution Method (Stead's). As this method is the method *par excellence* for the estimation of arsenic in alloys, where the element occurs in small amounts only, it will be detailed here. For further information, see under Arsenic Separation.

For arsenic in iron and steel and arsenic in copper alloys the principles are the same, but there is a difference in practice on account of the fundamentally different behaviour of iron and copper when acted upon with HCl.

(*a*) *Arsenic in Iron and Steel—Theory:* The metallic drillings are attacked with HCl, whereby most of the arsenic is carried off by the

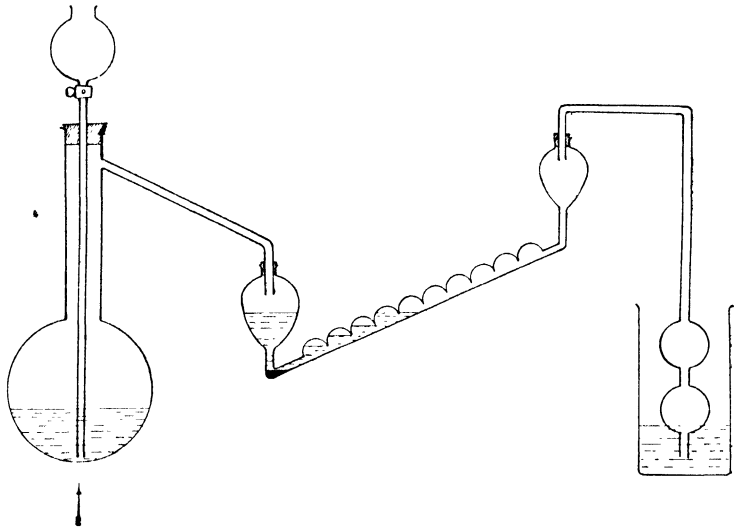


Fig. 11.—Apparatus for Determination of Arsenic in Iron and Steel.

hydrogen as arsine. This is absorbed in bromine water ; the whole is returned to the flask and the mixture distilled from HCl solution. The distillate contains all the arsenic as arsenious chloride, which may be titrated directly with standard iodine.

Method.—Weigh out 5 gms. of the iron or steel drillings and place them in a 250 cc. distilling flask fitted to a short condenser, the lower end of which is connected by a cork to a Meyer bulb containing bromine water and a few drops of liquid bromine (see fig. 11). One hundred cc. of 1 : 1 HCl are poured into the flask and the cork quickly placed in position. Hydrogen is evolved and bubbles through the bromine water, which oxidises any AsH_3 that may be formed. When the metal has dissolved (ignore silica and carbonaceous residues), the cork of the flask is removed and about 1 gm. of calcspar or marble is added, the cork being at once replaced. This causes an evolution of CO_2, which pushes the hydrogen (and AsH_3) that fills the flask and condenser out through the

bromine water. When the carbonate has dissolved, the Meyer tube is disconnected and its contents rinsed back into the distilling flask. Some of the Fe^{++} will be oxidised by the bromine, but there will always be sufficient to maintain thoroughly reducing conditions, and ensure the arsenic being present in the -ous condition.

A small flame is now set under the flask and the contents are distilled until the separating solids begin to bump (fig. 10). The distillate consists of strongly acid $AsCl_3$ solution. It is neutralised with conc. NaOH solution, using phenolphthalein as indicator, just reacidified with HCl, and after adding the $NaHCO_3$ as described, it is ready for titration with iodine. As the amount of arsenic in iron and steel rarely exceeds 0·05 per cent., it is usual to keep a special dilute iodine solution for this estimation. The dilute iodine is prepared by diluting the ordinary strong solution, and the arsenic equivalent is found by calculation. (See Volumetric Reagents.)

Note 1.—The bromine fumes are dangerous, and there should be a bromine trap in the shape of a thistle funnel or a broken bulb tube attached to the end of the Meyer bulbs and dipping below the surface of a conc. solution of NaOH.

Note 2.—Sometimes a little iron " bumps " over towards the end of the distillation. This may interfere with the titration. If this unfortunate accident should occur, the distillate is simply rinsed back into the flask and the distillation repeated ; or, if preferred, the arsenic can be separated by passing H_2S through the distillate and estimated gravimetrically as As_2S_3.

Note 3.—The bromine oxidises AsH_3 to arsen*ic* acid and water. The -ic acid is at once reduced to the -ous condition on returning the bromine water to the flask, which contains a large excess of Fe^{++}.

Note 4.—The end-point is taken at a full blue colour. At this dilution the colour change is not very sharp, and care should be taken to take the titration to the same end colour every time.

Note 5.—Although $AsCl_3$ boils at 119° C., this compound is sufficiently volatile to ensure all the arsenic being distilled by the time the solids separate. The acid boils at about 110° C., but the solution is, of course, several degrees hotter. See, however, Arsenic Separation.

(*b*) *Arsenic in Copper Alloys.*—Arsenic is added to many copper alloys as it has a toughening effect. Copper rods, tubes and boiler stays contain between 0·3 and 0·5 per cent. of arsenic, intentionally added.

Five gms. of the *fine* drillings, turnings or planings are weighed into a 250 cc. distilling flask and covered with 100 cc. of a strong solution (dens. 1·43) of $FeCl_3$ in 1 : 1 HCl. A condenser and receiver are connected to the side tube and the distillation carried out slowly over a small flame. As before, the distillation is stopped when the solids commence to bump in the flask ; the distillate is at once titrated with the dilute iodine solution after neutralising and adding $NaHCO_3$ as already described.

In this case, there is no need for the preliminary attack in the cold with the bromine bulbs to catch evolved arsine, since copper does not evolve hydrogen from HCl in the cold. The attack of the acid is very slow in the absence of the ferric chloride, and is rather slow in any case, so much so that if the drillings are not extremely fine they may

not be entirely dissolved by the time that the distillation is complete. In view of this possibility, it is safest, when the flask has cooled slightly, to add about 50 cc. of the 1 : 1 acid and shake until the Cu_2Cl_2 dissolves, when any undissolved particles of metal can easily be detected. If the attack has not been complete all that is necessary is that the second addition of acid be distilled, and the two distillates combined. See fig. 10, p. 79.

Note 1.—The ferric chloride is reduced by the copper and the hydrogen during the distillation, so that the dark colour fades before the end of the process. This is correct, as the final conditions must be strongly reducing in order to ensure the evolution of the arsenic.

Note 2.—There is sometimes some antimony in copper alloys as an undesirable impurity. This metal has an -ous chloride that begins to distil at temperatures above about 150° C., and some $SbCl_3$ may come over if the distillation is carried to a very low bulk. As a rule, however, with ordinary alloys, if the distillation is stopped at the first signs of bumping, there is no fear of this happening. $SbCl_3$ reads as $AsCl_3$ in the titration, of course.

An alternative method, which is specially useful when the amount of arsenic present is very small, or when antimony is also to be determined, is as follows: 5 to 25 gms. of the drillings, according to arsenic content, are weighed out into a large beaker and 20 cc. of HNO_3 for each 5 gms. of metal are cautiously added. When the reaction ceases (ignore any precipitate of the oxides of antimony and tin) the solution is evaporated to the point at which a crystalline scum begins to form, and is then diluted to about 500 cc. Five cc. of a 3 per cent. solution of ferric iron (nitrate) are added and solution neutralised carefully with a dilute solution of NaOH, until a permanent precipitate forms. This precipitate is cleared with a *few* drops of dilute HNO_3 (but care must be taken not to have the solution too acid) and 20 cc. of a saturated solution of sodium acetate are added. The solution is diluted to 750–800 cc. and, after adding two or three small pieces of broken porcelain (old crucible lids, etc.), the solution is brought to the boil. Basic ferric acetate will be precipitated, and will carry with it all the arsenic as arsenate, and the antimony as antimonate. The hot solution is allowed to settle for a minute or two and filtered through a large, open-textured filter paper. The insolubles are not washed, but the paper is allowed to drain as completely as possible. Meanwhile, the addition of the 5 cc. of ferric nitrate, followed by the sodium acetate, is repeated on the clear filtrate from the first operation ; the two precipitates are combined by opening out the papers in the funnels and pouring hot 1 : 1 HCl over them, thereby dissolving them off the papers. The chloride solutions are caught in the same beaker, the yellow stained papers washed alternately with *cold* water and *hot* dilute HCl until they give no perceptible yellow tint on adding the HCl, and the yellow solution, which contains all the arsenic and antimony, is concentrated on the hotplate, adding a little $KClO_3$ when the bulk has been considerably reduced. When the solution is nearly dry, it is diluted with 30 cc. of 1 : 1 HCl and the evaporation repeated, again adding $KClO_3$ near the end, in order to decompose the last traces of nitrates.

The solution is then transferred to a distilling flask (see fig. 10).

Five gms. of cuprous chloride (or ferrous chloride) are added, followed by 100 cc. of 1 : 1 HCl. The mixture is distilled over a small flame, and as a precaution against antimony coming over, a thermometer is fitted, with its bulb dipping into the liquid in the flask. The temperature is kept below 115° C. ; if the reading is found to rise above this, the receiver should be changed. It is perhaps safer to keep the temperature at 110° C. and perform a double distillation, that is, if antimony is present and is to be determined later. When the temperature rises above 110° C., remove the flame and allow the flask to cool until the thermometer reading drops to 50° C. or so. Then remove the cork and add 50 cc. of the 1 : 1 acid ; recork and redistil, again ceasing the operation when the temperature rises above 110° C.

The arsenic is then estimated in the distillate as already described. For the determination of the Antimony, see under that metal.

C. Evolution Method in Hydrogen.—This is the method used for the determination of very small amounts of arsenic, a matter which is often of great importance medically and industrially, owing to the poisonous nature of arsenic compounds and the rather wide distribution of the element in association with commercial metals and products. Thus, arsenic has been found to enter beer *via* the sulphuric acid used in brewing, the acid having been made from pyrites which contained arsenic. Small amounts are also liable to be found in baking powders, tinned meats, and the like, and, of course, some green paints and weed killers are commercially pure arsenic salts.

The original method of determination was Marsh's, which depended upon the reduction of arsenic to AsH_3 by nascent hydrogen under rigid conditions of experiment. The arsine was conducted through a capillary combustion tube heated by a small flame to above the temperature at which arsine decomposes. A ' mirror ' of metallic arsenic was thereby formed, and this was compared with a similar mirror prepared from a known amount of arsenic.

This method has been largely superseded by the Gutzeit method in which a stain is made by the escaping arsine upon a paper treated with a solution of mercuric chloride, the stain being then compared with a set of standard stains, prepared under rigidly defined conditions. An outline of this method will now be given, not because it is expected that the student will ever be called upon to perform a Gutzeit test, in an examination at least, but because it represents a type of quantitative estimation different from any hitherto given here.

It is of the utmost importance to maintain " standard " conditions, or at least uniform conditions, over a series of assays ; it does not matter greatly if the dimensions of the apparatus used by the student differ slightly from those recommended by the authors of the method, but it is absolutely essential that all the assays should be conducted in the same apparatus and with the same amounts of zinc, acid, etc., or the results will not be comparable.

The Gutzeit apparatus consists of a flask in which hydrogen (pure) is generated. When the vessels are full of the gas the arsenical solution is added, and any arsine produced is led through a small glass tube which holds a strip of the mercuric chloride paper. A stain is produced, which is compared with the stain made by a known amount of arsenic.

The authors of the method advise the use of two sizes of apparatus, the larger to estimate amounts of arsenic ranging from 0·02 to 0·50 mgm., and the smaller to estimate amounts ranging from 0·001 to 0·020 mgm. For convenience, the larger apparatus only will be considered here, the manipulations required for both being the same.

The form, size, and set-up of the apparatus may be seen from the dimensioned drawing (fig. 12). The necessary reagents and standards will now be considered:

1. *Standard Arsenic Solution.*—Dissolve 1·320 gm. of pure, resublimed As_4O_6 in 20–25 cc. of 20 per cent. NaOH. Dilute somewhat and neutralise with H_2SO_4, adding 10 cc. excess. Dilute to a litre. Dilute 50 cc. of this solution to 1 litre, and 100 cc. of the more dilute solution again to 1 litre, adding 10 cc. of H_2SO_4 before dilution. The final solution contains 0·005 mgm. of arsenic per cc.

2. *Sensitive Paper.*—A 3·5 per cent. solution of $HgCl_2$ is prepared, and a strip of smooth surfaced ordinary filter-paper is dipped into this, avoiding great excess of the solution. The paper is then placed flat upon a sheet of glass, and the excess solution expelled by rolling a large test-tube gently over it once forwards and once back, taking the roller completely across the surface each time. The glass sheet with the adhering paper is then placed inside the steam bath and dried at 100° C. As soon as it is dry, the paper is peeled off the glass and trimmed into a strip 13 cms. wide with a sharp knife ; (a photographic print-trimmer is ideal, especially if the edge of the table is graduated in centimetres). *Note.*—The mercuric solution tends to concentrate somewhat on the edges of the paper ; it is necessary, therefore, to trim off at least an inch all round the original strip in making the 13 cm. strip. The original should thus be at least 6 inches broad.

Having prepared the strip, it is cut across into smaller strips, 0·5 cm. wide, and these standard Gutzeit strips, 13 by 0·5 cm., are then placed in a stoppered bottle.

3. *Standard Iron Solution.*—To contain 0·1 gm. Fe in 5 cc. For this, 70 gms. of ferrous ammonium sulphate crystals are dissolved in 500 cc. of water, containing 5 cc. of H_2SO_4. A small piece of Armco iron wire is coiled into a spiral round a pencil and placed in the beaker while the solution is being made up, and before bottling. The acid solution may be allowed to act upon the iron for five or ten minutes to reduce any F^{+++} ; it is then poured off into a bottle.

4. *Sulphuric Acid.*—One part of the conc. acid is diluted with 4 parts of water. Ten gms. of pure NaCl should be dissolved in each litre of this acid.

5. *Lead Acetate Paper.*—A sheet of common filter-paper is soaked in a 10 per cent. solution of lead acetate, dried, and cut up into strips approximately 7 by 5 cms.

Method.—The apparatus is set up as indicated in the diagram ; *exact* dimensions are not important, but the apparatus used should approximate as closely as possible to the drawing, and all estimations *must* be made with the same set-up.

The arsenic solution is acidified with 50 cc. of the sodium chloride-sulphuric acid and diluted to 200 cc. 0·1 gm. of Fe, *i.e.* 5 cc. of the solution, is then added, followed by 30–40 pieces of pure zinc ' shot.'

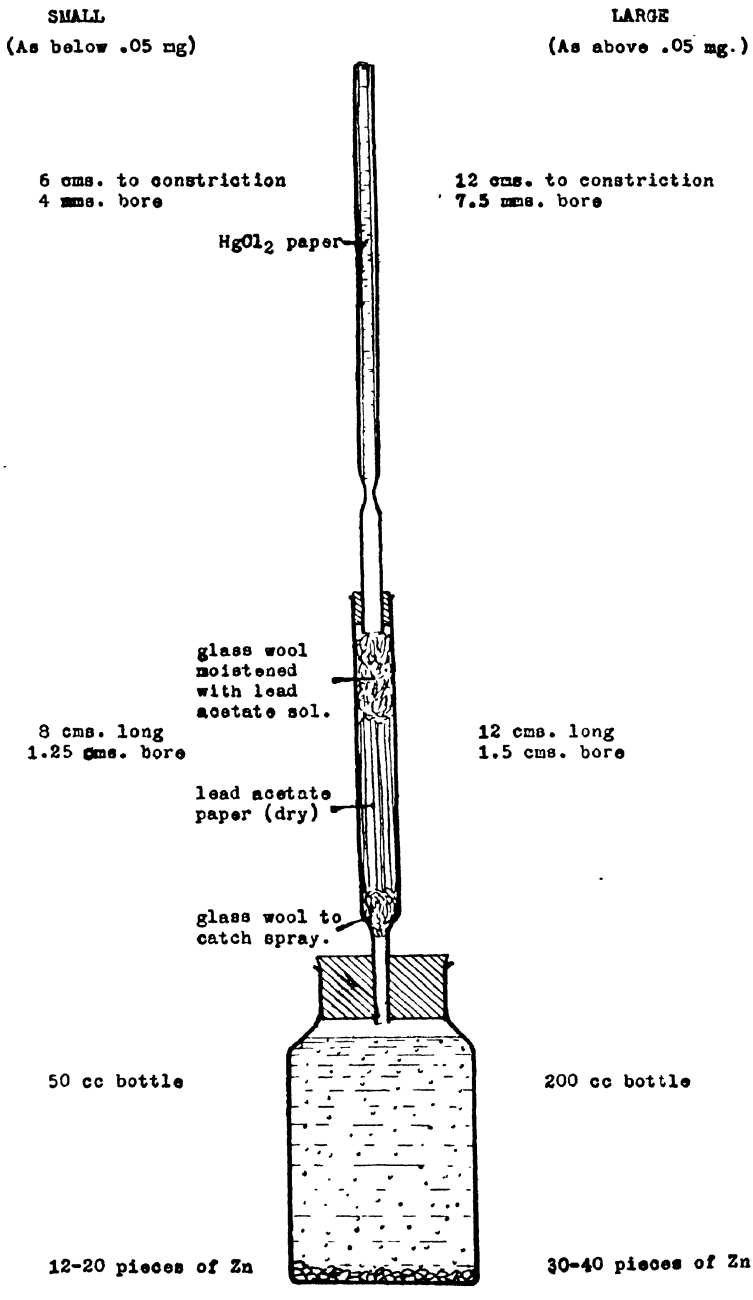


Fig. 12.—Gutzeit Apparatus for Arsenic Determination.

The rubber bung that carries the purification and absorption train is then quickly added, the apparatus shaken gently and placed in a water-bath heated to about 40–45° C.

After three-quarters of an hour, with occasional gentle shakings, the apparatus is disconnected and the solution poured away. The stained mercuric chloride paper is carefully removed from its tube and placed in a corked test-tube, which is set aside in a dark drawer or cupboard while the standard stains are prepared.

Standard Stains.—The stain is black at the lower end of the strip, shading off into brown, and finally yellow. The assay stain is measured, and two quantities of the standard arsenic solution corresponding to 0·1 mgm. below and 0·1 mgm. above the indicated amount are pipetted out. Two more " runs " with the apparatus are then carried through, using exactly the same volume of solution and acid, the same amount of ferrous solution, and the same number of zinc shot as were taken for the assay run. These should give stains one slightly longer and the other slightly shorter than the assay stain. Since the exact amounts of arsenic in these stains is accurately known, the amount of arsenic in the unknown solution can be ascertained by interpolation.

As a guide to choosing the volumes of the standard solution necessary, the following table is given:

Total Length of Stain (Including Yellow Tip).	Weight of Arsenic.	Volume of Standard Solution.
11·5 cms.	0·5 mgm.	100 cc.
9·8 cms.	0·4 mgm.	80 cc.
7·6 cms.	0·3 mgm.	60 cc.
5·3 cms.	0·2 mgm.	40 cc.
3·7 cms.	0·1 mgm.	20 cc.

These " lengths " are of course only intended as a guide, since they depend on a number of factors, apart from the dimensions of the apparatus. Thus, low concentration of $HgCl_2$ per sq. cm. in the strip, rapid evolution of the arsine, high temperature, much zinc, high acidity, all tend to give long, light-coloured strips, and *vice versa.*

Since the stains do not retain their tints sufficiently permanently to enable the worker to preserve them, they must be prepared afresh for each batch of assays ; they may, however, be kept for a day or two if preserved over phosphorus pentoxide in the dark. Some operators treat the tinted strips with dilute ammonia, which converts the colour into a deep black, but there is no obvious advantage in this.

Note.—If very small quantities of arsenic, suitable for the small apparatus, are to be determined, the following sizes, dimensions and volumes should be substituted for the aforegoing.

Volume of solution 50 cc., containing 12–15 cc. acid ; 5 cc. ferrous solution ; 12–20 pieces of zinc shot. The mercuric chloride is 0·5 per cent., and the strips are 7 by 0·4 cm. The evolution flask should be

2 oz. capacity and the tube that acts as strip holder 10 cms. long with 4 mm. bore. The other dimensions should be in proportion. It will also be necessary to make a standard arsenic solution by diluting 20 cc. of the intermediate solution to a litre; 1 cc. of this contains 0·001 mgm. As.

The approximate lengths of stain to be expected from various amounts of arsenic are appended as before ; in the case of the smaller apparatus, and weaker solution of $HgCl_2$, however, the stains are browner and yellower, owing to the greater dilution of the AsH_3.

Length of Stain.	Weight of Arsenic.	Volume of Standard Solution.
6·2 cms.	0·020 mgm.	20 cc.
4·7 cms.	0·015 mgm.	15 cc.
3·7 cms.	0·012 mgm.	12 cc.
2·8 cms.	0·008 mgm.	8 cc.
2·1 cms.	0·006 mgm.	6 cc.
1·6 cms.	0·004 mgm.	4 cc.
1·3 cms.	0·002 mgm.	2 cc.
1·0 cm.	0·001 mgm.	1 cc.

Note 2.—With a straightforward arsenious solution, the foregoing procedure may be carried out without preliminary manipulation. There are, however, a number of substances which cause trouble, such as oxidising materials, which prevent the evolution of the hydrogen and arsine, and some reducing agents, such as SO_2 and H_2S. The former is reduced to H_2S by nascent hydrogen, and this produces a black stain on the test paper, even though some of it be caught by the lead acetate trap. Oxidising agents, such as Cl_2, Br_2, HNO_3, may be removed by evaporating to fumes with H_2SO_4, there being no danger of loss of pentavalent arsenic, though trivalent arsenic would be driven off. Most reducing agents can be oxidised and made harmless by adding dilute permanganate solution from a burette until a slightly pink colour remains. This is then destroyed by a drop of oxalic acid solution, which will have no effect on the estimation. It is impossible to give directions to be followed in all possible circumstances ; the analyst must depend on his knowledge of Chemistry to guide him. After all, Chemical Analysis is applied Chemistry, and not, as is sometimes thought, a careful and slavish following of directions. The chief difference between an analyst and a routinist is that the former practises Chemistry, while the latter follows the book (which does not always help him).

Note 3.—Hydrochloric acid may be used instead of sulphuric acid, if desired. It occasionally happens that the material under analysis will neither dissolve in water nor sulphuric acid ; in this case, hydrochloric acid must be used, but remember that *$AsCl_3$ is volatile.* The amount of HCl used should correspond to the amount of H_2SO_4 previously recommended, *i.e.* the HCl solution should contain the same weight of the effective constituent—hydrogen ions. In other words, use an equivalent solution.

Note 4.—Remember that arsine is very poisonous, and take no risks of inhaling it.

TIN.

Metallic tin or tin in stanniferous alloys is readily soluble in hot dil. HCl, and in hot conc. H_2SO_4, yielding -ous compounds which are soluble in water and dilute acids. HNO_3, however, oxidises the metal to (meta-) stannic acid which is insoluble in water and HNO_3, soluble in conc. HCl and aqua regia, and in fused caustic alkalies. In very dilute nitric acid there is, however, some tendency for tin to form a soluble nitrate, but this decomposes, yielding the insoluble stannic acid when the solution is concentrated. Antimony behaves similarly, being oxidised to hydrated Sb_2O_5 (antimonic acid) by HNO_3.

Estimation of Tin.

A. Gravimetric Methods—1. *As Stannic Oxide.*—If the substance for analysis is an alloy, or metallic tin, 0·5–1·0 gm. is weighed out into a wide beaker and attacked with 20 cc. of 1 : 1 HNO_3, whereby the tin is oxidised to SnO_2, xH_2O. The solution is boiled and concentrated to half its bulk in order to decompose any nitrate of tin, and is then diluted to 100 cc., boiled, allowed to settle and the clear solution decanted through a close packed paper pulp; 50 cc. of 5 per cent. HNO_3 are added to the white insoluble residue, which is then boiled, and again decanted through the filter ; the precipitate is transferred and washed with hot 5 per cent. HNO_3. The pulp and precipitate are removed to a porcelain crucible with a pointed glass rod, the tip of a glass spatula, or a platinum wire, and the funnel wiped with a folded strip of moistened ashless filter-paper, adding this to the contents of the crucible. The paper and precipitate are dried in the mouth of the muffle, the paper charred off and finally the whole incinerated at red heat. There is no fear of any reduction of the SnO_2. The crucible is cooled and the tin weighed as SnO_2.

Note 1.—Any antimony that is present will be in the SnO_2 residue as Sb_2O_5, which roasts to Sb_2O_4 at 750°–800° C. If antimony is present, therefore, it is usual to roast the contents of the crucible at this temperature and weigh the mixed oxides ; the antimony is then estimated separately, calculated to Sb_2O_4, and this weight deducted from the total weight to give the SnO_2. In this case, however, care must be taken to keep the temperature of the muffle below 900° C. or the volatile Sb_2O_3 may be formed and antimony lost. Note also that if more than about half the residue is antimony, that metal will tend to be reduced by the charring paper, and the result will be unpleasant complications.

Note 2.—This method may also be adopted for tin originally present as $SnCl_4$. The solution is diluted to 400 cc. and ammonia is *cautiously* added until a slight opalescence is obtained ; 50 cc. of saturated NH_4NO_3 solution are then added and the solution boiled, when $Sn(OH)_4$ is thrown down as a finely divided precipitate. It is collected, filtered, ignited and weighed as SnO_2, as already explained.

Note on the Estimation of Tin as SnO_2 (see also Separation of Tin in

Bronze, p. 305).—The method already given is the usual one for estimating (and separating) tin when present in copper alloys, bronzes, gunmetals, special brasses, etc. The precipitate has, however, a tendency to contain small amounts of the other metals of the alloy, notably copper, lead and iron, while if the alloy contains phosphorus (phosphor bronze), all the phosphorus will be present in the precipitate as tin phosphate. In the latter case, the usual procedure is to estimate the phosphorus in a separate portion of the sample, calculate it to P_2O_5 and subtract this from the weight of the SnO_2 found ; the difference should be SnO_2. This method is not perfectly accurate, but is sufficiently so for the small percentages of phosphorus found in commercial alloys (rarely over 1 per cent. and usually not over 0·2 per cent.).

If, however, the precipitate of SnO_2 weighs more than about 0·12 gm. it is necessary for accurate work to purify it and extract the contaminating metallic oxides.

Procedure.—Ignite and weigh the SnO_2 as described. After weighing, return the precipitate to the crucible (porcelain), which must be sound and free from cracks. Add 3 or 4 gms. of a mixture of equal parts of Na_2CO_3 and resublimed sulphur, mix well with a platinum wire, cover the crucible with a tight-fitting lid and fuse the contents over a blast flame (*not* in the muffle, as if the crucible breaks or collapses, as is possible if the fusion is conducted at too high a temperature or for too long a period, the muffle lining will require replacement). After the crucible has been kept at a bright red heat for five or ten minutes, lift the cover, and if the contents are quietly liquid the crucible may be re-covered and removed from the flame to cool. It is most important that there should be excess of sulphur, and if a small blue flame of burning sulphur is not observed when the lid is raised, another gram of the fusion mixture should be added and the fusion repeated. When the fusion is cold, transfer the crucible and lid bodily to a 400 cc. beaker and extract with 200 cc. of hot water. Filter hot and wash with small quantities of dilute ammonium sulphide water. The precipitate is very liable to "go colloidal" (see under Theory) and pass through the filter. As a precaution, therefore, it is best to change the receiver for a clean beaker after the original yellow solution of thiostannates has passed through. The sulphides certainly *will* pass through if water alone is used for the washings, as soon as the electrolytes that coagulated the gels are removed ; if, however, dilute ammonium sulphide is used for washing, there is not much danger of this happening.

The solution contains all the tin as thiostannate, together with the antimony and the arsenic, also as thio-salts. The residue on the paper consists of the sulphides of such other metals as were carried down with the SnO_2 originally. The paper is transferred to a wide porcelain crucible and paper and precipitate dried in the mouth of the muffle. The whole is then carefully charred off just inside the muffle with ample air supply, or some of the metals, especially lead, will be reduced. When all the paper has burnt off, the sulphides are roasted at low red-heat to oxides, which are brushed out and weighed. This weight is deducted from the original weight of the SnO_2 precipitate, and the precipitate itself, after dissolving in a little 1 : 1 HNO_3 in the crucible, is transferred to the filtrate from the original SnO_2 precipitate for the rest of the assay.

It is bad working if there are more than a few milligrams of other oxides found in the SnO_2.

Note.—The "sulphur mixture" fusion will destroy the glaze on the inside of the crucible used, so that it will be of no use for ordinary purposes. It is best to set aside crucibles that have been used in this way, keeping them for this special process.

2. *As Stannic Sulphide.*—This method is not to be recommended, owing to the necessity of removing all other metals from the solution before precipitating, and as the volumetric methods do not require separations they are usually to be preferred. Occasionally, however, as for example in the complete analysis of an ore of a commercial metal, *e.g.* lead, these separations are necessary, and the final solution, after removing copper, bismuth, antimony and arsenic, contains nothing but tin. In this case the solution is nearly neutralised with ammonia and H_2S is passed in until all the tin is thrown down as a mixture of SnS and SnS_2. The precipitate is filtered off on a small pulp, washed with water, transferred to a porcelain crucible and the contents thoroughly dried in the mouth of the muffle. The paper is then burnt off, the carbon and the sulphur being oxidised by well roasting with full access of air. The tin is then weighed as SnO_2.

B. Volumetric Method—1. *Titration with Standard Iodine Solution.*—This is the best of all methods of estimating tin, but it demands great care in the manipulation. There are many methods published, which differ slightly in detail, principally in the nature of the metal used for the reduction. The following is the method preferred by the author, since it is comparatively simple in operation and has been proved to give excellent results.

The metal or alloy is obtained in the form of fine sawings or is granulated by melting it in a crucible under thick oil and pouring from a height of 3 or 4 feet into a basin of water. A quantity of the dried granulations is then carefully weighed out, such as will contain, as nearly as can be judged, 0·4 gm. of tin. The weighed sample is placed in a tall 300 cc. beaker and 50 cc. of 1 : 1 HCl are added ; the beaker is then covered with a clock-glass and set on the edge of the hotplate. Pure tin or alloys containing much tin dissolve quite readily in the hot acid, but if much copper or lead is present the process of solution may be very slow. In the latter case, when the evolution of hydrogen slackens, the addition of a little $KClO_3$ on the point of a spatula will send the insolubles into solution. The addition of chlorate should, however, not be overdone, as $SnCl_4$ boils at 114° C., and some tin may be lost by evaporation ; also, of course, the reduction takes longer. In the case of a comparatively pure sample of tin, the insolubles (copper, antimony and lead) will be present as a black residue ; if this is small it may be ignored and the addition of chlorate will be unnecessary, as there will be no tin in it.

When the sample is in solution, the contents of the flask are diluted to 200 cc. (rather over half way up the beaker ; it is important to keep to a standard dilution in order to make the 'blank' cancel out against the blank of the standard), and if the acid has become reduced in volume by evaporation in the course of solution, it should be replaced so that there may be 50 cc. of 1 : 1 acid always present. Two pieces of $\frac{1}{2}$ inch

Armco iron rod about 6 inches long are then placed in the solution and the cover replaced. Hydrogen is vigorously evolved (the solution should be kept just short of its boiling-point on the edge of the hotplate) and any tetravalent tin is reduced. For uniformity, the reduction is carried on for exactly one hour after the disappearance of the last traces of yellow colour due to the presence of Fe^{+++}. The beakers are then removed, still covered, to the cooling trough, and a rapid stream of cold water from the tap is circulated round them. As soon as the solutions are set to cool it becomes essential to preserve the Sn^{++} from oxidation by the atmosphere, as the evolution of the hydrogen at once slackens. For this purpose, a piece of white marble or calcspar about the size of a hazel nut is placed into each beaker, so that the free space may be filled with CO_2 during the cooling process.

Meanwhile, a 100 cc. burette filled with standard iodine solution (1 cc. $\equiv$ 0·05 gm. Sn) is set up, it is ascertained that the Kipp's apparatus for CO_2 is filled and working, and some fresh starch solution is prepared.

When the solutions are quite cold they are removed in turn to the titration bench, placed under the burette tap, and the cover removed. The instant the cover is off, the delivery tube of the Kipp is hooked over the lip of the beaker with its end just clear of the solution, and the CO_2 is turned on. The iron rods are quickly picked up with the fingers, and together with the fingers are rinsed down with a stream of cold, freshly boiled water from the washbottle ; the underside of the cover-glass is also rinsed ; the solutions are then titrated at once with the iodine, only adding the starch when the yellow colour of the iodine fades slowly. The end-point with this strength of iodine is sharp to less than one drop of the reagent. A standard is titrated with every batch of tin assays, or better, two standards, which should agree in their titre to within 0·1 cc. From the nature of the assay it is very nearly as quick to carry through a batch of three or four as one, but it is troublesome in the extreme to have to restart the whole manipulation because of a mishap to one beaker or solution. If only one tin assay has to be made, the writer advises weighing it out in triplicate, with two standards. For the standardisation of the iodine 0·4 or 0·45 gm. of pure tin (99·95 per cent. tin is available) is weighed out into a beaker similar to those used for the assays ; the reduction is then carried out in exactly the same manner and for the same time ; one standard should be titrated first and the other last and the mean value taken for the equivalent of the iodine.

Note 1.—Occasionally some yellow PbI_2 separates out owing to reaction between the KI in the iodine reagent and lead in the assay solution ; this may of course be ignored. It settles well.

Note 2.—Other reducing agents are sometimes advised, notably metallic nickel and lead, the reduction being carried out exactly as before. Powdered antimony is also used, the reduction being complete in a very short time, but the writer has not found that these metals give any more reliable results and the student is advised to keep to the original method as already detailed. The objection to the use of iron was its uncertain composition, but if Armco iron is used there can be no objection on this score.

Note 3.—None of the common metals interferes; certainly not those metals such as lead, copper and antimony, which may be expected to be found associated with tin in alloys. With iron as reducing agent, copper and antimony are precipitated as a black metallic mud on the rods; this does not affect the end-point and does not interfere in any way.

Note 4.—The Kipp is placed at a convenient distance, and the CO_2 is supplied to the assay beaker through a length of rubber tubing ending in a piece of glass tubing bent so that it hooks over the lip of the beaker. This results in delivery of the gas at the surface of the liquid, and the apparatus is out of the operator's way.

2. Tin is sometimes titrated with $FeCl_3$ solution; this method has no advantages over the iodine titration and is troublesome to manipulate on account of the solutions having to be kept boiling during the process. (*Vide*, also, Iron, Volumetric.)

GROUP III.

Iron, Aluminium, Chromium.

IRON.

Iron is everywhere in Nature; certainly it is to be found in the analysis of every commercial substance, either in traces as an impurity or in larger quantities as an essential component. More is known about this element than any other, and the methods used for its identification are well defined and accurate.

A. Gravimetric Method.—To the acid solution, which should contain ferric iron only, add about 5 gms. of NH_4Cl for each 1 gm. Fe present,* and neutralise carefully with ammonia, using an indicator (methyl orange or litmus). The barest excess is added and the now slightly ammoniacal solution is brought to the boil in a covered beaker. It is boiled until the precipitate coagulates well and until the gas bubbles which are entrapped in the large gelatinous flocks are expelled; stirring will help. The beaker is then removed from the centre of the hotplate and the precipitate allowed to settle out completely in a warm place. The liquid is filtered hot through a coarse-textured paper (41), *not* a pulp,† and the filter washed with boiling water until free from chlorides.

The paper and precipitate are transferred to a crucible, the water is dried out at the mouth of the muffle, the paper charred, and the precipitate finally ignited at dull redness, converting it to Fe_2O_3, in which form iron is invariably estimated gravimetrically.‡

* If ammonium salts are already present, or if the original solution is so acid that this amount of ammonium salts will be formed on neutralisation with ammonia, it is of course unnecessary to add NH_4^+. It should not be necessary to note that *any* ammonium salt will serve; the object of adding NH_4Cl is to supply NH_4^+ ions in order to reduce the ionisation of NH_4OH.

† Pulp filters must not be used for gelatinous precipitates when these amount to more than a few milligrams.

‡ The method relates, of course, to a solution containing iron only. If aluminium and/or chromium, or the metals of later Groups are present, the iron must first be isolated. See under Separations.

B. Volumetric Methods.—Iron is quantitatively oxidised from the ferrous to the ferric state by several reagents, but for volumetric analysis the only oxidants of importance are potassium dichromate and potassium permanganate.

As a rule, when separated, iron is in the ferric state, having been precipitated as ferric hydroxide by the addition of ammonia ; before it can be estimated volumetrically, therefore, it must be reduced. This can be effected in several ways, all quite efficient, so that the method adopted is determined by the analyst's personal preference, or, occasionally, by circumstances.

Methods of Reducing Ferric Iron to Ferrous Iron.

1. *By H_2S.*—This method is occasionally convenient, especially when metals of Group II have to be separated by this reagent and there are no metals of later groups except iron present.

H_2S gas is passed into the hot, slightly acid solution, until it becomes completely colourless and all sulphides have settled out completely. The solution is filtered through a small pulp filter, if necessary, but here note that a precipitate of amorphous sulphur, derived from the reaction

$$2FeCl_3 + H_2S = 2FeCl_2 + 2HCl + S$$

may be ignored, as sulphur has no effect on the cold titration liquid in either case. The filtrate is received in a flask which is afterwards heated to boiling on a gas ring or hotplate while a stream of CO_2 is bubbled rapidly through the liquid ; this serves to remove the excess H_2S much more rapidly than if the solution were merely boiled, and also prevents any possibility of reoxidation of the Fe^{++}. The solution is tested for the completeness or otherwise of the removal of the H_2S by taking a drop on the end of a glass rod and "spotting" it on a piece of lead acetate paper ; a brown or black stain indicates the presence of $S^{=}$. When free from the reducer, the solution is ready for titration.

2. *By SO_2.*—This is a useful method, but is apt to give trouble unless great care is taken to maintain the correct conditions. Its particular advantage lies in the fact that it may conveniently be employed if by mischance or carelessness the end-point is badly 'overshot' during the titration with dichromate or permanganate and the amount of material for analysis is limited in amount, so that a 'repeat' is out of the question.

The solution is first neutralised with ammonia (litmus *paper*) and then made just acid with HCl or H_2SO_4. Sulphur dioxide is bubbled into the hot solution until a drop removed on the end of a glass rod shows no coloration with a thiocyanate solution on the spot-plate (absence of Fe^{+++}). The excess of SO_2 is removed by boiling the solution on the hotplate while passing a stream of CO_2 through it. The solution is then cooled under the tap and titrated.

Note 1.—It is essential that the solution be only *just* acid before reducing with SO_2 ; if too much H^+ is present the reduction is always incomplete.

Note 2.—It may be convenient, on occasions, to use a crystal or two of a sulphite or a metabisulphite instead of the gas from a syphon; it

is always better, however, to refrain from burdening the solution with alien bases whenever possible.

Note 3.—SO_2 reduces Fe^{+++} to Fe^{++} but has no effect upon Cr^{+++}; a solution once titrated with dichromate may therefore be again reduced with SO_2 (or H_2S for that matter) and re-titrated if necessary, but the dark green of the Cr^{+++} ion accumulating in the solution sets a limit to this device in the long run.

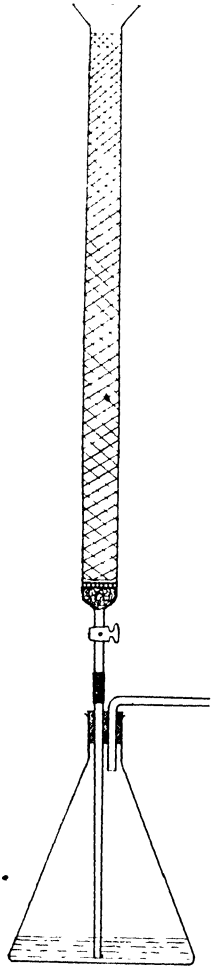


Fig. 13.—Jones' Reductor.

3. *By Metals—Jones' Reductor.*—The reductor consists of an 18″–24″ length of $\frac{1}{2}$″ glass tubing drawn out into a $\frac{1}{4}$″ taper at the lower end, for a length of about 10″. It is an advantage if there is a stopcock at the taper. The upper end is widened out into funnel form. (A burette can be used if a length of small bore tube is attached to the stopcock with rubber tubing). The tube is plugged at the taper with a wad of glass wool (or a perforated tile carrying a wad of asbestos) and is filled with 60 mesh zinc (zinc is easily powdered if heated to 210° C.) that has been "cleaned" in dilute acid and rubbed up in a mortar with a little mercury.

To clean the apparatus: Connect as shown in the diagram (fig. 13) with a flask and a water pump; close the stopcock and fill the tube with 50 cc. of dil. H_2SO_4 (1:4), drawing it through the apparatus with gentle suction. When the funnel empties add 50 cc. of water followed by 50 cc. of acid, and so on, each time adding the fresh liquid before the funnel has drained; the zinc must always be covered with either acid or water.

Method of Use.—The main tube being filled with water, connect a clean flask to the exit tube and pour the ferric solution into the funnel (volume, about 200 cc.). Open the stopcock and draw the solution slowly through the reductor, taking several minutes for the operation. When the funnel empties, and before the tube is empty, add the rinsings from the beaker which contained the solution, followed by another tube-full of wash water. The reduced solution is now ready for titration. It is worthy of note that this method is more adapted to the permanganate titration than the dichromate.

Note 1.—Should the original solution contain HCl or HNO_3, excess of H_2SO_4 must be added and the mixture taken down to copious fumes before reducing.

Note 2.—With any but the purest "analytical" zinc a "blank" titration must be carried out, and it is advisable to do this in all cases, in order that the end-point error may be discounted. Commercial zinc always contains iron derived from the ore, and this will naturally

appear in the solution flask to a greater or less degree. To carry out the blank, measure out the same volume (200 cc.) of 1 : 4 acid and wash the tube and flask in the same way, taking the same time and using the same quantities of reagents as described for the main assay. Any volume of $KMnO_4$ required to produce the standard end-point in the resulting solution must be deducted from the assay burette readings.

4. *By $SnCl_2$.*—Reduction of Fe^{+++} is rapid and complete with this reagent if the solution is (1) hot, (2) concentrated, and (3) strongly acid with HCl.

Method.—Precipitate the iron as $Fe(OH)_3$ and dissolve this in conc. HCl, or concentrate the HCl solution of the original substance to low bulk. While still hot, add a saturated solution of $SnCl_2$, drop by drop (use a dropping bottle), until the colour of the Fe^{+++} is just destroyed. Dilute to a convenient bulk, depending upon the amount of iron present, and "neutralise" the excess of $SnCl_2$ by adding excess of saturated $HgCl_2$ solution:

$$SnCl_2 + 2HgCl_2 = SnCl_4 + \underset{\text{(white precipitate)}}{Hg_2Cl_2};$$

if the solution is too hot, or too much $SnCl_2$ has been added, we have:

$$2SnCl_2 + 2HgCl_2 = 2SnCl_4 + \underset{\text{(grey precipitate)}}{2Hg}.$$

This grey precipitate of finely divided mercury interferes somewhat with the end-point observation; it is best, therefore, to dilute with cold water, and be careful to add the minimum of $SnCl_2$. The mercuric chloride should not be added until just ready to titrate, as the excess of the $SnCl_2$ serves as a very efficient protection against the Fe^{++} being oxidised by the air.

5. *Titanous Chloride* is also used, but this reagent has two serious disadvantages: (1) It is difficult to keep; (2) it is so powerful a reducer that many other compounds besides Fe^{+++} are reduced by it. See, however, under the Titration of Ferric Compounds.

(1) **Titration with Potassium Dichromate.**—In dilute acid solution ferrous iron is instantly and quantitatively oxidised to the ferric state by dichromate solution. Essentially, the reactions are:

1. $2FeO + O = Fe_2O_3$ (the oxidation of the iron), and
2. $2CrO_3 = Cr_2O_3 + 3O$ (the reduction of the dichromate).

In other words, 2 atoms of iron require 1 atom of oxygen for their complete oxidation, whereas 1 molecule of potassium dichromate can supply 3 atoms of oxygen; that is: 1 molecule of dichromate will oxidise 6 atoms of ferrous iron. The need for the presence of free acid (HCl or H_2SO_4) will be obvious from the complete equation:

$$\underset{\text{(orange-yellow)}}{K_2Cr_2O_7} + 6\,\underset{\text{(pale green)}}{FeSO_4} + 7\,H_2SO_4 = \underset{\text{(colourless)}}{K_2SO_4} + \underset{\text{(dark-green)}}{Cr_2(SO_4)_3} + 3\,\underset{\text{(almost colourless)}}{Fe_2(SO_4)_3} + 7\,H_2O.$$

As the reaction proceeds, the colour changes from a very pale green to a deep grass green, the end-point being marked by a spot-reaction with

dilute potassium ferricyanide solution. As this is the first time that the use of an outside indicator has been required, it is proposed to give very full details.

The indicator is made up fresh for every batch of titrations, as ferricyanide decomposes, yielding, in time, a certain amount of Fe^{++} which reacts with the excess reagent, producing a greenish colour change, and makes the correct end-point almost impossible to observe ; the ferricyanide must, also, be very dilute or the reaction loses sensitiveness ; a crystal of ferricyanide the size of a grain of wheat in 75–100 cc. water is suitable. A clean glass rod and a clean spot-plate of glazed white tile must be used ; both of these should be carefully cleaned and dried for the assay by the operator himself, as the least trace of " tramp " iron on either, picked up from the hands or the bench, will cause trouble with the end-point. The tile is washed with water or dilute ammonia if doubtful or if it is discoloured, and dried with a clean cloth, finishing with a piece of filter paper. The ferricyanide solution is applied to the tile in small, regular-sized, evenly spaced drops, not too close together, as the drops will be doubled in size when the test drops are added. The glass rod is rinsed under the tap before using it for the spot-tests or an all-obscuring blue coloration may be the result of placing a rod, wet with ferricyanide, into a ferrous solution.

With a small quantity of iron, the dichromate is run in a few drops at a time until the spot-test in the plate no longer gives a *deep* blue coloration. The solution is then run in more slowly (two drops at a time is suitable) until the blue is very faint ; then one drop at a time is added until the spot-test just fails to give a positive reaction.

When there is a larger amount of iron present, the solution should be diluted proportionally so that the dark green colour of Cr^{+++} does not obscure the end-point. This obscuring of the end-point is one great drawback to the use of dichromate ; the other is that there is no reliable means of knowing when the end-point is approaching. With small amounts of iron we can proceed a few drops at a time without much trouble, but for the titration of larger quantities of iron this cautious procedure would be terribly tedious, not to mention the error introduced by the removal of perhaps hundreds of drops of the solution before the end is finally reached. In this case it is quicker to weigh out three or four assays and proceed as follows:

To solution A, add the dichromate 5 cc. at a time and note the "interval" after which the end-point occurs; *i.e.* suppose a deep blue is obtained when 60 cc. have been run in, but that at 65 cc. the spot-test gives negative results ; we know then that the true end-point lies somewhere between 60 and 65 cc. To B, then, add 60 cc. quite boldly, and then add the dichromate in 0·5 cc. quantities. Suppose 62 cc. (*e.g.*) gives a blue spot and 62·5 no colour, then the end-point lies between 62 and 62·5 cc. Assays C and D may then be made ; 62 cc. are run in at once, the solution *well* stirred (important!) and the dichromate added two drops at a time until the blue pales, when one drop at a time is correct. This method will be found to be quicker in the long run, notwithstanding the fact that it entails additional weighings and manipulation.

It should not be necessary to add that if the strength of the dichromate is accurately known, and the amount of iron approximately known,

there is no need to make trial assays : Suppose it is calculated that 65 cc. ought to be necessary for the titration, add 62 and finish cautiously, as described. Also, of course, the analyst may be lucky and just hit the "paling of the blue" with one of his 5 cc. additions, but it is not worth while counting on this.

Note 1.—It is convenient to use two strengths of dichromate solution, viz. *Strong*, containing 8·782 gms. $K_2Cr_2O_7$ per litre ; 1 cc. will be equivalent to 0·01 gm. Fe. *Dilute*, containing 2·635 gms. $K_2Cr_2O_7$ per litre ; 1 cc. is equivalent to 0·003 gm. Fe.

The strong solution is used for iron in quantities of from 0·1 to 1·0 gm. and the dilute solution for smaller quantities of iron; or, if preferred, the strong solution may be used at the commencement of the assay, changing over to the diluter one for finishing, when the colour of the spot becomes perceptibly paler.

Note 2.—Potassium dichromate is usually supplied very pure. It may be further purified for making up the standard solution as follows: 1. Recrystallise by dissolving a large handful of the commercial salt in the minimum volume of boiling distilled water and cooling rapidly under the tap. Filter off the fine, powdery crystals on a Büchner funnel and suck them dry ; wash once or twice with small quantities of cold water, each time sucking the funnel dry. Then transfer the moist salt to a clean porcelain dish, dry on the hotplate and finally just fuse over a small Bunsen flame. Powder the re-solidified product and bottle for use as a standard reagent.

Note 3.—The standard dichromate should have its strength checked occasionally against pure ferrous ammonium sulphate solution to guard against change of strength by evaporation.

Note 4.—If there is much Fe^{++} in the assay, the green of the Cr^{+++} produced by the titration obscures the blue of the end-point. The final change may be detected by placing a spot of the assay solution on the spot-plate close alongside the doubtful test spot ; small differences of colour are more easily apparent if there is a " comparison spot." When the end-point is reached the tints should be identical, but care must be taken to use the same number of drops of assay solution for this comparison, and they should be spread out more or less flat with the glass rod, and not left with a pronounced meniscus, since such results in too many internal reflections to permit of a satisfactory comparison.

Note 5.—The end-point is reached when the test spot fails to produce an *immediate* blue colour. The spot tested will often turn blue on standing, owing to slow decomposition of the ferricyanide.

Note 6.—Clean the spot-plate immediately the titrations are finished or the blue precipitate in the spots will stain the plate. If this is neglected, a wash with a little dilute ammonia followed by a rinse with water will put the tile into condition again. Ammonia also removes the blue stains from the fingers.

Advantages of the Dichromate Method.

1. It can be used in HCl solution.
2. The solution is quickly prepared for the titration.
3. The rapid and efficient $SnCl_2$ reduction can be used.

Disadvantages.

1. An external indicator is a complication.
2. There is no indication of the approach of the end-point.

(2) **Titration with Potassium Permanganate.**—The essentials of the reaction are:

$2\,FeO + O = Fe_2O_3$ (oxidation of the iron), and
$Mn_2O_7 = 2MnO + 5O$ (reduction of the permanganate).

In other words, two atoms of Fe require 1 atom of oxygen and 1 molecule of permanganate will yield 5 atoms of oxygen. Thus, 1 molecule of permanganate will oxidise 5 atoms of Fe^{++} to Fe^{+++}.

The complete reaction is:

$$\underset{\text{(dark purple)}}{2\,KMnO_4} + \underset{\text{(very pale green)}}{10\,FeSO_4} + 8\,H_2SO_4 = \underset{\text{(colourless)}}{K_2SO_4} + \underset{\text{(very pale pink)}}{2\,MnSO_4} + \underset{\text{(very pale yellow)}}{5\,Fe_2(SO_4)_3} + 8\,H_2O.$$

The products of the reaction are so slightly coloured that ordinarily no colour is noticeable at working dilutions; the result is that the end-point is very easily observed by the relatively deep tint of the merest traces of excess MnO_4^- ion.

Ordinarily, the only acid present should be H_2SO_4, and it may be necessary to remove other acids by evaporation with excess of this reagent, but HNO_3 may be present in quantities less than 7 per cent. by volume provided the solution is kept cold, and, similarly, small percentages of HCl do not altogether prevent the quantitative titration, though in presence of this acid the end-point must be taken at that point at which the solution first takes a pink tinge through its entire volume, and the permanganate must on no account be added in a rapid stream. The reason for this is that HCl in the presence of Fe^{++} is slowly oxidised even in cold, dilute solutions, to water and free chlorine, the latter being detected by smell. Zimmermann has, however, investigated a method for the titration of solutions containing HCl which gives good results. His theory is as follows: (Summary)—$MnSO_4$ acts in two ways in the titration; first, by "slowing down" the reaction between FeO and $KMnO_4$, due to stabilisation of the intermediate product, Mn^{++++} (or possibly Mn^{+++}), and secondly, by acting as a catalyst between FeO and a hypothetical "ferric peroxide." The essential point is, however, that Mn^{++++} does not react very rapidly with HCl, and if $MnSO_4$ is present, Mn^{++++} appears to be produced.* The yellow colour of the $FeCl_3$, which is one of the end products, is apt to mask the end-point; phosphoric acid is therefore added. The $MnSO_4$-H_3PO_4 solution recommended by the investigators of the method is prepared as follows:

67 gms. of crystallised $MnSO_4$ are dissolved in 500 cc. of water and 140 cc. of syrupy phosphoric acid are added, (sp. gr. 1·7), followed by 130 cc. of conc. H_2SO_4 (sp. gr. 1·82), and the whole is diluted to 1,000 cc. One cc. of this solution is added for each cc. of HCl present in the solution.

* If $KMnO_4$ is boiled with $MnSO_4$, MnO_2 is precipitated as a black hydrate.

Method of Titration of Fe^{++} when HCl is present.—Add the $MnSO_4$-H_3PO_4 solution to the ferrous solution and dilute suitably. Titrate with standard $KMnO_4$, adding the reagent slowly from the burette in order to avoid local concentrations, and allowing the pink colour to fade completely before adding more permanganate. No chlorine will be evolved, and the method gives accurate results.

The ideal condition for titration with permanganate is, however, when no acid except H_2SO_4 is present (though HNO_3 in small concentrations does not interfere in the cold). The process is the simplest volumetric reaction there is, since no indicator is necessary, and the permanganate has such a deep colour that the faintest excess is visible immediately; also, the approach of the end-point is signalised unmistakably by the slower fading of the pink colour on adding the reagent, so that the titration can be carried out quite boldly practically up to the end-point.

Potassium permanganate is never quite pure, so that, unlike the dichromate, it cannot be weighed out directly to make up a solution the iron value of which is accurately known. In practice, a slight excess of the salt is weighed out and the exact titre worked out by standardisation.

Standardisation of $KMnO_4$.—1. *By Sodium Oxalate.*—This is perhaps the best method. Sodium oxalate is an excellent "standard reagent" as it is non-hygroscopic, non-efflorescent, does not decompose on keeping and may easily be prepared pure. Weigh out, accurately, 0·5 gm. of the salt and dissolve it in a little water. Add a few cc. of H_2SO_4 to combine with the potassium and manganese freed by the reduction of the permanganate, and titrate hot. The reactions are:

$$\begin{matrix}\text{COONa}\\ |\\ \text{COONa}\end{matrix} + O = 2\,CO_2 + Na_2O$$

and: $$Mn_2O_7 = 2\,MnO + 5O.$$

i.e., 2 molecules of $KMnO_4$ oxidise 5 molecules of sodium oxalate, or 10 atoms of Fe^{++}.

That is:

$$10 \times 56 \text{ gms. Fe} \equiv 5 \times 134 \text{ gms. } (COONa)_2$$

or: $$\frac{56}{134} \text{ gms. Fe} \equiv 0{\cdot}5 \text{ gm. } (COONa)_2 \equiv x \text{ cc. } KMnO_4 \text{ solution,}$$

whence:

$$\frac{56}{134} \times \frac{1}{x} \text{ gms. Fe} \equiv 1 \text{ cc. } KMnO_4 \text{ solution,}$$

which gives the required factor for the permanganate.

2. *By Ferrous Ammonium Sulphate.*—$FeSO_4 . (NH_4)_2SO_4 . 6\,H_2O$ is sometimes called Mohr's salt, after Mohr, who discovered that it is not oxidised by the air as $FeSO_4 . 7\,H_2O$ is. It is easily crystallised and purified, shows no tendency to absorb or lose water when kept in a stoppered bottle, and is therefore an excellent reagent for the checking of the strength of oxidising volumetric solutions.

Purification.—A hot, saturated solution of the commercial salt is made by placing excess of the crystals in a beaker or flask with a small quantity of water and standing the vessel on the corner of the hotplate to boil.

Note.—If preferred, the double salt may be made up by weighing out equivalent amounts of the two constituent salts ; *i.e.* 242 gms. of crystallised ferrous sulphate and 132 gms. of ammonium sulphate, or sub-multiples of these weights, instead of the commercial double salt.

While the solution is heating up, a few cc. of dil. H_2SO_4 and a small piece of Armco iron sheet or wire are added. The solution is gently boiled for a few minutes, the nascent hydrogen evolved from the iron and the acid serving to reduce any Fe^{+++} that may be present and to prevent oxidation in any case. When the water has become fully saturated with the salt, the solution is filtered rapidly through a wad of glass wool in the apex of a small glass funnel, catching the filtrate in a clean beaker which is placed inside a larger beaker full of cold water. The filtrate is rapidly stirred and the fine crystals are separated on a Büchner funnel. After sucking quite dry and washing once with about 50 cc. of 1 : 1 alcohol, added in small quantities, the crystals are removed and spread out on a folded wad of filter paper, which is then well squeezed to express as much water as possible. The paper is opened out and stood in a warm (not hot) place over-night, or until quite dry, when the fine crystals will pour like sand.

Ferrous ammonium sulphate contains almost exactly one-seventh of its weight of Fe^{++}. To standardise, weigh out 0·5 gm. of the salt into a beaker, dissolve in about 100 cc. of cold water and add 5–10 cc. dilute H_2SO_4. Titrate with the $KMnO_4$, and evaluate the "factor" as described under "Volumetric Reagents."

3. *By Pure Iron.*—This is still a popular method, but in view of the fact that there is no such thing as pure iron obtainable commercially, while perfectly pure sodium oxalate and ferrous ammonium sulphate are easily obtained, it is difficult to understand why this old-fashioned method is retained in text-books. For completeness, however, an outline of the method will be given.

Weigh out 0·5 gm. of "pure iron" wire and place it in a 250 cc. flask fitted with a bung through which passes a short, straight piece of glass tubing plugged with a wad of glass wool to catch any spray. Introduce 100 cc. of 1 : 4 H_2SO_4 and warm the flask on the corner of the hotplate until the metal is completely dissolved, then cool the solution quickly under the tap. There is absolutely no need for the elaborate precautions usually detailed to prevent oxidation, such as water seals or Bunsen valves ; ferrous sulphate solutions are by no means so susceptible to oxidation as was once thought, but if the operator has any doubt, it may ease his mind if, just as the last particles of iron are dissolving, he puts a crystal or two of sodium carbonate into the flask in order to fill the free space with CO_2. (It is obvious, of course, that no Fe^{++} can possibly oxidise while hydrogen is being generated in the solution.) When cold, rinse the glass wool with the wash-bottle jet to remove any spray that it has caught ; rinse down the underside of the bung and the sides of the flask and make up to 250 cc. in a calibrated flask. (It will save transference if the solution of the iron is carried out in a calibrated flask.) Remove 50 cc. and titrate with the permanganate.

Note 1.—It is not safe to depend on any iron being "pure"; even electrolytic iron contains some carbon. The purest commercial iron is "Armco," which is guaranteed to contain "not less than 99·84 per cent. Fe"; ordinary "pure" iron contains up to 0·2 or 0·3 per cent. of C, S, Si, P and Mn, and for standardising purposes it is really necessary to analyse the metal which it is proposed to use.

Note 2.—The iron rarely dissolves *completely*; there are usually a few specks of black substance left insoluble; this consists of the carbides of iron and manganese and, possibly, a little free arsenic.

(3) *Titration with Stannous Chloride or Titanous Chloride.*—Ferric iron may be titrated with either stannous chloride or titanous chloride, using thiocyanate on a spot-plate as outside indicator. In the former case the solution must be hot and concentrated, and in the latter there is considerable difficulty in keeping the reagent of known strength. In either case, the time saved in avoiding the reduction from ferric to ferrous iron is more than off-set by the trouble of manipulation; these methods will therefore not be discussed here, but the interested student may refer to one of the larger standard text-books.

For further details, see under Volumetric Analysis.

ALUMINIUM.

Aluminium hydroxide is precipitated together with the -ic hydroxides of iron and chromium when ammonia is added to the re-oxidised filtrate from the sulphide precipitate of Group II. Aluminium hydroxide is white, gelatinous, and troublesome to manipulate on account of its slimy nature and bulk when precipitated in the ordinary way. Like the hydroxide of ferric iron it can exist either as a sol or a gel, and as it shows some tendency to return to the sol state after precipitation, care must be taken in its manipulation. Unlike ferric hydroxide, aluminium hydroxide is "soluble" in excess of alkali hydroxides, forming "aluminates" from which the hydroxide may be reprecipitated by neutralising the alkali with an acid. Aluminium hydroxide is also somewhat soluble in excess of ammonia, so that the group reagent must not be added to excess; this is the reason for the often-repeated caution to use an indicator when making ammoniacal at Group III. On the other hand, if the just ammoniacal solution, containing precipitated aluminium hydroxide, is boiled so that the slight necessary excess of ammonia is driven off, some of the gel will return to the sol state, and the results will be low.

Aluminium is always estimated gravimetrically, and if the metal is present in considerable amount, some special device must be adopted to bring the hydroxide down in a form which can be easily handled and filtered.

1. *Precipitation as Hydroxide in presence of Paper Pulp.*—A little ashless filter paper is shredded and pounded in a small beaker with the tip of a glass rod until entirely disintegrated. The pulp is stirred up with water and a little of the suspension is added to the solution that contains the aluminium. Ammonia (and ammonium chloride) is then added until the solution is *just* alkaline (use methyl orange or litmus) and the whole brought to the boil for not more than a minute. The presence of the tiny particles of paper causes the precipitate to come down in a

more " granular " form, which is easier to filter and wash than the ordinary precipitate. After boiling, the precipitate is allowed to settle out completely, the solution is decanted through an open-textured paper (*not* a pulp) and the precipitate finally washed on with boiling water. The filter is washed with boiling water until the runnings no longer react with silver nitrate, but care should be taken to break up the slimy hydroxide well with the water jet on each occasion. The paper and precipitate are dried in the mouth of the muffle, the paper charred, and the precipitate finally ignited at redness to Al_2O_3. Needless to say, the paper pulp filtered off with the precipitate will make no difference to the result.

2. *Chancel's Method.*—Chancel conceived the idea of precipitating aluminium by controlling the usual hydrolysis of a salt of a weak base and a strong acid. In solution, aluminium salts hydrolyse:

$$AlCl_3 + 3\,H_2O \rightleftarrows Al(OH)_3 + 3\,HCl.$$

For this reason, the solutions of aluminium salts of strong acids possess an acid reaction and tend to throw down a " basic " salt as precipitate in spite of the fact that increasing hydrolysis tends to increase the percentage of free acid produced.

If, now, a substance is added which will combine with and " remove " the acid as fast as it is formed, it is obvious that the aluminium hydroxide will be progressively precipitated, and that without having added any excess of reagent or having created a tendency for the hydroxide to pass back to the sol state. Chancel used a thiosulphate, which reacts as follows:

$$2\,HCl + Na_2S_2O_3 = 2\,NaCl + H_2O + SO_2 + S.$$

The sulphur which is co-precipitated acts mechanically upon the precipitate like the paper pulp used in Method 1, and like the paper, it does not interfere with the weighing of the alumina after ignition.

Method.—The solution should contain not more than 0·5 gm. of Al per litre ; about 0·1 gm. Al in 250 cc. is suitable. Ammonia is added until a slight precipitate is formed ; this is then dissolved in a few drops of HCl and 1–2 gms. of sodium thiosulphate are added in concentrated solution. The solution is boiled until it no longer smells of SO_2, dilute ammonia is added cautiously, drop by drop, until a *very faint* smell of ammonia persists after blowing into the beaker to remove undissolved gas, and the precipitate is allowed to settle out on the corner of the hotplate. The solution is as far as possible decanted, and the precipitate washed with boiling water until free from Cl^-.

The hydroxide, so precipitated, settles well in a granular condition that permits of reasonably rapid filtration and washing.* If this method is to be used for the separation of aluminium from iron a complete separation can be effected by repeating the precipitation. After the first treatment with the thiosulphate and ammonia all the aluminium is in the precipitate together with a little of the iron as $Fe(OH)_3$. The

* If iron is present, the SO_2 reduces the Fe^{+++} to Fe^{++} and none of this metal will be precipitated if the final addition of ammonia is omitted. Unfortunately, in this case, the aluminium is not completely thrown down.

precipitate is dissolved in a little HCl and the precipitation is repeated, with the result that the final precipitate represents all the aluminium, while all the iron is in the combined filtrates. Note, however, that in ammoniacal solutions Fe^{++} oxidises quite rapidly and a rusty mess of basic ferric salt may separate out on the filter paper if the operation is not carried through with the utmost speed. The method is not recommended as a means of separating iron from aluminium.

General Remarks.—If there is not much aluminium present, the precipitation does not require any special precautions beyond the addition of ammonia with the aid of an indicator and the definite minute's boiling before filtration.

Another controlled hydrolysis method is *hydrolysis with a nitrite*, but this does not possess any important advantage over the foregoing.

3. *Precipitation as Phosphate.*—This is an excellent method, but suffers from the fact that the precipitant will throw down all the metals of Groups III, IV and V besides aluminium ; a separation of the aluminium must first, therefore, be made. The great advantage of the method is that aluminium phosphate is a crystalline precipitate, filters and washes very rapidly and shows very little tendency to adsorb alkalies.

Method.—To the acid solution add excess of Na_2HPO_4 or $(NH_4)_2HPO_4$ and sufficient ammonia to make the solution *just* alkaline to litmus. Digest the solution under a cover-glass on the corner of the hotplate with occasional stirring with a rubber-tipped glass rod until the flocculent precipitate changes over to the crystalline form, which will settle out excellently and filter rapidly. Decant the liquid through an open paper or pulp, and wash the precipitate with hot water until free from the acid radical of the original solution (usually Cl^-). Dry on the corner of the hotplate and ignite to $AlPO_4$, in which form the precipitate is weighed.

CHROMIUM.

Chromium may be presented to the analyst in three different states of oxidation, viz. CrO, basic, yields chromous salts ; Cr_2O_3, basic, yields chromic salts ; and CrO_3, acidic, gives chromates and dichromates. The lower basic oxides are roughly a parallel case to the two basic oxides of iron in that they form two series of salts and are precipitated by ammonia and alkalies as insoluble hydroxides, but they differ (in degree only) in that the chromous salts are of no importance analytically on account of their extreme instability and the ease and rapidity with which they are converted to chromic salts. The oxide CrO_3 and the chromates have no analogies in the case of iron.

The Group reagent, ammonia, precipitates $Cr(OH)_3$ from the filtrate from Group II. no matter what the original state of oxidation of the chromium, because any chromous salts are almost at once oxidised to chromic salts in solution, and any hexavalent Cr is reduced by the H_2S used in the separation of the metals of Group II. (*cf.* iron) ; the result of this is, that even if chromous salts and chromates were originally present, they will be chromic salts by the time ammonia is added.

$Cr(OH)_3$ is an apple green, gelatinous precipitate, strongly resembling

$Al(OH)_3$ and $Fe(OH)_3$ physically, in that it is very bulky for its weight, very slimy and slow filtering, and very prone to adsorb and carry down with it compounds of the metals of the later groups. The precipitation of $Cr(OH)_3$, like its group companions, demands careful adjustment of the quantity of precipitant used if the separation is to be quantitative ; only the barest excess of ammonia is allowable, as the hydroxide is more than a little soluble in excess and the filtrate from strongly ammoniacal solutions will be found to be coloured pink-violet from the formation of a soluble complex with ammonia.

Estimation of Chromium.

A. Gravimetric Methods—1. *As Chromic Oxide.*—It is necessary that the chromium shall be in the -ic state. If the solution contains hexavalent chromium this must first be reduced.

Reduction of 6-Valent Chromium—(*a*) By H_2S.—The reaction is, essentially:

$$2\,CrO_3 + 3\,H_2S = Cr_2O_3 + 3\,H_2O + 3\,S.$$

The colour changes to dark green, and sulphur (which does not interfere) is precipitated.

(*b*) By SO_2.—Similar to the reduction of Fe^{+++} by this reagent, A sulphite, thiosulphate or metabisulphite may also be used. (See Iron.)

(*c*) By Alcohol.—10 cc. of alcohol are added to the solution for every 0·1 gm. of chromium present and the solution is evaporated in the presence of HCl or H_2SO_4 until the colour changes to the characteristic dark green of the chromic salts. If necessary, the process may be repeated with more alcohol.

Having obtained all the chromium in the trivalent condition, NH_4Cl and NH_4OH are added, the latter cautiously, until the solution reacts just alkaline to litmus. The beaker is then covered and the solution boiled until the smell of ammonia is barely perceptible. The precipitate is allowed to settle and the liquid decanted carefully through an open-textured paper. The precipitate is washed with very hot water, care being taken to stir it well with the jet each time. The paper and precipitate are dried in the mouth of the muffle and the paper charred off ; the precipitate is finally ignited at the full heat of the muffle to Cr_2O_3, in which form the chromium is weighed.

2. *As Lead, Mercurous or Barium Chromate.*—These methods are not to be recommended except in special circumstances, as 6-valent chromium is so much more rapidly and conveniently estimated volumetrically. The chromate solution is neutralised with ammonia (or HNO_3, as the case may be), using litmus paper, and is brought to the boil. Excess of 10 per cent. $BaCl_2$ solution (10 cc. for each 0·1 gm. Cr) is added *drop by drop* with steady stirring until the supernatant liquid is no longer yellow. The precipitate is digested for a quarter of an hour on the hotplate and filtered hot through a tared Gooch crucible, washed with cold water containing 10 per cent. of alcohol and dried in the air oven. The dry precipitate and crucible are then fitted inside a larger crucible by means of a piece of asbestos sheet with a hole that just fits the Gooch, so that the latter is not in contact with the outer crucible, and the whole

is heated to bright redness in the open muffle. The chromium is weighed as $BaCrO_4$.

The method with a lead salt as precipitant is similar.

Neither of the foregoing precipitants can be used in the presence of $SO_4^=$. If this acid is present, the chromium may be precipitated with a slightly acid (HNO_3) solution of $HgNO_3$. In this case the precipitate decomposes on ignition, the mercury being volatilised, so that the chromium is weighed as Cr_2O_3.

B. Volumetric Methods.—Unless the chromium is in the hexavalent condition, it must be oxidised.

Oxidation of Trivalent Chromium.—(*a*) By fusion with Na_2O_2.—This is a common method in the case of refractory ores. The mineral is fused with the peroxide in a copper, nickel, iron or silver crucible until no gritty particles can be detected on stirring with a platinum wire. The melt is then extracted with hot water and carefully acidified with either HCl or H_2SO_4, after which the solution is well boiled to destroy the excess of peroxide and to expel oxygen. The solution is then cooled and titrated.

(*b*) By Fusion with Na_2CO_3 + KNO_3.—If very little KNO_3 is added and the fusion conducted at a moderate temperature, a platinum crucible may be used without doing much damage. This method is often convenient when it is desired to separate iron, aluminium and chromium as precipitated in Group III. The precipitate is filtered off, dried and ignited at low redness ; the carbonate and a pinch of nitrate are then added and well mixed with the precipitate, and the whole just fused. On extraction with water, Fe_2O_3 remains insoluble whilst Al_2O_3 and Cr_2O_3 pass into solution, the former as sodium aluminate and the latter as sodium chromate. The chromium may be titrated in the filtrate after removing iron. In this case, of course, there is no excess reagent to be decomposed, but the solution must be acidified (HCl or H_2SO_4) before titrating. If there is much iron, some chromium may be occluded in the oxide remaining on the paper. In any case, if the insoluble residue is large it is best to dissolve it in dil. HCl and reprecipitate by saturating the solution with bromine and then pouring it into a hot solution of NaOH (10 per cent.). The filtrate, after acidifying, is boiled to decompose BrO^- and then added to the main chromium solution.

(*c*) By Hot Permanganate Solution.—The solution, which should contain only $SO_4^=$ or NO_3^- (*no* Cl^-), is diluted to at least 400 cc. in a tall beaker, and brought to the boil. When boiling freely, a saturated solution of $KMnO_4$ is added, drop by drop, until a precipitate of MnO_2, H_2O persists after five minutes' boiling. 3-Valent chromium is thus oxidised to 6-valent chromium and the 7-valent manganese reduced to 4-valent manganese, which appears as a black, flocculent precipitate of hydrated MnO_2. Having completed the oxidation, the colour of the liquid must be observed, in case some undecomposed MnO_4^- remains. The beaker is held above the head, tilting it slightly, and looking through the thin layer of the solution, as shown in the diagram (fig. 14), it is usually quite easy to detect the least traces of pink in this manner.

If a pink colour persists after boiling, the excess MnO_4^- must be destroyed. This is best achieved by adding a few drops of saturated $MnSO_4$ solution to the still boiling mixture, boiling for five minutes

and again observing the colour of the solution as before. If the pink colour is not discharged, a few more drops of $MnSO_4$ are added and the procedure repeated, but avoiding excess of $MnSO_4$. The reactions are:

$$Mn_2O_7 \rightarrow MnO_2$$

and

$$MnO \rightarrow MnO_2.$$

The hot solution is now filtered through an asbestos pulp filter, the filter washed with hot water until the liquid in the stem of the funnel is no longer coloured yellow, and the filtrate set on the hotplate to evaporate down to a more convenient bulk for titration, say, 150–200 cc. Having boiled the filtrate down to this bulk, it is cooled and titrated with ferrous sulphate solution.

Note. The liquid shows a strong tendency to violent "bumping" if a heavy precipitate of hydrated manganese dioxide is allowed to

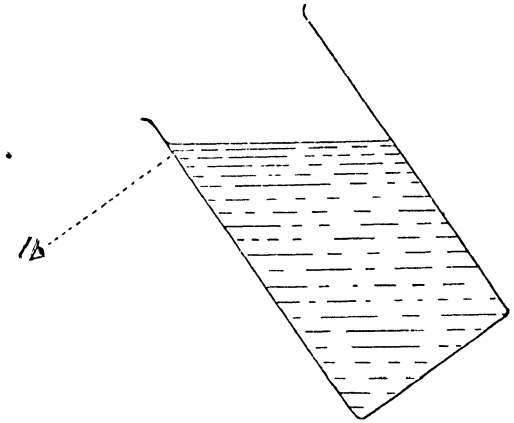


Fig. 14.—Observation of Solution to Detect Presence of Traces of Permanganate.

accumulate. It will therefore be necessary to place two or three small pieces of broken pot or porcelain in the beaker and to watch carefully until the convection currents become powerful enough to keep the precipitate circulating. It is best to have the solution boiling strongly *before* adding the permanganate, and then to add the latter so slowly that the liquid never ceases to boil. A judicious stir with a glass rod will often cure a bumping solution by setting a settled-out precipitate in motion.

(*d*) By Solid Sodium Peroxide added to a Suspension of the Group III Precipitate in Water.—The precipitate from the ammonia group is washed to separate the metals of later groups and then rinsed back into the precipitation beaker. About 1 gm. of dry sodium peroxide is tipped into the suspension and well stirred in with a glass rod. Aluminium and chromium pass into solution as aluminate and chromate respectively, and may be filtered from the iron. The filtrate is acidified with sulphuric acid and the solution vigorously boiled for ten minutes

to decompose the excess of peroxide. After cooling, the solution is ready for titration. If desired, aluminium may first be separated by making the solution just ammoniacal after acidifying. $Al(OH)_3$ is reprecipitated and may be filtered off, while the chromium, now hexavalent, is not affected.

(*e*) By Hydrogen Peroxide in the presence of Alkali.—This is essentially the same as the foregoing. The chromium is precipitated by KOH or NaOH together with the iron and aluminium, and H_2O_2 is added. The solution is acidified as described and boiled to destroy the excess of peroxide, when, after cooling, the chromium may be estimated by titration.

Note that in both cases it is unnecessary to remove iron and aluminium since these do not interfere with the titration of 6-valent chromium in acid solution, but on account of the fact that this method of oxidation may incidentally be used for the quantitative separation of the metals of Group III, it has been described in some detail. See also later, under Separation of Chromium.

(*f*) By Bromine in Alkaline Solution.—Acidify with HNO_3, preferably, but if the solution should chance to be very alkaline (it should not be, if Group III has been properly precipitated) either H_2SO_4 or HCl is to be preferred. To the acid solution add a few drops of Br_2 and stir until the liquid takes on a deep orange tint. Add a slight excess of NaOH (or KOH), stir, and bring to the boil to decompose the hypobromites. *In the absence of ammonium salts* this procedure results in the following reactions with the various metals which may be present :

Fe, . . .	$Fe(OH)_3$ . .	precipitated, (red-brown)
Al, . . .	$Na_2Al_2O_4$, .	in solution, (colourless)
Cr, . . .	Na_2CrO_4 . .	in solution, (yellow)
Ni, . . .	$Ni(OH)_3$ . .	precipitated, (black, flocculent)
Co, . . .	$Co(OH)_3$ . .	precipitated, (black, flocculent)
Mn, . .	Na_2MnO_4 and $NaMnO_4$ . .	in solution, (green ; purple)

[If much Mn is present, some will be precipitated as MnO_2, H_2O (black, flocculent). If alcohol is added and the solution boiled, all the Mn is precipitated.]

Zn, . . .	Na_2ZnO_2 . .	in solution, (colourless)

In the presence of ammonium salts, and using NH_4OH as precipitant, the reactions of the metals are slightly different, viz. :—

Fe, . . .	$Fe(OH)_3$ . .	precipitate, (red-brown)
Al, . . .	$Al(OH)_3$ . .	precipitate, (white)
Cr, . . .	$(NH_4)_2CrO_4$.	in solution, (yellow)
Ni, . . .	is not precipitated,	(deep blue solution)
Co, . . .	is not precipitated,	(pink or blue solution)
Mn, . .	$MnO_2 . H_2O$.	precipitate, (black, flocculent) (complete)
Zn, . . .	is not precipitated,	(colourless solution)

These reactions are of the greatest importance in the analysis of alloy steels. They are inserted here under the appropriate heading, but they are more fully discussed later under Separations.

Titration of Chromate and Dichromate Solutions.

1. *With Ferrous Sulphate Solution.*—CrO_3 is titrated with a standard solution of ferrous sulphate using a solution of potassium ferricyanide on a spot-plate as an outside indicator. This is the reverse of the titration of Fe^{++} with standard dichromate solution, and the same precautions are to be observed. In this case, of course, the end-point is detected by the first appearance of an *immediate* blue coloration on the test-spot and not by the fading of the blue colour as before ; the titration is, however, much easier in reverse, as there is, to the experienced worker, quite a definite indication of the approach of the end-point in the slow and progressive fading of the yellow lights in the solution that is being titrated, especially when the solution is a *pure* chromate, as is the case if the chromium has been separated from iron, notably, since ferric salts are yellow. The addition of the ferrous salt from the burette results in an immediate change of colour in the reaction beaker to green, which shade deepens as the reaction proceeds and more and more 6-valent chromium is reduced to Cr^{+++}, while at the same time the yellow of the chromate fades in intensity. This latter change enables the operator to follow the course of the reduction, and with experience it is possible to run in the reagent quite boldly right up to within 1 cc. or so of the end-point. It is a considerable aid to the eye to place a beaker that has been already titrated to the end-point beside the one that is being titrated and to compare the colours by looking through the green solutions at a reflection of a window on the bottom of the beaker. The beakers should be placed upon a white tile in order to obtain a neutral background. If, however, the operator is not accustomed to the titration, it is safer to conduct it with the same precautions as were advised under the titration of Fe^{++} with a chromate solution, *i.e.* to do a rough titration first to discover approximately where the end-point may be expected, and then to repeat with a duplicate assay solution, finishing slowly.

Standardisation of the Iron Solution.—Ferrous sulphate oxidises slowly on keeping and the solution requires re-standardisation, say, once a week. If only occasional chromium assays are to be carried out, the solution should be standardised afresh each time. The "standard" should be titrated first so that it may be used as a comparison standard for the assays. In this case, since the strength of the ferrous solution is known very closely, the titration of the standard can be carried out very quickly by calculating approximately how much ferrous solution should be required and adding the solution boldly from the burette to within about 1 cc. of the necessary amount.

For the standard, 0·1 or 0·2 gm. of purified potassium dichromate is accurately weighed into a beaker, dissolved in the same bulk of water as the assay solutions, and titrated at once. Free acid is necessary, but need not be added as in the case of the reverse titration because there is sufficient H_2SO_4 already present in the ferrous sulphate solution.

Note 1.—It is important to keep the bulks equal, and to choose an amount of standard as near as possible to the amount of chromium in the assays. The reason for this is that there is often quite a considerable "blank" due to personal factor with this titration, and if standards and assays are equal in bulk and CrO_3 concentration the blank may be made to cancel out.

Note 2.—If the end-point is overshot, the assay may be "back-titrated" with standard dichromate solution from another burette, but if this is necessary, *excess* of dichromate should be added and the titration finished with the ferrous solution in order that the "blank" may cancel against the blank of the standard ; do not rely on the end-point obtained by the exact back titration, as its "blank" is different.

Note 3.—There may be a difficulty in the case of solutions containing much chromium, occasioned by the deep green of the chromic salt obscuring the blue of the ferricyanide. If any doubt is felt, it is safest to place a spot of the solution from the beaker close beside the ferricyanide spot which is suspected of showing the end-point ; any slight difference of colour can easily be detected by this means.

2. *By Titration with Sodium Thiosulphate after adding Excess of Potassium Iodide.*—The reaction is:

$$2\,CrO_3 + 6\,KI = Cr_2O_3 + 3\,K_2O + 3\,I_2$$

and:

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

The solution of the chromate must be free from iron, so that one of the oxidation methods which entails a separation should be chosen. The solution is then acidified with H_2SO_4, adding 5 per cent. by volume excess, and well boiled to decompose the excess of oxidant. After cooling completely, 1 gm. of KI (solid) is added for each 0·1 gm. of chromium, the solution is stirred well, and the liberated iodine titrated with standard thiosulphate, only adding the starch indicator when the yellow of the dilute iodine solution begins to fade. With experience, the end-point is quite definite, even in the presence of much chromium, the dark green colour of which tends to mask the final disappearance of the blue of the indicator. This titration has, however, no real advantages over the titration with a ferrous salt, and in view of the difficulty with the end-point, the latter, in the writer's opinion, is always to be preferred.

GROUP IV.

Nickel, Cobalt, Manganese, Zinc.

This group consists of the above four metals. Nickel and cobalt are very closely alike in their properties, both chemical and physical, and both resemble iron in many respects, iron being the third member of the first Group 8 Triad in the Periodic Classification. Manganese and zinc come from groups that are wide apart in the Periodic System. All four metals show a great variety of reactions that can be used for their estimation, so that, on the whole, this analytical group is perhaps the most interesting of all as far as the Analyst is concerned.

The differences between this group and the previous one, by which the two groups can be separated, are not great, chemically ; in fact,

the quantitative separation of Groups III and IV is by no means so simple an operation as is often supposed by chemists who have had no experience in the analysis of iron and steel. All four metals are precipitated as hydroxides by ammonia and the alkalies, just as iron, aluminium and chromium are, but $Ni(OH)_2$ and $Co(OH)_2$ are soluble in a moderate excess of ammonia, while none of the four is precipitated by this reagent provided there is a sufficiency of ammonium salts present in the solution. This is the chief reason for the addition of ammonium chloride when precipitating Group III ; but whether ammonium salts are present or not, the hydroxides are always *liable* to come down in Group III, especially if there are large amounts of the metals of either (or both) groups present. Thus, in the analysis of a steel, if an attempt is made to remove the iron as $Fe(OH)_3$ *by* ammonia before proceeding to the estimation of the manganese which is invariably present, it will be found that little or no manganese will be in the filtrate from the iron, practically the whole of it being carried down by the ferric hydroxide ; and the same applies to the other metals. Special methods of separation must, therefore, be adopted when the bulk of the Group III precipitate is at all large, or when the amounts of the metals of Group IV are more than a few milligrams. These methods will be considered under Separations (*q.v.*).

Group IV is separated from Groups V and VI by the precipitation of the sulphides of the metals from the filtrate from the ammonia group, these sulphides being insoluble in ammonia and in ammonium sulphide. (See, however, under Nickel and Cobalt.)

The slightly ammoniacal filtrate from Group III is saturated in the cold with H_2S ; nickel and cobalt are precipitated as NiS and CoS, which are black, Zn as ZnS, which is white (though pure white ZnS is an analytical rarity, because of contamination with traces of black or coloured sulphides), while MnS is pink or green, according to conditions. These sulphides are not precipitated in the presence of quite small concentrations of strong acids, though ZnS may be quantitatively precipitated from H_2SO_4 or HCl of extreme dilution and quite easily precipitated from dilute acetic or formic acid solutions, from which NiS, CoS, and MnS show no tendency to come down. MnS is the most susceptible, even the slightest concentration of H^+ completely preventing its precipitation ; NiS and CoS come next in the scale, being thrown down in very dilute solutions of the " weak " acids, while ZnS may be precipitated from very dilute " strong " acids. NiS and CoS have, however, the strange peculiarity of being insoluble, when once precipitated, in concentrations of acid which would be quite sufficient to prevent their original precipitation ; indeed this is made use of in the separation of these two metals from the other members of the group. All four sulphides are first precipitated by H_2S from alkaline solution, the precipitate is filtered off and washed, and then treated on the filter with 5–7 per cent. HCl. The ZnS and MnS dissolve easily and completely, leaving the black sulphides quite unaffected. The latter dissolve, however, in hot dilute HNO_3 and in $HCl + KClO_3$.

Nickel and cobalt form two series of salts which are derived from the oxides NiO, Ni_2O_3 and CoO, Co_2O_3 respectively. In both cases the -ous salts are the more stable, and of the two series of -ic salts,

those of cobalt are the more stable. Manganese has a whole series of oxides, of which only the lowest, MnO, is stably basic, forming manganous salts. (Manganic salts from Mn_2O_3 do exist, but these compounds are so unstable that their reactions are of no importance analytically.) The higher oxides MnO_3 and Mn_2O_7 are acidic, yielding manganates and permanganates respectively, while MnO_2 is a peroxide. Zinc forms only one normal oxide, ZnO, which forms a series of zinc salts with the acids; in the presence of strong alkalies, this oxide can act as an acid, forming salts, the "zincates."

It is worthy of note that MnO, though its salts are eminently stable, is readily and fairly rapidly oxidised in alkaline solution by the air to MnO_2. This fact is occasionally of importance in analysis, and has been made the basis of one method of estimation of oxygen in aqueous solution.

NICKEL.

Nickel resembles its congener cobalt extremely closely in ever, respect; so much so that until the discovery of the organic precipitants dimethylglyoxime and α-nitroso-β-naphthol, which have the specific property of precipitating nickel and cobalt respectively, each without contamination by the other, there was no really satisfactory method of separating the two metals. Apart from cobalt, nickel resembles iron and copper more closely than it does any other metal; the resemblance to iron is general and just what might be expected from the relative positions of the two elements in the Periodic Classification. The analogies with copper are not so close, but the analyst always remembers that these are the two metals which have greenish-blue ions (cupr*ic* and nickel*ous*), and which form deep blue solutions when ammonia is added in excess to their solutions.

Estimation of Nickel.

A. Gravimetric Methods—1. *As NiO.*—To the solution, which must not contain any NH_4^+ ions, add about 1 cc. of bromine and stir until a deep orange colour is permanent. Now add, slowly and carefully, a bare excess of 10 per cent. KOH solution, and bring the mixture to the boil, when the nickel separates out as black nickelic hydroxide, $Ni(OH)_3$, which settles and filters well. Pour the solution through an open-textured filter and wash the precipitate thoroughly with hot water, first by decantation, and then on the filter. Transfer paper and precipitate to a porcelain crucible and after charring off the paper, ignite to black NiO. Unfortunately, this precipitate adsorbs electrolytes rather strongly, and since "fixed" alkali must be used for the precipitation, the oxide will be contaminated with some KOH. Most of this may, however, be removed by extracting the oxide after ignition with a little boiling water and re-filtering; the oxide does not adsorb as the hydroxide does, and in any case after ignition the alkali is no longer held in bondage by ionic forces. Also, of course, there will only be a relatively minute amount of alkali present, so that even if NiO did adsorb, say, 1 per cent. of the alkali, this amount would always be negligible. The extracted NiO is filtered off, washed once or twice and re-ignited.

If the oxidation with bromine is omitted, green gelatinous $Ni(OH)_2$ is precipitated by the KOH. This may also be ignited to NiO, but the nickelic compound is very much to be preferred, as the green hydroxide is very slimy and filters extremely slowly, besides which, it is much more strongly adsorbent than the black compound.

This method is convenient when the solution contains several of the Group IV metals originally, especially when nickel is to be separated from zinc, as, for instance, in the analysis of Nickel Silver, to which the student is referred.

2. *As Nickel Dimethylglyoxime.*—Dimethylglyoxime, $\begin{matrix} CH_3 - C = NOH \\ | \\ CH_3 - C = NOH \end{matrix}$, forms a compound with nickel, two adjacent oxime hydrogen atoms from two molecules of the reagent being replaced by one atom of nickel. The compound is rose-red in colour and very voluminous. The great point about this method is that the corresponding cobalt compound is not precipitated even from a solution containing much cobalt and but little nickel; it constitutes, therefore, an excellent method of separating these metallic twins.

Method.— Dilute the solution to such a bulk that cobalt, if present, is at a concentration of not more than 0·1 gm. to each 100 cc. Neutralise with ammonia and then make just acid with HCl. Boil, and add the dimethylglyoxime in 1 per cent. alcohol solution until there is sufficient present to combine with all the nickel and all the cobalt and leave a slight excess. This done, either make the solution just ammoniacal, or add sufficient ammonium acetate to bring the H^+ concentration to a negligible value. Digest on the hotplate until the precipitate settles out well and then decant through a weighed Gooch crucible (paper or asbestos). Rinse the precipitate into the crucible and wash well with hot water, having an eye to possible creeping of the precipitate. Dry in the air oven to constant weight at 110° C.

Note 1.—Much HNO_3, nitrates, or free mineral acids interfere. The precipitate is slightly soluble in ammonia, so that an excess is to be avoided; also in alcohol, hence the volume of the solution must be adjusted so that not more than 50 per cent. of its bulk consists of alcohol.

Note 2.—The precipitation with glyoxime constitutes a complete separation from all metals which are not precipitated by ammonia, (except palladium).

Note 3.—A useful "rapid" end method is as follows. Filter off on to a small hardened paper (No. 50) and wash on the pump, rinsing the precipitate to the apex of the paper. When washed, open the paper out and spread wet upon a clean glazed tile which is placed in the air oven and dried at 110° C. From the hardened paper the whole of the precipitate can usually be detached in a single piece if the paper is carefully bent and a small spatula inserted under the edge of the precipitate, thus saving considerable time. Traces of precipitate adhering to the paper may be ignored, since only 20 per cent. of this is nickel, and an error of 1 mgm. on a 1 gm. sample only represents 0·02 per cent.

B. Electrolytic Method.—This is an excellent method for the estimation of nickel; cobalt is completely co-precipitated on the kathode, but no other metal ordinarily interferes under the conditions of the experiment. The fact that cobalt is deposited with the nickel is not

entirely a disadvantage, as it enables these two metals to be separated easily and accurately from relatively large amounts of, for example, zinc, in the analysis of nickel silver. The two metals are weighed together, and the nickel or cobalt, whichever is the less, is determined separately after dissolving the deposit from off the kathode, the other metal being estimated by difference.

Method.—7 to 10 gms. of ammonium sulphate should be present for each 0·25 gm. of nickel (cobalt), and NO_3^- must be absent. If this anion is present, *e.g.* in the solution of an alloy which has been attacked with nitric acid, or when the acid has been added to oxidise Fe^{++} in Group III, about 5 cc. of H_2SO_4 are added from a burette and the solution evaporated to copious fumes of SO_3. Five cc. of the acid represent roughly 9 gms. of H_2SO_4, which is chemically equivalent to 12 gms. (approx.) of ammonium sulphate, so that after fuming, cooling and diluting, the mere neutralisation of the solution with ammonia will secure the presence of sufficient ammonium sulphate in the final solution. If there is less than 1 gm. of nickel present, it need not be allowed for, but if more than this amount is present, it should be remembered that each gram of nickel will combine with roughly 1·6 gms. of sulphuric acid.

The diluted solution is neutralised with ammonia and, after cooling, 30–40 cc. of 0·880 sp. gr. ammonia are added. The solution is now electrolysed at about 3 volts and 1–2 ampères for one hour (rotating electrode) in which time complete deposition of the nickel should be effected.

Note.—The deposited nickel is best dissolved in hot 1 : 1 HNO_3. It is somewhat difficult to remove completely and the completeness of its removal or otherwise is not easily detected on account of the similarity in colour between nickel and platinum. If a cupro-nickel copper is being analysed, the nickel may be deposited directly on the copper which has previously been estimated electrolytically, thus saving a weighing, and greatly facilitating the removal of the nickel.

C. Volumetric Method.—The author has not found this method altogether satisfactory for the determination of nickel in pure nickel solutions (in these the electrolytic method is to be preferred), but for the estimation of nickel in alloy steels it is rapid, accurate, and completely satisfactory. Fe, Mn, V, Mo, W, Zn and Cr do not interfere, but cobalt does ; in fact, cobalt may be roughly titrated by this method in solutions that are free from nickel.

Theory.—In very faintly ammoniacal solutions nickel reacts with KCN to form potassium nickelocyanide [$K_4Ni(CN)_6$], and the nickel being in the complex anion, no $Ni(CN)_2$ is precipitated in the course of the process. If a cyanide is added to a solution containing nickel, this reaction takes place, but there is no visible end-point ; in order, therefore, to employ the reaction for titration purposes, an artificial end-point must be devised. For this, a precipitate of AgI is produced in the solution to be titrated, and this precipitate is " dissolved " by the excess of KCN after the nickel has been quantitatively converted into nickelocyanide. The reaction is:

$$AgI + 2\,KCN = KAg(CN)_2 + KI,$$

the potassium silver cyanide being soluble in water.

Solutions Required.—1. 5 gms. KCN + 5 gms. KOH dissolved in 1,000 cc. water.

2. 5 gms. $AgNO_3$ in 1,000 cc. water.

3. 350 gms. $(NH_4)_2SO_4$ + 50 gms. KI in 1,000 cc. water.

Method.—The nickel solution should have a volume of about 100 cc. and should be in a Phillip's flask or a tall beaker. Dilute ammonia is added until the solution smells very faintly of the gas. This operation requires some care as the neutral point *must not* be overshot or the assay will have to be restarted. The method of adding the ammonia (1 : 4) is to introduce it drop by drop, and after each addition blow the ammonia gas out of the beaker before applying the nose to the mouth of the vessel to ascertain whether the neutral point has been reached. The correct end of neutralisation is that point at which the operator can take a deep inhalation of the gas in the beaker without bringing tears to his eyes. I have always found that if, by accident, excess of ammonia is added, the indicator precipitate comes down in a coarsely crystalline condition and the end-point cannot be observed properly owing (1) to retarded attack by the KCN, and (2) to the rapid settling of the denser precipitate.

The solution is cooled thoroughly and 20 cc. of the $(NH_4)_2SO_4$-KI solution added (use an ordinary 25 cc. graduated cylinder), followed by exactly 2 cc. of the $AgNO_3$ from a burette. A turbidity at once forms (AgI). The cyanide solution is now added from the burette, several cc. at a time at first, but more cautiously as the reaction proceeds. Care must be taken that the end-point is not overshot, as there is no sign of its approach until the AgI begins to dissolve, and this does not happen until the main reaction is complete. When the latter is the case, the turbidity slowly clears and distinct "clear spaces" in the turbid solution may be observed after each addition of cyanide. To observe the end-point the flask should be placed upon a dull black surface in a good light. The solution is rotated gently (not shaken), and when the turbidity commences to clear, the cyanide is added drop by drop, arranging matters so that the liquid is rotating slowly and that the drops strike the surface at a point about midway between the centre and the outside. The final clearing of the last traces of turbidity may be detected when the addition of a drop of the cyanide fails to produce a perceptible "clear space" in the solution. This is a method which requires practice and experience, but is one which gives quick and accurate results in practised hands.

Cobalt interferes, as a similar reaction takes place with the cyanide, and here there is a further possible complication due to the fact that cobaltocyanides are oxidised by the oxygen of the air to cobalticyanides, slowly but quantitatively.

For the application of this method to the analysis of Nickel Steels see under Steel Analysis.

Standardisation of the KCN Solution.—Add 10 cc. of the $AgNO_3$ solution from the burette to a solution that has just been titrated and again add cyanide until the end-point is attained. This gives the cyanide equivalent of the $AgNO_3$ solution and shows how much KCN must be deducted from the cyanide burette reading to allow for the 2 cc. added at the

commencement of the titration. This amount remains a constant blank throughout a series of estimations.

It is worthy of note here, that if by accident the end-point is overshot, more $AgNO_3$ may be (at once) added and the end-point again looked for. If this device is used, the blank corresponding to the extra $AgNO_3$ added must, of course, be deducted in addition to the usual blank.

A standard nickel solution is made up by dissolving 0·2 gm. of nickel ammonium sulphate in a little water, making just ammoniacal as explained, and titrating with the cyanide after adding the 2 cc. of $AgNO_3$. This standard will require approximately 22 cc. of the foregoing cyanide solution. In the case of the estimation of nickel in a steel it is best to use a standard steel for standardisation. Steels standardised by British Chemical Standards are supplied by chemical dealers together with certificates of analysis.

Note.—An excellent device for detecting the end-point of this titration is to arrange a small enclosed electric light so that a beam of light is focussed to a point of intense luminosity inside the solution. If a turbidity exists, it is shown up by the luminous path in the solution, *cf.* dust particles showing up a beam of sunlight. At the end-point, the solution appears empty, and no luminous path is visible.

COBALT.

Cobalt is not very often met with in analysis, though it is a constituent of a few alloys; cobalt steels are also growing in importance. Analytically, as already noted, it closely resembles nickel, so much so that the separation of the two metals is a matter of some difficulty, or was, before the discovery of the applicability of dimethylglyoxime as a precipitant for nickel and of α-nitroso-β-naphthol for cobalt. Nickel and cobalt are the closest twins chemically and physically that exist outside the " rare earth " group of metals, and as the two are always found together, nickel being an invariable impurity in a cobalt compound, and *vice versa*, their separations are vitally important. A careful study of the reactions given later under Separations is therefore necessary.

Estimation of Cobalt.

A. Gravimetric Methods—1. *As Metal.*—Cobalt forms three oxides, of which CoO, cobaltous oxide, and Co_2O_3, cobaltic oxide (or cobaltous cobaltite) are the important ones as being the basis of the -ous and -ic series of salts respectively. There is, however, a third oxide which is of importance, viz. Co_3O_4, which is the " cobalt oxide " of commerce and is perhaps the most stable of the three oxides under ordinary conditions. Both CoO and Co_2O_3 are converted into this oxide when heated in air, but, unfortunately, the conversion is never quite quantitative and the residue on ignition is of too intermediate a composition to be of much value for the accurate gravimetric estimation of cobalt. To overcome these objections it is usual to estimate cobalt gravimetrically as metal, by preparing either of the oxides CoO or Co_2O_3, heating the mixture to char off the paper, etc. after filtering, whereby Co_3O_4 is formed to a greater or less extent, and finally reducing the mixture of oxides in coal gas or hydrogen to the metal.

Procedure.—To the cobalt solution add one or two cc. of bromine and stir until a deep orange colour is obtained. (The solution must be acid.) This done, add excess of KOH solution and bring to the boil. Cobalt is precipitated as black cobaltic hydroxide, which, like the nickel compound, settles and washes well. Allow to settle on the corner of the hotplate and filter through an open-textured paper. Wash well with hot water and after drying and charring off the paper, ignite to oxide. After ignition brush the precipitate out into a small beaker and extract with several small washes of hot water to remove, as explained under Nickel, the alkali which invariably contaminates the precipitate. The mixture of oxides is finally caught on a small pulp filter and re-ignited to destroy the paper. The crucible is then placed on a pipe-clay triangle over a small Bunsen flame and the oxides reduced by directing a stream of hydrogen from a bent hard glass tube upon the bottom of the crucible while continuing the heating. (A Rose crucible is to be preferred.) The reduction is complete at redness, but the reduced cobalt must be cooled off in hydrogen before brushing out and weighing, as it is pyrophoric.

2. *Estimation as* $CoSO_4$.—If preferred, the oxides, obtained as above, may be converted into the anhydrous sulphate for weighing. The mixed oxides are treated in the crucible with a slight excess of 1 : 1 sulphuric acid and gently heated until completely dissolved. Heating is continued on the hotplate until acid fumes cease to come off, when the crucible is placed in the mouth of the muffle and slowly worked back to a low red heat. Water of hydration is finally expelled before the sulphuric acid commences to fume, and this part of the manipulation requires some care to avoid loss of sulphate by spitting. The heating in the muffle must not be carried above low redness or the sulphate may commence to decompose.

Note that in both these methods cobalt may be originally precipitated by KOH as cobaltous hydroxide, which is blue or pink according to conditions, but this compound is not so satisfactory as the one advised, owing to its gelatinous nature, which means that it is not only very slow in filtering, but that it adsorbs electrolytes powerfully. Cobaltous hydroxide, like ferrous hydroxide, is oxidised to the brown-black -ic compound by the air.

Note 2.—The precipitation is incomplete in the presence of ammonium salts. (These are eventually completely decomposed by the bromine.) Preliminary separation of the cobalt as CoS is therefore essential.

Note 3.—Co in small amounts *may* (but α-nitroso-β-naphthol is greatly to be preferred) be estimated more or less directly from the group precipitation as CoS, provided no other metals of the group are present, by filtering off the sulphide and igniting it to oxide in an open crucible. The oxide, containing a certain amount of residual sulphide, is then treated with sulphuric acid as already described and the cobalt finally weighed as sulphate.

3. *Estimation as Phosphate.*—No other metals having insoluble phosphates may be present. The method is, however, a useful one, owing to the great "handiness," analytically speaking, of properly prepared phosphate precipitates.

Method.—The $(NH_4)_2HPO_4$ used for the precipitation must be free from the di-hydrogen phosphate. To ensure this, the reagent is dissolved

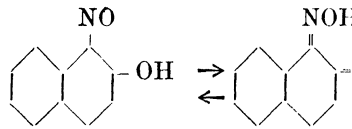
in water and a drop of phenolphthalein is added, followed by ammonia, until a faint pink colour is obtained ; the mono-hydrogen salt is neutral to phenolphthalein.

Cobalt phosphate is more " insoluble " in water than magnesium phosphate so that a large excess of ammonia is not required, in fact, the precipitate dissolves in excess of ammonia, owing to the formation of complexes, *cf.* Zinc, *q.v.* In the case of cobalt there is another possible complication, since this metal is exceedingly prone to the formation of complexes with a variety of substances, and these are somewhat " indeterminate " analytically. On this account, some analysts advise against the use of the phosphate method for cobalt ; the following procedure has, however, been thoroughly tested, and will be found to give reliable results provided the method is closely followed:

To the slightly acid cobalt solution add excess of the tested mono-hydrogen solution, warm, and add dilute ammonia drop by drop until a slight precipitate is formed. Now add 15 cc. of ammonium acetate solution and a drop or two of ammonia until the solution shows a slight but noticeable alkaline reaction to litmus or methyl orange.

The precipitate first formed is lavender blue and flocculent ; it is of no value analytically as it clogs the filter badly, and is therefore converted into the compact crystalline variety as follows : Place the beaker on a boiling water-bath and stir vigorously until the condition of the precipitate commences to change. Digest at 100° C. for about half an hour, stirring occasionally, until the change is complete and the precipitate is entirely converted into the crystalline purple-rose phosphate. Filter hot and wash well with hot water. Transfer to a porcelain crucible and char the paper as rapidly as possible ; then ignite at full redness (800° C.) to $Co_2P_2O_7$. The filtrate should be tested for cobalt with a little $(NH_4)_2S$ solution. If a dark coloration is produced, the solution is digested on the hotplate until the precipitate settles out. The sulphide is then filtered off and if it only amounts to a mgm. or so, it is roasted to oxide ; (assume all is Co_3O_4 ; the error on a mgm. will be unimportant) ; if, however, there are more than mere traces of cobalt in the filtrate, the sulphide must be roasted to oxide and then converted to $CoSO_4$ in a weighed crucible as described under Gravimetric Methods. The " extra cobalt " is added to the cobalt as calculated from the phosphate precipitate. If cobalt is found in the filtrate it is a sign of bad working.

Note.—For details and theory of Phosphate Precipitations, see under Magnesium.

4. *Estimation as α-Nitroso-β-Naphthol Compound.*—The reagent has the formula, 

the two forms being tautomeric. It forms a red, flocculent precipitate with cobalt but not with nickel in acid solution, and is therefore a valuable means of separating small quantities of cobalt from large amounts of nickel. The compound also precipitates copper and iron completely, and silver, bismuth, tin and 3-valent chromium partially ; these metals must,

therefore, be absent. In the case of a complete analysis these metals will have been already separated in the ordinary routine.

The standard reagent is prepared by dissolving 8 gms. of the crystals in 300 cc. of glacial acetic acid and diluting to 600 cc. with water. The cobalt solution, which may contain nickel, manganese, zinc and any of the metals of the later groups, besides the previously unmentioned metals of Groups I and II, is acidified with HCl (5–10 per cent.) and the precipitant added slowly until no further precipitate is formed. The beaker is placed on the hotplate and the contents digested until the red compound has settled out completely ; a little more of the reagent is added to make sure that all the cobalt is down and the precipitate is allowed to settle further for at least three hours. The solution is decanted through an open-textured filter, or weighed Gooch, and the precipitate washed as far as possible by decantation with cold water, then with three or four small quantities of 10 per cent. HCl to dissolve out any nickel that may have been carried down by the cobalt precipitate, and finally with hot water to remove the acid. The precipitate and paper are dried on the hotplate or in the mouth of the muffle, the paper charred off and the precipitate ignited carefully to oxide. The oxide is finally reduced in a stream of hydrogen, as described under Method 1, to metallic cobalt, using a Rose's crucible. The cobalt is weighed as metal.

Note 1.—The red organic compound tends to volatilise slightly as a whole, carrying the cobalt away. It is sometimes advised that the first ignition should, in consequence of this, be conducted over a small flame in a Rose's crucible into which a slow current of oxygen is passed. This has the effect of burning up the organic part of the precipitate before any cobalt is lost by volatilisation. If, however, the ignition is conducted carefully, charring the paper and precipitate in the mouth of the muffle first and then gradually working back to the full heat, there should be no danger of loss.

Note 2.—Small quantities of cobalt may be estimated much as was described under Nickel, by filtering the bulky precipitate off on to a No. 50 paper and drying at 100° C. in the air oven. The dried precipitate is then detached with the blade of a penknife or a small spatula, and weighed direct.

Note 3.—Owing to the very bulky nature of the precipitate, it is not recommended that this method be used for quantities of cobalt greater than about 0·1 gm.

5. *Separation as Potassium Cobaltinitrite*, $K_3Co(NO_2)_6$, xH_2O. — This compound is useful in connection with the analysis of some cobalt alloys, particularly as neither nickel nor iron forms a similar insoluble compound. The cobalt is, however, not estimated as cobaltinitrite, as this compound does not lend itself to quantitative work ; the method is used rather as a means of separation, and as such will be considered under Separations, *q.v.*

B. Electrolytic Method.—Cobalt is very conveniently and accurately estimated by the electrolysis of strongly ammoniacal solutions of cobalt containing ammonium sulphate. The details are exactly similar to those detailed for the electrolytic estimation of nickel and will not be repeated here ; the student is referred to the section on Nickel. As was mentioned under that heading, this method is useful in analysis where

nickel and cobalt are together in a solution containing other metals as a preliminary means of isolating these metals. In practice, the two metals are weighed together after the electrolysis, the deposit is dissolved off the kathode with a little 1 : 1 HNO_3 (hot), and either the nickel or the cobalt, whichever is the less, estimated in the solution by glyoxime or nitroso-naphthol, after expelling the nitric acid by evaporating with HCl.

Note.—If $Co(OH)_3$ deposits as a black stain on the anode, more ammonia is necessary.

C. Volumetric Method.—A method has been devised on the lines of that detailed for Nickel, but it is not satisfactory.

D. Colorimetric Method.—Potassium thiocyanate yields a deep blue colour with solutions of cobalt salts. This coloured compound is soluble in alcohol-ether, and may be extracted from the cobalt solution in this manner. The coloured extract is then compared with the colour, similarly produced, of a standard cobalt solution. Ferric iron interferes. The method has no advantages over, *e.g.* the nitroso-β-naphthol method for small quantities of cobalt, and is only mentioned for completeness.

MANGANESE.

Analytically, two oxides of manganese are of primary importance, the basic oxide MnO, which forms a complete series of salts, and the acid oxide Mn_2O_7 which yields permanganic acid and the permanganates. Two other oxides must, however, be considered: MnO_2, which is frequently met with as the result of a reduction of permanganic acid or as the oxidation product of MnO ; and Mn_3O_4, which bears considerable resemblance to Fe_3O_4 and Co_3O_4 in that it is the final product when the other oxides are heated in air. Unlike Co_3O_4, however, it is constant in composition if properly prepared. $MnO_2 . H_2O$ is a black insoluble substance which resembles $Ni(OH)_3$ physically.

There are a great many methods, most of them extremely reliable, for the estimation of manganese. Here, attention will be directed particularly to a selection of the best methods.

Estimation of Manganese.

A. Gravimetric Methods—1. *As Mn_3O_4.*—This is the most generally applicable method for the estimation of manganese, as it involves the separation of this metal from all others that are not precipitated as hydroxides by ammonia in the presence of ammonium chloride, *i.e.* from nickel, cobalt, zinc, and the later groups. The manganese is precipitated as $MnO_2 . H_2O$ and weighed as Mn_3O_4.

Procedure.—To the solution, which should have a bulk of some 400–600 cc., and be slightly acid (any acid), 2 or 3 cc. of bromine are added and the solution stirred with a glass rod until the bromine is dissolved to a deep orange solution. When thoroughly brominated, the solution is made just ammoniacal and brought to the boil, whereby hydrated MnO_2 is thrown down as a black precipitate which settles out well. The solution is decanted through an open-textured paper and the precipitate washed well with hot water, the whole transferred to

a weighed platinum crucible, the paper charred in the mouth of the muffle and the precipitate finally ignited to Mn_3O_4 at full orange heat (1,000–1,100° C.).

It has been stated that the precipitate is not entirely Mn_3O_4, but the author has used this method as standard for the estimation of manganese in ferro-manganese (80 per cent. Mn) and there has never been any difficulty in making the results total up to within a fraction of 100 per cent. If any doubts are entertained, however, the precipitate may be treated with a few cc. of 1 : 1 H_2SO_4 in the crucible (as described under Cobalt) and the oxide converted to the anhydrous sulphate exactly as described. The sulphate is stable at dull redness, and the manganese may be weighed in this form. Or, alternatively, the precipitate may be dissolved in a little hot H_2SO_4 and the manganese precipitated as phosphate as described below.

Note 1.—Do not attempt to dissolve the precipitate out of the crucible with HCl. Chlorine ruins platinum!

Note 2.—Ammonium persulphate in ammoniacal solution, or bleaching powder in the presence of zinc chloride in neutral solution may also be used as precipitant.

Note 3.—The method is an exact parallel with the method already given for nickel as $Ni(OH)_3$ except, and this is an important point, that the nickel must be precipitated by KOH or NaOH in the *absence* of ammonium salts, whereas manganese, when oxidised, will not as a rule be precipitated by the "fixed" alkalies. The precipitation may, however, be effected if alcohol is added to the solution before boiling; alcohol has the effect of reducing alkaline manganates and permanganates to MnO_2 (*cf.* Chromates). These facts may be made the basis of a separation of nickel from manganese.

2. *As Phosphate.*—As was remarked in the case of aluminium and cobalt, this method is only possible when no other metal with an insoluble phosphate is present in the solution. It is, however, an excellent method for the estimation of manganese after its separation from other metals. The precipitated phosphate is converted into pyrophosphate before weighing.

Method.—To the cold solution, which should not contain more than about 0·2 gm. of manganese, add considerable NH_4Cl (20 gms.), followed by 10 cc. of a saturated solution of Na_2HPO_4 or NH_4NaHPO_4. This done, add ammonia until the solution reacts just alkaline to methyl orange. Add one or two drops excess and bring the solution to the boil, digesting the precipitate on the hotplate until the original flocculent masses are converted into the crystalline variety. Filter through an open-textured paper, or preferably through a weighed (asbestos) Gooch. Wash with dilute NH_4NO_3 solution until free from Cl^-, dry in the mouth of the muffle and finally ignite at full redness to $Mn_2P_2O_7$ in the muffle, (not over a burner). The residue should be quite white when it is weighed.

B. Volumetric Methods.

1. *Ferrous Ammonium Sulphate and Permanganate or Dichromate Method.*—The manganese is precipitated as $MnO_2.H_2O$ with bromine and

ammonia, or by $KClO_3$ in HNO_3 solution (*vide* Steels). The precipitate is filtered off and washed well with hot water, then transferred together with the paper bodily to a beaker or conical flask containing excess of a standard solution of ferrous ammonium sulphate acidified with H_2SO_4 ; the ordinary standard solution serves well.

The MnO_2 dissolves, oxidising an equivalent amount of the ferrous salt, thus:

(1) $MnO_2 = MnO + O$, and

(2) $2\,FeO + O = Fe_2O_3$; or as one equation

(3) $MnO_2 + 2\,FeSO_4 + 2\,H_2SO_4 = MnSO_4 + Fe_2(SO_4)_3 + 2\,H_2O$.

The excess of $FeSO_4$ is titrated with standard permanganate or dichromate solution. As this is the first example of a volumetric method involving a back titration, an example will be given.

Suppose 100 cc. of the standard ferrous ammonium sulphate were taken, and suppose 25·2 cc. of permanganate solution have to be added to oxidise the excess of the ferrous sulphate after the reaction with the MnO_2.

The next stage is to titrate the ferrous sulphate solution against the permanganate (or dichromate). Run 20 cc. of the ferrous sulphate solution into a beaker ; dilute it to about the same bulk as the assay and titrate it with the permanganate ; calculate the ferrous sulphate value of each cc. of the permanganate solution. Suppose 1 cc. permanganate solution ≡ 1·06 cc. ferrous sulphate solution, then 25·2 cc. permanganate solution ≡ 26·7 cc. ferrous sulphate solution, and consequently, 100 − 26·7 cc. (= 73·3 cc.) of ferrous sulphate solution were used to oxidise the unknown amount of MnO_2. From the reaction equation it follows that each molecule of MnO_2 will oxidise two molecules of FeO to Fe_2O_3, *or*:

1 Mn is equivalent to 2 Fe (in this reaction).

$2 \times 55{\cdot}84$ gms. Fe ≡ 54·93 gms. Mn.

i.e. 111·68 gms. Fe ≡ 54·93 gms. Mn.

The iron (ferrous) content of the ferrous sulphate solution is then calculated from the standardisation figures for the solution, and its manganese equivalent per cc. follows. This equivalent, when multiplied by the volume (net) of the ferrous sulphate solution consumed (here, 73·3 cc.), gives the weight of manganese in the unknown solution.

If the solution used is the ordinary permanganate of which 1 cc. ≡ 0·0006 gm. Mn, the calculation is as follows: The above equivalent is for the reaction $Mn_2O_7 = 2\,MnO + 5\,O$; here we are only reducing $2\,MnO_2$ to 2 MnO, *i.e.* only using 2 O, so that each cc. of ferrous sulphate solution will completely reduce $\frac{5}{2}$ times the amount of Mn (as MnO_2) that it will reduce when the Mn is present as Mn_2O_7, (*i.e.* as in $KMnO_4$). The manganese factor will, therefore, be $0{\cdot}0006 \times \frac{5}{2}$. Whence the amount of manganese present is $73{\cdot}3 \times 0{\cdot}0006 \times \frac{5}{2}$ gms.

It is simpler, perhaps, and possibly more accurate, at least in the case of a steel, to standardise the ferrous sulphate solution against a manganese solution of known strength, *i.e.* a solution of a steel of known manganese content.

2. *Sodium Bismuthate Method.*—This is the best known and most accurate of all methods of estimating manganese. For the estimation of manganese in iron and steel it is the best method by far, but for the estimation of manganese in other substances it has two drawbacks which may render it impracticable. The difficulties are: (1) the solution must contain only nitric and sulphuric acids (the latter is not essential); HCl must be removed completely before the oxidation can be performed; and (2) the amount of manganese must be less than about 0·02 gm. or precipitation of MnO_2 may take place.

Procedure.—The cold solution of manganese, which may contain almost any other metal (except cobalt in appreciable amounts), should have a bulk of not more than 100 cc. and should contain not less than 2 per cent. nor more than 7 per cent. of HNO_3 by volume. To this is added sufficient sodium bismuthate to leave a decided excess of the unused solid compound at the bottom of the beaker or flask. (About 1 gm. usually suffices.) The solid reagent is shaken up with the solution for not more than two minutes, when all the manganese will be completely oxidised to permanganate. The purple solution is then decanted through a prepared asbestos filter, and when the clear solution has run through, the reaction vessel is rinsed out with a cold 2 per cent. solution of HNO_3, the washing with the dilute acid being continued until the liquid in the stem of the funnel shows no sign of pink colour. The filtrate from the excess bismuthate is then immediately titrated with standard ferrous sulphate solution, taking the reduction a cc. or two past the end-point. The reduced solution is then titrated back to a faint pink with standard permanganate solution.

Calculation of Results.—It is necessary to know the permanganate equivalent of the ferrous solution; for this purpose 20 cc. of the ferrous solution are run out of the burette into a beaker, a little dilute HNO_3 is added and the bulk made up approximately to that of the assay, arranging matters so that the concentration of the HNO_3 in the solution is between the limits already mentioned. The ferrous solution is then titrated with the permanganate to faint pink, and the permanganate equivalent of each cc. of ferrous sulphate solution is calculated. The volume of ferrous sulphate solution used for the assay is then worked out in terms of the permanganate solution and the volume of permanganate added for the back titration is deducted from the result. The final "permanganate" volume is multiplied by the manganese factor of the solution (0·0006 gm. Mn per cc.) which gives the weight of manganese in the assay. The actual standardisation of the solutions is carried out by titrating the ferrous solution against 0·2 gm. of potassium dichromate, or by carrying out the whole process with a solution of known manganese content, such as a weighed amount of pure manganous sulphate or a steel the manganese content of which is accurately known.

Note 1.—Nitric acid is necessary for the oxidation with bismuthate; if the permanganate colour refuses to develop in a minute or so after

adding the reagent, the first thing to be suspected of being wrong is the HNO_3 concentration, and a cc. or two of strong acid should be added to the solution. The total volume of HNO_3 should, however, not exceed about 7 per cent., or the acid will tend to oxidise the ferrous sulphate. For this reason it is advisable to carry through the titration as rapidly as possible.

Note 2.—In the case of the estimation of manganese in a steel or iron sample, which will invariably contain more or less carbon, it is necessary to remove this before the final oxidation. For this purpose, proceed as follows: The *hot* HNO_3 solution, boiled free from nitrous fumes, is treated with small doses of the bismuthate until either some solid remains or a permanent pink colour persists. This treatment converts carbon into carbon dioxide. The solution must then be reduced to dissolve excess bismuthate and MnO_2, which is effected by treating it with a crystal of ferrous sulphate, or of thiosulphate or sulphite, the latter being preferred. When reduced, the solution is thoroughly boiled under cover to expel SO_2 and nitrous gases before being cooled for the final assay oxidation, which is carried out as described.

Note 3.—Chromium and vanadium interfere unless great care is taken, as they are also oxidised by bismuthate, albeit slowly in the cold. For further details of the procedure in the presence of these metals refer to Steel Analysis.

Note 4.—Cobalt interferes also, partly because it also tends to become oxidised, but also on account of its pink colour in dilute solution, which prevents the operator from detecting the first faint trace of excess permanganate.

Note 5.—It is desirable to carry out all the operations as rapidly as possible as the permanganate has a decided tendency to be reduced in concentrated solution to MnO_2. Do not, therefore, exceed the time limit of two minutes' contact with the bismuthate, arrange the filter to run as rapidly as possible, and titrate immediately the washing is completed. The back titration also should not be delayed, owing to the possibility of oxidation of the Fe^{++} by the HNO_3 present.

Note 6.—It is necessary to use an asbestos pulp filter owing to the fact that permanganate solution attacks paper, being reduced to MnO_2 in the process.

3. *Volhard's Method.*—This method is suitable for the estimation of manganese in larger quantities than can be titrated by the bismuthate method. It has been much criticised as giving inaccurate results, and is in consequence not very much used by English chemists ; in Germany, however, it is almost the standard method of estimating manganese, and since it depends upon a somewhat peculiar reaction and is capable of yielding perfectly correct results if the manipulation is conducted correctly, the process will be described here, especially as it involves some interesting manipulation.

The underlying reaction is:

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

whereby it will be seen that manganous manganese is capable of reducing the permanganic ion. Only sulphuric acid and sulphates may be present.

Volhard's method being particularly applicable to the estimation of manganese in such alloys as *ferro-manganese* (80 per cent. Mn), and *spiegeleisen*, and as in both cases the other main constituent of the material is iron, the method is usually considered to involve the separation of this latter metal. Similar remarks may be applied to manganese ores. The theory of the separation will be more fully discussed under the Separation of Group III metals from those of Group IV (*q.v.*); here, only the bare outline of the method will be given.

Procedure.—2 gms. of spiegeleisen or 1 gm. of ferro-manganese are weighed into a 400 cc. beaker and dissolved in 20 cc. HNO_3 + 10 cc. HCl. When the reaction is complete, 5 cc. of H_2SO_4 are added and the solution evaporated to fumes to expel the unwanted acids. The solution is then diluted after cooling, and boiled, if necessary, until the dehydrated sulphates are dissolved. It is then rinsed out into a 500 cc. graduated flask and diluted to about 300 or 350 cc. with cold water.

In the mean time an emulsion of $Zn(OH)_2$ is prepared by dissolving about 10 gms. of pure zinc sulphate in 250 cc. of cold water and adding KOH until the mixture reacts *just* alkaline to methyl orange. This emulsion is added in small quantities to the manganese solution with constant shaking and swirling of the flask until all the iron is precipitated as hydroxide and a slight excess of the white zinc precipitate is seen to remain mixed with the brown ferric precipitate. The solution is allowed to stand for a few minutes with the mixture still in slow swirling movement, and the precipitate examined carefully to see whether the excess of zinc hydroxide still remains. If not, more of the reagent is added, repeating if necessary until excess zinc oxide is noticeable mixed with the precipitate; but it is important to have no more than the barest excess of reagent, or the results will be low, owing to the precipitation of some of the manganese with the iron.

The solution is made up to the mark, with 2–3 cc. over; the latter is to allow for the volume of the precipitate. (*Note.*—2 cc. may seem too little considering the *apparent* bulk in the flask, but the actual bulk is quite small, as may be proved by pouring the precipitate on to a large filter, draining completely, and finally drying for a day or two in the air oven at 100° C.) The whole is then well mixed by shaking, and poured out into a tall 500 cc. measuring cylinder; do *not* wash the precipitate out. The precipitate and solution are allowed to stand for an hour or so in the cylinder, or until the precipitate has settled out well. It pays to give this part of the process plenty of time, as good settling saves a filtration; the precipitate may be considered as sufficiently settled when the upper surface of the iron precipitate has sunk to the 200 cc. mark, and the upper liquid is quite clear and colourless.

An aliquot part of the solution is now transferred to a 400 cc. Phillip's beaker. This is effected by attaching a length of rubber tubing to a large pipette, the lower end of which is dipped into the clear solution (taking care not to disturb the precipitate; on no account relax the suction until the pipette is clear of the cylinder), and applying suction until the pipette is full. The rubber tube is then clipped by the thumb and finger and the clear solution removed to the selected beaker.

100 cc., $= \frac{1}{5}$ of the solution, $\equiv$ 0·2 gm. of ferro-manganese or 0·4 gm.

of spiegeleisen. Of course, more or less than 100 cc. may be taken, the aim of the operator being to obtain not more than about 0·15 gm. of manganese in the assay. A small equal aliquot part is then pipetted out in the same manner and placed in a second beaker, the idea being to have two solutions for titration, the first for an approximate run in and the second for an accurate determination.

The two assays are diluted to about 200 cc. and heated to boiling on the hotplate, covering them with glasses and placing one or two small pieces of broken porcelain in each to prevent bumping during the later boiling, when the precipitate has formed. 3 4 cc. of HNO_3 are added to each assay and the assays are titrated hot with the standard permanganate solution. To the first beaker the permanganate is added in quantities of about 1 cc. at a time, shaking constantly and vigorously. After each addition of the permanganate the assay is examined against a white surface, looking through the liquid near the surface ; the heavy black precipitate of MnO_2 settles well and the least trace of excess of $KMnO_4$ is readily detected. Having established the end-point to within a cc., the same operation is carried out on the second solution, except that this time, knowing exactly how much permanganate may be added safely, this amount should be run in at once and the last cc. of the titration made drop by drop. When a permanent pink colour is attained, the contents of the beaker are again brought just up to the boiling-point and the solution is re-examined for excess of permanganate, and if the pink colour is found to have disappeared, another drop of permanganate should be added, continuing the process until a pink colour remains for a minute or so in the almost boiling solution. Avoid actual boiling, as this decomposes permanganate slowly and may lead to a false end-point.

Standardising.—The usual permanganate solution may be used, though a more dilute solution is sometimes advised. Standardise against sodium oxalate in hot solution of about the same bulk as the assay (acidified with sulphuric acid, of course). Use 0·5 gm. of the oxalate for the ordinary solution ; this will give a sufficiently large burette reading.

The manganese factor may also be calculated from the iron factor of the solution, bearing in mind the fact that the two reactions differ in the degree to which the permanganate is reduced. The equations are:

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

and: $2\,KMnO_4 + 10\,FeSO_4 + 8\,H_2SO_4 = K_2SO_4 + 2\,MnSO_4 + 5\,Fe_2(SO_4)_3 + 8\,H_2O,$

i.e. in Volhard's method 2 $KMnO_4$ oxidise 3 MnO, whereas in the iron titration the same amount of $KMnO_4$ oxidises 10 Fe ; whence: 3 Mn ≡ 10 Fe, or

558·4 parts of Fe ≡ 164·8 parts of Mn.
i.e. 1 part of Fe ≡ 0·295 part of Mn.

To obtain the manganese factor from the iron factor multiply by 0·295. Note, however, that this is a different reaction from that used in the

bismuthate method, and *this factor will not serve to standardise the bismuthate permanganate.*

The method may be used for the estimation of manganese in a manganese ore provided that the solution is treated so that only H_2SO_4 is present at the time of the treatment with zinc hydroxide ; the HNO_3 added later is to acidify the neutral solution and to make the MnO_2 precipitate settle better.

Note 1.—The zinc hydroxide acts by removing the acid formed by the hydrolysis of the ferric salt, thereby permitting the precipitation of the iron to proceed to completion in a neutral solution. The equation explains this:

$$Fe_2(SO_4)_3 + 6\,HOH \rightleftarrows \underset{\text{precipitate}}{2\,Fe(OH)_3} + 3\,H_2SO_4$$

$$H_2SO_4 + Zn(OH)_2 = ZnSO_4 + 2\,H_2O.$$

Note 2.—The rubber tubing attached to the pipette is a useful device as it enables the operator to watch the open end of the pipette while applying suction.

4. *Estimation of Manganese by Oxidation to MnO_4^- with $(NH_4)_2S_2O_8$ and Titration with an Arsenite.*—If the substance for analysis is an alloy, such as iron or steel, or a manganese " bronze," dissolve 1 gm. (less if the manganese exceeds 1 per cent. of the whole) in 20 cc. of HNO_3 (sp. gr. 1·2) and boil to expel nitrous fumes. Dilute to 100 cc. If a mixture of salts, separate the manganese by any of the methods given under Separations, preferably as MnS (or $MnO_2 . H_2O$), and dissolve it in 15 cc. of 1·2 sp. gr. HNO_3 after boiling off nitrous fumes if necessary.

To the nitric acid solution add about 2 gms. of solid ammonium persulphate and 10 cc. of $AgNO_3$ solution (5 gms. per litre). Place the beaker or flask on the edge of the hotplate and warm gently until the MnO_4^- colour is fully developed and oxygen is being evolved freely. Cool under the tap and titrate with a solution made by dissolving 2 gms. of As_4O_6 in a little NaOH, acidifying with H_2SO_4 and diluting to 1,000 cc. Standardise this solution against a solution of a standard steel of known manganese content (for a steel or iron), or against a known weight of pure $MnSO_4$ (for a salt mixture).

It is unfortunate that the end-point is not very definite in some cases, but with practice good results are obtainable. Traces of AgCl in the solution may be ignored. It is important that the standard should be titrated to the same end colour as the assay ; the titrated standard should be set on the titration bench as a guide to the eye in estimating the end-points of the other assays.

This method is a fairly rapid routine method for the estimation of manganese in iron and steel ; it has no advantages over the bismuthate method, however, and the indefinite end-point is a decided disadvantage.

C. Colorimetric Methods.—Advantage is taken of the fact that manganese can be oxidised to the deeply coloured permanganic state by several reagents, chief of which are $(NH_4)_2S_2O_8 + AgNO_3$ (catalyst), and solid PbO_2, both of which operate in warm solution, and sodium bismuthate, which oxidises in the cold. The colour produced is then compared with that of a standard produced in the same manner and

with the same reagent. The method is not applicable to amounts of manganese exceeding about 0·0015 gm. HCl should of course always be absent on account of its action on MnO_4^- ; $SO_4^=$ is allowable, and HNO_3 is essential.

Procedure.—The solution, containing not more than the prescribed amount of manganese, is brought to low bulk (10–15 cc.), transferred to a test-tube, and as much ammonium persulphate as will cover a sixpence is added, followed by 10 cc. of $AgNO_3$ solution (1·5 gms. per 1,000 cc.) ; the standard, a solution of pure $MnSO_4$ of known strength, to which 5 cc. of 1·2 sp. gr. HNO_3 have been added, is treated similarly. Or, in the case of a steel, a similar weight of a steel of known manganese content should be used.

The two test-tubes are heated in a beaker of water which is brought to the boil on the hotplate, the heating being continued until the characteristic colour of MnO_4^- develops and oxygen is coming off freely. The solutions are then cooled under the tap and transferred to Eggerz comparison tubes. The standard is made up to a definite bulk with distilled water, arranging matters so that there is a definite concentration of manganese per cc., *e.g.* if the standard $MnSO_4$ solution contains 1 gm. of Mn per litre, and 10 cc. have been taken for the comparison, the standard contains 0·01 gm. of Mn dissolved in 15–20 cc. of liquid, depending on the amount of water used for rinsing out the test tube and the amount of evaporation during the heating. The standard is made up to 20 cc. exactly, when each cc. will contain 0·0005 gm. Mn.

The assay tube is then diluted with water, added from a burette or separating funnel, until the solutions appear of the same depth of colour when viewed against a translucent white surface. When the colours match, the concentrations of manganese are equal in the two tubes, and, knowing that the assay solution contains 0·0005 gm. Mn per cc., the total manganese content is found by multiplying this factor by the volume of the diluted solution. See fig. 8, p. 68.

Note 1.—Do not compare in direct sunlight. A good background for the comparison tubes is made by wetting a piece of filter paper and applying it to a window-pane.

Note 2.—The tubes should be viewed both ways, *i.e.* first with the standard and then with the assay tube on the right. As a rule the eyes have unequal colour sensitiveness ; if this is the case, the end-point is taken when the standard appears just darker when on the right and just lighter on the left (or *vice versa*).

Note 3.—The foregoing volumes are not intended to be taken as standard. The volume of the standard manganese solution taken will depend upon the amount of manganese in the assay solution; always aiming at using slightly less standard than assay (as to weight of manganese), so that the assay tube may be diluted. Of course it does not really matter which tube is diluted, but it is more convenient for calculation if the concentration of the manganese in the standard tube can be arranged so that it is some simple figure, such as that given.

Note 4.—If the original solution contains Cl^-, add 1 cc. (or a sufficient excess) of H_2SO_4 and evaporate to fumes ; but remember to add the nitric acid, which is essential to the reaction.

Note 5.—The estimation of manganese in a steel is a matter of great ease when this method is used, and it is a useful check on the reliability of the results obtained by other methods to run a colour manganese estimation along with the colour carbon test. As standard take a steel of known manganese content ; the slight colour of the ferric nitrate makes no difference to the results. Nickel, cobalt and chromium in the steel interfere by reason of their coloured solutions. A rough approximation to the colour due to traces of $CrO_4^{=}$ may be obtained by adding dichromate to the standard by drops from a burette until the yellowish tints of the solutions match. The red-purple of the MnO_4^- may then be compared, but the results are not very reliable.

Note 6.—Instead of ammonium persulphate and silver nitrate, a pinch of solid PbO_2 may be used for the oxidation (always in the presence of HNO_3). The PbO_2 being heavy, settles completely and rapidly, and the solution may be decanted without any need for filtration.

Bismuthate can also be used, and is even to be preferred to either of the foregoing oxidants as it oxidises in the cold, thereby saving time. Like PbO_2 it permits of complete decantation. The persulphate method is described because it is the usual standard method.

ZINC.

Zinc differs from the other metals of its group in that it has only one oxide of importance analytically. This oxide is usually basic, yielding salts with the acids, but in the presence of the strong bases, ZnO functions as an acid, forming " zincates," which are soluble in water. $Zn(OH)_2$ is thrown down as a white precipitate in the absence of ammonium salts by ammonia and the alkalies, but the hydroxide readily dissolves in excess. In this it resembles aluminium, but aluminium is only slightly soluble in excess of ammonia.

Zinc is usually determined gravimetrically, but there is a volumetric method which gives good results in practised hands, provided conditions are rigidly controlled.

Estimation of Zinc.

A. Gravimetric Methods—1. *As Oxide.*—Small quantities of zinc, *e.g.* up to 0·01 gm., may be precipitated as ZnS (in ammoniacal solution, provided nickel, cobalt and manganese are absent) ; the precipitate is filtered off and washed, and finally ignited with free access of air to ZnO. It is impossible to roast the sulphide completely to oxide, and usually from 2 to 5 per cent. of the sulphur remains unoxidised. This, however, only represents a weight of 0·0005 gm. at the worst, making an actual error of no more than 0·00025 gm. or 0·025 per cent. on a 1 gm. sample (since O = ½ S).

The method serves to estimate small quantities of zinc left over after the separation of the other metals in the analysis of some alloys, such as gunmetals.

Note.—ZnS, precipitated from alkaline solution, passes back into the " sol " state as soon as the coagulating electrolyte is washed out of the precipitate and paper ; usually, therefore, only one wash is safe. This does not greatly matter in the case of the analysis of an alloy, as the

metals of the later groups are very rarely constituents of ordinary alloys (though barium, calcium, magnesium and sodium are sometimes used). There is, therefore, nothing but ammonium salts to be washed out of the precipitate, and as these are all volatile, the residue will contain nothing but the zinc. The student is warned, however, that some zinc may be lost if the precipitate contains much mechanically held Cl^-; hence one washing is advised.

2. *As Pyrophosphate.*—At least one writer characterises this method as the most accurate one for the estimation of zinc, and the method is one to be thoroughly recommended, but there is the invariable difficulty inherent to phosphate precipitations, that all the metallic phosphates, except those of the alkalis, are insoluble in water, and it is therefore necessary to effect a complete separation of the metal to be determined before converting it into phosphate for weighing. In the case of zinc, the metal is separated as ZnS (but see Separations), and this, after filtering and washing, is dissolved in a little dilute HCl; H_2S is boiled out of the solution, a few drops of methyl orange are added and the solution carefully neutralised with dilute ammonia in a bulk of about 300 cc. Meanwhile, a solution of $(NH_4)_2HPO_4$ is prepared by dissolving 8–10 gms. of the salt in 100 cc. of water, adding a drop of phenolphthalein, and then NH_4OH until a faint pink colour is produced. This converts any $NH_4H_2PO_4$ into the di-ammonium compound which is neutral to phenolphthalein. The zinc solution is brought to the boil on the hot-plate and the phosphate added in a steady stream, stirring constantly, until an excess has been added and no further precipitate is thrown down when a drop or two of the phosphate is added to the clear liquid over the rapidly settling precipitate. The solution is digested on the hotplate with occasional stirring until the precipitate which at first separates in a bulky, gelatinous condition, has been converted into the compact, crystalline form. The precipitate is allowed to settle and the solution decanted through a weighed Gooch crucible (asbestos pad), washing with hot water containing 1 per cent. ammonium phosphate until the filtrate runs free from Cl^-, then four or five times with very small quantities of cold water, sucking the crucible dry each time.

The crucible and contents are dried carefully in the mouth of the muffle, guarding against spitting and loss of precipitate; the crucible is gradually worked further and further back into the muffle until it is at the full temperature of the furnace (at least 900° C.). The residue should be perfectly white. (*Note* here, that if the phosphate is filtered off on paper, as may be done if desired, the last traces of the carbon require prolonged heating to consume them, and the precipitate may be slightly discoloured.) The zinc is weighed as $Zn_2P_2O_7$.

3. *As Sulphide.*—Weiss has shown that ZnS may be quantitatively precipitated from a dilute H_2SO_4 solution containing not more than 500 mgms. H_2SO_4 per 100 cc. Under these conditions the sulphides of the other metals of the same group are not thrown down. Cl^- and NO_3^- should be absent.

The procedure to be adopted depends upon the previous history of the solution; three cases will be considered.

Case 1.—The solution is the ordinary filtrate from Group III. It will be ammoniacal and will certainly contain Cl^-, probably also NO_3^-,

and large amounts of ammonium salts, apart from (possibly) nickel, cobalt, manganese and the metals of Groups V and VI. In this case, H_2S is passed to saturation at once, the precipitate allowed to settle, and filtered off. It is washed *once* only if the metals of Groups V and VI are known to be absent or if they are not to be estimated. If they are present and are to be estimated, the precipitate should be washed twice with cold dilute NH_4Cl solution, through which H_2S has been bubbled for five minutes. The filter and precipitate are transferred back to the original beaker and extracted with cold 3 per cent. HCl. Any dark residue that remains is treated for nickel and cobalt. The filtrate is diluted and H_2S boiled off; the solution is made ammoniacal, ignoring any precipitate unless there is much magnesium present, in which case $Mg(OH)_2$ may be thrown down. The remedy is to add NH_4Cl. The solution is again saturated with H_2S.

The precipitate is filtered off and washed twice as before, combining the two filtrates for the estimation of calcium, barium, magnesium, etc. The precipitate is again dissolved in a little dil. H_2SO_4, the solution neutralised with ammonia and made just acid with H_2SO_4 from a burette or dropping funnel, so that there are 400–500 mgms. of the acid in each 100 cc. of solution.

Note that the acid liberated in the reaction:

$$\underset{64}{ZnSO_4} + H_2S = ZnS + \underset{98}{H_2SO_4}$$

must be allowed for; 1·5 mgms. H_2SO_4 for every 1 mgm. Zn is sufficiently accurate.

Example.—A sample contains roughly 30 per cent. Zn and 1 gm. of it was taken, *e.g.* in the analysis of a brass.

i.e. 0·3 gm. or 300 mgms. of Zn are present.

This will yield 1·5 × 300 mgms. of H_2SO_4 on saturating with H_2S, or 450 mgms. Taking 10 per cent. acid for the process, each cc. contains 0·1 cc. H_2SO_4 or (about) 184 mgms. H_2SO_4.

If, then, 3 cc. excess acid have been added, the total acid will be 450 + (3 × 184) mgms., or 1,000 mgms. The safe upper limit of acid concentration being 500 mgms. per 100 cc., a bulk of at least 200 cc. is required for complete precipitation.

Case 2.—The metals of Groups I and II have been removed by HCl and H_2S, leaving metals of Groups III to VI still in the solution.

Excess of H_2SO_4 is added, *i.e.* sufficient to combine with all the metals present and leave 2–3 cc. over. (With a 1 gm. sample, about 5 cc. is correct.) The solution is evaporated to copious fumes, taking particular care to avoid spitting when the bulky salts begin to separate, then cooled completely and 150 cc. of water added, followed by boiling until the solution is quite clear. This process may take some time, especially if there is much iron present, as the anhydrous sulphates are only very slightly soluble. If barium or much calcium and strontium are present they will remain as a fine white precipitate which cannot fail to be recognised by the way in which it settles to the centre of the beaker when the liquid is swirled. If such a precipitate remains after

half an hour's boiling, it is filtered off on a close-textured pulp and the filtrate treated as described under Case 1 for the precipitation of the zinc. The metals of Group III do not interfere.

Case 3.—Zinc only is required ; *e.g.* in evaluating a zinc ore. When the solution has been prepared and the acidity adjusted properly, the liquid is cooled to room temperature (the precipitation is incomplete above 50° C. and the precipitate is more compact when thrown down from a cold solution), and H_2S is passed in a *rapid* stream (8-10 bubbles per second ; *i.e.* faster than can be counted). It is an advantage to admit the gas by means of a tube that has been drawn out at the tip and bent over at right angles. This is then arranged so that the gas enters tangentially to the side of the beaker, producing a slow rotation of the solution, and thus completing the precipitation in shorter time. About 40 minutes will suffice for the complete precipitation of 1 gm. of zinc. The precipitate is filtered off on to an asbestos Gooch and washed with hot water. The crucible and contents are dried on the corner of the hotplate and a pinch of pure sulphur stirred into the precipitate with a fine platinum wire. The crucible is placed inside a larger crucible to shield its contents from direct heat, and a stream of dry hydrogen is passed into the inner Gooch by means of a bent hard glass tube. A wash bottle containing strong H_2SO_4 placed in series with the hydrogen supply serves at once to dry the gas and enable the speed of flow to be estimated ; 3-4 bubbles per second is correct. The outer crucible is then heated over an ordinary Bunsen flame until the sulphur added has been distilled off and burnt. When the flame of burning sulphur fails, the burner is removed and the flow of the hydrogen increased to 8 bubbles per second, maintaining this rate of flow until the crucible is quite cold. The zinc is weighed as ZnS.

If preferred, the zinc can be weighed as $ZnSO_4$. The final precipitate of ZnS is placed in a tared crucible and the paper charred off. The crucible is cooled, and 4 cc. of 1 : 1 H_2SO_4 per gm. of Zn added. The solution is evaporated cautiously to fumes on the hotplate and the crucible set in the mouth of the muffle until fumes cease to be evolved. Then it is gradually introduced into the muffle, finishing at a dull red (not more). The $ZnSO_4$ is weighed.

See also p. 310 for other acid solution methods.

B. Electrolytic Method.—This is an excellent method for use in some circumstances. It is possible, for instance, to make the complete analysis of a nickel silver sample by electrolysis, plating copper, nickel and zinc successively on the kathode. The zinc is separated by any method, but preferably as sulphide from acid solution; the sulphide is dissolved in HCl, and after adding 5 cc. of H_2SO_4 the solution is evaporated to fumes. 70 cc. of hot water are added and the solution boiled until the $ZnSO_4$ is dissolved, then neutralised with NaOH, using methyl orange as indicator, and finally just acidified with acetic acid. Five grams of sodium acetate are added and the solution cooled completely, then made up to 100-120 cc. and electrolysed, using a rotating kathode and 0·5 amp. at 5 volts.

Alternatively, a strongly alkaline solution (20 cc. excess N NaOH per 100 cc.), free from NH_4^+, may be electrolysed, using a current of 3 to 4 ampères at 5 to 6 volts, and depositing the zinc on a rapidly rotating gauze kathode.

Note.—Zinc should not be deposited directly upon platinum. If a platinum kathode is used, a thin film of copper should first be deposited.

C. Volumetric Method.—This is probably the best general method for the estimation of zinc in quantities of more than about 0·05 gm. The titration reagent is potassium ferrocyanide, which throws down zinc ferrocyanide as a white (pale blue or green) precipitate from hot acid solutions. Metals which form insoluble or coloured ferrocyanides must be absent ; these are : Pb, Al, Fe, Mn, Cu, Sb and Cd ; oxidising agents must also be absent.

Procedure.—It is always best to separate the zinc as sulphide first, from acid solution if manganese, nickel or cobalt are present. This is not, however, absolutely necessary, provided that none of the interfering metals is present in the solution and there is not much HNO_3 present. If the separation of iron, etc. has been carefully performed, the solution should barely smell of ammonia ; it is diluted to 250 cc. and brought to the boil ; methyl orange is added and then HCl until neutral, then 3 per cent. excess (7·5 cc. in this case). A few drops, 4–6, of ammonium sulphide are then added to the hot solution, which reduces any traces of NO_3^- and precipitates copper, lead, antimony and cadmium sulphides if present. The solution should now be at 75°–80° C.

Titration.—Reserve about one-quarter of the solution in a small beaker, placing it under a glass cover on the corner of the hotplate. Run the standard ferrocyanide solution into the main solution from a burette in a fine stream and with constant stirring. A voluminous pale blue precipitate is thrown down, which, when the ferrocyanide is in excess, changes to nearly white, and with experience the change may be taken as a warning of the approaching end-point. It is, however, not altogether to be relied upon, firstly because the change is very abrupt, and secondly because it is often obscured by traces of Fe^{+++} in the assay, which is naturally tinged a faint blue thereby, and this colour will not fade. It is, therefore, necessary to use an outside spot-indicator consisting of a 10 per cent. solution of uranium nitrate or acetate, which gives a deep brown colour when the ferrocyanide is in excess.

Add the ferrocyanide in 5 cc. quantities until one drop of the assay solution yields the brown coloration. At this point quickly add the reserved portion of the solution, noting the volume of ferrocyanide already added. Suppose this to be V cc. Without rinsing out the beaker that contained the reserved portion, run in a further quantity of ferrocyanide amounting to $\frac{1}{4}(V - 5)$ cc. (Note, $V - 5$ cc. was insufficient ; V cc. was in excess.) Test on the spot plate ; no coloration should be observed. It is now known that the end-point will be reached with less than $5 - \frac{5}{4}$ cc., say with 3·5 cc.

From this point proceed cautiously, adding the reagent from the burette at the rate of 4–5 drops at a time until the brown coloration is again obtained. Now rinse out the small beaker with hot water and finish the titration drop by drop, stopping at the first sign of a brown tinge on the spotplate. Stir vigorously once more and again test the solution on the spotplate. This is necessary as sometimes the burette reagent gets in pockets in the precipitate and a false end-point may be obtained.

Note 1.—It is important to keep a constant bulk for the titrations, at least throughout a batch, and, of course, the standard must be similar. The reason for this is that there is a distinct "blank" depending upon the degree of dilution, and it should be the aim of the operator to cancel this out against the blank in the standard as far as possible. It is sufficiently accurate to use the same type of beaker for all the assays, a 400 or 600 cc. tall beaker being suitable. Mark the 250 cc. line on the outside with a grease pencil and always work to this bulk.

Note 2.—Oxidising agents decompose ferrocyanides in hot solution; HCN may be detected by smell if HNO_3 is added to a finished assay.

Note 3.—Back titration does not give accurate results in this assay; it is therefore necessary to adopt the device of reserving part of the solution, since the titration must be carried out quickly or the temperature will fall below 75° C.

Note 4.—Below 75° C. a secondary reaction begins to interfere, and above 80° C. there is danger of decomposition of the reagent. Accurate temperature control is therefore necessary. The student is advised to use a thermometer with the bulb protected by a piece of rubber tubing as a stirring rod. If necessary the solution may be warmed up on the hotplate during the course of the titration. When above 75° C. the precipitate is $Zn_3K_2[Fe(CN)_6]_2$.

Note 5.—With pure zinc solutions the procedure is much simpler, and this is why the operator is advised to separate the zinc first. If the zinc is separated as ZnS, this is rinsed back into the precipitation beaker and dissolved in 10 cc. of HCl and a little water; H_2S need not be boiled off. If there is much zinc, more HCl will have to be taken, and if any doubt as to the exact degree of acidity exists, the solution should be neutralised with ammonia and re-acidified with HCl to 3 per cent. excess, using a single drop of methyl orange as indicator.

In a solution containing nothing but zinc the colour change usually works well and the titration can be carried out much more quickly and confidently.

The titration can also be carried out in alkaline solution. In this case, ferric chloride and citric acid are added to the assay (the latter to keep the iron from being precipitated when the solution is made alkaline), and glacial acetic acid is used on the spot plate. The solution is made alkaline with ammonia and ferrocyanide is added until a drop gives a blue colour on the spot plate, the blue being due to the formation of ferric ferrocyanide when the acetic acid neutralises the ammonia, no colour being obtainable in the assay solution owing to the excess of the latter. The method has no advantages over the titration in acid solution, and the writer has found it give very erratic results without any apparent reason, though it is useful in certain cases, notably the determination of zinc in its blende ores. The precipitate is of a different composition from that obtained in acid solution, and the factor of the ferrocyanide solution is therefore also different.

Standardisation.—Weigh out sawings of pure zinc to an amount roughly equal to that of the zinc in the assay. Dissolve in HCl, neutralise, and re-acidify to the standard excess with HCl. Titrate, observing exactly the same precautions as were used in the case of the assays.

Ferrocyanide Solution.—A solution of 43·2 gms. crystalline ferrocyanide in 1,000 cc. of water has a factor approximating to 0·01 gm. Zn per cc.

Indicator.—Ten per cent. solution of uranium nitrate or acetate.

GROUP V.

Barium, Strontium, Calcium, (Magnesium).

Calcium and barium are the only members of this group frequently met with analytically. The Alkaline Earths may practically be ruled out of consideration as far as alloys are concerned, but calcium is an almost invariable constituent of minerals, ores and technical by-products such as slags. It is an essential constituent of cement, frequently of glass, and is almost always found dissolved in water. Barium is important not so much as a constituent of ores or commercial products as on account of its very " insoluble " sulphate, which is so frequently required for the estimation of sulphur and its compounds.

BARIUM.

A. Gravimetric Methods—1. *As $BaSO_4$.*—Barium is almost invariably estimated as $BaSO_4$. On the addition of sulphuric acid or a soluble sulphate to a solution of a barium salt slightly acidified with HCl (not HNO_3) the barium is thrown down as $BaSO_4$ in the form of a finely crystalline white powder. Owing to the precipitate being so finely divided, the precipitation is best conducted in hot, dilute solution and the separating sulphate digested for some time at or near the boiling-point before filtering, in order to obtain the crystals as coarse as possible (see Theory) ; also, in this case, because freshly precipitated solutions show supersaturation phenomena to a marked degree.

After digestion, filter off upon a close paper (No. 40), or better, on a compact paper pulp, washing with hot water until the runnings show no reaction with $AgNO_3$. (*Note.*—The precipitate tends to creep.) Transfer paper and precipitate to a crucible (platinum, silica or porcelain) and after drying, char off the paper and ignite at redness for ten minutes, taking care that there is an ample supply of air, or some $BaSO_4$ may be reduced to BaS.

2. *As Barium Chromate.*—See under Separations. If barium has been separated as chromate it will save time to estimate it in that form.

The $BaCrO_4$ in the Gooch crucible is ignited at dull redness and weighed as $BaCrO_4$. If a green tinge develops, it is an indication that some CrO_3 has become reduced to Cr_2O_3. This will not take place if an asbestos pad is used in the Gooch

B. Volumetric Estimation.—If desired, the washed precipitate of $BaCrO_4$ can be thrown, filter and all, into a tall 400 beaker, acidified with sufficient H_2SO_4 to decompose the chromate and leave a small excess (the process of decomposition is easily watched), and the whole titrated with standard ferrous sulphate solution. Or, if preferred, excess of ferrous sulphate (solid or standard solution) may be added and the excess titrated with permanganate or dichromate.

Example.—The precipitate is transferred to a beaker containing 50 cc. of standard ferrous sulphate solution, of which 1 cc. is equivalent to 0·01 gm. Cr (as CrO_3). The back titration requires, say, 12·5 cc. of permanganate, and 10 cc. of permanganate oxidise 11·4 cc. of the ferrous solution as found by a separate titration.

Then, 1 cc. $KMnO_4 \equiv 1{\cdot}14$ cc. ferrous sulphate solution,

and 12·5 cc. ,, $\equiv 14{\cdot}25$ cc. ,, ,,

Whence:

50 — 14·25 cc., = 35·75 cc., ferrous sulphate solution have been used in reducing the CrO_3.

$\equiv 35{\cdot}75 \times 0{\cdot}01$ gm. Cr.

$\equiv \frac{35{\cdot}75 \times 0{\cdot}01 \times 137{\cdot}4}{52}$ gm. Ba (since Ba : Cr = 137·4 : 52 in $BaCrO_4$).

STRONTIUM.

This metal is estimated as $SrSO_4$ in a manner similar to that described under Barium, except that the solution should contain 50 per cent. of alcohol, and the washing should be conducted with the 1 : 1 water-alcohol mixture. The precipitate is allowed several hours in which to separate out.

Strontium may also be estimated as $SrCO_3$ by precipitation with ammonia and ammonium carbonate from a solution which contains no other metal but strontium. The carbonate is estimated gravimetrically as $SrCO_3$ after ignition at dull redness (*not more*), or volumetrically by throwing the washed precipitate into an excess of standard HCl and titrating the unneutralised acid with standard alkali. Either N or $\frac{N}{10}$ solutions are used, according to the amount of strontium present.

Another possible method is to titrate the sulphuric acid solution of washed strontium oxalate in a manner exactly analogous to that described for the titration of Calcium Oxalate (*q.v.*).

CALCIUM.

A. Gravimetric Methods—1. *As CaO.*—Bring the slightly ammoniacal solution, containing 4–5 gms. of ammonium chloride, to boiling and add a slight excess of ammonium oxalate. Digest on the hotplate for an hour, or until the precipitate has settled out well. Decant through a No. 40 paper or a small pulp filter, rinse the precipitate on to the filter and wash with several doses of warm water, keeping the bulk of wash water down as far as possible, since $Ca(COO)_2$ is slightly soluble in water. It is best to use a pulp filter as this requires less wash water,

and every drop is effective. Six or eight washes of 10 cc. each should give a filtrate that will not reduce permanganate solution acidified with sulphuric acid. Transfer paper and precipitate to a crucible (platinum is best), and after charring off the paper, gradually bring the temperature up to full redness (at least 800° C.). Cool in the desiccator and weigh quickly, as CaO absorbs CO_2 and water from the air.

2. *As* $CaSO_4$.—Owing to the fact that CaO increases in weight during the process of weighing, it is preferable to finish the operation by converting the oxide to sulphate and weighing the calcium in this form. Weigh the crucible before placing the precipitate in it. Char the paper and ignite at a low temperature ; cool, and cover the white residue with a few drops of conc. H_2SO_4. Place the crucible upon the hotplate until fuming ceases, then transfer it to the mouth of the muffle, keeping it there until no more fumes are driven off (as a rule, a little more SO_3 comes off here even when the crucible has been heated on the hotplate). Finally push the crucible back into the hotter regions of the muffle, finishing at low red heat. Note that $CaSO_4$ decomposes above 900° C. Weigh as $CaSO_4$.

B. Volumetric Method.—This is the best and most accurate method for the ordinary estimation of calcium in quantities of more than about 0·05 gm.

Precipitate the calcium as oxalate as already described, washing until 10 drops of the filtrate no longer discharge the colour from a test solution made by adding a drop of permanganate solution to 5 cc. of hot water and acidifying with a drop of H_2SO_4 ; but use as little water as possible.

When the filtrate runs free from $(COO)_2^{=}$, open out the paper and rinse the precipitate back into the original beaker with hot water ; do not trouble to remove the last traces of precipitate from the paper. Add 20 cc. of 1 : 1 H_2SO_4 and heat until the oxalate is dissolved ; dilute to 150–200 cc. with hot water and titrate with standard permanganate at a temperature of about 80° C. It will be found that the colour of the MnO_4^- ion is discharged but slowly at first, even though there be a large excess of oxalate present, but when a little Mn^{++} has been formed, the fading is quite rapid, only slowing up again as the end-point is approached. (Mn^{++} acts as a catalyst.) Titrate boldly right up to the end, and when a permanent pink colour has been obtained, transfer the paper and the adherent precipitate to the titration beaker and stir well with a glass rod, breaking up the paper as far as possible. The remaining oxalate will usually discharge the colour of the small excess of permanganate left, and the titration may now be completed a drop at a time until the pink colour is just perceptible.

Standardise the permanganate against pure sodium oxalate acidified with sulphuric acid and dissolved in approximately the same bulk of water.

Note.—The oxalate may be filtered off upon a pulp filter ; this is advisable on account of less wash water being needed. It has the disadvantage, however, of necessitating the paper being in the hot dilute acid during the whole of the titration, and permanganate attacks paper (and all organic matter) with the separation of MnO_2 (black or brown stain). At the dilution recommended, however, there will not be any serious error from this cause provided the permanganate is added rather

slowly, and with constant stirring in order to avoid local concentrations of the reagent which might attack the paper pulp.

MAGNESIUM.

This metal is intermediate between the alkaline earths and the alkalis. It differs from the former by having a very soluble sulphate, and from the latter by the fact that its phosphate and (basic) carbonate are insoluble in water. The carbonate is, however, not precipitated by ammonium carbonate in the presence of ammonium salts, and for this reason magnesium is not thrown down with the alkaline earths in the ordinary qualitative separation.

Quantitatively, magnesium is invariably determined as phosphate (or pyrophosphate) after the alkaline earths have been separated. The previous remarks as to phosphate precipitates apply here also. Magnesium has the additional peculiarity of being uncertain in its reactions as far as precipitation is concerned when there is much NH_4^+ in the solution. For this reason it is usually advisable either to remove ammonium salts or to begin again with a fresh solution, as was advised under Alkaline Earths (see Separations).

Removal of Ammonium Salts.—Transfer the solution to a large porcelain dish and evaporate on the hotplate or over a Rose's burner until salts begin to crystallise out. Add 10–50 cc. conc. HNO_3 (according to the bulk of the crystals). A vigorous reaction will usually set in, so the acid should be added with caution. The reaction is:

$$NH_4Cl + HNO_3 = NH_4NO_3 + HCl$$

and:

$$NH_4NO_3 = N_2O + H_2O, \text{ which are both expelled as gases.}$$

Continue the evaporation, adding more HNO_3 if necessary, and finally take to dryness. Dissolve the residue in HCl, and, if necessary, filter through a small pulp filter ; wash with hot water.

Note.—This procedure is often necessary owing to the reagents attacking the glass vessels in which the manipulations have been hitherto conducted. The separated SiO_2 is discarded.

The magnesium may then be precipitated as phosphate. As this is the characteristic phosphate precipitation, the theory will be discussed at some length.

Theory of Phosphate Precipitations.—Owing to the fact that H_3PO_4 is a tribasic acid, and the three H^+ ions possess widely different dissociation constants (see under Theory), it is only to be expected that phosphate precipitations are liable to complications, often unsuspected by the " follow the book " analyst. The actual equilibria have been very thoroughly investigated by several chemists, and the student will find an excellent summary in Bassett's " Theory of Quantitative Analysis," to which the writer is largely indebted for the following outline. Magnesium is estimated by adding excess of a phosphate in acid solution to the solution of the metal, containing no other metals except potassium and sodium, in the presence of a moderate concentration of NH_4^+, and then rendering the mixture decidedly alkaline with ammonia.

During the process the following equilibria are operative:

1. $(NH_4)_2HPO_4 \rightleftarrows H^+ + NH_4^+ + NH_4PO_4^=$.

2. $MgCl_2 \rightleftarrows Mg^{++} + 2Cl^-$.

Whence:

3. $Mg^{++} + NH_4PO_4^= \rightleftarrows \underset{\text{(dissolved)}}{MgNH_4PO_4} \rightleftarrows \underset{\text{(solid)}}{MgNH_4PO_4}$.

It is the concentration of $NH_4PO_4^=$ ions which regulates the precipitation, and of the several phosphate ions and complexes, this is the one which predominates.

From the above primary equilibria, the following secondary ones may arise:

4. $NH_4PO_4^= \rightleftarrows$ (*a*) $NH_3 + HPO_4^=$
(*b*) $NH_4^+ + PO_4^{\equiv}$.

5. $H^+ + PO_4^{\equiv} \rightleftarrows HPO_4^=$.

6. $NH_4^+ + NH_4PO_4^= \rightleftarrows (NH_4)_2PO_4^-$.

7. $MgNH_4PO_4 \rightleftarrows MgPO_4^- + NH_4^+$ (to a slight degree).

Also, in the presence of ammonium salts (NH_4Cl, for example) and NH_4OH, the following also occur:

8. $NH_4Cl \rightleftarrows NH_4^+ + Cl^-$.

9. $NH_4OH \rightleftarrows$ (*a*) $NH_4^+ + OH^-$
(*b*) $NH_3 + H_2O$.

Of the possible compounds which might arise from these equilibria, the following have low solubility products and may be precipitated:

(*a*)	$MgNH_4PO_4$	depending	upon	the concentration	of $NH_4PO_4^=$
(*b*)	$MgHPO_4$	,,	,,	,,	,, $HPO_4^=$
(*c*)	$Mg_3(PO_4)_2$	,,	,,	,,	,, $PO_4^{\equiv}$
(*d*)	$Mg(OH)_2$	,,	,,	,,	,, OH^- and Mg^{++}
(*e*)	$(NH_4)_3PO_4$	,,	,,	,,	,, NH_4^+ and $PO_4^{\equiv}$

As ordinarily performed, the precipitation produces $MgNH_4PO_4$ almost entirely, from which fact it follows that in solutions of $(NH_4)_2HPO_4$ the main ionisation is $(NH_4)_2HPO_4 = H^+ + NH_4^+ + NH_4PO_4^=$, as already stated. The conditions that cause the above-mentioned "false precipitations" will now be briefly discussed.

1. $HPO_4^=$ is formed from $NH_4PO_4^=$ if the concentration of NH_4^+ is too low. It is for this reason that an ammonium salt (usually NH_4Cl) is added to the solution before making alkaline. $MgHPO_4$ is more soluble than $MgNH_4PO_4$ and its formation is therefore to be avoided, in spite of the fact that both compounds ignite to the pyrophosphate.

This compound also results if the precipitate is washed with pure water, hence the employment of 2·5 per cent. ammonia.

2. The precipitation of $Mg_3(PO_4)_2$ is caused by an undue concentration of $PO_4^{\equiv}$ and/or of $MgPO_4^-$. This is avoided by the presence of excess of NH_4 salts, so that the high concentration of NH_4^+ may drive equilibria 4 (*b*) and 7 from right to left. The separation of this compound is particularly liable to occur at the beginning of the precipitation by ammonia and is an important reason why the addition of the ammonia should be slow and "with stirring." As $[Mg^{++}]$ decreases and $[NH_4^+]$ increases, any tribasic phosphate will pass over into $MgNH_4PO_4$, which is the final stable form, but if ammonia is added rashly, some $Mg_3(PO_4)_2$ may become 'enveloped' and the desired change may not be able to take place. Needless to say, the tribasic phosphate will *not* ignite to the pyrophosphate.

3. $Mg(OH)_2$ has a relatively high solubility product, but may form if $[Mg^{++}]$ is very high and ammonia is added too rapidly. Its separation is prevented by:

(*a*) Adding ammonia slowly, so that the magnesium is thrown down as $MgNH_4PO_4$.

(*b*) Having an adequate concentration of an ammonium salt in the solution, thereby throwing the ionisation of the ammonia back towards the undissociated condition. In the absence of an ammonium salt, the concentration of OH^- in aqueous ammonia is high enough to reach the solubility product of $Mg(OH)_2$ if the concentration of Mg^{++} is high, but in the presence of much NH_4^+ ion, the concentration of OH^- becomes too low to permit of the hydroxide being precipitated.

4. The solubility product $[NH_4^+]\,[(NH_4)_2PO_4^-]$ is relatively small, and if $[NH_4^+]$ is unduly high (*i.e.* too much NH_4Cl or NH_4OH present) $(NH_4)_3PO_4$ may be precipitated. This separation is also obviously favoured by a high concentration of phosphate.

The optimum conditions for the quantitative precipitation of magnesium as $MgNH_4PO_4$ are, therefore:

(*a*) Bulk of 50 cc. per 0·1 gm. MgO (30 cc. per 0·1 gm. Mg.).

(*b*) Add 1 gm. of $(NH_4)_2HPO_4$ for each 0·1 gm. MgO in the solution.

(*c*) Add 5–10 cc. of 2*N* NH_4Cl (= 0·5–1·0 gm. of the solid, approx.).

(*d*) The solution should be sufficiently acid (with HCl) to prevent any permanent precipitate forming when the phosphate is added, before neutralisation.

(*e*) The solution may be hot or cold. (Hot preferred for speed.)

(*f*) Add dilute ammonia drop by drop with constant stirring, until the solution becomes markedly alkaline to litmus or methyl orange.

(*g*) Stand for 6–12 hours at room temperature.

The precipitate is washed with 2·5 per cent. ammonia and ignited to $Mg_2P_2O_7$, which is pure white in colour. If the ignited residue is grey, more heating is required.

GROUP VI.

The Alkali Metals.

The alkali metals consist of *Sodium*, *Potassium* and "*Ammonium.*" There is no group reagent since there are no "insoluble" compounds of these metals in the analytical sense (except, perhaps, the platinichlorides of potassium and ammonium, and $KClO_4$). The alkali metals, therefore, remain in solution when all the other metals have been removed, and special methods have to be adopted for their isolation and estimation.

In the first place, it is almost always the best practice to commence the estimation of the alkali metals in a separate portion of the sample in order to ensure a solution which shall be analytically "clean," uncontaminated by ammonium salts and other reagents, all the impurities in which will become concentrated in this last soluble residue. If this is impracticable for any reason, the ammonium salts should be expelled as explained under Magnesium, the excess phosphate brought down in combination with Fe^{+++} (see Phosphates), and the residue, which contains all the alkalis originally present, redissolved in acid (HCl usually). The solution, after filtering off any SiO_2 derived from the inevitable attack of the reagents previously used upon the vessels employed in the analysis, now contains sodium and potassium only and is weighed in a tared platinum dish as a preliminary to the precipitation of the potassium ; sodium is estimated by difference.

The above outline method will, however, give a solution which is very impure in spite of the greatest care taken ; reagents are never perfectly pure, and even if pure originally, are always liable to take up solids from their containers. One of the worst offenders in this respect is ordinary ammonia solution, which invariably contains SiO_2 (and consequently sodium, and/or potassium, calcium, lead, etc.) from the glass bottles in which it is stored. Another source of trouble is, that if magnesium has to be separated, the excess phosphate is not volatilised by the evaporation treatment with HNO_3. The two chief methods of separation will be considered here at some length. It is assumed that the analyst is endeavouring to isolate the alkalis in a separately weighed portion of the sample.

The separation of Groups I–IV is the same in both cases:

(1) Obtain a solution of the sample by any method ; preferably by solution in HCl. If Group I metals are present, add sufficient HCl to throw them down completely, and then 3 cc. in excess per 100 cc. of solution. Filter and wash.

(2) Saturate with H_2S, first in the cold, slowly bringing the solution to the boil and cooling again, still passing the gas. Allow to settle, filter and wash.

(3) Add a drop of methyl orange (*N.B.*—The indicator is a *sodium* salt !) and make just alkaline with ammonia. Hydroxides of chromium and aluminium will be thrown down plus sulphides of Fe^{++}, Ni, Co, Mn, and Zn, if present. The reaction of the solution may change over to acid during this process ; if it does, add ammonia drop by drop until the mixture reacts just alkaline again. It will not do to add an excess

of ammonia to start with, as $Al(OH)_3$ and $Cr(OH)_3$ are somewhat soluble in this reagent, and it would be too much a matter of guesswork to judge how much acid is going to be liberated by the H_2S. Allow to settle, filter, and wash with very dilute ammonia solution which has been gassed with H_2S for a minute or two. Acidify with HCl and

(4) Boil to expel H_2S. Evaporate to low bulk. The final separations are now to be applied.

(*a*) *The Gooch and Eddy Method.*—This method is probably the best of all. A special reagent is required:

Reagent.—Mix 1,000 cc. distilled water,
1,200 cc. " rectified spirit " (95 per cent. alcohol),
200 cc. ammonia solution (0·880 sp. gr.),

in a large bottle and introduce powdered, pure " ammonium carbonate," shaking occasionally until the liquid mixture is saturated. This reagent precipitates the alkaline earths as normal carbonates, and magnesium as $MgCO_3.(NH_4)_2CO_3.6H_2O$ in crystalline form.

Application.—Treat the concentrated solution (filtrate from Group IV) with conc. HNO_3 in a porcelain dish and evaporate to dryness, adding more HNO_3 to the dry crystals repeatedly, if any reaction takes place. Finally, take quite dry. Extract with HCl and again take dry. Dissolve the crystals in a little distilled water and filter ; the alkalis being all soluble, the insoluble residue, if any, consists of silica, and possibly traces of basic chlorides. In any case it may be discarded. Add an equal volume of 95 per cent. alcohol and then the Gooch and Eddy reagent until no further precipitate is obtained. Stir and shake the solution vigorously for a minute or two to promote crystallisation and subsequent settling, and then set aside in a cool place for an hour. Filter through a pulp filter and wash with Gooch and Eddy reagent until free from Cl^-.

If more than 0·2 gm. of total alkalis is present, the precipitate must be dissolved off the filter with a few cc. of HCl and, after dilution, the precipitation with the Gooch and Eddy reagent must be repeated. The combined filtrates contain all the alkalis.

(*b*) *The Barium Hydroxide Method.*—Extract the dried residue, after expelling ammonium salts, with a little water. To the extract containing, possibly, some insolubles (basic salts, hydroxides) add a saturated solution of $Ba(OH)_2$ until no further precipitation is observed. Boil the mixture and rinse it on to a filter (not a pulp) ; wash the filter well with hot water. Concentrate the filtrate if necessary and add ammonia and ammonium carbonate solution in a bare excess. The first precipitate contains all the magnesium, and the second the excess of barium as carbonate. The other alkaline earths (if present) will also be in the second precipitate as carbonates, though some calcium and strontium may be with the magnesium in the hydroxide precipitate as hydroxides. The final filtrate contains alkalis only.

(*c*) *The Mercuric Oxide Method.*—To the dry residue, containing magnesium and the alkalis only, add 20–30 cc. of HCl and evaporate to dryness. When dry, moisten the residue with a little water and add 1 or 2 gms. of freshly precipitated HgO, $[Hg(OH)_2]$. Mix well

with a glass rod or a small pestle. (It is convenient to perform the evaporation in a porcelain dish ; the residue is more easily got at.) Take dry on the water-bath or the edge of the hotplate, and finally transfer the dish to the hotter parts of the plate. $MgCl_2$ is converted entirely into MgO, the chlorine escaping as $HgCl_2$. (*Note.—The fumes are poisonous!*)

When nearly all the HgO has disappeared, extract the mixture with water and filter. Wash well with hot water.

The insolubles are HgO and MgO ; the solution contains the alkalis as chlorides. If desired, the residue after filtering off the alkalis may be ignited in a crucible, whereby the mercury is driven off and MgO left. The latter may be weighed as such.

In cases where it is desirable to estimate the alkalis in an entirely fresh solution, or when the alkalis only are required the following method is by far the best.

(*d*) *Lawrence Smith Method.*

Take 1·44 gms. of the sample, ground to a very fine powder, and mix it intimately with 1 gm. of resublimed NH_4Cl and 5 gms. of precipitated $CaCO_3$. Place the mixture in the bottom of a tall platinum crucible (the original was a sort of platinum test-tube), and cover with a further 4 gms. of the $CaCO_3$. Heat the bottom of the tube to bright redness for 1 hour (700° C.), keeping it closely covered and avoiding heating the upper portion. When the heating is complete, tap the contents out into a porcelain dish and digest the mixture in 250 cc. of hot water for an hour, breaking up any lumps with a glass rod or small pestle. Make up to 302 cc., transferring the mixture to a tall measuring cylinder for the purpose ; the odd 2 cc. represent the estimated volume of the solids. Filter off 250 cc. through a dry filter paper ; this filtrate represents 1·20 gms. of the original sample, and contains all the alkalis together with the alkaline earth chlorides ; all the other metals will be in the insolubles.

Boil the filtrate down to 220 cc. and add a slight excess of ammonium oxalate solution and a few drops of ammonia. Digest until the precipitate has settled out completely and again transfer precipitate and solution to the measuring cylinder ; make up to 301 cc. and filter off 250 cc. through a dry paper. This bulk represents 1·00 gm. of the original sample. This fractional filtration should be noticed ; it is a very useful device when bulky and slow filtering precipitates are concerned, as no washing is necessary.

Boil down to low bulk (50 cc.), add 3–4 drops of conc. $(NH_4)_2HPO_4$ solution and 10 cc. NH_4OH. Shake well and stand for at least one hour on the corner of the hotplate. Filter off the $MgNH_4PO_4$, washing it with 2·5 per cent. ammonia. Make the filtrate acid with HCl, boil, and add 5 cc. of 5 per cent. $FeCl_3$ solution. Make *just* ammoniacal and again filter after boiling to coagulate the iron precipitate, which removes the excess of phosphate.

The final filtrate contains the alkalis plus the ammonium salts that have been added. To remove these, add 50 cc. conc. HNO_3 and evaporate to a syrup, if necessary adding more HNO_3. Rinse into a weighed porcelain crucible or dish (not platinum), and take to complete dryness. Add 10 cc. HCl and again evaporate to dryness. A third evaporation

may be necessary if there is much residue, in order to expel the last traces of NO_3^-. Weigh the mixed chlorides of sodium and potassium.

Note 1.—This method is the best for such materials as sands, rocks, soils, cement, ashes, etc. In the analysis of a made-up mixture, the ordinary group separations, followed by the expulsion of NH_4^+ and precipitation of magnesium as $MgCO_3$ with Gooch and Eddy's solution, is more suitable. See also Water Analysis.

Note 2.—In all cases it is *essential* to perform a " blank " assay using the same weights and volumes of the reagents as were taken for the main estimation. Unfortunately, there is always a blank, though with pure reagents and proper care on the part of the analyst, it should be small.

Lawrence Smith's method involves very considerable manipulation, and if the operator can obtain good results for an estimation of small amounts of alkalis in a mineral, he may congratulate himself that he is well on the way to becoming an analyst. It is perhaps needless to mention that it is extremely unlikely that a " Lawrence Smith " will be demanded of a candidate in a practical examination ; certainly not unless two or three days are available.

SODIUM.

Sodium has no " insoluble " compounds suitable for the gravimetric estimation of the metal. It is usually determined " by difference " after the separation of potassium. Volumetric estimations of sodium are, however, possible, since this metal is so strong a base that many of its compounds possess an alkaline reaction such as will permit of their determination by titration with standard acid. The most obvious example is sodium carbonate ; for the estimation of this and other compounds such as NaOH, $NaHCO_3$ and the like, see under Estimation of Acid Radicles.

POTASSIUM.

Potassium may be separated and estimated as K_2PtCl_6 (or Pt), or as $KClO_4$.

1. *Estimation as Platinichloride (or Platinum).*—The alkali chlorides, which must be free from ammonium salts, are dissolved in the minimum amount of water in a small porcelain dish, and treated with a solution of chloroplatinic acid (platinum chloride) sufficient to precipitate the whole of the mixture if it were all KCl. The mixture is evaporated to a syrup on the water-bath. On cooling, a crystalline yellow crust forms. 5–10 cc. of 80 per cent. alcohol are added, the mixture stirred well with a glass rod and decanted through a Gooch crucible (asbestos pad). The golden-yellow precipitate is washed six times by decantation with small quantities of the 80 per cent. alcohol, and then the precipitate is transferred to the crucible, using an alcohol jet from a small wash bottle. The precipitate is washed four or five times more with a few cc. of alcohol, and finally dried at 130° C. in the air oven.

Or, if preferred, the crucible and contents may be heated in the muffle until the compound decomposes:

$$K_2PtCl_6 = 2KCl + Pt + 2Cl_2.$$

The crucible is cooled and the KCl extracted with water. The residue is dried, and after igniting, the platinum remaining is weighed.

Note.—The potassium platinichloride is somewhat soluble in water and slightly so even in alcohol. It is essential, therefore, to keep down the bulk of the wash liquid as far as possible, remembering that a number of small washes are more effective than a few big ones, even though more wash liquid be used in the latter case.

2. *Estimation as Perchlorate.*—This method is available in the presence of the alkaline earths, magnesium and $PO_4^{\equiv}$, but sulphates interfere.

To the neutral solution add twice as much $HClO_4$ as is necessary to combine with all the bases present, and take the solution to a syrup on the water-bath. Add 5 cc. of hot water and continue the evaporation until heavy fumes of $HClO_4$ are evolved, by which time all Cl^- and NO_3^- will have been removed. When actively fuming, remove the solution from the water-bath and cool completely. Add 20 cc. of alcohol (97 per cent. at least) to which a few drops of $HClO_4$ have been added (5 drops to 100 cc.), stir, and break up the crystalline precipitate with the tip of a glass rod. Allow the crystals to settle and decant through a weighed Gooch crucible (asbestos). Wash once more by decantation and then evaporate off the alcohol on the water-bath. Dissolve the residue in a little hot water and, after adding 0·5 gm. of $HClO_4$, again evaporate to fumes. Wash once with the perchlorated alcohol (by decantation) and transfer the crystals to the Gooch with a jet of the wash liquid from a small wash-bottle. Wash four times, using as little wash liquid as possible, as the potassium perchlorate is appreciably soluble. Finally, wash once with pure 97 per cent. alcohol and suck quite dry at the pump. Dry the residue at 130° C. and weigh.

If sodium is to be determined, the weight of $KClO_4$ is calculated to KCl and the result subtracted from the total weight of the mixed chlorides as originally obtained.

If potassium and sodium are present in approximately equal quantities, a fair approximation to their percentages in the residue may be obtained as follows, by taking advantage of the fact that the chlorides and sulphates have weights which differ considerably. The estimation is indirect and is interesting from a theoretical point of view.

(1) Weigh the dry mixture of chlorides (= W gms.).

(2) Treat the chlorides with 1 cc. H_2SO_4 and evaporate to dryness in the mouth of the muffle. Expel the last traces of acid by heating to dull redness and weigh the mixed sulphates (= w gms.). Then, if the mixture contains x gms. Na + y gms. K, the following relations hold:—

$$x \text{ gms. Na} \equiv \frac{x \times 58{\cdot}5}{23} \text{ gms. NaCl } \textit{or } \frac{x \times 142}{46} \text{ gms. } Na_2SO_4.$$

$$y \text{ gms. K} \equiv \frac{y \times 58{\cdot}5}{39} \text{ gms. KCl } \textit{or } \frac{y \times 174}{78} \text{ gms. } K_2SO_4.$$

$$\text{Now: } \frac{x \times 58{\cdot}5}{23} + \frac{y \times 58{\cdot}5}{39} = W, \textit{ and } \frac{x \times 142}{46} + \frac{y \times 174}{78} = w.$$

Solving these equations for x and y (W and w being known) gives the

weights of sodium and potassium individually present. The accuracy is not very good.

A rough separation of potassium from sodium which is useful when small amounts of the former have to be estimated in the presence of comparatively large amounts of the latter, is as follows, advantage being taken of the slight solubility of NaCl in saturated HCl solution.

The mixed chlorides are dissolved in the minimum quantity of cold water contained in a tall beaker or Phillips' flask. HCl gas, obtained by dropping conc. H_2SO_4 from a tap funnel into conc. (commercial) HCl, is then passed into the solution by means of a wide tube *just* dipping below the surface of the solution ; an inverted thistle funnel serves very well. If a narrow bore tube is used two sources of trouble are found; first, the tube becomes clogged up with fine NaCl crystals and, second, there is some danger of the solution sucking back into the generating flask, owing to the great solubility of HCl gas in water.

NaCl is precipitated in small crystals, while KCl remains in the solution. When no more NaCl is deposited, remove the flask and filter through a pad of glass wool or asbestos, washing with a few small doses of pure conc. HCl. The potassium may easily be estimated in the filtrate now that the bulk of the sodium has been removed.

AMMONIUM.

" Ammonium " is the name applied to the radicle NH_4 which behaves, analytically, as an alkali metal, closely resembling potassium in the reactions of its compounds.

It is perhaps unnecessary to observe that ammonium must always be estimated in a separate portion of the sample for analysis, if only because ammonium salts are being added at every stage of the systematic separation of the metals.

Ammonium may be estimated gravimetrically as $(NH_4)_2PtCl_6$, the manipulations being similar to those detailed under Potassium, but this is not common practice ; it is more usual to estimate the radicle by expelling NH_3 gas from the compound under analysis and absorbing this in excess of standard acid. The excess acid is then titrated with standard alkali.

For small quantities of NH_4^+ the colorimetric method, using Nessler's solution is best.

Estimation of Ammonium.

A. Gravimetric Method.—*As Platinichloride.*—The manipulations are exactly the same as those given under Potassium. $(NH_4)_2PtCl_6$ is also stable at 130° C. When heated strongly, the platinichloride breaks up into NH_4Cl, Cl_2 and Pt, and, the two volatile compounds having been driven off by heat, the platinum may be weighed instead of the yellow compound if desired.

B. Volumetric Method.—The sample is placed in the flask A (fig. 15) and dissolved in 200 cc. of water that has been freshly distilled from alkaline permanganate, rejecting the first 100 cc. or so. The condenser and receiver are arranged so that the tip of the former just dips below

the surface of a suitable volume of standard acid. The strength of this acid will depend upon the amount of ammonia to be absorbed. If small amounts are being estimated, 25 cc. of $\frac{N}{10}$ acid will suffice ; this will absorb, theoretically, 0·04 gm. NH_3, equivalent to 4 per cent. NH_4^+ on a 1 gm. sample. If the sample under analysis is an ammonium salt the purity of which is being determined, the acid must be such that 0·6 gm. NH_3 will be absorbed ; for this, 50 cc. of N acid will be sufficient.

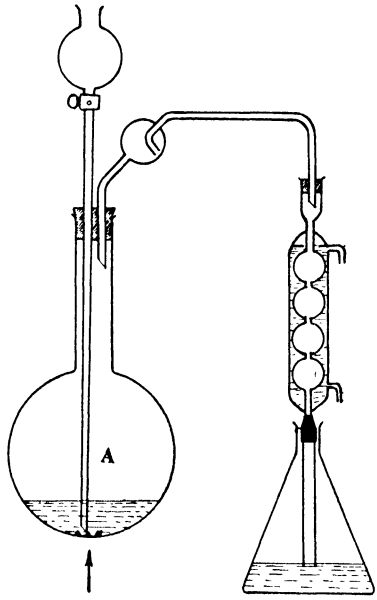


Fig. 15.—Absorption of Ammonia Gas.

The following table will serve as a guide for all cases:—

1,000 cc. N acid	are	equivalent to	17 gms. NH_3
50 cc. N	,,	,,	0·85 gm. NH_3
50 cc. $\frac{N}{10}$	,,	,,	0·085 gm. NH_3
25 cc. $\frac{N}{10}$	,,	,,	0·042 gm. NH_3.

Of course, in all cases a suitable excess must be allowed.

A suitable volume of standard acid having been pipetted out into the receiver (Phillips' flask or tall beaker), and the apparatus tested for gas leakage, the caustic soda is run in *via* the tap funnel and the distillation flask cautiously heated with a small burner held in the hand so that it may be instantly withdrawn if the evolution of the gas becomes unduly violent. When the evolution of ammonia slackens, the contents of the

flask are slowly brought to the boil and distilled until the volume has been reduced to one-half. The evolved ammonia is rapidly taken up by the standard acid, and if it is driven over too rapidly there is considerable danger of sucking back ; it is for this reason that the tip of the condenser is arranged to dip only just below the surface of the acid. If sucking back does occur, the liquid will fall back into the flask when the exposure of the tip permits air to enter and relieve the reduced pressure.

In setting up the apparatus all joints must be carefully made and tested for their gas-tightness ; the cork or bung of the flask A should also be boiled in dilute NaOH solution before use.

The bulk of the ammonia comes off at a fairly low temperature and great care must be taken with the heating at the commencement of the operation ; when the evolution slackens, the heating may be pressed somewhat, but the whole analysis demands careful and constant attention.

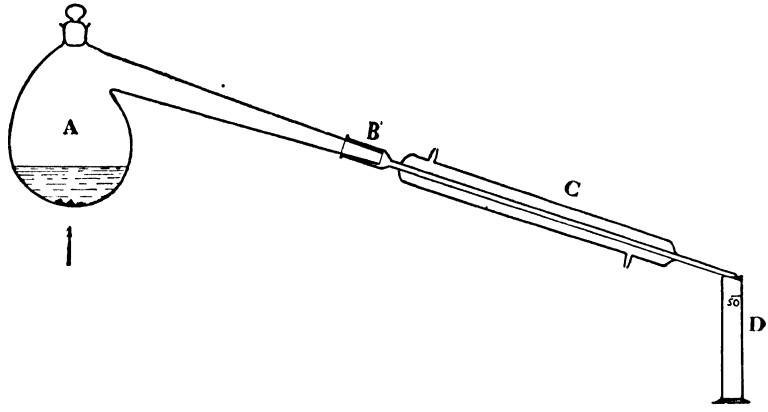


Fig. 16.—Colorimetric Method for Estimation of Ammonia.

When the bulk has been reduced by half, the flask is disconnected from the condenser and a few cc. of water are run through the latter to rinse it out, the rinsings being caught in the flask containing the acid.

Next, methyl orange is added to the distillate in the receiver and the solution titrated back with standard alkali, calculating the weight of ammonia (ammonium) as follows: (Example):

Used 50 cc. N H_2SO_4 in the receiver ; 15 cc. N NaOH were required for the back titration. Then: 50-15 cc. or 35 cc. were neturalised by the ammonia evolved. Whence:

$$\frac{35 \times 17}{1{,}000} \text{ gms. } NH_3 \text{ or}$$

$$\frac{35 \times 18}{1{,}000} \text{ gms. } NH_4^+ \text{ were present in the sample.}$$

C. Colorimetric Method.—For very small amounts of ammonia, *e.g.* in drinking water, the following method is used:

The apparatus is set up as in fig. 16. A is a large retort (1,000 cc.) which fits closely into B, the wide end of a glass condenser C. D is a Nessler tube (50 cc.) to catch the distillate. Three or four of these tubes, carefully washed out with freshly distilled water, will be necessary.

300 cc. of recently distilled water and one or two small pieces of clean broken porcelain are placed into A and the mixture is boiled until at least 200 cc. have passed over. This "cleans" the apparatus from traces of ammonia or nitrogenous substances which might decompose and yield ammonia on heating. The preliminary distillation is extremely important and should on no account be omitted, as it is amazing how large a blank can be obtained with the most carefully washed apparatus if it has been exposed to the laboratory atmosphere for any length of time ; for the same reason it is advisable to conduct the whole estimation in a separate room ; the ordinary laboratory is too completely permeated with ammonia and ammonium compounds to be safe when traces of these compounds are being estimated.

A measured volume of the water sample (or weighed portion of the sample if a solid, dissolved in a little recently boiled 1 per cent. cold NaOH solution) is then placed in the retort and the slow distillation is commenced.

Note.—The volume in the retort should be about 350–400 cc. With ordinary drinking water, this will serve very well as the entire sample, but if the water is contaminated, a smaller volume of sample is necessary or the result will be precipitation instead of coloration in the first Nessler tube. If a smaller sample is taken, it is always necessary to dilute it to the proper bulk with ammonia-free water (water that has been recently distilled from a retort containing alkaline $KMnO_4$, the first third being rejected). In the case of the solid sample, the weighed solid should first be dissolved in a little cold, recently boiled, 1 per cent. NaOH, and diluted to 350 cc. as explained. 350 cc. is a good volume to take, as the calculation to "grains per gallon" is simplified, there being 70,000 grains in an English gallon.

Each 50 cc. as it collects is removed and a fresh receiver placed in position. The distillates are transferred (in turn) to a 75 or 100 cc. Eggertz carbon tube and exactly 2 cc. of clear Nessler solution added from a small pipette. If ammonia is present, a yellow or brown colour is developed, the intensity of which is proportional to the amount of the NH_3. The colour is compared with that of a standard which consists of 50 cc. of freshly distilled ammonia-free water to which 2 cc. of Nessler solution have been added. A burette is filled with a dilute solution of NH_4Cl of such a strength that 1 cc. $\equiv$ 0·0001 gm. NH_3, and this solution is added to the "standard" tube until the two colours match when viewed against a white illuminated background, daylight being essential for the comparison. When the tints agree, the amount of ammonia present in the distillate is equal to the amount of ammonia added from the burette. This is recorded and the second tube of distillate is treated in exactly the same way, and so on, in succession, until the addition of Nessler solution no longer produces a coloration. The successive totals are then added together, giving the total ammonia present in the sample. See fig. 8, p. 68.

Nessler's Solution.—Dissolve 61·75 gms. KI in 250 cc. of cold water.

Add cold saturated $HgCl_2$ until the colour is a permanent bright red (about 400 cc.). Clear the solution by adding 0·75 gm. KI and then add 150 gms. KOH in 250 cc. water. Dilute to 1,000 cc. with recently distilled water ; settle, and decant off the clear solution.

Standard Ammonium Chloride.—Dissolve 3·15 gms. of sublimed NH_4Cl in 1,000 cc. of distilled water. Pipette out 10 cc. and dilute to 1,000 cc. One cc. of this solution contains 0·0001 gm. NH_3.

Note.—The distillation may be conducted from an ordinary distillation flask, but the retort is preferable, as it enables the apparatus to be set up without the use of corks.

SECTION IV.

THE ACID RADICLES.

GROUP I.

THE SULPHUR ACIDS.

General.—In all compounds of sulphur the sulphur may, if desired, be converted into $SO_4^{=}$ and estimated by weighing as $BaSO_4$. In the case of acids in which the sulphur is in a lower state of oxidation than

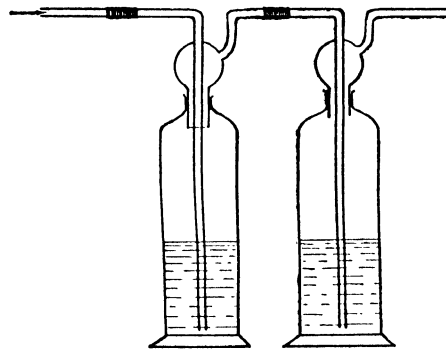


Fig. 17.—Washbottles for Estimation of H_2S.

in $SO_4^{=}$, it is usually oxidised to the higher state by treatment with one of the following reagents: Conc. nitric acid, aqua regia, bromine, chlorine, or ammoniacal hydrogen peroxide, that is, if a gravimetric method is to be used ; needless to say, it is frequently possible to devise excellent volumetric methods in many cases, depending upon the quantitative oxidation of the compound of the lower oxide to the hexavalent state.

H_2S AND THE SULPHIDES.

1. (*a*) **The Free Gas**—*Method* 1.—Free H_2S is best estimated by bubbling it through a series of wash-bottles containing either lead acetate or alkaline cadmium chloride, whereby PbS or CdS is precipitated.

Set up a series of wash-bottles containing lead acetate solution (fig. 17) and allow a measured volume of the gas to pass through them from a

calibrated container. When a suitable volume has been driven through the reagent, wash out the contents of the bottles into a large beaker and collect the precipitate by digesting on the corner of the hotplate. The volume of gas taken for the experiment depends, of course, upon the amount of H_2S present. The best plan is to have a definite amount of lead in each bottle, so that when one bottle is saturated and the lead sulphide begins to be precipitated in the second bottle, a suitable weight of PbS will have been thrown down ; 10 cc. of 10 per cent. lead acetate will absorb approximately 0·09 gm. of H_2S, so that a reasonable quantity of reagent would be 10 cc. of 10 per cent. lead acetate, diluted to, say, 200 cc. in each of the wash-bottles. The absorption would be continued until the second bottle showed signs of discoloration by the black PbS.

When the precipitate has settled out completely, the clear liquid is carefully decanted off through a small pulp filter, and the PbS finally washed on to the filter, then washed well with water that contains a little HCl, 2 or 3 cc. per litre. When all the soluble lead has been washed out of the filter, and the runnings show no coloration with H_2S water, the receiver is removed and a clean beaker is put in its place. The black sulphide is rinsed off into the beaker and any adherent precipitate is dissolved off in 10 cc. of hot 1 : 2 HNO_3, which is poured over the opened-out paper. A reaction commences at once and nitrous fumes are evolved, the precipitate dissolving as $Pb(NO_3)_2$. At the same time a spongy mat of discoloured sulphur is formed, and this, buoyed up by the liberated gas, floats on the acid. The acid wash is followed with 10 cc. of cold water and the treatment repeated with water and acid alternately three or four times. To the clear liquid in the beaker 10 cc. of H_2SO_4 are added and the solution set on the hotplate to evaporate to fumes. The filter paper and the mat of sulphur are transferred to a small, clean crucible that has been previously weighed, and gently heated on the centre of the plate until charring commences ; the sulphur will probably catch fire and burn ; this is necessary, so that if the hotplate is not hot enough to start the combustion, the crucible should be held just inside the muffle with the tongs for a moment, replacing it on the hotplate the instant the sulphur takes fire. When the sulphur has been burnt off the crucible is placed on its side in the mouth of the muffle so that any unburnt carbon may be consumed, while admitting plenty of air. If the original treatment on the hotplate has been carried out properly, all combustibles should burn off without any of the lead being reduced to metal. The crucible is then removed from the muffle and cooled ; two drops of H_2SO_4 are added and the crucible placed on the centre of the plate until the acid fumes strongly. It is cooled once more and set aside until the beaker containing the main precipitate shows copious fumes. Usually, the two processes finish almost simultaneously.

When the contents of the beaker are sufficiently cool to permit of dilution, rinse the contents of the crucible into the beaker and dilute to 200 cc., no more. Set the solution aside to cool and settle. When quite cold and clear, decant the solution off through a weighed Gooch crucible and wash several times with cold 5 per cent. H_2SO_4. Put the crucible on the hotplate to dry, and finish in the mouth of the muffle until all traces of acid are expelled. Push it into the dull red zone

for a minute or two to make certain that no acid remains, cool in the desiccator, and weigh as usual.

303·25 gms. $PbSO_4$ ≡ 239·25 gms. PbS ≡ 43·0 gms. H_2S ≡ 32·0 gms. S.

Note 1.—PbS is chosen for several reasons: 1. Because it does not tend to form basic sulphides. 2. It is dark coloured and traces of it in the second bottle are easily detected. 3. It is very easily soluble in dilute acids. 4. If it oxidises on the filter (as sulphides usually do) the oxidation product is a "safe" one, viz. $PbSO_4$, which is "insoluble" and will not be lost by passing through the filter during the washing. 5. PbS is dense and settles well and quickly. 6. Pb has a high atomic weight, so that a little H_2S means a fairly heavy precipitate, thereby minimising errors in weighing.

Note 2.—This method of conversion of PbS into $PbSO_4$ will be found to work excellently; the recovery of the Pb as $PbSO_4$ from the filter paper and the mat of freed sulphur is quite good. It is necessary to burn the paper, as the HNO_3 tends to produce $PbSO_4$ by direct oxidation of the PbS, and there is always some sulphate in the filter pad. The combustion of the paper and the sulphur must, however, be carried out carefully, giving the process plenty of time and the residue plenty of air. The final product may contain sulphate, oxide and sulphide of lead. All these are converted into sulphate by fuming with acid. If reduced metal is noticed, treat the contents of the crucible with HNO_3 before adding the H_2SO_4, though the latter acid will attack lead and convert it into sulphate at its boiling point. The sulphates are easily transferred to the main solution in the original beaker.

Method 2.—If the amount of H_2S is less than about 0·005 gm. its absorption in an ammoniacal solution of $CdCl_2$ is quicker to carry through as the CdS can be estimated by the titration of the H_2S liberated when it is dissolved in dilute HCl. The method is one which has been adapted for the estimation of sulphur in steel and iron, and further details will be found under that heading.

Usually one washbottle suffices to catch all the H_2S, but it is safer to arrange two in series; an alternative method is to use a capacious absorption bulb for the cadmium solution; Meyer's bulbs are the best, as they wash the gas very thoroughly and are easily cleaned out.

When the gas has all been driven through the solution, the liquid, containing CdS in suspension, is rinsed out into a tall 600 cc. beaker and excess of moderately concentrated HCl is added; 1 : 2 acid one-quarter of the bulk of the cadmium solution will serve well. The yellow sulphide dissolves immediately; 0·1 *N* iodine solution is then run in from a burette until the mixture is coloured decidedly yellow by the iodine, this excess of iodine being then titrated with standard thiosulphate from another burette. When the yellow of the iodine is discharged, a few drops of starch solution are added, and the titration with the iodine continued until a faint blue colour is attained. If necessary, the mixture may be back-titrated with the thiosulphate and the end-point again found with the iodine. The reactions are:

1. $H_2S + CdCl_2 = CdS + 2\,HCl$, absorption of the H_2S.
2. $CdS + 2\,HCl = CdCl_2 + H_2S$, reliberation of the H_2S.

There is obvious danger of loss of H_2S here if the iodine is not run in immediately. The addition of the HCl should only be made on the titration bench when everything for the titration is ready.

3. $H_2S + I_2 = 2\,HI + S$, - - reaction with the iodine solution.

4. $I_2 + 2\,Na_2S_2O_3 = Na_2S_4O_6 + 2\,NaI$, the excess iodine titration.

After the titration proper, the two solutions are titrated against each other, using at least 20 cc., and the iodine equivalent of the thiosulphate is calculated. The equivalent of the volume of thiosulphate used is deducted from the total iodine required, and the amount of H_2S calculated from the factor of the iodine solution. This solution is standardised against the H_2S evolved from a known weight of ZnS, or better, if the sulphur in a steel or iron is being estimated, a standard steel with a known percentage of sulphur is used to check the strength of the iodine solution. If ZnS is used, the following procedure is adopted: The ZnS is weighed into a small flask connected to the absorption train and dilute HCl is admitted by means of a dropping funnel. H_2S is quantitatively evolved and absorbed by the $CdCl_2$, being finally estimated as already described, after sweeping the flask clear of H_2S as follows: The evolution being completed, add 15 cc. conc. HCl *via* the funnel, followed by a saturated solution of 5 gms. of anhydrous Na_2CO_3 in water, admitted a little at a time, as the reaction slackens. 0·1 gm. of ZnS should be taken for the standardisation ; this will yield 0·035 gm. of H_2S ; this quantity is really rather great, but it is inadvisable to weigh less than 0·1 gm. ZnS for standardisation purposes, as the lower the weight of the standard taken the more any errors of weighing become multiplied in the calculation of the result. The standardisation by comparison with the H_2S evolved from a standard steel is very much to be preferred.

Solutions required:

0·1 *N* iodine.
0·1 *N* thiosulphate.
1 : 2 HCl for the solution of the CdS.
Fresh starch solution.
Ammoniacal cadmium chloride solution.

1. (*b*) **H_2S in Solution.**—The best and safest method is to transfer a measured volume of the solution to a small flask, add one or two pieces of pot or porcelain to ensure a steady stream of bubbles, and then boil the solution while a slow stream of CO_2 is bubbled through it. By this means all the H_2S will be carried over into the $CdCl_2$ absorption train, where it is estimated as already described.

If the solution contains nothing except the gas, or at least nothing that will interfere with the subsequent procedure, an alkaline solution of $CdCl_2$ may be added to the solution itself; CdS will be precipitated. This is collected by digestion on the hotplate for a while, and is then filtered off and washed once or twice. The precipitate and pulp filter are then transferred to a beaker, excess of dilute HCl is added, and the solution immediately titrated with iodine and thiosulphate as before.

This method will answer well for the estimation of free H_2S (or a soluble sulphide) in a sample of water, for instance.

2. **Gravimetric Estimation of Sulphur in a Sulphide.** This is the method generally adopted for the estimation of a sulphide, as it is applicable whether the percentage of sulphur in the sample is high or low. The weight of the sample to be taken depends upon the amount of sulphur present. In the case of a sulphide mineral or a more or less pure artificial sulphide, a weight of 0·5 gm. is sufficient, while in the case of the estimation of sulphur in a metal or alloy, a weight of 5 to 10 gms. will be necessary. The mineral must be very finely ground, especially if there is silica present, or it will be only very slowly attacked by acids ; a metallic sample need not be so finely divided as solution is usually even and rapid ; ordinary drillings or turnings will do.

Weigh the sample out into a wide, 600 cc. beaker.

A. *Sulphur in a Mineral.* Add 20-30 cc. of conc. HNO_3 and a few drops of bromine to the sample. Cover the beaker and set aside in a cool place so that the bromine is not lost ; it may be necessary to stand the beaker in a dish of cold water if the reaction with the acid is at all violent. As a rule, a scum of free sulphur is formed ; when the first reaction slackens or ceases, the beaker may be placed on the edge of the hotplate, where the digestion is continued until the sulphur is seen to have disappeared ; more HNO_3 and bromine may be necessary. When all the sulphur has been oxidised, and the sample is completely in solution except for any silica that may be present, the cover may be removed and the mixture taken slowly to dryness on the hotplate, care being taken that no spitting occurs.

The preliminary digestion should result in the complete solution of the material, but some substances, notably roasted ores and the like, do not dissolve readily in HNO_3. If, then, the silica refuses to clear after, say, an hour's digestion, a few cc. of conc. HCl must be added at intervals until the sample is completely in solution and the silica is pure white. Note especially that HCl must not be added until the HNO_3 has had a fair opportunity of oxidising the sulphur, and in any case, the HNO_3 must be in excess or there is danger of loss of sulphur as H_2S. In this case also, when the sample is dissolved, take the mixture slowly to dryness. When the mixture is quite dry, cautiously work the beaker into the centre of the hotplate, keeping it at a temperature of between 200° and 300° C. for half an hour to dehydrate the silica and render it insoluble in acid ; too high a temperature for baking will result in the loss of some SO_3 by decomposition of the sulphates present ; too rapid a transference to the centre will result in a cracked beaker.

After baking, the beaker is removed and set aside on an asbestos sheet to cool (it will crack if placed on a good conductor of heat while it is still hot and it will char wood). When cool enough to bear touching with the hand, 20 cc. of HCl are added and the beaker covered with a clock-glass. It is then set on the edge of the hotplate and the contents digested until all the basic nitrates are completely in solution ; the silica should "clean" well and rapidly in the HCl. When this has been effected, 100 cc. of hot water are added and the solution filtered immediately through an open-textured paper (No. 41), catching the filtrate in a Phillips' flask. The residue is washed thoroughly with cold water and

hot 5 per cent. HCl alternately, four times with each, and finally with hot water until the filtrate is free from Cl^-. This is not so important if the silica is not to be estimated ; it is unlikely (though possible) that the basic chloride of iron which is liable to be formed if the acid wash is dispensed with will contain $SO_4^=$. The silica on the filter may be ignited and weighed if desired. The filtrate contains the sulphur as $SO_4^=$.

Place the solution on the hotplate and bring to the boil. Add excess (usually about 15–20 cc.) of 10 per cent. $BaCl_2$ solution in a steady stream, preferably boiling at the same time ; cover the flask and digest the precipitate just below the boiling-point for at least an hour, or until the $BaSO_4$ settles out completely. Filter off through a small compact pulp (not too compact ; a very compact filter is not necessary if the precipitation has been properly conducted) and wash with *cold* water until free from Cl^-. Transfer paper and precipitate to a crucible, (porcelain, silica, or platinum) and after charring off the paper in the mouth of the muffle where there is plenty of air, ignite at redness. Cool in the desiccator and weigh as $BaSO_4$.

Note 1.—$BaSO_4$ contains, roughly, one-eighth of its weight of sulphur. As the final precipitate should not weigh more than about 1 gm. the weight of sample taken must be chosen accordingly.

Note 2.—The digestion with $HNO_3 + Br_2$ should be long enough to ensure all the sulphur being oxidised ; the evaporation should not be commenced if there is any free sulphur visible in the beaker ; its presence is unmistakable.

Note 3.—Silica may be in either or both of two forms: (*a*) Sandy particles, representing free silica in the sample ; (*b*) a rather bulky, gelatinous residue resulting from the decomposition of silicates.

Note 4.—Washing $FeCl_3$. This compound tends to "go basic" and deposit insoluble iron compounds in the pores of the filter paper when it is washed with hot water ; the treatment recommended will prevent this. Do not use too much HCl, as the acidity of the filtrate should not be higher than about 5 per cent. by volume, or appreciable amounts of $BaSO_4$ may be dissolved.

Note 5.—The Phillips' flask is recommended on account of the lower loss by evaporation during the long digestion near the boiling-point. The solution must not be permitted to boil ; this is not from fear of loss, or attack of the precipitate by the hot acid, but is to prevent the formation of splashings of basic compounds on the sides of the flask. These will not easily dissolve in the acid of the solution and stronger acid must not be used for fear of loss of the precipitate by solution ; the actual splashings would not matter were it not for the fact that they invariably wash off into the filter and contaminate the precipitate.

Note 6.—The $BaSO_4$ must be precipitated *hot* ; this is to delay complete precipitation by having a solution in which the sulphate is appreciably soluble. The result is that small crystals of the $BaSO_4$ dissolve and are later deposited upon the larger ones, small crystals having a greater solubility than large ones. The net result is to obtain a coarsely crystalline precipitate which will filter and wash without causing any trouble ; when precipitated hot, $BaSO_4$ comes down so coarsely divided that there is usually no need to wait more than an hour or so for the precipitate to settle.

B. *Sulphur in an Alloy or Metal.*—Many metals are smelted from sulphide (pyritic) ores, and are liable to contain sulphides ; for example, copper, lead, antimony. Other metals, though not derived from sulphide ores, nevertheless pick up " tramp " sulphur from fuel, fluxes, or from impurities in the ores during smelting ; the chief example of this type is iron. The exact details of the estimation may vary slightly in different cases, depending on the nature of the metal concerned, but as a rule, the main principles are the same. Here, the case of iron and steel will be considered.

Weigh 2·5 gms. of cast iron or 5 gms. of wrought iron or steel. (Also copper, copper alloys, lead.) Place the drillings in a large, wide beaker (600 cc.) and add 20 cc. of HNO_3 followed by 15 cc. HCl, adding the latter acid carefully and a little at a time as the reaction is liable to become violent, especially with fine drillings. It is advisable, as a precaution, to have a wash-bottle with cold water handy to use in case of violent upheaval of the mixture in the beaker.

The HNO_3 *must* be added first, on account of the reactions:

$$FeS + 2\,HCl = FeCl_2 + H_2S$$
$$MnS + 2\,HCl = MnCl_2 + H_2S$$

which entail loss of sulphur. The HNO_3 oxidises all the sulphur to $SO_4^{=}$, none being lost.

When the action ceases, complete the estimation as described under A ; *i.e.* bake, take up in HCl, evaporate off excess acid, dilute, filter off silica, precipitate $BaSO_4$, allow to settle, filter, wash, and weigh.

Note that ordinary " pure for analysis " HCl and HNO_3 are always liable to contain H_2SO_4 derived from the method of manufacture ; a " blank " must, therefore, be carried through with the assay, using a similar beaker, the same treatment, and exactly the same volumes of the same acids. A pinch of pure KNO_3 (KCl, etc., etc.) is placed in the blank to combine with the $SO_4^{=}$, which would otherwise be lost when the acid is evaporated to dryness with the assays. All volumes must be exactly measured in order that the blank may be accurate. With good quality acids the blank will amount to about 0·003 gm. or less ; this is a serious matter when percentages as low as 0·03 per cent. are being estimated, but hardly affects the results of the assay when 20, 30 or 40 per cent. of sulphur is concerned, as in the case of sulphide ores. This is why the blank is insisted upon here but was not mentioned in Method A. Some commercial analysts redistil their acids for sulphur estimations ; this is hardly necessary when the blank sulphate is small; recent blanks with ordinary analytical acids in the author's laboratory average 0·003 gm. only.

Note 2.—It should be unnecessary to mention that proximity to beakers evolving H_2S, SO_2, SO_3, etc., is to be avoided, and fuming H_2SO_4 even several yards away will completely spoil the results of this method of estimation.

Note 3.—The precipitation of $BaSO_4$ is a process which contains many pitfalls which are often unsuspected by the unthinking. It must be remembered that no precipitate is absolutely " insoluble," and even $BaSO_4$, though its solubility in pure water is extremely low, is

completely soluble in a sufficient volume of concentrated HCl. The problem of adsorption also comes into the process to a considerable degree. For refined work, elaborate precautions must be taken to ensure accurate results ; in some cases, the metals of Group III have to be removed before precipitating the $BaSO_4$, since these have a great tendency to become adsorbed by the finely divided sulphate. For ordinary purposes, and to obtain a result correct to within 0·1 or 0·2 per cent. of the total sulphur, sufficient accuracy is attained by the exercise of the following precautions:

1. The solution should be boiling.
2. It should be fairly dilute (at least 400 cc.).
3. The acidity should be low (1–2 per cent. HCl by volume).
4. No HNO_3 or NO_3^- should be present.
5. The precipitant should be added *hot*, and run in in a steady stream while the solution is stirred or swirled.

The observation of these conditions will give a minimum of error, negligible for ordinary work. The chief sources of error are:

1. Adsorption of $BaCl_2$ and other metallic salts, notably $FeCl_3$. Adsorbed substances cannot be washed out with water, and must be weighed with the precipitate. If iron is adsorbed to an excessive extent, the ignited precipitate will appear pink (due to Fe_2O_3). This may, if necessary, be allowed for by boiling the precipitate with 5 cc. of conc. HCl until all is in solution or until the undissolved $BaSO_4$ is perfectly white. The mixture is then diluted to 300–400 cc., and boiled. 1 or 2 cc. of $BaCl_2$ are then added, and the precipitate, after settling as usual, is filtered off and finally weighed. If preferred, the precipitate may first be weighed, then treated with hot conc. HCl, and the Fe^{+++} reduced with $SnCl_2$. The iron is then titrated with standard dichromate, the figure obtained calculated to Fe_2O_3, and this weight deducted from the original weight of the impure $BaSO_4$. This is not so good as the former method, however, as only adsorbed iron is allowed for.

The above method is a common one for minimising the effect of adsorption. Adsorption is least in dilute solutions ; if (for example) 0·01 gm. of iron be adsorbed from a solution containing 2 per cent. of iron, on the second precipitation the concentration of the iron is only 0·01 gm. in 300 cc., *i.e.*, 0·0033 per cent., and if adsorption takes place to the same degree, only 0·000017 gm. will be taken up, a negligible amount.

2. The solubility of $BaSO_4$ in acid and neutral salts. Keep the acidity low and work at the indicated dilutions.

3. Mechanical occlusion. Precipitation in hot solution minimises this and gives a coarse-grained precipitate which is less soluble in acids. As a refinement, the solution of $BaCl_2$ may be diluted to 100 cc. from the 10-12 cc. advised, boiled, and then added hot ; this will keep down mechanical occlusion.

Wet oxidation methods for the estimation of sulphide sulphur are usually very convenient, but may be tediously slow ; the very accurate dry oxidation method will now be described.

Dry Oxidation Method for Sulphide Sulphur.—The sample is very finely powdered and mixed with about 5 to 7 times its weight of a mixture

of 3 parts Na_2CO_3 with 1 part KNO_3 in a nickel or iron crucible, and the whole covered with a layer of the same mixture. The crucible is covered with its lid and heated in a muffle or electric crucible furnace (*not* over a flame, on account of the sulphur which is invariably present in coal gas). The mixture fuses, and is kept in a state of quiet fusion for 15 minutes. At the end of this time the crucible is cooled, and the mass extracted with hot water, washing well with hot water until all soluble salts are removed. The filtrate is acidified with HCl and taken to dryness. The residue is cooled, moistened with HCl, and again taken to dryness, baked for a few minutes (10) in the centre of the hotplate and once more dissolved in a few cc. of hot HCl and water. The silica, if any, is filtered off on a small pulp, the filtrate diluted to 400 cc., boiled, and precipitated with $BaCl_2$, preferably diluted, keeping the solution stirred during the addition.

This method is of quite general application and gives excellent results.

Note 1.—A blank determination is usually necessary to check the purity of the fusion mixture.

Note 2.—Na_2O_2 is sometimes used in place of the KNO_3 in the above mixture. This substitution obviates the necessity for two evaporations with HCl to destroy the NO_3^-; one, however, is necessary, in order to separate the SiO_2. A suitable mixture is 6 parts Na_2CO_3 + 1 part Na_2O_2. As a rule the blank is very small if the carbonate has been made by the ammonia-soda process; the peroxide is made from the metal, and is, or should be, free from sulphur; both reagents, however, will take up sulphur, especially *acid* sulphur, when exposed to the air, hence the need for the blank.

SULPHATES.

Sulphates are invariably estimated gravimetrically as $BaSO_4$. The weight of sample taken is arranged so that not more than about 0·2 gm. of sulphur is present, or, say, 0·6 gm. $SO_4^=$; this will yield about 1·4 gms. of $BaSO_4$, which is about the upper limit of weight that can be comfortably handled. This being so, in the case of a pure sulphate, take about 0·2–0·25 gm., or more in proportion as the percentage of sulphate is less.

All sulphates, except those of barium, strontium, calcium and lead, are soluble in water; in the case of the sulphate of any other metal, or free sulphuric acid, dissolve the sample in water and dilute the solution to 400 cc. If neutral, add not more than 10 cc. of HCl; if acid, neutralise with ammonia and add this excess of HCl; bring the solution to the boil and add excess of 10 per cent. $BaCl_2$ solution, also hot. Cover the beaker and stand in a hot place with the solution not quite boiling until the precipitate settles out well. Filter through a pulp filter, wash precipitate with cold water until free from Cl^-, dry, char, and finally ignite; weigh as $BaSO_4$.

For details and precautions to be observed, see under Sulphur in Sulphides, Gravimetric.

In the case of an insoluble sulphate, such as $BaSO_4$, etc., the metal is converted into carbonate as follows.

0·2–0·25 gm. of the sulphate of barium, strontium or calcium is weighed out into a platinum crucible and mixed with 5 gms. of anhydrous Na_2CO_3. The mixture is further covered with about 1 gm. of the carbonate and fused in the muffle, *not* over a flame owing to the inevitable contamination with sulphur from the gas. When quietly fused, the mixture is removed and the crucible carefully swirled with the tongs so that the molten carbonate solidifies in a thin film on the sides of the crucible ; as soon as the contents are solid, the crucible is dipped into a little water in a porcelain dish without allowing the water to enter, and when the whole is cold, the crucible is laid on its side in the water. The fusion converts the original sulphate into the carbonate, the metallic radicles changing partners, so that the extract in the dish now consists of a solution of Na_2SO_4 and an insoluble residue of $BaCO_3$. The solution is filtered hot through an open paper and the residue washed with a hot, dilute (1-2 per cent.) solution of Na_2CO_3. The filtrate is carefully acidified with HCl, 1 to 3 per cent. excess being added, then boiled, and excess of $BaCl_2$ added. The $BaSO_4$ is then weighed as before.

In the case of $PbSO_4$ it is not always safe to carry out the fusion in platinum unless a qualitative test has been made on the mixture ; a mere trace of a reducing agent will cause a hole in the crucible. $PbSO_4$ is, however, sufficiently soluble in water to enable the transposition of the radicles to be made in solution. The weighed sample is, therefore, digested at near boiling-point with a concentrated solution of Na_2CO_3 ; $PbSO_4$ is decomposed and $PbCO_3$ formed, the latter compound being less soluble, especially in a solution of carbonate, than the sulphate, apart from the usual Mass Action effect of the excess of carbonate. The solution is filtered as already described, acidified, and the SO_4^{--} estimated.

To judge the volume of 10 per cent. $BaCl_2$ solution to be added to precipitate a given weight of sulphate, the following ratios are given:

$BaCl_2$, 2 H_2O	$BaSO_4$	SO_4^{--}	S
244·3 gms.	≡ 233 gms.	≡ 96 gms.	≡ 32 gms.
10 cc. ≡ 1 gm.	≡ 0·955 gm.	≡ 0·039 gm.	≡ 0·013 gm.

i.e. 10 cc. of 10 per cent. $BaCl_2$, 2 H_2O solution will precipitate the above weights in grams of the indicated compounds ; an excess of 1 cc. is ample to ensure complete " insolubility " of the $BaSO_4$ produced.

Free Sulphuric Acid.—The free acid may, of course, be estimated by titration with standard alkali ; for details, see under Acidimetry. In the presence of other acids, the gravimetric method is, however, the only method available.

Conc. Sulphuric Acid and the Fuming Acid.—The sample must be weighed. The acid is very hygroscopic and all weighings must be carried out in a stoppered weighing bottle. The bottle is dried carefully, cooled, and weighed. The stoppered sample is then opened and about 5 cc. drawn out with a pipette (use a long rubber tube to apply the suction, not only to avoid all possibility of drawing the acid into the mouth, but to avoid introducing moisture from the breath). The acid is quickly run out into the weighing bottle, which is at once stoppered

and re-weighed. Five cc. of conc. H_2SO_4 represent about 9 gms. of the acid.

The weighed sample is then carefully poured into 100 cc. of cold water in a large beaker, the bottle rinsed out several times with water from the wash-bottle, and the mixture cooled to room temperature. It is then diluted somewhat, transferred to a graduated 500 cc. flask, and the solution made up to the mark with cold water. The solution is poured backwards and forwards between the beaker and flask several times to ensure thorough mixing ; 25 cc. are then withdrawn with a calibrated pipette for the estimation. The pipetted volume represents one-twentieth of the weight taken, *i.e.*, about 0·5 gm. H_2SO_4. The acid may be estimated either by titration with standard alkali, or gravimetrically by precipitation with $BaCl_2$.

For the fuming acid, the same method is adopted, but the acid should be diluted to 1,000 cc. Great care must be taken in diluting the fuming acid, and it may be safer to stand the sample in a dish exposed to the air overnight to enable it to hydrate itself without danger to the operator. To prevent the entry of dirt and dust, it is suggested that the dish containing the acid, the weighing bottle (unrinsed, of course) and a dish of water be placed together under a bell jar ; the acid will have diluted itself down to about 1·4 sp. gr. in 12 hours or so. It is then safe to dilute, but the operator is warned to be cautious even then.

FREE SULPHUR.

Free sulphur in a mixture is estimated by extracting with CS_2 or CCl_4 in a Soxhlet apparatus. The extracting liquid must have been recently distilled.

One gram of the mixture (more if the percentage of sulphur is low) is weighed out into the thimble and the extraction with the reagent is started. After 10 or 12 syphonings, the flask into which the solution returns is removed and the reagent distilled off on the water-bath. The flask and the extracted sulphur are then weighed. After weighing, the flask is placed on the water-bath for half an hour longer and then re-weighed, continuing until the weight is constant.

This is effective only if there is nothing else present in the sample which is soluble in the reagent used for the extraction. If impurities are present, the residue in the flask (which need not be weighed in these circumstances) is treated with a solution of bromine in CCl_4, or, if CCl_4 was used for the extraction, a few cc. of bromine are added to the extract as soon as the apparatus is disconnected. (CCl_4 is safer to use than CS_2 as it is not inflammable ; it has the other advantages of not being so offensive to use and not being liable to decomposition with the formation of sulphur, which goes into solution in the excess of the liquid. Moreover CS_2 must be distilled off before the oxidation with the bromine can be carried out. The tetrachloride has, therefore, every advantage.)

The bromine mixture is slowly evaporated on the water-bath, and towards the end 20 cc. of HNO_3 are added together with about 1 gm. of KNO_3 to combine with the H_2SO_4 which is being formed. The

mixture is finally taken quite dry and a second evaporation carried out with 20 cc. HCl to destroy the excess of HNO_3. After the second evaporation, the dry mixture of K_2SO_4 and KCl is taken up in a little water, 10 cc. of HCl are added and the whole diluted to 500 cc. The $SO_4^=$ is then precipitated with $BaCl_2$ as has been described under Sulphides.

THIOSULPHATES.

Thiosulphates may be estimated by means of three reactions:

1. $H_2S_2O_3 = H_2O + S + SO_2$, the SO_2 being estimated as described under Sulphites.

2. $H_2S_2O_3 + 6\,O \rightarrow H_2O + 2\,SO_4^=$, the $SO_4^=$ being precipitated as $BaSO_4$.

3. $2\,Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2\,NaI$.

Reactions 1 and 3 are useless in the presence of sulphites or metabisulphites.

Reaction 2 is not available in the presence of any other sulphur compound.

To estimate thiosulphates by either of the first two reactions proceed in exactly the same way as described under Sulphites; the calculations are, of course, different.

The third method is a standard volumetric method and is described in great detail under Copper (and in other places). The solution is titrated with standard iodine, the strength of which may be checked against pure copper, or against a standard thiosulphate solution.

SULPHUROUS ACID AND THE SULPHITES.

1. **Free SO_2.**—(*In a Gas Mixture*).—(*a*) A measured volume of the gas is aspirated through an acid solution of $KMnO_4$ of known volume and strength. The excess of $KMnO_4$ is then titrated with ferrous sulphate.

(*b*) The gas is aspirated through excess of bromine water containing free bromine, in a Meyer bulb. The bromine solution is then rinsed out into a beaker, the bromine boiled out, and the SO_2, now sulphuric acid, precipitated with $BaCl_2$.

2. **Free SO_2.**—(*In Solution in Water.*—(*a*) A solution of SO_2 is very rapidly and conveniently estimated by an iodometric method, depending on the reaction.

$$H_2SO_3 + I_2 + H_2O = 2\,HI + H_2SO_4.$$

Under certain conditions, however, the secondary reaction

$$SO_2 + 4\,HI = 2\,I_2 + 2\,H_2O + S$$

sets in, and the results obtained are inaccurate. This is prevented by keeping the iodine in excess, adding the solution of SO_2 to a measured

quantity of standard iodine solution (in excess) and titrating the excess left after the reaction with standard thiosulphate.

Method.—Excess of the standard iodine solution is measured into a tall beaker and a measured volume of the SO_2 solution added. After gently stirring to mix the two solutions, the excess of iodine is titrated with thiosulphate until only a faint yellow colour remains ; starch indicator is then added and the titration continued until the blue colour is just discharged.

From the equation given,

$$80 \text{ gms. } SO_3^{=} \equiv 64 \text{ gms. } SO_2 \equiv 254 \text{ gms. } I_2.$$

If the usual " strong " iodine solution be used, 1 cc. is (approximately) equivalent to 0·0034 gm. $SO_3^{=}$, = 0·0027 gm. SO_2.

The standard iodine solution may be directly titrated with the sulphurous acid. The latter is placed in a burette and run into a measured volume of standard iodine until the yellow colour is faint ; starch indicator is then added, and the titration continued until the blue colour is just discharged.

(*b*) Potassium permanganate may be used in the place of iodine in the foregoing methods. The reaction is, in skeleton:

$$1.\ Mn_2O_7 = 2\,MnO + 5\,O, \text{ and}$$

$$2.\ SO_2 + O = SO_3.$$

Thus, $2\,KMnO_4 \equiv 5\,SO_2$, and since $2\,KMnO_4 \equiv 10\,Fe^{++}$, $SO_2 \equiv 2\,Fe^{++}$ when titrated with permanganate. In gram equivalents this becomes: 64 gms. SO_2 = 111·7 gms. Fe ; the iron factor of the permanganate must therefore be multiplied by $\frac{64}{111{\cdot}7}$ to obtain the factor for SO_2, (by $\frac{80}{111{\cdot}7}$ for $SO_3^{=}$).

The method is exactly the same as that given under Iodine ; *i.e.*, either a measured volume of the sulphurous acid is added to excess of the permanganate and the excess titrated with ferrous sulphate, or the SO_2 solution may be run into a measured excess of the permanganate from a burette. Of the two, the latter is the more accurate procedure in both cases, as there is less liability to loss of SO_2 from a burette than from a beaker, though, if the mixture be made quickly, there should be no serious trouble from this cause.

Standardising the Iodine Solution.—Four grams of resublimed arsenious oxide are weighed out accurately into a small porcelain dish and a little conc. NaOH solution added. When the oxide has dissolved, the sodium arsenite is rinsed out into a 1,000 cc. flask and 1 drop of phenolphthalein is added. The solution is then exactly neutralised with H_2SO_4 (dil.) and 5 or 6 gms. of pure $NaHCO_3$ are added. After cooling, the solution is made up to the mark. There should be no pink colour when the bicarbonate is added ; a pink colour is due to the normal carbonate, which interferes with the reaction ; if a pink tint is obtained, one drop of the dilute acid will discharge it. The iodine

used for the estimation is then titrated with this solution using starch as indicator.

1 cc. arsenite solution ≡ 0·01026 gm. I_2
and 254 gms. I_2 ≡ 64 gms. SO_2 or 80 gms. $SO_3^{=}$.

Soluble sulphites (and metabisulphites) may be estimated by the iodine method by acidifying the iodine solution with a suitable amount of HCl so that SO_2 is generated *in situ*. The permanganate method is also applicable if the permanganate solution is similarly acidified with H_2SO_4. In these cases the volume of the solution should be sufficiently great to prevent the loss of SO_2. On the whole, it is best to proceed as follows in the case of a soluble sulphite:

Weigh out 0·25 gm. and dissolve it in 100 cc. of water. If the sample is Na_2SO_3 anhydr., the calculation is as follows:

126 gms. Na_2SO_3 ≡ 64 gms. SO_2 ≡ 111·7 gms. Fe^{++}, whence:
0·25 gm. Na_2SO_3 ≡ 0·225 gm. Fe^{++}.

Now 1 cc. of standard* $KMnO_4$ ≡ 0·00305 gm. Fe^{++}, so that 100 cc. will supply an ample excess.

Measure out 100 cc. of the permanganate solution with a pipette and transfer to a tall 600 cc. beaker, add 5 cc. H_2SO_4, previously diluted and cooled, and then the sulphite solution in a slow stream with constant stirring. The dark colour fades considerably; when the reaction has completed itself, which is a matter of seconds only, provided the stirring and mixing are properly conducted, the excess of permanganate is titrated with standard ferrous sulphate solution. From the cross titration of the two solutions, the volume of standard permanganate reduced by the SO_2 is calculated, and the weight of SO_2 follows from the above relations. It does not matter, of course, that the permanganate has been diluted twice since it was measured; the solution will have the same oxidising power whatever its dilution, within reason; *i.e.*, there will be the same excess *weight* of $KMnO_4$ no matter what the volume may be, and it is the excess *weight* we are titrating with the Fe^{++}.

Similar methods may be employed for the iodine reaction.

Gravimetric Method.—This is of general application. In the case of a soluble sulphite, 0·25 gm. (or more, if the sample is impure) is weighed out into a tall beaker or conical flask; 100 cc. of water are added and a few drops of bromine. The solution is digested in a warm place for half an hour, adding more Br_2 is necessary; it is then just acidified with HCl, and precipitated with hot $BaCl_2$ solution as detailed under Sulphides.

Insoluble sulphites are treated in the same manner exactly, as (provided the sample is finely divided) the bromine will oxidise a suspension just as well as a solution. Complications are, of course, possible, *e.g.* in a solution containing lead or calcium, or a metal such as silver, which gives a precipitate with HCl and Br_2 ($Br_2 + H_2O = 2HBr + O$). In these cases the volumetric method must be used; the formation of a precipitate will not affect the result.

* See Section on Volumetric Analysis.

GROUP II.

THE HALOGEN ACIDS.

HYDROCHLORIC ACID AND THE CHLORIDES.

The chlorides are all soluble in water with the exception of AgCl and Hg_2Cl_2. $PbCl_2$ is only slightly soluble in cold water, and is precipitated unless the concentration of Pb^{++} or Cl^- is very low ; TlCl is similar to $PbCl_2$, and $BaCl_2$ and NaCl, though easily soluble in water, are precipitated from concentrated solutions on the addition of conc. HCl.

Cl^- is estimated gravimetrically by the precipitation of AgCl from a solution made slightly acid with HNO_3 ; volumetrically, it is estimated by titration with standard $AgNO_3$ solution.

A. Gravimetric Estimation.—To the solution in a conical flask a few drops of HNO_3 (or H_2SO_4) are added (if neutral or alkaline) and excess of a moderately dilute solution of $AgNO_3$. The mixture is shaken vigorously ; this has the effect of bringing the precipitate together in quick-setting clots, leaving a clear layer of liquid which may be tested for excess of $AgNO_3$ by the addition of a drop of the reagent, when no further precipitation should take place.

The clear solution is decanted through a weighed Gooch crucible, preferably with an asbestos pad, though paper dried at 100° C. may be used. The precipitate is then rinsed into the crucible with a little cold water and the whole washed until the filtrate gives no precipitate or cloudiness when tested with a little HCl in a test-tube. The precipitate is dried in the air oven and finally heated to below redness in the mouth of the muffle, but only if asbestos pulp has been used ; do not overheat, as AgCl fuses at 451° C. Weigh as AgCl.

The precipitate may be filtered off on paper in the ordinary way, but this entails a manipulation which takes time and gives several chances for accident. If this method be adopted, however, the precipitate is washed into the apex of the paper, and when it is free from Ag^+ by test, the paper is opened out and placed flat upon a glazed tile in the air oven, or on a piece of asbestos board on the edge of the hotplate. When the paper and precipitate are quite dry, the AgCl is brushed off on to a piece of smooth paper, preferably dark coloured, and the filter paper is loosely folded and placed in a weighed porcelain crucible which is set in the mouth of the muffle for the paper to be charred and ashed. This done, the crucible is removed, and, after cooling, 1 drop of HNO_3 is allowed to fall from a small pipette on to the ash. This converts any reduced silver into the nitrate, which is then converted into chloride by the addition of a drop of HCl. The acids are evaporated off in the mouth of the muffle and the bulk of the AgCl from the paper is brushed into the crucible, the whole being heated to the point at which the mass just fuses, then cooled, and the crucible weighed again.

This procedure was once used for all precipitates which were thought to be reducible by glowing carbon ; nowadays, of course, the analyst employs a Gooch crucible fitted with an asbestos pad, or still more

recently for acid solutions at least, a Gooch crucible with a filter pad of ignited, pure silica. A platinum Gooch with a filter of platinum sponge is also used occasionally for special work, but it is expensive and not always applicable.

Note 1.—The white precipitate of AgCl slowly darkens when exposed to light and it is occasionally advised to perform the precipitation in the dark, or in a dark glass vessel, or at least in a flask surrounded by a roll of brown paper. Unless the darkening, which is usually considered to involve the formation of a small quantity of a sub-chloride of silver is very intense, the change in weight is so small as to be undetectable by the ordinary analytical balance. All the usual precautions are, therefore, quite unnecessary, though it is advisable to carry out the precipitation in the dimmest lighted corner of the laboratory and not to allow the AgCl to stand exposed to the light for longer than is necessary.

Note 2.—To remove the fused precipitate from the crucible, add a piece of granulated zinc and fill the crucible with HCl or H_2SO_4 (dil.). Silver is precipitated as a spongy mass, the chloride being disintegrated in the process.

Note 3.—To estimate Cl^- in an insoluble chloride or in a mixture of AgCl and $PbCl_2$, for example, a fusion with Na_2CO_3 is carried out, the Cl^- being estimated as before after extracting with water, filtering, washing, and acidifying with HNO_3.

Free Hydrochloric Acid.—This may be estimated either gravimetrically or volumetrically ; in the latter case, the method chosen may be titration either with $AgNO_3$ solution or with a standard alkali ; for the latter, see Acidimetry.

The concentrated acid is weighed into a bottle, but without special precautions unless the sp. gr. is over 1·16, when it is advisable to use the pipette with a long rubber tube attached, and effect the transference as quickly as possible.

Volumetric Method.—This is the titration of the solution with a standard solution of $AgNO_3$ in dilute HNO_3 solution. It is the exact reverse of the method which has already been given under Silver for the estimation of that metal by titration with standard NaCl solution, and the student is referred to that section for details.

BROMIDES AND IODIDES.

The free acids and their salts are estimated Gravimetrically and Volumetrically in exactly the same way as has been detailed under Chlorides, except, of course, that the precipitates are, respectively, AgBr and AgI.

In the case of salts of hydrobromic and hydriodic acids, however, there is an important reaction, which, though possible in the case of chlorides, is, nevertheless, never employed in analysis for obvious reasons. The reaction is, in the case of a bromide:

$$KBr + Cl = KCl + Br,$$

i.e. the more electronegative chlorine expels bromine quantitatively from its compounds. In the case of iodides, both chlorine and bromine

are capable of replacing the iodine. The reaction is employed in the indirect estimation of chlorine (or bromine) when in the free state, but is of general application in the assay of compounds which can yield chlorine when treated with a reagent, usually HCl. Its application to the estimation of Cl^-, Br^-, and I^- when present in the same sample will be discussed under Separations of the Acids.

Iodides have one special reaction which differentiates them from the other halide salts, and that is their interaction with a soluble palladium salt, to give a precipitate of PdI_2.

Precipitation of I^- as PdI_2.—Make the solution slightly acid with HCl and add a solution of $PdCl_2$ until no more precipitation takes place. Place the beaker on the edge of the hotplate or on the top of the air oven for two or three hours to allow the palladous iodide to settle out well ; then filter through a weighed paper or asbestos pad Gooch crucible that has been dried in the steam oven at 100° C. Wash with water until the filtrate ceases to react with a solution of $AgNO_3$. Dry the crucible and precipitate at 100° C. in the steam oven ; weigh as PdI_2.

This method is important as it enables iodides to be estimated in the presence of either Br^- or Cl^- or both, since $PdCl_2$ and $PdBr_2$ are both soluble.

HYPOCHLOROUS ACID AND HYPOCHLORITES.

These are invariably estimated volumetrically. The commonest example of the estimation of hypochlorites occurs in the evaluation of bleaching powder, and as this is of some theoretical interest, and affords practice in a method which is somewhat out of the ordinary, full details will be given.

Evaluation of Bleaching Powder.—Weigh 10 gms. of the bleaching powder as rapidly as possible, and transfer to a lipped beaker. Add 300 cc. of water (cold) and shake and stir gently until the mixture is homogeneous ; then transfer to a litre graduated flask, rinsing the beaker out with successive quantities of water until all the insolubles are in the flask. Make up to the mark with water and pour to and from the original beaker once or twice to mix the suspension-solution thoroughly, finally transferring the mass to the flask.

Shake and mix by inverting the stoppered flask once or twice, and quickly pipette out 50 cc. of the milky liquid, transferring it to a tall 300 cc. beaker or flask ; add 3 gms. of KI in a little water. Make the solution just acid with acetic acid and titrate at once with standard thiosulphate. The results are calculated from the following relation:

127 gms. I ≡ 35·5 gms. " available " Cl.

The reactions are:

$$Cl_2 + 2KI = 2KCl + I_2 \text{ and}$$
$$HClO + 2\,KI = KCl + KOH + I_2,$$

so that the " available " chlorine is derived from the hypochlorite present ; the total available chlorine is probably a measure of the hypochlorite present, but the latter decomposes in air under the influence

of the CO_2 which is invariably present, and some free chlorine is always detectable in the powder and its milky extract. The free chlorine, of course, registers as hypochlorite, but as from a technical point of view the value of the powder is measured by the amount of "available" chlorine in it, this does not matter.

An alternative method is to titrate the 50 cc. of the sample, which represent 0·5 gm., with standard arsenite solution, using strips of potassium iodide-starch paper as an outside indicator. As the reaction nears completion, a drop of the liquid is removed on the tip of a glass rod and touched on the paper; when a blue colour no longer immediately develops, the reaction is complete.

Note 1.—It is necessary to take a large sample as the powder is never sufficiently homogeneous to render a small weight a satisfactory sample of its composition.

Note 2.—If free chlorine and hypochlorous acid are to be estimated separately when present in the same solution, the procedure is as follows:

1. To the solution add a slight excess of standard HCl (N or 0·1 N). Then add the KI and titrate with thiosulphate as described. This gives the measure of *chlorine + hypochlorous acid.*

2. Now add to the solution 3 drops of methyl orange and titrate the excess of acid with standard alkali (N or 0·1 N). The difference between the volume of standard acid originally added and the volume of standard alkali used in this titration measures the amount of KOH liberated by the second reaction. This difference is calculated to grams of KOH from the relation:

1 cc. N KOH contains 0·056 gm. KOH, which is equivalent to 0·0525 gm. HClO.

Now calculate the weight of iodine this weight of HClO will liberate from KI, from the relation:

$$52{\cdot}5 \text{ gms. HClO} \equiv 254 \text{ gms. } I_2$$

and deduct this weight from the total iodine found. The difference represents the iodine liberated from the KI by the free chlorine, and the weight of this follows from the relation:

$$127 \text{ gms. I} \equiv 35{\cdot}5 \text{ gms. Cl.}$$

Unfortunately, this method cannot be applied to bleaching powder owing to the free $Ca(OH)_2$ that is present.

Note 3.—The theoretical percentage of "available" chlorine in bleaching powder is 48·9, but the best specimen that has been obtained in the laboratory contained 48·7 per cent. The commercial product never has as much chlorine as this.

CHLORATES.

Chlorates are readily reduced to chlorides either by Fe^{++}, by nascent hydrogen or by sulphur dioxide.

1. *By Ferrous Iron.*—Take 0·25 gm. of a sample of a chlorate (or a volume of chlorate solution or chloric acid that will contain approximately this weight), and dissolve it in 100 cc. of water. Add 5 gms. of ferrous sulphate dissolved in 50–60 cc. of water and bring the solution

to the boil, keeping it at the boiling-point or thereabouts for 15 minute Add sufficient dilute HNO_3 to clear the solution from any deposite basic salts and precipitate the Cl^- with $AgNO_3$ as described unde Chlorides.

2. *By "Nascent" Hydrogen.*—The solution should be rather dilute about 500 cc. is advisable. Add acetic acid until the reaction is distinctl acid and then zinc dust to excess. Digest the mixture at the boilin point for at least an hour ; then dissolve the excess of zinc in a litt HNO_3 and precipitate the Cl^- as AgCl as described under Chlorides.

3. *By Sulphur Dioxide.*—The solution is saturated with SO_2 in the col The excess of sulphur dioxide is then boiled off, HNO_3 added as usua and the Cl^- precipitated as AgCl.

Note.—Heating an alkali chlorate until all the oxygen has bee expelled does not give accurate results, as some chlorine is invariab lost.

PERCHLORATES AND PERCHLORIC ACID.

The sample is weighed into a platinum dish and mixed with fo times its weight of pure sublimed ammonium chloride. The mixtu is covered with a cover-glass and gently heated over a small flame a temperature short of the melting point of KCl, but sufficiently hig to expel all the NH_4Cl. A second admixture with NH_4Cl is made ar the heating repeated ; finally, the residue is extracted with wate about 5 cc. of HNO_3 are added, and the Cl^- that is now present precipitated with $AgNO_3$ as described under Chlorides.

The weight of the sample taken should not be too great ; 0·25 gr is convenient. The reaction seems to be helped by the presence platinum, which acts as a catalyst ; if, therefore, a platinum dish not available, a drop or two of platinichloride solution should be add to the mixture.

Perchlorates are not reduced by ferrous salts or by SO_2.

Perchloric acid is first neutralised by the addition of dilute KO or NaOH, and the solution then taken to dryness on the edge of t hotplate before admixing with the NH_4Cl.

Note.—Mixtures of perchlorates with organic matter are liable explode if heated.

FLUORIDES.

Hydrofluoric acid very rarely occurs in analysis for estimation important quantities. In the analysis of a soluble fluoride the F^- precipitated as CaF_2, in which form it is weighed.

Method.—The solution, if acid, is neutralised with Na_2CO_3 solutio adding about 1 cc. of the 10 per cent. solution in excess. The soluti is brought to the boil and excess of $CaCl_2$ solution added, slowly a with stirring. The resulting white precipitate is allowed to settle a then filtered through a close-textured paper, washing with hot wat until free from Cl^-.

The above method, as can be seen at a glance, involves the c precipitation of some $CaCO_3$; the object of this is to open out t fluoride precipitate and allow it to come into contact with the wa

liquid, as otherwise the CaF_2 will not permit the water to pass through except with extreme slowness.

The combined precipitates are transferred to a platinum crucible and ignited as usual, not allowing the temperature to exceed a bare redness. The crucible is cooled, and the white residue brushed out into a small beaker, where it is extracted with 1 : 3 acetic acid, which removes the $CaCO_3$ as soluble calcium acetate. The mixture is then re-filtered and washed free from the acetate ; this time, however, the fluoride will be found to filter quite well. It is important to avoid the use of too much acetic acid, as the CaF_2 is appreciably soluble even in the dilute acid. The residue, after gentle ignition, is weighed as CaF_2.

The most important commercial product in which fluorine is involved is the mineral fluorspar, which is CaF_2 with varying amounts of impurities. Fluorspar is not completely broken up by fusion with alkalis, and the accurate estimation of F^- in this compound is a long and difficult process, of which an outline only can be given here.

Mix the finely powdered mineral with three times its weight of SiO_2 and six times its weight of Na_2CO_3, and fuse at bright redness for half an hour in a platinum crucible. Extract with water and filter. The residue is $CaCO_3 + SiO_2$, etc., while the filtrate contains the alkali fluoride and silicate. To the filtrate add 5 gms. of solid $(NH_4)_2CO_3$ and stand for 6–8 hours in a warm place. Filter off the precipitated SiO_2 and discard it. Then evaporate the filtrate to dryness and take up the solid residue in a few cc. of water to which a little HCl has been added to produce a slight acidity. Boil the solution and add $CaCl_2$ to precipitate the fluorine.

Note.—The difficulty lies in the complete removal of the SiO_2, and, as a rule, further operations are required to remove the last traces. The foregoing method is, however, accurate enough for all but the finest work.

GROUP III.

NITROGEN ACIDS.

NITRIC ACID AND NITRATES.

There are no insoluble metallic nitrates. NO_3^- may, however, be determined gravimetrically, by precipitation with *Nitron*, an organic base the nitrate of which is only slightly soluble in water.

"Nitron" Method.—"Nitron" is diphenylendoanilohydrotriazole, the nitrate of which contains 16·5 per cent. of NO_3^-.

Take sufficient of the sample to contain about 0·1 gm. of NO_3^-, and dissolve in 100 cc. of water, adding 3 or 4 drops of dilute HCl. Boil the solution and add excess of the reagent (about 10 cc.) in a steady stream. Stir the mixture well and then cool completely in ice water. Filter the crystalline precipitate on to a weighed Gooch crucible, washing it with *small* doses of ice water. Dry at 100° C. and weigh.

Note 1.—The precipitate is appreciably soluble even in ice cold water, and the minimum quantity of wash liquid must be used ; the

Gooch crucible is specially suitable for complete washing with the least possible amount of water, as every drop must pass *through* the precipitate, and the porcelain is easily washed clean.

Note 2.—HBr, HI, HNO_2, $HClO_3$, $HClO_4$ and a few less common acids interfere, owing to the formation of very slightly soluble compounds with the reagent. HBr and HI may be eliminated by adding excess of chlorine water and boiling out Br_2 and I_2; HNO_2 and H_2CrO_4 may be reduced with hydrazine before precipitating the NO_3^-.

Note 3.—The reagent is made up by dissolving 10 gms. of the " nitron " in 100 cc. of 5 per cent. acetic acid. It should be kept in a dark coloured bottle, as it slowly decomposes in light.

Volumetric Estimation of Nitrate.—It is possible, in the absence of other oxidising agents, to estimate NO_3^- volumetrically by boiling it with a ferrous salt in excess and titrating the unoxidised Fe^{++}, but the following method is of universal application and is of some importance analytically.

Devarda's Method.—Pentavalent nitrogen can be completely reduced by nascent hydrogen to ammonia, the nascent hydrogen being furnished by the Al-Zn or the Al-Hg couple in a solution of NaOH or NOH.

0·2 to 0·25 gm. of the nitrate is weighed out into a 500–600 cc. flask and dissolved in about 100 cc. of water. About 5 cc. of ethyl alcohol and 50 cc. of a 33 per cent. KOH solution are then added, followed by 2–3 gms. of *Devarda's Alloy* (Al-Hg couple). The flask is connected by a bent glass tube, with which is incorporated a spray trap, to two large absorption bulbs, the first containing 20 cc. and the second 5 cc. of 0·5 N H_2SO_4 or HCl. A modified form of the apparatus shown in fig. 15, p. 150, is suitable.

When all is ready, and the apparatus has been proved gas-tight, the flask is gently warmed to start the reaction. Hydrogen is at once evolved and it may be necessary to steady the reaction down by cooling the flask. When the reaction ceases, bring the contents of the flask to the boil and distil off about half the solution. Disconnect the bulb tubes and rinse their contents out into a beaker. Add a drop or two of methyl orange and titrate with standard alkali.

The alkali titration result is subtracted from the total volume of standard acid placed in the absorption tubes, giving the amount of acid neutralised by the ammonia evolved. The weight of NO_3^- in the sample is calculated from the relation: 1 cc. 0·5 N acid $\equiv$ 0·0315 gm. of NO_3^-.

Gasometric Estimation of Nitrate.—This depends upon the reaction:

$$MNO_3 + 3\,FeCl_2 + 4\,HCl = MCl + 3\,FeCl_3 + 2\,H_2O + NO.$$

The solution of the metallic nitrate is boiled with a concentrated acid solution of ferrous chloride until all the NO is evolved. The NO is collected over water in a graduated cylinder.

The method is accurate, but very tedious owing to the numerous corrections necessary.

For the estimation of nitrates in drinking water see under Water Analysis.

NITROUS ACID AND THE NITRITES.

Nitrous acid is best estimated by a volumetric method, making use of the reducing action of "N_2O_3" by titrating warm permanganate with the nitrous solution. The reaction is:

$$2\,KMnO_4 + 5\,HNO_2 + 3\,H_2SO_4 = K_2SO_4 + 2\,MnSO_4 + 3\,H_2O + 5\,HNO_3.$$

As was mentioned under the titration of H_2SO_3, when one of the solutions in a volumetric process is liable to decompose or to lose strength by the escape of a dissolved gas, it is always best to use that solution as the titrating liquid, running it into a known volume or known excess of the standard with which it is being compared, the latter being preferable if practicable.

In the estimation of a nitrite, N_2O_3 is very liable to be lost in acid solution, and the following method is adopted to overcome this. The neutral nitrite is placed in the burette, while in a beaker underneath is an excess of standard $KMnO_4$, acidified as indicated in the equation with a little conc. H_2SO_4, which will heat up the solution somewhat. The proper temperature to work at is about 40°–50° C., and the solution of $KMnO_4$ must be moderately dilute.

Method.—The unknown nitrite solution, or an aliquot part, is poured into the burette, and excess of standard $KMnO_4$, diluted to 300–400 cc., and acidified with 10 cc. of conc. H_2SO_4, is placed underneath, after warming to 50° C. The nitrite solution is added slowly and cautiously, stirring or swirling vigorously in order to avoid local concentrations. As the reaction approaches completion, the reduction is very slow, and care must be taken not to overshoot the end-point, which is signalised by the final sudden discharge of the last trace of pink colour.

The concentration of the nitrite solution may be calculated from the iron factor for the permanganate, as follows:

316 parts $KMnO_4 \equiv 235$ parts HNO_2.
2 mols. FeO require 1 atom of oxygen.
1 mol. HNO_2 requires 1 atom of oxygen.
$\therefore$ $HNO_2 \equiv 2$ FeO,
or 47 parts $HNO_2 \equiv 111{\cdot}7$ parts Fe,

whence: the HNO_2 factor $= \frac{47}{111{\cdot}7}$ of the iron factor.

The method of adding the nitrite solution to excess of warm $KMnO_4$, acidified with H_2SO_4, and titrating the excess with a ferrous solution cannot be used owing to the HNO_3 that is formed by the reaction.

For the estimation of NO_2^- in water, see Water Analysis.

GROUP IV.

CARBON, CARBONIC ACID, CARBONATES.

Carbonic acid is a very weak acid and cannot be titrated as such, though the fact that the acid is so weak enables the alkaline carbonates

to be titrated as though the bases were uncombined, if methyl orange is used. For details, see under Acidimetry and Alkalimetry.

CARBONATES AND CARBONIC ACID.

Carbonates of the metals are estimated either by measuring the loss of weight that takes place when they are ' decomposed ' by a ' strong ' acid or by weighing the carbon dioxide that is evolved in the course of this reaction.

Method 1.—*Loss of Weight Method for Carbonates.*—One gram of the carbonate, or more if the sample is not pure, is weighed out and introduced into the lower bulb, A, of the apparatus shown in fig. 18 through the stoppered hole. Excess of acid, usually HCl, though HNO_3 or

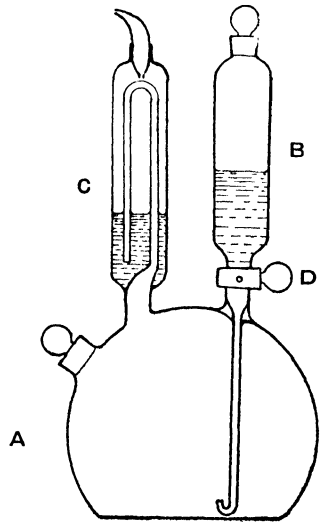


Fig. 18.—Apparatus for Estimation of Carbonates by Loss of Weight.

H_2SO_4 (dil.) may be used, is placed in the upper bulb B, the cock D being closed, and 1 or 2 cc. of conc. H_2SO_4 to act as a combined spray trap and drier, are introduced into bulb C. The reacting acid is chosen so that the salt which results from the decomposition shall be " soluble " ; *i.e.*, if the carbonate is $CaCO_3$, HCl is used, not H_2SO_4 ; if $PbCO_3$, HNO_3 must be used, but note that some chlorides and nearly all nitrates are very slightly soluble in their respective *concentrated* acids. (If the wrong acid is chosen, the reaction may cease by reason of the sample becoming coated with an insoluble layer.) The whole apparatus is carefully wiped over with a soft linen cloth and accurately weighed.

The stopcock at D is then opened and the acid allowed to enter A slowly, so that the reaction is always under control. CO_2 is evolved, and this escapes through the scrubber-drier, C. When the reaction is over, and all the acid has been admitted, a sodalime-calcium chloride

tube is attached to the upper opening of B, a rubber tube to the corresponding opening of C, and a gentle stream of dry, CO_2-free air is sucked through the apparatus, driving out the CO_2 which still remains and replacing it with air. The apparatus is then allowed to cool completely in a desiccator, after which it is again carefully wiped over and weighed. The loss of weight represents CO_2.

Method 2.—Estimation of Carbonate by Absorption of Evolved CO_2.—This is the converse of Method 1.

One gram of the sample is weighed out accurately and placed in a

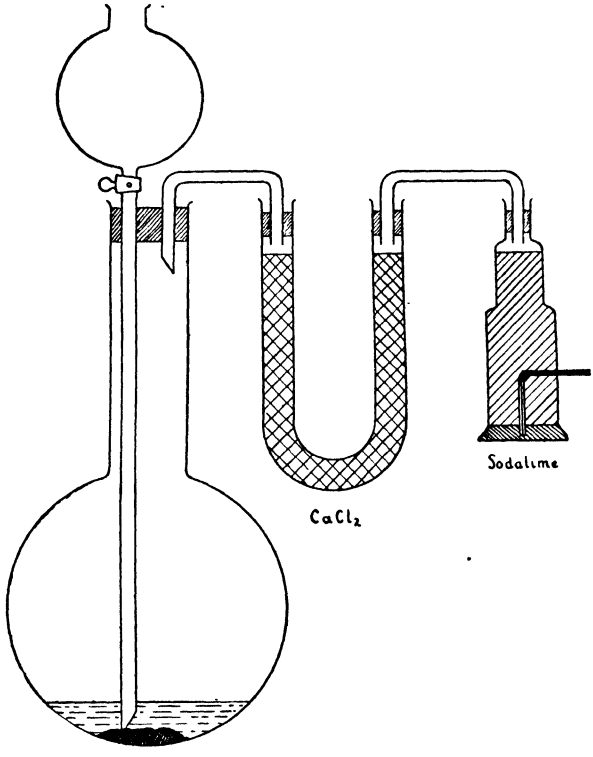


Fig. 19.—Apparatus for Estimation of Carbonates by Absorption of Evolved CO_2.

small (50 cc.) flask closed by a 2-hole rubber bung carrying (*a*) a tap-funnel reaching to the bottom of the flask, and (*b*) a glass tube connected through a drying tube to a weighed absorption bulb (see fig. 19). Any type of bulb will serve ; for a short discussion of the various types, see under the Estimation of Carbon in Steel.

1 or 2 cc. of water are added *via* the tap-funnel to act as a trap and to prevent any CO_2 being lost, and then 10 cc. of 1 : 1 HCl are run into the flask. When the reaction has ceased, the bulb is attached to an aspirator, the tap-funnel being connected to a sodalime-calcium chloride tube as before, and about 1 litre of dry, CO_2-free air is drawn

through the whole apparatus to drive the last traces of the CO_2 over into the absorption bulb, which is then disconnected, and after wiping, reweighed. The increase in weight represents CO_2.

Method 3.—"*Calcimeter*" *Method.*—This is a rough commercial method for the rapid estimation of CO_2 ; it is used in cement works for checking the limestone content of mixtures.

The sample (1 gm. is usual) is weighed out into the small flask A (see fig. 20), and an excess of acid is pipetted into the tube B, which is

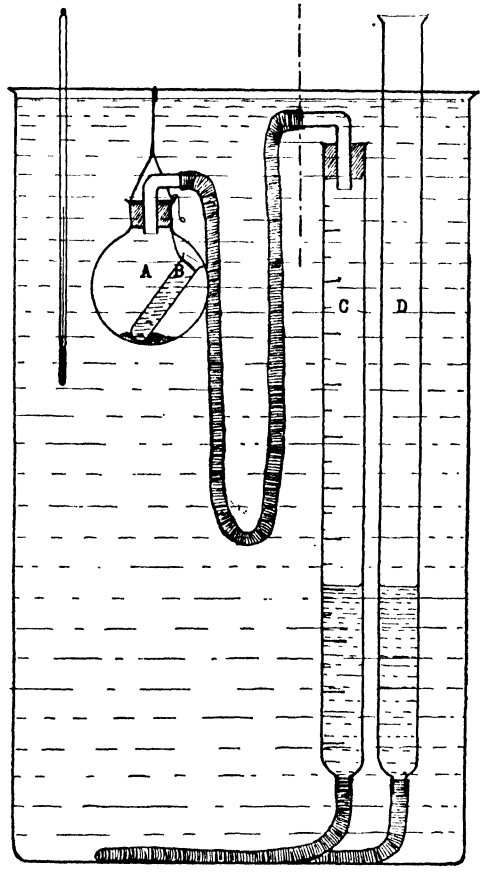


Fig. 20.—"Calcimeter" Method for Estimation of Carbonate.

held in an oblique position by a fine thread gripped by the cork. The flask is connected by a piece of bent tubing to a graduated cylinder C, in communication with a second similar cylinder D, the whole usually being contained in a large vessel of water which acts as a temperature equaliser ; the flask A should also be immersed in this water-bath, being hung from the rim by a wire hook ; this last precaution is quite necessary, as most of the heat changes take place in the flask.

The tube D is raised until the water stands at the zero mark in the cylinder C ; the cork in A is then quickly loosened and replaced, allowing the acid tube to fall upon its side and spill the acid upon the sample. CO_2 is briskly evolved, and the level of the water in C rapidly falls, the operator preserving the internal pressure of the apparatus as nearly as possible to atmospheric pressure by manipulating the balance tube D. When the reaction is complete and the temperature has equalised itself, the tube D is adjusted so that the levels in C and D are equal, the volume is read off, and the percentage of CO_2 calculated.

The calculation is by no means a simple one, and if full accuracy is desired there will be many corrections to apply, since the final volume depends upon temperature (which rises during the reaction), pressure (which may change during the operation), solubility of CO_2 in water (and in HCl containing $CaCl_2$), and the vapour pressure of the water (which again depends upon temperature and pressure). The calculation will make a nice little exercise for the student ; the cement analyst, however, is in a hurry, and reads the percentage of limestone direct from a complicated chart of variables calculated in advance, and usually supplied with the apparatus by the makers.

Method 4.—*Estimation of Carbonate as* $BaCO_3$.—The CO_2 in a gas mixture, or evolved during the reaction between an acid and a carbonate, is bubbled through a clear, recently filtered solution of $Ba(OH)_2$, which captures the CO_2 and holds it as white, precipitated $BaCO_3$. This may be filtered off (in an atmosphere free from CO_2), washed with CO_2-free water, and weighed as $BaCO_3$ after gentle ignition. The method of filtering and washing without exposure to the atmosphere is as follows:

The $Ba(OH)_2$ solution is measured out into a Meyer bulb-tube, one end of which is attached to the apparatus in which the CO_2 is being generated and the other to a sodalime tube to keep out CO_2. Any form of evolution flask will serve, but it is best to make it as small as possible, so that the washing out with air may be easier ; for this purpose a tap-funnel dipping to the bottom of the flask is a necessary adjunct. When all the gas has passed through the Meyer tube and the evolution vessel has been " washed out " by drawing CO_2-free air through it, the absorption bulbs are detached and quickly connected by means of clean rubber tubing with a large vessel full of recently distilled water (therefore free from CO_2) on the one side, and a Gooch filtering apparatus on the other, as indicated in fig. 21.

The $BaCO_3$ is filtered off and washed and the crucible and precipitate ignited to a dull redness, the CO_2 being weighed as carbonate.

Or, the precipitate may be filtered off on a paper pulp supported by a porcelain filter disc in the ordinary way, using the special cylindrical funnel as shown. When washed free from the excess of $Ba(OH)_2$, it is rinsed out into excess of standard HCl and the excess acid titrated with standard alkali.

Another method, not so good, consists in absorbing the CO_2 in a known volume of standard $Ba(OH)_2$ solution in the Meyer bulbs, and, having filtered off the precipitate, titrating the excess of hydroxide with standard acid. The difficulty here is that the hydroxide very rapidly picks up CO_2 from the air and becomes covered with a film of carbonate

during the titration ; this does not matter in theory, as the same volum of acid will be used in converting the $BaCO_3$ to $BaCl_2$ as will be neede by the $Ba(OH)_2$, but the film is a nuisance in practice owing to i

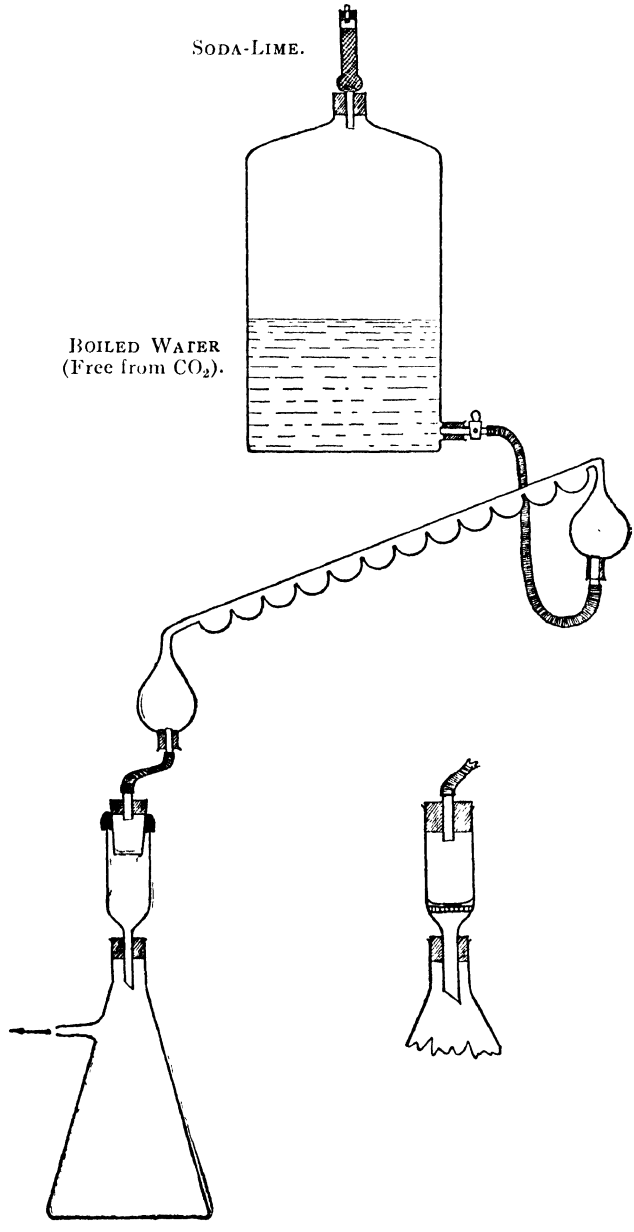


Fig. 21.—Apparatus for Estimation of Carbonate as $BaCO_3$.

creeping propensities, though the titration can be conducted by over-titrating with the standard acid, thereby dissolving the clinging carbonate from the sides of the beaker, and then back-titrating with standard alkali. There is really very little to choose between the two routines in theory, except for the slight trouble mentioned, which necessitates the use and reading of two burettes, but the other possible source of error, at the commencement, when the known volume of $Ba(OH)_2$ is being measured out, is more serious. For, unless the pipetting out and transference of the solution be very rapidly performed, some $BaCO_3$ will be formed during the process, and this will be filtered off with the $BaCO_3$ produced in the estimation, giving a high result for the CO_2. The additional " accurate " measurement also gives opportunity for a mistake.

Method 5.—*Titration with Standard Acid.*—Any carbonate, in the absence of salts of other weak acids and bases or basic salts, may be estimated rapidly by dissolving in a measured excess of standard N acid and titrating the excess of free acid with standard alkali. This applies to insoluble carbonates ; the soluble carbonates are always titrated directly with standard acid, and details are to be found under Acidimetry and Alkalimetry. This section should be referred to if any of the foregoing methods involving a volumetric process be selected, as the titration involves an understanding of the theory of indicators (see Section II., p. 35) ; CO_2 has a slight effect upon methyl orange, more upon litmus, and a considerable effect upon phenolphthalein.

CARBON.

The estimation of free carbon or carbon combined as carbide, is one upon which a very great deal of investigation has been carried out, in view of the extreme importance in practice of an accurate knowledge of the amount of carbon present in iron and steel.

Free carbon is always estimated by oxidising it to CO_2 and measuring the latter, either volumetrically, by collecting the gas in a graduated vessel, or, more usually, gravimetrically, by measuring the increase in weight when the CO_2 is absorbed by a suitable reagent. A variation of the latter method is to absorb the gas in a solution of $Ba(OH)_2$ and weigh the $BaCO_3$ that is precipitated ; or, to dissolve it, after filtering and washing, in excess of a standard acid solution and titrate the excess of acid. One other method, which is of academic interest only, is to collect the CO_2 by freezing it out in a bath of liquid air and measure the increase of pressure in a vessel of known volume when the liquid gas is allowed to vaporise.

There is no difference, except in obvious details, in the methods of estimating free carbon and carbide carbon by combustion in a current of oxygen.

Details of the estimation of carbon in iron and steel are given in the following, this being by far the most important estimation of the kind.

Estimation of Carbon in Iron and Steel.—A furnace, preferably electrically heated, is used for heating the combustion tube ; the combustion tube is a cylindrical tube made of silica or porcelain and about 1 inch in diameter. A purification train is set up as shown in fig. 22

to free the entering oxygen from traces of CO_2 before its admission to the furnace. The sample of steel is placed in the hot tube, where the carbon burns to CO_2 in the current of oxygen, and the issuing gas is passed through another train of vessels to purify it from other compounds that might influence the results (*e.g.* SO_2, oxides of phosphorus, and the like), before being passed through the final absorption vessel where the CO_2 is taken up.

There have been, in the past, many patterns of apparatus designed for this estimation, and many different trains of purifying and absorbing reagents have been proposed and used. A great deal of difference of opinion as to the necessary conditions has also obtained, but the alterations and modifications have all tended to simplify the apparatus and to shorten the time required for the estimation. At one time, not so long ago, it was considered necessary to separate the carbides before entering upon the combustion ; this was effected by attacking the steel (or iron) with a solution of the double chloride of potassium and copper (-ic), slightly acidified with HCl. The action was slow and the carbides that were left behind when the iron dissolved had to be filtered and washed free from Cl^- on an asbestos pad, which then had to be dried at not too high a temperature before it was ready for combustion. It was then shown that the same results could be obtained by direct combustion of the metal drillings or turnings in oxygen, provided that the temperature in the furnace was sufficiently high to burn the metal. Iron, in a moderately finely divided condition, readily catches fire and burns in oxygen at temperatures above about 800° C., but as it is usually considered necessary that the Fe_3O_4 which is formed shall fuse, the furnace is worked at 1,000° ± 50° C.

Purification Trains. - Oxygen nowadays is prepared commercially from liquid air, so that its chief impurity is argon ; nitrogen comes next, and then, perhaps, CO_2, but this latter, which is the only one that need be considered, is never present in serious amounts in oxygen produced in a modern air liquefying plant. Still, it must be guarded against, as also must small amounts of organic matter which are occasionally present. The author tests each oxygen cylinder supplied for purity as follows: The preliminary purification train of the carbon combustion furnace is temporarily disconnected and the bottle E filled with the gas by displacement from the cylinder T. The rubber tube connecting E to the oxygen cylinder is detached from the latter and connected to a short combustion tube of hard glass or silica containing a roll of fine " copper oxide " gauze between two plugs of loosely packed asbestos. The " copper oxide " gauze is prepared by heating a compact roll of ordinary copper gauze to redness with a small burner while oxygen is passing over it ; the oxide serves to convert carbon monoxide and organic matter into CO_2. The tube containing the gauze is attached to a tall washbottle containing 100 cc. of $Ba(OH)_2$ solution. The tap D is closed and 5 litres of oxygen are bubbled through the baryta. E is then once more filled with oxygen, the copper oxide tube is brought to redness, and the gas again bubbled through the baryta (after filtering off $BaCO_3$ if much is precipitated during the first test). From the results of these two trials it is easy to see if there are serious amounts of (*a*) CO_2, and (*b*) other carbon compounds in the oxygen supply. As a rule

little or no $BaCO_3$ is thrown down in the first test, and only traces in the second test. The sodalime tower H will absorb these small amounts of CO_2, but if the second test with the copper oxide gauze working, shows more than traces of $BaCO_3$ a heated gauze tube must be introduced permanently into the preliminary train between E and H. If this test shows positive results on several cylinders, the analyst has a legitimate grievance against the oxygen suppliers. Volatile carbon which is not present as CO_2 will appear as a " blank " in the final absorption bulb R ; the existence of a blank, provided it is not too large, is easily allowed for, as a definite volume of oxygen is used for all combustions.

The following is a complete description of the train in use in the author's laboratory (see fig. 22) :

A, E. Glass bottles holding about 5–6 litres and graduated roughly in litres. E is closed with a 3-holed bung carrying glass tubes communicating with A (closed by tap B), F (closed by tap C), and T (closed by tap D).

F, P. Sulphuric acid bubblers each containing about 5 cc. of concentrated acid. P enables the operator to observe the velocity of the issuing gases.

G. Drier containing about 100 cc. of strong acid.

H. Sodalime (" Sofnolite ") tower to absorb final traces of moisture and any accidental CO_2, (etc.). Glass-wool in base ; soda-asbestos at top.

J. Pierced stopper communicating with side tube.

K. Soft rubber bung, a good fit in the combustion tube.

L. Combustion boat and shield.

M. Filling of ignited asbestos. Acts as (*a*) filler to reduce dead space in the combustion tube, (*b*) filter to stop passage of Fe_3O_4, SO_3 and P_2O_5, and (*c*) protects the bung N from heat.

N. Rubber bung carrying a capillary glass tube the aperture of which is adjusted so that only 200–250 cc. of oxygen can pass per minute under a full head of water in A.

O. 80-Mesh zinc to act as final filter for solids in the gas stream and to stop any acidic oxides that may still be in the vapour state.

R. Absorbent (" Sofnolite " with soda-asbestos). Three types of tube are shown: The Midvale, Dennstedt's, and a plain U-tube. Tubes with two stoppers are to be preferred.

Q, S. Stoppers.

T. Oxygen cylinder with reducing valve, etc.

U. Spring clamp.

V. Sliding resistance.

W. Ammeter.

Method of Conducting the Estimation.

Required: 1. A supply of recently ignited fireclay boats.
2. Spray-shields. Two if sheet nickel is used ; one only, if alundum.
3. Piece of asbestos board about 6″ square.
4. Tool of stout copper wire furnished with a hook at one end.
5. Two similar absorption tubes.

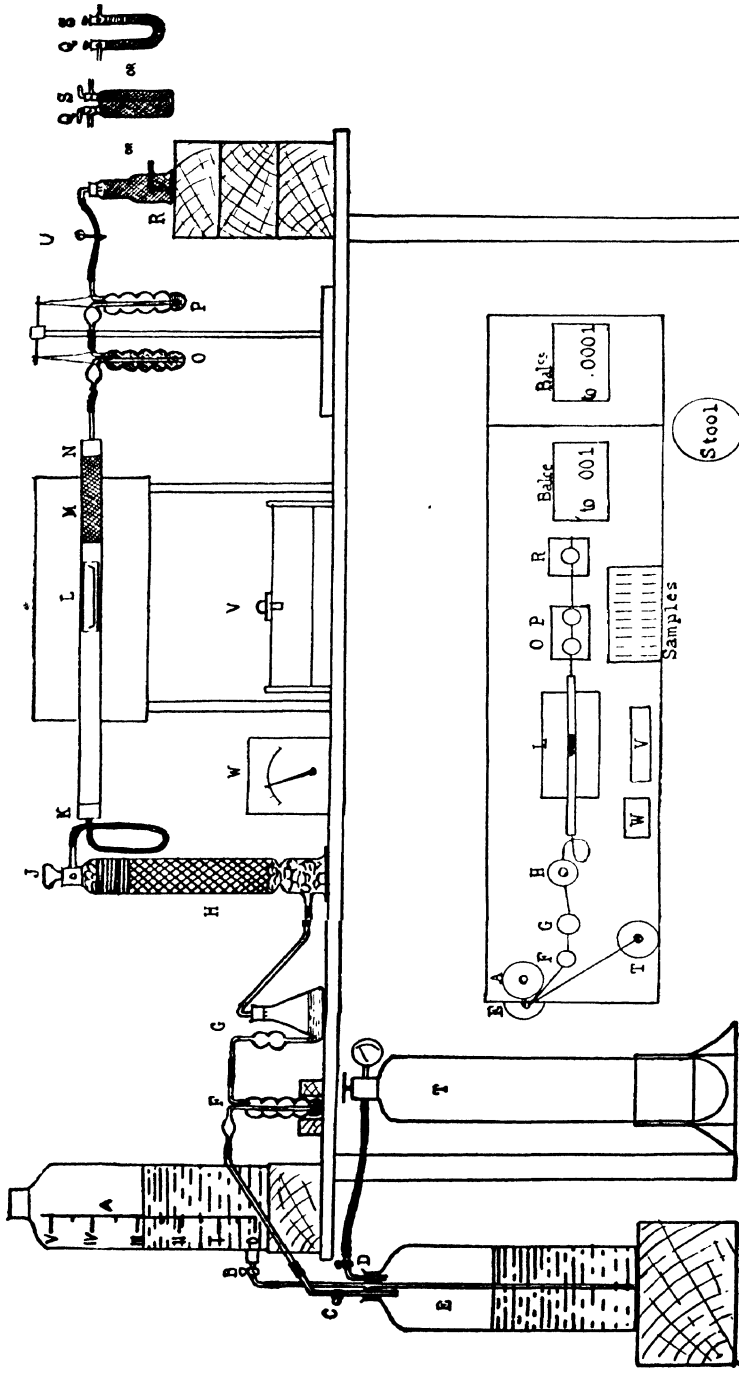


Fig. 22.—Apparatus for Carbon in Steel by Combustion.

1. Fill E with oxygen by opening B and D, C being closed. When A is full of water displaced from E, close the oxygen cylinder valve and tap D.

2. See that clamp U is shut, then *cautiously* open tap C (if this is not done with care the pressure may blow sulphuric acid into the rubber connections). Watch the bubblers F and P. When the pressure is equalised throughout the apparatus no gas will pass through either bubbler if the apparatus is free from leaks. (Note, however, that leaks between E and K do not affect the results and that *small* leaks between K and S are not of much importance owing to the short time taken for the combustion. But it is very slovenly and unworthy of Chemistry to work with defective apparatus.)

3. Switch on the furnace. The proper temperature is 1,000° C., and it is important to work at or near this temperature in every case. As a rule the makers of electric furnaces supply calibration charts for use with each furnace in conjunction with the ammeter and resistance in the circuit. Attention to the tables of Current/Temperature will enable the operator to select the temperature he desires by altering the resistance until the current is correct, but it will be found that as the furnace ages and the heating coils oxidise, the tables no longer give correct results, and it is advisable to check the actual temperatures inside the tube occasionally by means of a pyrometer. If a pyrometer is not available, small pieces of gold and silver wire will serve as temperature indicators. Silver melts at 960° C. and gold at 1,063° C., so that when the furnace is working properly, the silver will fuse and the gold will not. The two pieces of metal, in the form of strip or wire, are propped up in an inclined position inside a fireclay boat and watched through the open tube at the end. With a little practice the operator can learn what 1,000° C. " looks like " and adjust his furnace accordingly ; it is advisable for him to test his judgment periodically with the pyrometer or the metal wires, and always note the current which gives the correct temperature.

It takes about 40 minutes to 1 hour to heat the ordinary type of furnace from atmospheric temperatures to 1,000° C.

4. Attach an absorption tube to the exit end of P, taking care that both stoppers are shut. Remove the spring clamp U from the rubber connection.

5. Open S *slightly* and allow a slow stream of oxygen to pass through the apparatus (about 1,000 cc. in 30 minutes). At the end of this time, close J and remove the absorption tube. Wipe it carefully with a clean cloth (the author uses Selvyt cloth) and weigh it accurately. Re-attach it and pass a second litre of oxygen, more rapidly this time. Again weigh after wiping. The two weighings should agree to within 0·0002 gm. If the weight is constant, put R into the desiccator and attach tube R′. Repeat the foregoing until R′ comes to constant weight. *Always* wipe the absorption bulb before weighing it.

6. While tubes R and R′ are being brought to constant weight and the furnace is heating up, the samples of steel or iron are weighed out ; these should consist of turnings, drillings, or planings, the latter being preferred, as the sample can be taken right across the section of the metal for analysis instead of out of one hole only ; moreover, the metal

planes off in small, chunky pieces which are ideal for combustion. Too coarse pieces do not necessarily burn right through, and very thin shavings are apt to catch fire before the tube can be closed, and CO_2 may be lost. A balance sensitive to about 0·001 gm. only need be used. This is sufficient for all ordinary purposes, and more accurate weighing is waste of time. The reason for this apparent carelessness is as follows: Unless the greatest precautions are taken to ensure that there shall be no adsorbed moisture on the surface of the absorption bulb R (glass adsorbs strongly), and all weighings of this bulb be reduced to "*in vacuo*" conditions, the error in weighing the CO_2 will necessarily be about ± 1 mgm. (Hence the instruction to weigh the absorption bulb to the nearest mgm. only.) One mgm. of CO_2 represents, on a 2-gm. sample, about 0·014 per cent. of carbon, which is quite near enough for practical purposes. Now in weighing out a 2-gm. sample that contains, say, 1 per cent. of carbon, an error of 10 mgms. represents the same error in the final result, so that with low carbon steel, weighing to the nearest cgm. is all that is necessary, and more refined weighing is not only unnecessary but is an analytical crime which affects the tidy-minded man as painfully as the spectacle of a student multiplying a weight of, say, 0·8742 gm. of $PbSO_4$ by the factor 0·6832 and obtaining nine figures in his product simply because he has never heard of contracted methods of multiplication, or of logarithms. The above may be excused in the very young, but when the student proceeds to set down his result to the sixth decimal place per cent., then speech fails! The writer adopts the following plan when dealing with a batch of samples. A sheet of paper is placed beside the balance case and the reference numbers of the samples are written on it. Each number is then covered up by placing a fireclay boat upon it. A standard steel and the samples are then weighed out to the nearest mgm. For samples of metal containing over 1 per cent. carbon, a 1 gm. sample will give sufficient increase in weight to the absorption bulb ; for wrought iron and very soft steels, 3 gms. or even 4 gms. may be necessary. As each sample is weighed it is transferred to its appropriate boat, the number on the sample container being compared with that under the boat as the latter is replaced.

A recently ignited unglazed fireclay boat is employed in which a shallow layer of ignited silica sand has been placed. Some analysts cover their sample with more sand or a layer of alundum ; some use a cylinder of nickel sheet or alundum, and some a roll of ignited asbestos ; the object is to protect the combustion tube from spatterings of fused oxide when the metal catches fire. There is no harm in the metal spattering a little, but if the oxide is allowed to collect upon the inside of the tube, the latter may be cracked by uneven contraction when the furnace cools. If a large 'blob' of oxide falls on the silica tube the cracking will be certain and immediate. One analyst advises the covering of the metal in the boat with another boat which is slightly smaller, and which has had its ends knocked off, so that it forms a sort of tunnel over the sample. This device works well, but the writer prefers a shield made out of a piece of nickel sheet. The sheet is cut and rolled into a cylinder of such size that it will slip easily into the combustion tube, the length being sufficient to overlap the boat by about 1″ each end. A small piece

of the metal bent up at the end of the cylinder serves admirably for the copper hook to catch hold of. Nickel will contain a little carbon and the shield must, therefore, be ignited in oxygen in the furnace for at least an hour before putting it into use.

7. All samples having been weighed, the furnace being at 1,000° ± 50° C., both tubes being at constant weight and E being full of oxygen, J is closed and tube R is attached. The boat containing the standard steel is then slipped into one of the ignited shields and bung K is removed. (*Note*, the rubber tube here should be of such a length that when K is out and hanging down, it just does not touch the bench. This enables the operator to let the bung dangle within easy reach without risking its acquiring dirt or dust by contact with the table.)

The boat and shield are boldly pushed into the hot zone and bung K is replaced. (*Note.*—There is no need for a hasty scramble here; the steel will not start to burn for at least 30 seconds, and no CO_2 can possibly be lost up till this time.) Taps C and Q are opened but S is kept closed.

8. Watch the bubbler F. At first, owing to cold air entering with the sample, there will be a small back pressure, but in half a minute or so the gas will begin to press from left to right owing to the combination of the gas inside the tube with the steel sample. Now open S cautiously, allowing the oxygen to bubble steadily through P. Almost immediately, especially if the sample consists of thin drillings, flashes of light will be seen inside the tube, and oxygen will begin to rush through F and G at great speed until about 350 cc. have passed, when the bubbles once more pass F and P at the same rate.

9. "Sweep out" the apparatus by passing a further 600 cc. or so of oxygen, making one litre in all per 1 gm. sample (one and a half litres for 2 gms.; two litres for 5 gms.). This will take about 3 or 4 minutes. When one litre has been admitted, close J, and when no more bubbles pass through P, close both Q and S and remove R, replacing it immediately by R′. Open Q′ and S′.

10. Remove bung K and insert the copper hook, by its aid removing the boat from the tube in one steady movement, catching the red hot piece of apparatus on the piece of asbestos board. Be careful not to let the hot boat linger at the mouth of the combustion tube or the bung will be charred when it is replaced, not to mention the certainty of the operator burning his fingers.

11. Meanwhile the next sample has been brought forward. It is then inserted and pushed into the hot zone and the cycle of operations 7 to 10 repeated, using bulbs R and R′ alternately.

General Remarks.—1. Each combustion takes about 4 minutes to carry through. During the combustion the apparatus requires no attention, so that time is available for the weighing of the absorption tube that has just been removed; no time whatever need be wasted.

The writer finds that he is able to carry through at least ten combustions per hour with the apparatus described, including time taken for refilling E with oxygen after each five cycles. This means that a one-tube furnace keeps one operator fully occupied, and nothing is gained by having two or four tubes available. As a matter of practical detail, however, the writer uses a two-tube furnace, but the connections

are so arranged that only one tube is heated. If the winding fails, therefore (as it must in time), there is no delay whatever in carrying on the work, as the simple changing over of the power wires brings the reserve tube into use.

2. In practice it frequently happens, especially with a newly filled absorption tube, that the first one or two combustions give low results. If the apparatus is properly set up, however, this cures itself in time, and the precaution of first 'combusting' a standard steel shows up any defects at once.

3. Always make duplicate determinations, and arrange matters so that originals and duplicates are absorbed in different tubes. This automatically checks any differences in behaviour between the bulbs.

4. The writer has obtained very good results with "Sofnolite" as absorbent. This material has an indicator incorporated with it so that it changes colour as it is 'used up' and there is no uncertainty as to how the tube is functioning.

The Sofnolite bottle must be kept very securely stoppered or moisture will be absorbed, which will cause trouble when the reagent is put into the bulbs, as there will be a *loss* in weight between two blank weighings, unless a drier is incorporated. This presents some difficulty, as Sofnolite, which is essentially sodalime, does not work well if quite dry, whilst if excessive moisture is present, the drier loses its value rapidly if in contact with the reagent. An excellent method is to fill the *exit* side of the tube with soda-asbestos (two or three inches), separating the two reagents by a wad of asbestos about half an inch thick ; $CaCl_2$ may also be used, but it has not the advantage of being an absorbent for CO_2 as well as being a drier. Better still, perhaps, is to use a tube with a separate compartment for the drier, capable of being shut off by a stopcock when the tube is idle, so that moisture is not transferred uselessly.

5. If many combustions are to be carried out, as is the case in commercial working, two balances, one sensitive to 0·001 gm. for weighing out the samples, and one sensitive to 0·0001 gm. for weighing the absorption tubes, are a great help to rapid working. It is always wasteful of time to have to replace weights in the box because one has to change over from weighing tubes (which weigh 50–70 gms.) to samples (1 gm.), and of course it is quicker to make a weighing on the less sensitive balance. The sensitive balance must be protected from the heat of the furnace (to save the operator's steps it should be close at hand, if possible on the same bench), a sheet of asbestos board making an effective shield.

6. Periodically, say after every 500 combustions, when finished with a batch of determinations, clear the asbestos plug filter M from entrapped SO_3 and P_2O_5 by removing bung N and withdrawing the combustion tube from the furnace until M is in the hot zone. Hold it there with the gas still passing for about a quarter of an hour, when the acid oxides will be effectively expelled.

7. Always keept the combustion tube closed when not in use, so that dust cannot enter, but do not switch off and leave the apparatus as it is while the furnace cools. If this is done, there will be a partial vacuum inside the tube, which, when subsequently released will probably suck acid up into the rubber connections. The writer removes K and substitutes a similar one-holed bung until the furnace is cold.

The foregoing represents the author's method and apparatus for the estimation of carbon in iron and steel ; it has been well tested in the author's laboratory and has proved rapid and accurate. At the same time it cannot be ignored that there are other forms of combustion apparatus which are in use in up-to-date laboratories, and which give excellent and rapid results.

The salient features of a combustion train have been discussed amply in the foregoing, and here it may be stated that as far as the purification train for the ingoing gas is concerned, the following are the essentials:

1. A steady stream of oxygen. 2. Reasonable freedom from CO_2, CO and other volatile carbon compounds. 3. Freedom from moisture. 4. A means of estimating the rate of admission of the oxygen is desirable.

As regards the exit train the following points are to be noted: 1. The issuing gas must be free from SO_2, SO_3 and other compounds which will be absorbed in the final bulb. 2. The gas must be dry.

There is another important method of absorbing the CO_2 which is in use in many of the important commercial laboratories, in America particularly. This method uses a train similar to that described already for the purification of the entering gas, but the CO_2 is absorbed in a Meyer bulb train containing $Ba(OH)_2$ solution. The Meyer bulbs are sufficiently capacious to enable the gas to be passed through them fairly rapidly and still give up all its CO_2 ; the $BaCO_3$ thereby precipitated is filtered off with due precautions to prevent the access of stray CO_2 from the laboratory, and the CO_2 is finally estimated either by ignition and weighing of the carbonate, by solution of the carbonate in excess of standard acid and titrating excess acid volumetrically, or by an electrometric method which, though it is very rapid and sufficiently accurate, demands special apparatus and experience on the part of the analyst. For this reason it will not be described here, and the interested student is advised to refer to the original papers of Cain and Maxwell.

Cain and Maxwell use a 10 bulb Meyer tube containing $Ba(OH)_2$, $8\,H_2O$ solution (25 gms. per litre), the volume of the solution used for each estimation being sufficient to fill all the small bulbs and half fill the pear bulb at the exit end. This arrangement enables the gas to be passed through the furnace at a rate of a litre in 5 or 6 minutes ; the small bulbs break up the stream of gas and wash it very efficiently. There is, however, the usual serious objection to the use of baryta ; theoretically it is an easy matter to filter off and wash the precipitate, but in practice it demands so many special precautions to avoid contamination with atmospheric CO_2 that unless the method is used in a regular routine, with a regular supply of CO_2-free water and the like, it is a method which is not to be recommended.

Method.—When the combustion is complete, the contents of the Meyer bulbs are poured out into a suction filter and washed with CO_2-free water, which is passed through the Meyer tube from end to end to rinse it. Sufficient 0·1 *N* HCl to dissolve any remaining $BaCO_3$ is then added to the bulb tube and rinsed out into a beaker with a little water ; the washed precipitate is added to the beaker, paper and all, and the rest of the standard volume of acid is added. *E.g.*, if 25 cc. HCl are necessary to dissolve all the carbonate, and 5 cc. have been used to clean

the bulb tube, add 20 cc. to the beaker. It is as well to use a burette for the acid and to have its twin alongside, containing standard alkali with which to titrate the excess acid after dissolving the carbonate.

From the equations:

$$Ba(OH)_2 + CO_2 = BaCO_3 + H_2O$$

and

$$BaCO_3 + 2\,HCl = BaCl_2 + H_2O + CO_2$$

it is seen that 1 gm.-atom of Carbon ≡ 2 gm.-molecules of HCl ; *i.e.* 2 litres of N HCl are equivalent to 12 grams of Carbon ; whence:

$$1 \text{ cc. } 0.1\ N\ HCl \equiv 0{\cdot}0006 \text{ gm. Carbon.}$$

If desired, the HCl solution may be made up of such a strength that each cc. is equivalent to a definite percentage of carbon when a 2 gm. sample is used for the combustion.

Estimation of Free Carbon.—Carbon can in many cases be estimated by the simple process of weighing the sample before and after ignition in a free supply of air, the loss in weight being taken to be carbon. Needless to say, this simple method is only applicable when there can be no other loss or change taking place in the sample on heating ; it serves, for instance, to estimate lampblack in a black or grey paint when the base of the material is barytes or something inert, but it will not serve if the base be white lead, which would lose both CO_2 and H_2O on heating.

Free Carbon in Iron.—The commonest case where free carbon has to be estimated in practice is the estimation of graphite in cast and pig iron. In cast iron the carbon is always present in two forms ; partly as graphite and partly as carbon combined with iron as carbide, Fe_3C, which is the form in which carbon is met with in steel. The complete estimation of carbon in cast iron or in one of the rare instances where steel contains both forms, involves two determinations, that of *total* carbon, *i.e.* graphite plus carbide carbon, and that of *free* carbon (graphite), the combined carbon being invariably measured by taking the difference between the two.

The estimation of total carbon is carried out in exactly the same way as has been described for combined carbon in steel, except that as the total carbon usually amounts to over 3 per cent., it is only necessary to weigh a 1 gm. sample. The separation of the free from the combined carbon is performed as follows:

Weigh out 1 gm. of the sample in the form of drillings, taking particular care to obtain a representative portion of the metal. This warning is necessary owing to the fact that the chips of cast iron are friable by reason of the graphite plates which break up the continuity of the metal ; the fine powder, therefore, contains a higher percentage of graphite than the larger pieces, and a proper proportion of the two must be present in the sample taken for analysis. Place the sample in a tall 300 cc. beaker or Phillips' flask and add 30 cc. of 1·2 sp. gr. HNO_3 ; cover the vessel and digest on the corner of the hotplate (on a piece of asbestos board), or on the water-bath, until the reaction with the iron ceases. The iron passes into solution as nitrate, leaving the graphite behind as an insoluble residue, since graphitic carbon is unattacked by

the diluted acid. (*Note*, graphite is slowly dissolved by hot conc. HNO_3). The digestion needs some care as it is necessary to be certain that the combined carbon has all gone into solution before filtering, and this takes an hour or more as a rule. It is difficult to see exactly what is taking place in the beaker owing to the suspended graphite, but if the sediment be undisturbed the carbide iron can be seen in the acid as a flocculent suspension, reddish-brown in colour, rather like ferric hydroxide. This substance, which seems to have no very definite composition, will pass into solution in time, and as it undoubtedly contains all or most of the combined carbon, it is obviously essential that the digestion be continued sufficiently long to effect complete solution. On the other hand, if the solution be overheated or concentrated by evaporation, gelatinous silica will separate out in such a form as will make the filtration extremely slow owing to the clogging of the asbestos mat.

When the solution is clear, and free from the brown flakes of carbide complex, it is poured on to a small asbestos filter and washed, first with a little hot dilute HNO_3 and then with water until the runnings are reasonably free from iron ; the filter is sucked dry on the pump and together with the graphitic residue is packed into a combustion boat. The funnel is wiped carefully with a wet swab of asbestos, using an upward spiral motion, and the swab added to the contents of the boat, which is then set in the air oven to dry completely at 110° C. When it is dry, (do not overheat, as it has been suggested that graphite is slowly oxidised by hot air), it is ready for the combustion, which process is carried out in exactly the same way as has been described for the direct estimation of carbon in steel, except that it must be remembered that the graphite will catch fire almost instantly when the boat reaches the hot region of the furnace, and will burn very rapidly in the oxygen ; the operator must, therefore, be ready with the stopper of the input end of the gas train lest some CO_2 escapes backwards.

Having estimated *total carbon* (*i.e.*, graphite + carbide carbon) and *graphite* alone, the amount of *combined* carbon (as Fe_3C) follows by subtraction. It is quite useless to try to estimate the combined carbon directly by colour in the filtrate, as this colour, even when a standard of cast iron of known combined carbon content is used for comparison, seems to bear no close relation to the amount of carbon present. The solution, which contains HNO_3 only, is, however, useful for the estimation of the manganese either by the bismuthate or the arsenite method.

The other methods that have been proposed for the estimation of carbon in iron and steel are of less importance and will not be discussed here except in general terms. The old-fashioned method of separating the carbides by solution of the sample in " double chloride " solution is never used nowadays, as the direct combustion method is far more rapid ; in the case of alloy steels, which are not always amenable to the " double chloride " attack, the direct combustion method is essential. The " wet combustion " method, in which the carbon is oxidised to CO_2 by a solution of CrO_3 in H_2SO_4, is also passing. The necessary apparatus is complicated and it is not adapted to rapid working, apart from the fact that the results obtained are not accurate unless elaborate precautions against incomplete oxidation are taken.

Where alloy steels are concerned, especially those containing the metals chromium, manganese and tungsten, the sample requires a higher temperature for its complete combustion. In these cases it is usual to spread a layer of some compound such as Mn_3O_4 or Pb_3O_4 on the bottom of the boat, on the sand, and a similar layer on the top of the drillings ; a temperature of 1,100° C. at least should be employed (but note that this rapidly destroys the windings of the furnace if nichrome wire is used). It will also be desirable to prolong the combustion somewhat, running the oxygen at a slower rate, all these devices aiming at the oxidation of the refractory carbides of the alloying metals. The above-mentioned metals have carbides which are much more difficult to burn than Fe_3C. Nickel and cobalt, when alloyed, do not present any difficulty, as their affinity for carbon is less than that of iron.

The estimation of combined carbon by combustion is one of the simplest operations in analysis and one of the most important commercially ; it has, however, a diabolical habit of going " wrong " without any obvious cause, and constant vigilance is necessary to ensure that the results are reliable. It is a good thing to check results occasionally by the " colour " method, and estimations should always be made in duplicate, running the duplicates through on different trains if the furnace is designed for simultaneous working, or, if a single tube only is in use, the duplicates of a batch of assays should be burnt off in irregular order, so that if a fault occurs, it may be detected by the disagreement between the pairs of results.

GROUP V.

MISCELLANEOUS ACIDS.

HYDROCYANIC ACID AND CYANIDES.

The methods used for the estimation of the cyanides resemble those for the halogens.

A. Gravimetric.—To the cold solution, which should be free from halogens, add excess of $AgNO_3$ solution and a few drops of HNO_3. Stir vigorously to make the white precipitate of AgCN coagulate, and test the clear supernatant liquid with a drop of $AgNO_3$ solution to see whether all the CN^- is precipitated ; filter through a tared Gooch crucible (paper or asbestos) and wash with water to which a few drops of HNO_3 have been added ; dry at 100° C. when the runnings no longer show the presence of Ag^+ when tested with a drop of HCl.

If preferred, the precipitate may be filtered off on an ordinary filter and transferred to a weighed porcelain crucible. On heating, the AgCN decomposes, yielding metallic silver, which can be weighed after extracting with water. The heating should be performed gradually, slowly raising the temperature of the crucible to the melting-point of silver (960° C.).

B. Volumetric—*Volhard's Method.*—To the solution of the cyanide add a measured excess of standard $AgNO_3$ solution, followed by a drop or two of HNO_3. Stir well and allow the precipitate to settle ; filter, and wash with very dilute HNO_3, finally titrating the excess of Ag^+

with a standard solution of NaCl. See under Halogens and Silver for further details.

Liebig's Method.—If $AgNO_3$ be added to a solution of KCN, white AgCN is momentarily formed ; this redissolves on stirring, the Ag^+ ions disappearing to form an anodic complex $Ag(CN)_2^-$. When, however, all the CN^- has been converted into $K^+.[Ag(CN)_2]^-$, further addition of Ag^+ produces a turbidity due to the re-formation of AgCN.

$$AgNO_3 + KCN = \underset{\text{(precipitate)}}{AgCN} + KNO_3$$

$$AgCN + KCN = \underset{\text{(soluble)}}{K^+.[Ag(CN)_2]^-}$$

$$K^+.[Ag(CN)_2]^- + AgNO_3 = 2\,\underset{\text{(precipitate)}}{AgCN} + KNO_3.$$

Procedure.—Dissolve the cyanide in water and add a little KOH ; dilute to about 100 cc. Add the standard $AgNO_3$ solution from a burette, with constant stirring, observing the solution against a dark background in a good light, and taking the end-point when the first sign of permanent turbidity is produced. A drop or two of KI solution makes the end-point more definite.

Then: $Ag \equiv 2\ CN^-$,

whence: 108 gms. $Ag \equiv 52$ gms. CN^-.

OXALATES.

The oxalates are important analytically owing to the fact that they react sharply and quantitatively with $KMnO_4$. The reaction may be formulated:

$$\begin{matrix}COOH\\|\\COOH\end{matrix} + O = \begin{matrix}CO_2\\+\\CO_2\end{matrix} + H_2O$$

or more completely:

$$5\,(COOH)_2 + 2\,KMnO_4 + 3\,H_2SO_4 = K_2SO_4 + MnSO_4 + 10\,CO_2 + 8\,H_2O.$$

Method.—The oxalic acid or oxalate is weighed out into a beaker, taking such a weight as will give a suitable reading on the burette with the standard $KMnO_4$ solution. The sample is dissolved in 75–100 cc. of water, if it is soluble ; if not, this amount of water is added ; in both cases sufficient 1 : 1 H_2SO_4 to combine with the K and the Mn of the $KMnO_4$ is poured into the beaker, the mixture being heated until insoluble oxalates pass into solution. The solution is then titrated with standard $KMnO_4$ at a temperature of 80° C. At first the reaction is slow, and the pink colour of the first $KMnO_4$ added remains for some time without reacting with the excess of oxalate. As soon as some Mn^{++} is formed, however, the $KMnO_4$ reacts very rapidly, being " catalysed " by the Mn^{++} ion. As soon as the first few drops are decolorised,

therefore, the permanganate may be added much more rapidly, and in the hot solution the end-point is very sharp and distinct.

The permanganate is standardised against pure, recrystallised $(COONa)_2$, which is easily prepared pure, and crystallises without water. Pure oxalic acid ($2\,H_2O$) may also be used, but this is somewhat efflorescent and the sodium salt is to be preferred. The method of standardisation is exactly as described above; in all cases sufficient H_2SO_4 must be present. As a guide to the judging of the weight of sample to be taken for the estimation:

630 gms. $(COOH)_2.2\,H_2O \equiv 450$ gms. $(COOH)_2 \equiv 670$ gm.
$(COONa)_2 \equiv 316$ gms. $KMnO_4$;

whence:

0·0063 gm. $(COOH)_2\,2\,H_2O \equiv 0{\cdot}0045$ gm. $(COOH)_2 \equiv 0{\cdot}0067$ gm.
$(COONa)_2 \equiv 1$ cc. $\frac{N}{10}$ $KMnO_4$.

This method is of extreme importance in analysis owing to its application to the estimation of certain metals, notably calcium. Any metal which forms an "insoluble" oxalate, may be separated by the addition of ammonium oxalate, the precipitate filtered off, washed, and titrated as described, after solution in hot dilute H_2SO_4. This is the usual method for the estimation of calcium (*q.v.*).

PHOSPHATES AND PHOSPHORIC ACID.

In the case of free phosphoric acid, or the phosphate of an alkali metal, the $PO_4^{\equiv}$ is best estimated by precipitation with magnesia mixture. The method is the exact converse of that already detailed under Magnesium, the only difference being that whereas in the former case a phosphate was added to the magnesium solution, here, the magnesia mixture is added to the phosphate solution; the treatment and weighing of the precipitate are identical in both cases.

If, however, other metals are present, it will be necessary to isolate the $PO_4^{\equiv}$ before the final precipitation, owing to the fact that all metals except the alkalis form phosphates (or hydroxides) insoluble in alkaline solutions, and unless the substance under analysis be perfectly pure, a precipitate of indefinite composition will be formed when ammonia is added.

Method 1.—Separation as Phosphomolybdate.—This method is easy to carry out, but it is essential that strict attention be paid to details of temperature and concentration, owing to the fact that the composition of the yellow precipitate varies with these factors. The following is Woy's method, as recommended by Treadwell.

Solutions Required.

1. 3 per cent. ammonium molybdate, prepared by dissolving 120 gms. of the salt in 4,000 cc. of water. 1 cc. of this $\equiv 0{\cdot}001$ gm. P_2O_5.
2. 340 gms. of ammonium nitrate in 1,000 cc. of water.
3. HNO_3 of 1·153 sp. gr. (*i.e.*, 25 per cent.).
4. Wash liquid: 200 gms. NH_4NO_3 + 160 cc. HNO_3 in 4,000 cc. water.

Procedure.—If a solid is to be analysed, weigh out accurately into a 400 cc. tall beaker a quantity that shall contain not more than 0·1 gm. P_2O_5 ; dissolve in water if soluble, or in dil. HNO_3 if (as is usual) it is insoluble in water ; make up to about 50 cc. with water. If a solution be given, take an aliquot part such as shall contain the specified amount of P_2O_5, and dilute or concentrate as necessary.

Add 30 cc. of the NH_4NO_3 solution and 10–20 cc. of the HNO_3. Heat until N_2O just begins to come off and immediately add the proper amount of the molybdate reagent, also heated to boiling. The molybdate should be added in a steady stream, while rotating the beaker.

Yellow $(NH_4)_3PO_4.12\,MoO_3.2\,HNO_3.H_2O$ is at once thrown down. Shake and swirl the solution for a short time longer, and then set aside in a warm place until the precipitate settles out completely. Decant off the clear liquid through a filter, add 50 cc. of the wash liquid to the precipitate in the beaker, shake, allow to settle, and again decant. Then add 10 cc. of 8 per cent. NH_4OH to the precipitate in the beaker, which brings it into solution. Re-precipitate by adding 20 cc. NH_4NO_3, 30 cc. water and 1 cc. molybdate solution. Heat, as before, until the nitrate commences to evolve N_2O, and throw the phosphate down by pouring 20 cc. of hot HNO_3 into the ammoniacal solution, while swirling the liquid. The second precipitate is entirely free from the base which was previously combined with the $PO_4^{\equiv}$. The $PO_4^{\equiv}$ may now be determined, either directly or by dissolving the precipitate in dilute ammonia and precipitating the phosphate with magnesia mixture, the former method being preferred for small percentages of phosphate and the latter for larger ones.

(*a*) *Direct Method.*—Filter through a tared Gooch crucible (asbestos), washing with the acid NH_4NO_3 solution until free from the excess of molybdate. Dry the crucible and contents in a current of air at 160° C. If the precipitate turns greenish in colour add a small crystal of NH_4NO_3 and one of $(NH_4)_2CO_3$, again heating the crucible to 160° C.

For very small amounts of phosphorus the yellow precipitate may be filtered off on to a small " toughened " filter paper (No. 50), and washed on the suction pump. When the filtrate is free from excess of molybdate, the paper is sucked dry and spread out flat on a smooth tile (spot-plate) in the air oven or on the corner of the hotplate. When it is quite dry, the precipitate is gently detached from the paper with the tip of a knife-blade or spatula and shaken off on to the weighing pan of the balance, any undetached particles being brushed off with light strokes of a small brush. With a dry precipitate and the hardened paper, practically 100 per cent. of the yellow compound is easily detached for weighing, and the method has the advantage of rapidity.

(*b*) *As Magnesium Pyrophosphate, $Mg_2P_2O_7$.*—Dissolve the reprecipitated phosphomolybdate in dilute ammonia and add dilute HCl until the precipitate which is formed only just dissolves on shaking. Add excess of magnesia mixture and bring the solution to boiling. Cool slightly and add ammonia to the extent of one-fifth of the bulk of the solution. Cover the beaker and stand it in a warm place until the precipitate settles out well and completely. Filter, wash, ignite and weigh as described under Magnesium.

Note.—The correct amounts of the reagents to be added are indicated below:

Weight of P_2O_5.	3% Molybdate.	NH_4NO_3.	25 % HNO_3.
0·100 gm.	120 cc.	30 cc.	20 cc.
0·010 gm.	15 cc.	20 cc.	10 cc.
0·001 gm.	10 cc.	15 cc.	5 cc.

For practical methods of estimating phosphorus in alloys, see under the respective headings.

Volumetric Estimation.—There is also a volumetric method for the estimation of $PO_4^{\equiv}$, based on the reaction:

$$K_2HPO_4 + (CH_3COO)_2UO_2 = 3\,CH_3COOK + CH_3COOH + UO_2HPO_4.$$

(white precipitate)

The titration is conducted at 100° C. and the end-point is observed by the spot reaction on a white plate, using potassium ferrocyanide as outside indicator.

SECTION V.

VOLUMETRIC ANALYSIS.

ACIDIMETRY AND ALKALIMETRY.

The student is referred to the section on Theory of Indicators (under Theoretical Considerations), which should be read carefully to obtain a thorough understanding of what follows.

Normal Solutions.—In Acidimetry and Alkalimetry it is usual to work with Normal (Semi-normal, Deci-normal) solutions, though, on occasions, it may be desirable to possess solutions of special " strengths " in order to avoid calculations in working out results.

A Normal Solution is defined as one which *contains one gram-equivalent of the solute (referred to hydrogen) in one litre of solution.* Thus, a solution containing 1 gm.-molecule of HCl (35·47 gms.) per litre is Normal (generally written N). A solution of sulphuric acid to be Normal will contain not 1 gm.-molecule of H_2SO_4 per litre, but half of this, because sulphuric acid is dibasic. Similarly, a solution of NaOH containing 1 gm.-molecule per litre will be normal (since Na is equivalent to H), while a normal solution of sodium carbonate will contain half of 1 gm.-molecule of sodium carbonate per litre. A semi-normal solution contains half these quantities of solute, a deci-normal solution one-tenth these quantities, etc.

Note.—Phosphoric acid introduces a difficulty. The acid is tribasic in that it has three atoms of ionisable hydrogen, but, in practice, the acid itself never behaves in more than in dibasic fashion, since the third H^+ is so very little ionised (see table). To methyl orange, phosphoric acid reacts as though it has only *one* ionisable H^+, and a normal solution (using methyl orange) would have to contain 1 gm.-molecule per litre instead of one-third of that amount as might be expected. To phenolphthalein, however, phosphoric acid behaves as though it were dibasic, and a normal solution (using phenolphthalein) will have to contain two-thirds of 1 gm.-molecule per litre. Phosphoric acid is, however, never used for the titration of alkalis, nor is it ever estimated by titration, so that the above is, strictly speaking, outside ordinary analytical practice.

The usual acids and alkalis used in analysis are: HCl, H_2SO_4, $(CO.OH)_2$, NaOH, Na_2CO_3, $Ba(OH)_2$. HNO_3 and KOH are less frequently met with.

In making up a set of volumetric reagents for acidimetry and alkalimetry, the usual starting point is the sodium carbonate solution ; from this the acids HCl and H_2SO_4 are standardised, and by comparison with the standardised acids, the NaOH and the $Ba(OH)_2$ solutions are then checked. It is possible, however, to standardise the acids directly,

by methods which will be explained, and even to prepare a standard HCl solution of known strength without standardisation against alkali.

Standard Sodium Carbonate Solution.—It is usual to prepare the carbonate for this solution from the bicarbonate, which, when made by the "ammonia-soda" process, is an extremely pure product, even without recrystallisation. To recrystallise $NaHCO_3$, prepare a saturated solution at 40°–45° C. (this will contain, roughly, 13 per cent. of the salt), filter, and evaporate slowly at not more than 45° C. by immersing the beaker or dish as deeply as possible in a water-bath containing warm water. When about half the salt originally dissolved has separated, the solution is cooled under the tap and the mother-liquor poured off. The crystals are scraped out on to a Buchner funnel and sucked dry, one rinse of cold water is poured over them and they are again sucked as dry as possible. They are then spread out on a clean tile and left overnight in a desiccator to dry completely.

The dry bicarbonate is then converted into carbonate. The powdered crystals are placed in a platinum dish or crucible embedded in sand or asbestos (a thermometer is used as a stirrer) and heated over a very small flame to 270°–300° C., but not much above this or the Na_2CO_3 may be decomposed. Steam and CO_2 are copiously evolved, and after half an hour at 300° C., only pure Na_2CO_3 remains. This is cooled in the desiccator; 5·300 gms. are then accurately weighed out into a beaker, dissolved in water* and made up to a litre for the usual $\frac{N}{10}$ solution. Normal Na_2CO_3 solution is not usually employed in volumetric analysis; to standardise Normal acids a separate weighing of the solid carbonate is made; see below.

In making up the solution, shake the powder with 100 cc. or so of water for a minute or two, and pour the solution off into the measuring flask. Add more water to the residue that is left undissolved, in successive small portions, each time shaking for a minute and then pouring off the solution. The 5·3 gms. will all be dissolved long before a litre of water has been used. Make up to the mark with successive rinsings from the beaker used for the solution, adding the last few cc. very carefully, so that the liquid in the narrow neck of the flask is pure water only. Then, if the mark be accidentally overshot in making up, the excess water can be removed with a pipette without affecting the "strength" of the solution. Pour the solution into a *dry* 1,200 cc. beaker and retransfer to the flask. Repeat this latter process and the solution is ready for use, being thoroughly mixed.

For very accurate work, the temperature of the solution at the time of making up should be taken and noted on the bottle in which the solution is to be kept. This is to permit of corrections for expansion being made if the other solutions, used in conjunction with the Na_2CO_3, should not have been made up at the same time. It is easy to see that a solution made up in a laboratory the temperature of which is, say, 90° F., will be "too strong" when the laboratory temperature falls to, say, freezing-point, as there will be the same weight of reagent in a smaller bulk of liquid. If all the solutions are made up at approximately the

* Distilled water is of course used in all analytical processes.

same temperature (of solution and measuring flask) their alterations in strength will roughly keep pace with one another ; even then, however, an error is introduced owing to the fact that aqueous solutions do not expand and contract equally with water or with one another ; but the differences are small, and for ordinary volumetric volumes no readable error will come in. To save trouble in the matter of corrections, it is best to arrange matters so that if the set of solutions is not being made up at the same time, a standard temperature is selected for the water of solution. It does not matter greatly what this is, provided that it is constant, but it is decidedly preferable that the temperature at which the measuring vessels, flasks, burettes, pipettes, etc., are graduated be chosen. This temperature may either be 15° C., 60° F. (English practice), 20° C. (U.S.), or 84° F., which latter is used in hot countries.

Standard Hydrochloric Acid.—Normal HCl contains 36·47 gms. HCl per litre ; ordinary " conc. HCl " is, roughly, 12 *N*. The approximate HCl content of the laboratory " conc. acid " is found by taking its sp. gr., and a measured volume (about 100 cc.) is then diluted with the calculated amount of water. It is usually best to make the acid up at slightly above *N* strength if it is to be adjusted to exact normality later, as it is easier to calculate how much water to add than it is to work out the proper amount of acid if the solution is too weak.

Example.—Sp. gr. of acid = 1·19. This represents 37·23 per cent. of HCl. Pipette out 100 cc. and transfer to a 1,200 cc. beaker. The weight of HCl present = 37·23 gms., and it is required to make up a solution containing 36·47 gms. per litre.

$$\therefore \text{ Solution should be made up to } \frac{1{,}000 \times 37{\cdot}23}{36{\cdot}47} \text{ cc.}$$

$$= 1{,}021 \text{ cc.}$$

The dilution is best carried out in a litre graduated cylinder as great exactness is unnecessary at this point, the additional 20 cc. of water being added with a pipette. The mixture is cooled completely (*or* adjusted to the standard temperature) and mixed thoroughly by pouring backwards and forwards between cylinder and beaker twice.

Standardisation.—(1) Weigh 2 gms. of Na_2CO_3 *exactly* into a tall 400 cc. beaker. Dissolve in 100 cc. of water and add, from a dropper, 2 or 3 drops of methyl orange solution. Fill a 50 cc. burette to the zero mark with the acid and, after having seen that the delivery end is free from bubbles of air, titrate the carbonate solution with the acid, stirring the whole time with a glass rod tipped with rubber. When the red colour produced by the acid changes back to yellow but slowly, and well marked areas of pink are formed at each addition of HCl, titrate more cautiously, stopping when the solution shows a pink blush throughout its bulk. It is well to have a " matching standard " on the bench close to hand. This is prepared as follows: Take 140 cc. of water and add the same 2 or 3 drops of the indicator, followed by 1 drop of the acid. Stir well, and in each titration match the colour at the end-point with that of the " standard."

Note 1.—The indicator added should always be measured, as it uses a definite amount of acid to produce the change of colour.

Note 2.—The liberated CO_2 has but little effect on the end-point with normal solutions. See, however, under the Titration of $\frac{N}{10}$ Na_2CO_3 for a further note on this.

(2) The strength of the HCl can also be checked gravimetrically, and some analysts insist on this. 25 cc. are pipetted out into a beaker, diluted to 100 cc. approximately, and excess of $AgNO_3$ is added. The Cl^- is then estimated exactly as described under Chlorides (*q.v.*).

(3) Standardisation with $CaCO_3$. Calcspar is very pure $CaCO_3$ and may be used for an indirect standardisation of the HCl. Weigh out exactly 2 gms. of the not too finely crushed crystals into a tall 400 cc. beaker, and add 100 cc. of water, followed by 50 to 60 cc. of the (roughly) N HCl from a burette. Cover the beaker, and when the reaction is completed, and no more undissolved particles of the spar remain, rinse the cover and the sides of the beaker down with a few drops of water from the washbottle. Add two drops of methyl orange and titrate the excess acid with N NaOH (or KOH). Take the titration to a decidedly yellow end-point and then just restore the pink colour with a drop of acid from the HCl burette. Keep this titration as the "matching standard." *Note.*—The NaOH need not be *exactly* Normal, nor need its exact strength be known.

Read the burettes; suppose the volume of HCl added is V cc. and that of the NaOH, v cc.

Run 40 cc. of the NaOH into a similar beaker and dilute it with 100 cc. of water; add two drops of methyl orange and titrate with the acid until the colour matches the standard. Suppose x cc. of HCl are used for this titration. Then:

$$40 \text{ cc. } N \text{ NaOH} \equiv x \text{ cc. } N \text{ HCl},$$

whence:

$$v \text{ cc. } N \text{ NaOH} \equiv \frac{v\,x}{40} \text{ cc. } N \text{ HCl}.$$

Now, V cc. = (acid required for the calcspar) + (acid required for the NaOH).

$$\therefore \left(V - \frac{v\,x}{40}\right) = \text{(acid equivalent to the 2 gms. of calcspar)}.$$

But 2·0 gms. of $CaCO_3 \equiv$ 40 cc. of NHCl (*accurately* N).

If the HCl is exactly N, $\left(V - \frac{v\,x}{40}\right) = 40$, but if the expression in the bracket is greater than 40 the acid is below normal, and *vice versa*. In either case, the normality of the acid is: $\frac{40V - v\,x}{1{,}600}$.

(4) Acid solutions may be standardised by titrating them with the NaOH solution produced when a known weight of sodium is allowed to react with water, sodium being usually obtained in a high state of purity.

For N acid, weigh accurately about 1 gm. of the bright metal; it should be freshly cut and must be quickly weighed in a stoppered bottle. The metal is then dissolved in CO_2-free water by the ether method (see p. 203). The ether is removed as explained, and the alkali titrated

with the acid, using methyl orange or phenolphthalein as indicator. The normality of the acid is calculated from the fact that 23·00 gms. of Na correspond to 1 litre of N HCl. (1 gm. will take $\frac{1,000}{23}$ cc. = 43·5 cc. approx. of the acid.)

For the standardisation of $\frac{N}{10}$ acid, weigh 1 gm. of the metal and, after having prepared the NaOH, dilute it to 500 cc. with CO_2-free water. Take 50 cc. (= 0·1 gm.) of this solution for the titration; this, of course, also takes about 43 cc.

Direct Preparation of Normal Hydrochloric Acid.—(1) If a solution of HCl be boiled in an open vessel, the first vapours evolved will be either H_2O or HCl according as the concentration of HCl is below or above 20·24 per cent.; as the boiling proceeds, the solution gradually attains that concentration (at 760 mm. pressure). At this point the acid neither gains nor loses strength, but distils at a constant temperature (108·54° C.) and with a constant composition, provided the atmospheric pressure remains steady. This composition of 20·24 per cent. HCl corresponds to a sp. gr. of 1·10. To prepare "constant boiling-point acid," therefore, dilute the conc. acid to a sp. gr. of 1·10 and boil it in a large open beaker for 10 to 15 minutes. It will then contain exactly 20·24 per cent. HCl (at 760 mm.). Cool completely and weigh out 180·17 gms., which will contain 36·47 gms. HCl; now, on diluting to 1 litre, acid of exactly normal strength is obtained.

Note.—The exact composition of the constant boiling point acid depends on the atmospheric pressure. According to Hulett and Bonner the composition changes with pressure as follows:

Pressure in mm.	Per cent. HCl.	Gms. Distillate for 1 Mole HCl.
770	20·218	180·390
760	20·242	180·170
750	20·266	179·960
740	20·290	179·745
730	20·314	179·530

At 760 mm. the sp. gr. is 1·10 and the B. Pt. 108·5° C.

For intermediate pressures, interpolation will give correct figures. It should be noted that the composition does not alter greatly with pressure.

(2) An ingenious and accurate method of preparing standard HCl is to pass HCl gas into water and weigh the amount absorbed.

About 100 cc. of water are placed in a large absorption bulb, a Meyer bulb, for preference, and a fairly large $CaCl_2$ guard tube is attached to the exit end. The bulb and guard tube are weighed to the nearest 0·01 gm., and are then placed in a trough of cold water. A steady stream of HCl gas (dry) is bubbled through the water. The HCl is generated dry by adding conc. H_2SO_4 to coarsely crushed rock salt in a large flask warmed on the water bath, or, if preferred, it may be produced by adding conc. H_2SO_4 from a dropping funnel to 200–300 cc.

of conc. (commercial) HCl contained in a large flask. In the latter case it will be necessary to dry the gas by passing it through a little conc. H_2SO_4 in a small wash-bottle.

During the absorption the Meyer bulb is periodically disconnected and the whole roughly weighed, so that the process of absorption may be followed. Under ideal conditions 100 cc. of water will take up about 39 gms. of HCl, but here, 20–30 per cent. of absorption will suffice. If the bulb tube will hold more than 100 cc. it is suggested that an increase in weight of about 35 gms. should be aimed at, but it must be remembered that the absorption is accompanied by a considerable increase in volume ; about 50 per cent. should be allowed for this.

In any case, whatever the volume chosen (the actual volume does not matter), when the HCl appears to pass through the water without much absorption, the bulb and guard tube are disconnected, thoroughly wiped, and again weighed to the nearest 0·01 gm. From the increase in weight (= HCl) the volume required to contain 36·47 gms. is easily calculated ; the acid is rinsed out of the bulb and diluted to this bulk ; accurately N HCl results.

Normal Sulphuric Acid.—The molecular weight of H_2SO_4 is 98·08, and its normal solution contains $\frac{98{\cdot}08}{2} = 49{\cdot}04$ gms. per litre. The sp. gr. of the concentrated acid of the laboratory is taken with a hydrometer, and the corresponding percentage of H_2SO_4 is found from a Table. Acid of 1·84 sp. gr. contains 95·6 per cent. H_2SO_4, whence 49 gms. occupy $\frac{4{,}904}{95{\cdot}6 \times 1{\cdot}84}$ cc. = 27·88 cc. (Or another volume if the sp. gr. of the conc. acid is not 1·84).

28 cc. of the conc. acid are pipetted out and diluted with about 200 cc. of water, the solution is cooled, and then made up to 1,000 cc. (approximately).

The acid is standardised against 2 gms. of the pure Na_2CO_3 exactly as described for N HCl, and, if desired, made up to exact normality by the addition of water. H_2SO_4 is not much used in volumetric analysis; it has no advantages over HCl and has the disadvantage that there are more " insoluble " sulphates than there are chlorides.

Decinormal Hydrochloric and Sulphuric Acids.—100 cc. of the N acids (= 3·647 gms. HCl or 4·904 gms. H_2SO_4) are pipetted out and diluted to 1,000 cc. If desired, the $\frac{N}{10}$ acids may be made up directly, by taking one-tenth quantities. The $\frac{N}{10}$ acids are checked against the $\frac{N}{10}$ Na_2CO_3 solution if made up independently of the standardised N acid.

Decinormal Oxalic Acid.—The molecular weight of $(COOH)_2{\cdot}2\,H_2O$ is 126·06, and its $\frac{N}{10}$ solution will therefore contain 6·303 gms. per litre. This weight of the pure, dry, recrystallised acid is weighed out, and after dissolving in water, is made up to a litre.

This solution can be used to check the $\frac{N}{10}$ NaOH solution (using

phenolphthalein), just as pure Na_2CO_3 is used to check the strength of the acids. $\frac{N}{10}$ oxalic acid may itself be checked against standardised permanganate, after adding sufficient sulphuric acid to combine with the potassium and the manganese.

Normal Sodium Hydroxide (free from carbonate).—This is best prepared from the metal, though ordinary " stick caustic " may be used. N NaOH contains 40·01 gms. NaOH per litre. This represents 23·0 gms. Na.

(1) From the metal: About 1 litre of recently boiled, and therefore CO_2-free water, is placed in a 2-litre beaker and a layer of ether, about 2 cms. deep, is floated on the surface. Ordinary metallic sodium is used ; each lump, on being removed from the naphtha, is placed on a piece of coarse filter or blotting paper and roughly dried ; the outer skin is then sliced off with a knife, and each piece of clean, dry sodium is transferred immediately to a large weighing bottle which is at once stoppered, the bottle standing, tared, on the pan of a balance reading to 0·1 gm. Before commencing to prepare the sodium, an additional weight of 23·5 gms. is placed on the other scale pan, and after transferring each piece of sodium, the beam is momentarily released. When the weighing bottle and sodium outweigh the tare, the last piece of metal added is removed and cut in halves, one-half is replaced in the weighing bottle and the weight again tested. The process is repeated, either halving the last piece of sodium added and rejecting one-half or halving the last piece removed and adding one-half, until the beam is more or less balanced.

The roughly weighed metal is then cut into cubes of about 0·5 cm. sides, and these are cautiously added to the liquid in the beaker, being careful not to let the sodium enter the water. The metal floats on the surface of the ether and is slowly converted into NaOH by reaction with the small amount of water dissolved in the ethereal layer ; as the metal dissolves, the caustic sinks and enters the water. This is a very safe method of preparing pure NaOH, but the usual precautions must be taken to avoid an ether fire, which may be a serious matter.

When all the sodium has dissolved, the bulk of the ether is removed by means of a pipette ; the last traces are expelled by warming the solution to above 40° C. on the water-bath in a place where no abnormal amount of CO_2 is present. (The water-bath should not be anywhere near a gas burner. If an electrically heated water-bath is not available, the water should be boiled in a separate vessel and poured into the bath round the beaker.)

NaOH solution must be kept in a bottle provided with a soda-lime guard tube, and should be in direct communication with the burette in order to avoid absorption of CO_2 from the air during transference to the burette. Note, however, that the solution has the same alkalinity to methyl orange whether it has taken up CO_2 or not, but phenolphthalein only registers half the carbonate (*i.e.* $NaHCO_3$ is neutral where phenolphthalein is concerned) and where this indicator must be used, *e.g.*, in titrating a weak acid, the NaOH solution must be free from carbonate. (*Note.*—It is possible to titrate a carbonate solution with the use of phenolphthalein if the solution be boiled ; see p. 205).

(2) From " stick caustic ": A rough estimate of the amount of

carbonate present is first made. About 1" of the stick is broken off and quickly transferred to a tared weighing bottle, in which it is weighed to the nearest 5 mgms. The caustic is then dissolved in about 100 cc. of water (free from CO_2) and excess of $BaCl_2$ solution is added. The precipitate of $BaCO_3$ is collected on a filter, washed well with CO_2-free water and finally weighed after ignition at not more than 700° C., (low redness). Suppose the stick contains 92 per cent. NaOH ; weigh out $\frac{40 \times 100}{92}$ gms., breaking the sticks to make up this weight to the nearest gram, and weighing to 0·1 gm. Dissolve in 500 cc. of CO_2-free water in a flask and add the $BaCl_2$ solution. Allow the $BaCO_3$ to settle completely and decant the clear solution into another flask. Calculate the volume of water that will give a solution containing rather more than 40 gms. per litre, and dilute to this bulk with CO_2-free water. The solution is then ready to titrate with the standard HCl ; H_2SO_4 is inadmissable, owing to the presence of Ba^{++}.

Note.—If, instead of $BaCl_2$ solution, excess of $Ba(OH)_2$ solution were added to precipitate the $CO_3^=$, only 40 gms. of the stick caustic should be taken and not the larger weight as recommended above. The reason for this is seen on considering the reaction:

$$Ba(OH)_2 + Na_2CO_3 = BaCO_3 + 2\,NaOH.$$

The preliminary estimation is saved, therefore, if baryta solution be used in place of the usually recommended $BaCl_2$, but it is necessary to add no more than the barest excess, as baryta solution is a "strong" alkali, and will react like NaOH. It is fairly easy to judge when the precipitation is complete if the baryta be added from a burette or dropping funnel to the hot solution, allowing the precipitate to settle each time before adding more baryta.

Decinormal Sodium Hydroxide is prepared in exactly the same manner except that one-tenth quantities are taken. Note that $\frac{N}{10}$ NaOH can be standardised directly against $\frac{N}{10}$ oxalic acid using phenolphthalein as indicator. Pure, resublimed benzoic acid can also be used with the same indicator.

To test whether NaOH solution contains $CO_3^=$, titrate it cold with HCl using (*a*) methyl orange and (*b*) phenolphthalein. If no $CO_3^=$ is present, the two titrations will give identical results. In the presence of $CO_3^=$ the second will take a smaller volume of HCl than the first. The difference represents half the carbonate present. See also under Titration of Carbonate and Hydroxide when co-present.

Some Applications of Acidimetry and Alkalimetry.

A. Estimation of the Acid Content of Fuming Acids.—Fuming acids must always be weighed, not measured, and the weighing must be rapidly conducted, using a closed container, owing to the ease with which the fuming acids either take up water or lose the excess of their acid content.

Method: Accurately weigh a dry weighing bottle. When this is done, and not before, unstopper the acid container and as quickly as

possible remove one or two cc. of its contents with a dry " fountain-pen filler." (*Note.*—If the laboratory equipment does not include such a thing, an effective substitute can be made out of a piece of glass tubing drawn out to a fine point. The other end is fitted with a piece of rubber tubing about 2″ long, the open end of which is closed by the insertion of a small piece of glass rod. Note that an ordinary pipette must not be used, for obvious reasons.) Squirt the acid into the weighed bottle, stopper it at once, and re-weigh accurately.

Having weighed the sample, pour the acid, drop by drop, but quickly, into a beaker containing 100 cc. of water, finally dropping the empty bottle, unrinsed, into the diluted acid. Add 3 or 4 drops of methyl orange and titrate the solution with *N* alkali.

B. Estimation of the Acid Content of Ordinary Acids.—Take the specific gravity of the acid and form a rough estimate of the concentration by reference to the Tables. For ' conc.' acids, the sample should be weighed as described above ; for dilute acids a sample may either be weighed or measured according to dilution.

C. Estimation of an Alkali Hydroxide.—This is a simple direct titration with standard acid. Either phenolphthalein or methyl orange may be used as indicator.

D. Estimation of an Alkaline Earth Hydroxide.—This is an ordinary direct titration with standard acid, using phenolphathalein as indicator.

E. Estimation of Alkali Carbonate.—This is a straightforward titration ; see under Standard Alkalis.

F. Estimation of Alkaline Earth Carbonate.—See Standardisation of HCl by Calcspar. Excess acid is added to the weighed sample of the solid carbonate, and after boiling until the attack is complete, the excess acid is titrated with standard alkali.

G. Estimation of Alkali Bicarbonate.—Bicarbonates react neutral to phenolphthalein in the cold, but they may be accurately titrated, using this indicator, if the solution be boiled to expel CO_2.

Method: Boil the solution. Add two drops of phenolphthalein and titrate until the solution is colourless. Again boil. The colour will re-appear as the CO_2 is removed. Continue the titration until the indicator is again colourless, and again boil, repeating the process until boiling fails to reproduce the pink colour of the indicator. With methyl orange, titration is as usual if *N* acid is used ; with 0·1 *N* acid, however, carry the titration to the orange-red point, and then, since the indicator is slightly affected by the CO_2 present, boil the solution and continue the titration to the orange-red point in the cooled liquid. Only one boiling is necessary here.

H. Alkaline Earth Bicarbonates.—The presence of these causes the ' hardness ' of water. For their estimation, see under Water Analysis.

I. Estimation of Alkali Carbonate and Bicarbonate when Co-present.—*Method* (*a*): (1) Estimate total alkali in one portion of the sample by titration with standard acid (HCl) using methyl orange as indicator.

(2) To another portion (equal), add a measured volume of standard NaOH (free from carbonate), when the following reaction takes place:

$$NaHCO_3 + NaOH = Na_2CO_3 + H_2O.$$

The excess of NaOH is then determined by precipitating the carbonate

by the addition of a solution of $BaCl_2$, filtering off the $BaCO_3$ in a small pulp (or Buchner funnel, using the pump), and titrating the filtrate with standard acid as before.

Calculation:

Suppose (1) requires a cc., and (2) requires b cc. of standard acid (N or 0·1 N according to the weight of the sample taken), and that c cc. of standard NaOH have been added. Then:

$(c - b)$ cc. = volume of standard NaOH used to convert the bicarbonate into normal carbonate.

From the relation:

1 cc. of N NaOH ≡ 1 cc. N $NaHCO_3$ = 0·084 gm. $NaHCO_3$,

there were $(c - b) \times 0{\cdot}084$ gm. $NaHCO_3$ in the sample originally. Similarly, $a - (c - b)$ cc. is the measure of the Na_2CO_3, and since normal acid is equivalent, volume for volume, to normal alkali, and the weight of Na_2CO_3 per cc. of its N solution is 0·053 gm.,

$(a - c + b) \times 0{\cdot}053$ gm. of Na_2CO_3 was originally present.

Method (*b*).—(1) Titrate a measured volume of the solution with standard acid, using phenolphthalein as indicator. This indicator reacts neutral to $NaHCO_3$, so that if a cc. be required, this is the measure of half the Na_2CO_3, according to the reaction:

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

(2) Methyl orange is then added, and the titration is continued to completion with this indicator. Suppose b cc. are used; this is the measure of the bicarbonate plus half the carbonate (since this indicator reacts alkaline to bicarbonates).

Then: $2a$ cc. represent carbonate

and $(b - 2a)$ cc. represent bicarbonate.

The calculation is simple.

Note.—$NaHCO_3$ reacts neutral to phenolphthalein provided that CO_2 is not lost. The titration must, therefore, be conducted under the following conditions:

1. Very cold solution.
2. Moderately dilute solution.
3. Titrating acid not stronger than 0·1 N.
4. Titration conducted very slowly.
5. Tip of burette touching the solution (to avoid stirring up the mixture).
6. Gentle stirring during titration; no bubbles should be produced.

J. Estimation of Alkali Carbonate plus Hydroxide.—Use the same amount of sample for each determination, withdrawing 25, 50 or 100 cc. each time with a pipette.

Method (*a*).—Estimate total alkali by titration to orange-red with standard acid, using methyl orange as indicator. (a cc.)

To a separate portion, add excess of $BaCl_2$ solution, so that the $CO_3^=$ is precipitated as $BaCO_3$. *Either* filter off the $BaCO_3$ and titrate the NaOH in the filtrate with acid, using methyl orange as indicator (see *I*), *or* add phenolphthalein and titrate with acid without filtration. If this titration be conducted slowly and with proper stirring, the end-point for the NaOH can be detected before any $BaCO_3$ is attacked. (*b* cc.)

Then: *b* cc. measures the hydroxide and
$(a - b)$ cc. measures the carbonate.

The calculations are simple.

Alternatively, a method similar to *I*(*b*) may be used.

Method (*b*).—Titrate with phenolphthalein as indicator. This measures the total NaOH plus half the carbonate. (= *a* cc.)

Titrate with methyl orange as indicator. This measures the other half of the carbonate. (= *b* cc.). Then:

$2b$ cc. measures carbonate and $(a - b)$ cc. measures hydroxide.

K. Estimation of NaOH in Stick Caustic.—The sample (about one-quarter of a stick, or approximately 5 gms.) must be transferred quickly to a tared weighing bottle, which is then stoppered and re-weighed.

Dissolve the caustic in 500 cc. of cold, recently boiled, water (*i.e.* free from CO_2) in a measuring flask. After mixing, 100 cc. are pipetted out and a few cc. of $BaCl_2$ solution are added in order to precipitate any carbonate that may be present. The solution is then titrated with standard acid, using phenolphthalein as indicator.

Similar methods may be adopted for caustic solutions as were advised for the acids. After taking the specific gravity of the sample and roughly estimating the amount of NaOH present from the Tables, a few cc. of a conc. solution are weighed out, diluted with CO_2-free water, the $CO_3^=$ precipitated with $BaCl_2$, and the mixture titrated with standard acid. More dilute solutions may be measured out by volume.

L. Estimation of Alkaline Earth Carbonate plus Oxide (Hydroxide).—For example, in a sample of quick or slaked lime.

Quickly weigh out 10 gms. of the roughly crushed sample and transfer to a 500 cc. flask; after slaking with a little CO_2-free water, and cooling, dilute the solution to the mark, also with CO_2-free water. Shake the mixture vigorously, so that the lime is evenly suspended throughout the liquid; quickly pipette out 50 cc. of the turbid liquid and transfer to a second measuring flask (500 cc.); again make up to the mark with CO_2-free water. Each 50 cc. of the more dilute suspension will contain 0·10 gm. of the original sample.

Pipette out 50 cc. (after well shaking) and titrate slowly, in the cold, with 0·1 *N* HCl, using phenolphthalein as indicator. $CaCO_3$ is neutral to this indicator, but $Ca(OH)_2$ is alkaline to it. If the titration be conducted slowly, and with steady stirring, no $CaCO_3$ will be attacked until all the hydroxide has been converted into chloride. Suppose *a* cc. of acid are required for this purpose; then this quantity is the measure of the $CaO.[Ca(OH)_2]$.

Pipette out another 50 cc. and transfer to a 400 cc. beaker. Add excess (say 50 cc.) of the standard HCl. Boil the solution until no

more CO_2 comes off, and until clear (ignore silica). Titrate the excess acid with standard alkali (suppose *b* cc.). Then:

50 − (*b* + *a*) cc. is the measure of the carbonate, and
a cc. is the measure of the oxide.

The calculation is simple, but remember that *N* CaO ($CaCO_3$) contains only one-half of a gram-molecule in a litre.

Note.—The foregoing solutions are, of course, impossible in practice owing to the slight solubility of the compounds, but that does not matter in theory, since the suspensions behave like solutions.

OXIDATION AND REDUCTION.

Potassium Permanganate.

$KMnO_4 = 158{\cdot}06$.

In visualising the reactions of $KMnO_4$, and particularly in calculating the results of permanganate titrations, it will be found very helpful to revert to the old dualistic conception of a salt, and to consider this reagent as $\frac{1}{2}(K_2O, Mn_2O_7)$.

When potassium permanganate has completely fulfilled its oxidising functions it is itself reduced (in the presence of an acid) to a mixture of potassium and manganous salts; according to the dualistic theory it becomes $\frac{1}{2}(K_2O, 2\,MnO)$, losing $\frac{5}{2}$ atoms of oxygen in the process. Bearing this in mind, it is easy to formulate any permanganate reaction in terms of chemical equations, though this is rarely necessary as it is always possible to set down the essentials of any permanganate reaction in the form of two or more fragmentary equations, one of the oxidation(s) and the other of the reduction, which are then "balanced" with regard to oxygen. Examples will make this clear:

1. *Potassium Permanganate/Ferrous Salt.*

(*a*) *Reduction*: $2\,KMnO_4 (= K_2O, Mn_2O_7) = K_2O + 2\,MnO + 5\,O$.
(*b*) *Oxidation*: $2\,FeO + O = Fe_2O_3$.

Whence: $2\,KMnO_4 \equiv 5\,O$
or $10\,FeO$
or $10\,Fe^{++}$.

In terms of weights:

$2 \times 158{\cdot}06$ gms. $KMnO_4$ are equivalent to $10 \times 55{\cdot}84$ gms. Fe^{++}
i.e. $316{\cdot}12$ gms. $KMnO_4$ „ „ $558{\cdot}4$ gms. Fe^{++}.

The equation with (*e.g.*) H_2SO_4 follows simply. We can write at once, for the left hand side of the equation (leaving a blank for the "unknown" amount of acid):

$$2\,KMnO_4 + 10\,FeSO_4 + ?$$

For the right hand side we can write

$$K_2SO_4 + 2\,MnSO_4 + 5\,Fe_2(SO_4)_3 + ?$$

since we know that Mn_2O_7 becomes 2 MnO and that FeO becomes Fe_2O_3. [If desired, the student can retain the dualistic system of formulation, thus: K_2O, SO_3 + 2 MnO, SO_3 + 5 (Fe_2O_3, 3 SO_3), etc.]

Totalling up the SO_3 on the right hand side, we obtain 18 SO_3; there are already 10 SO_3 on the left, so that 8 more are required. These are obtained by adding 8 H_2SO_4. Filling in the blanks, therefore, we obtain:

$$2\,KMnO_4 + 10\,FeSO_4 + 8\,H_2SO_4 = K_2SO_4 + 2\,MnSO_4 + 5\,Fe_2(SO_4)_3 + 8\,H_2O.$$

The foregoing supplies the reason why acid is always added to a solution before titrating with permanganate; the K_2O and MnO must have something to combine with.

2. *Potassium Permanganate/Oxalic Acid (or an Oxalate).*

(*a*) *Reduction* as before.

(*b*) *Oxidation.*—Oxalic acid is written: $\begin{matrix}COOH\\|\\COOH\end{matrix}$; the molecule is oxidised completely by one atom of oxygen into water and 2 CO_2, thus:

$$\begin{matrix}COOH\\|\\COOH\end{matrix} + O = \begin{matrix}CO_2\\\\CO_2\end{matrix} + H_2O$$

whence:

$$2\,KMnO_4 \equiv 5\,O \equiv 5\,\begin{matrix}COOH\\|\\COOH\end{matrix}$$

or: 316·12 gms. $KMnO_4 \equiv 5 \times 90{\cdot}02$ gms. $(COOH)_2$
$\equiv 5 \times 126{\cdot}05$ gms. $(COOH)_2, 2\,H_2O$
$\equiv 5 \times 134{\cdot}00$ gms. $(COONa)_2$
$\equiv 5 \times 128{\cdot}09$ gms. $(COO)_2Ca$
$\equiv 5 \times 56{\cdot}09$ gms. CaO.

In the case of sodium and calcium oxalates, the oxidation is quite similar, and may be formulated:

$$\begin{matrix}COONa\\|\\COONa\end{matrix} + O = \begin{matrix}CO_2\\\\CO_2\end{matrix} + Na_2O$$

and:

$$\begin{matrix}COO\\|\\COO\end{matrix}\!\!>\!Ca + O = \begin{matrix}CO_2\\\\CO_2\end{matrix} + CaO.$$

3. *Potassium Permanganate/Hydrogen Peroxide.*—Here, the oxidation may be written:

$$H_2O_2 + O = H_2O + O_2$$

whence:

$$2\,KMnO_4 \equiv 5\,O \equiv 5\,H_2O_2$$

or: 316·12 gms. $KMnO_4 \equiv 5 \times 34{\cdot}02$ gms. H_2O_2.

4. *Potassium Permanganate/Nitrous Acid.*—The oxidation may be written:

$$HNO_2 + O = HNO_3,$$

but nitrous acid is usually considered, commercially, as "N_2O_3," the dualistic idea persisting, and we may write:

$$\tfrac{1}{2}(H_2O, N_2O_3) + O = \tfrac{1}{2}(H_2O, N_2O_5)$$

whence:

$$2\,KMnO_4 \equiv 5\,O \equiv 5\,HNO_2 \equiv \tfrac{5}{2}\,N_2O_3$$

or:

316·12 gms. $KMnO_4 \equiv 5 \times 47{\cdot}01$ gms. HNO_2, or $2{\cdot}5 \times 76$ gms. N_2O_3.

5. *Potassium Permanganate/Sulphurous Acid, SO_2, etc.*—The oxidation reaction is:

$$H_2SO_3 + O = H_2SO_4$$

whence:

$$2\,KMnO_4 \equiv 5\,O \equiv 5\,H_2SO_3 \equiv 5\,SO_2$$

or:

316·12 gms. $KMnO_4 \equiv 5 \times 82{\cdot}08$ gms. $H_2SO_3 \equiv 5 \times 64{\cdot}06$ gms. SO_2.

6. *Potassium Permanganate/Iodine and Thiosulphate.*—The oxidation is:

$$2\,KI + O = K_2O + I_2.$$

The liberated iodine is then reduced by thiosulphate:

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

whence:

$$2\,KMnO_4 \equiv 5\,O \equiv 10\,I \equiv 10\,Na_2S_2O_3$$

or:

316·12 gms. $KMnO_4 \equiv 5 \times 16$ gms. $O \equiv 10 \times 126{\cdot}93$ gms. I
$\equiv 10 \times 248{\cdot}2$ gms. $Na_2S_2O_3 . 5H_2O$.

This reaction is of interest, as it links up the iodine reactions with the permanganate reactions.

7. *Potassium Permanganate/Antimonious Compounds.*—The oxidation is:

$$Sb_2O_3 + 2\,O = Sb_2O_5,$$

or

$$Sb \equiv O$$

whence:

$$2\,KMnO_4 \equiv 5\,O \equiv 5\,Sb$$

or:

316·12 gms. $KMnO_4 \equiv 5 \times 16$ gms. $O \equiv 5 \times 121{\cdot}76$ gms. Sb.

8. *Potassium Permanganate/Manganese* (Volhard's Reaction).—The oxidation is:

$$2\,MnO + 2\,O = 2\,MnO_2.$$

The reduction is:

$$Mn_2O_7 - 3\,O = 2\,MnO_2.$$

So that:

$$2\,KMnO_4 \equiv 3\,Mn^{++}.$$

In this case the permanganic acid is not completely reduced and the whole case is different. A solution which is 0·1 N as far as Fe^{++} solutions (etc.) are concerned, is 0·15 N in the case of the Volhard reaction.

From the above:

$$316{\cdot}12 \text{ gms. } KMnO_4 \equiv 3 \times 54{\cdot}93 \text{ gms. Mn} = 164{\cdot}79 \text{ gms. Mn.}$$

9. *Potassium Permanganate/Hydrogen* (for "Normality").

$$2\,KMnO_4 \equiv 5\,O \equiv 10\,H$$

or: $316{\cdot}12$ gms. $KMnO_4 \equiv 5 \times 16$ gms. $O \equiv 10$ gm.-atoms H

i.e. $31{\cdot}612$ gms. $KMnO_4 \equiv$ one gm.-atom H,

whence: $N\,KMnO_4$ contains 31·612 gms. per litre. This solution is, however, impossible, as the solubility of $KMnO_4$ at 0° C. is only 28·3 gms. per litre. In any case the solution would be too concentrated for practical purposes; three different "strengths" are in use in the author's laboratory:

(i) 0·1 $N\,KMnO_4$, containing 3·16 gms. per litre.

(ii) $KMnO_4$ for Fe, Sb and Mn (bismuthate). This is made up of such a "strength" that 1 cc. ≡ 0·0006 gm. Mn. The latter is equivalent to 0·00305 gm. Fe and 0·003325 gm. Sb, the same solution being used for all three metals. The even 0·0006 gm. of Mn per cc. was chosen because in the author's laboratory the manganese estimations are the most numerous. In other cases it might be best to alter the "strength" slightly and make 1 cc. ≡ 0·00300 gm. Fe (or 0·00300 gm. Sb). The "manganese solution" contains 3·452 gms. $KMnO_4$ per litre.

No. (iii) solution, for Ca (CaO) and oxalate titrations, is a stronger solution, containing 5·639 gms. per litre. 1 cc. of this ≡ 0·005 gm. CaO.

Standardising Permanganate Solutions.—$KMnO_4$ is best standardised against pure sodium oxalate. The titration is a straightforward matter, and will not be further discussed here, but something must be said concerning the weight of standard salt taken and the calculation of the "strength" of the permanganate solution concerned from the

results obtained. The calculations are given rather fully, and may be skipped by advanced students.

$5 \times 134{\cdot}00$ gms. sodium oxalate $\equiv 316{\cdot}12$ gms. $KMnO_4$

i.e. $0{\cdot}5$ gm. ,, $\equiv 0{\cdot}23591$ gm. ,,

$0{\cdot}1\,N$ $KMnO_4$ contains $3{\cdot}1612$ gms. per litre $= 0{\cdot}0031612$ gm. per cc.

$\therefore$ 1 gm. sodium oxalate $\equiv \frac{0{\cdot}47182}{0{\cdot}0031612}$ cc. of $0{\cdot}1\ N$ $KMnO_4 = 149{\cdot}25$ cc.

To calculate the normality of the $KMnO_4$, weigh accurately $0{\cdot}5000$ gm. of pure sodium oxalate, dissolve it in 100 cc. of water, add 5 cc. of conc. H_2SO_4 (previously diluted), heat to 70°–80° C. and titrate to the first trace of pink. If the solution is accurately $0{\cdot}1$ *N*, $74{\cdot}63$ cc. will be required ; suppose $73{\cdot}1$ cc. is the actual reading of the burette, the solution is, therefore, slightly too strong and its normality is obviously $\frac{74{\cdot}63}{73{\cdot}10}$ of $0{\cdot}1$ *N*. If desired, the solution may be diluted to the exact decinormal strength, but this is really unnecessary, as it only takes a second or two to calculate a result with a slide rule after the " factor " has been evaluated. In any case, $0{\cdot}1\ N$ $KMnO_4$ has no " even number " factors for calculating the result of any assay, and one more term in the multiplication makes very little difference.

For specific assays, especially when there are many to be made, it is often advisable to use a special solution, such as No. ii. already mentioned, of which 1 cc. $\equiv 0{\cdot}0006$ gm. of Mn (by the bismuthate method). The titration is actually carried out with a ferrous solution of which the exact concentration need not be known, as it is titrated back against the permanganate, the " strength " of which in terms of Mn is known. For details, the student is referred to the estimation of manganese in steel, but the following is an outline.

In the assay, the MnO is oxidised to Mn_2O_7, *i.e.* to permanganic acid, and this is then titrated with a solution of ferrous sulphate until the colour is discharged. Suppose x cc. of ferrous sulphate are required for this ; then, if a second x cc. of the ferrous solution be taken and titrated with a standard solution of permanganate, taking, say, y cc., it is obvious that y cc. of the standard solution of $KMnO_4$ must contain the same amount of Mn as is present in the assay sample. Then, knowing the Mn equivalent per cc. of the standard solution, the weight of Mn in the assay follows. In practice one does not exactly duplicate the ferrous titration in reverse ; it is sufficient to titrate, once and for all (with each batch of assays), a definite volume, *e.g.* 25 cc., of the ferrous sulphate solution, against the standardised permanganate and reduce the result to a " factor " per cc., thus:

If 25 cc. ferrous sulphate solution require 22 cc. $KMnO_4$

Then 1 cc. ,, requires $\frac{22}{25}$ cc. $KMnO_4$

and x cc. ,, require $\frac{22}{25}\,x$ cc. ,,

which is equivalent to y cc.

Calculation of the Strength of the $KMnO_4$ by Titration with Sodium Oxalate.—Weigh out 0·25 gm. of pure sodium oxalate, dissolve and titrate. Suppose x cc. $KMnO_4$ are required. We know from the foregoing that 0·25 gm. of sodium oxalate ≡ 0·11795 gm. $KMnO_4$, and remembering that 158·06 gms. $KMnO_4$ contain 54·95 gms. of Mn, we see that:

$$0{\cdot}25 \text{ gm. sodium oxalate} \equiv \frac{54{\cdot}95 \times 0{\cdot}11795}{158{\cdot}06} \text{ gm. Mn}$$

$$= 0{\cdot}040990 \text{ gm. Mn.}$$

This quantity is in x cc., and therefore, 1 cc. contains $\frac{0{\cdot}04099}{x}$ gm. Mn.

Also, if the factor is to be exactly 0·0006, x will equal $\frac{0{\cdot}04099}{0{\cdot}0006}$ cc.

$$= 68{\cdot}32 \text{ cc.}$$

The actual factor may be calculated from this as was described for the 0·1 N $KMnO_4$ Thus, if 65·0 cc. are required instead of 68·32 cc., the factor will be $0{\cdot}0006 \times \frac{68{\cdot}32}{65{\cdot}00}$ gms. Mn. per cc. This is, in fact, the short cut to the rapid working out of volumetric solution factors.

No. iii. Solution.—Sodium oxalate may also be used for the standardisation of this solution. No. iii. $KMnO_4$ solution (5·639 gms. per litre; 1 cc. ≡ 0·005 gm. CaO) is used in commercial laboratories for the determination of the CaO in such products as cement, in which the weight of CaO handled in an ordinary analysis is about 0·6 gm. For lesser amounts of CaO or Ca the 0·1 N solution or the No. ii. solution may be used. No. iii. solution is standardised against 1·0 gm. of the oxalate.

5×134 gms. sodium oxalate ≡ 316·12 gms. $KMnO_4$ or

$5 \times 128{\cdot}07$ gms. calcium oxalate or $5 \times 56{\cdot}09$ gms. CaO.

∴ 1 gm. sodium oxalate ≡ 0·47182 gm. $KMnO_4$ or 0·41843 gm. CaO.

Whence: (1) $0{\cdot}005$ gm. CaO $\equiv \frac{0{\cdot}47182}{0{\cdot}41843} \times 0{\cdot}005$ gm. $KMnO_4$

$$= 0{\cdot}005639 \text{ gm. } KMnO_4 \text{ per cc.}$$

$$= 5{\cdot}639 \text{ gms. per litre.}$$

and (2), If 1 cc. of the solution ≡ exactly 0·005 gm. CaO,

1 gm. sodium oxalate will require $\frac{0{\cdot}47182}{0{\cdot}005639}$ cc. $KMnO_4$

$$= 83{\cdot}67 \text{ cc.}$$

From the actual titration results the exact factor may be calculated as before.

Calculation of the Factors for Fe^{++} and Sb^{+++} when Standardising with Oxalate.

670·0 gms. oxalate ≡ 316·12 gms. $KMnO_4$ ≡ 558·4 gms. Fe^{++}
≡ 608·8) gms. Sb^{+++} ≡ 109·90 gms. Mn^{++} ≡ 280·35 gms. CaO.

1 gm. oxalate ≡ 0·47182 gm. $KMnO_4$ ≡ 0·83345 gm. Fe^{++}
≡ 0·90866 gm. Sb^{+++} ≡ 0·16403 gm. Mn^{++} ≡ 0·41843 gm. CaO.

From these factors the weight of the substance to be determined that corresponds to 1 gm. of oxalate is evaluated. This gives the weight of the substance to be determined that corresponds to a known number of cc. of the $KMnO_4$ solution.

Example.

To find the " antimony factor " for a solution of $KMnO_4$.

Weigh out and dissolve 1 gm. of sodium oxalate (or 0·5 gm., 0·25 gm., according to the " strength " of the permanganate). Suppose x cc. of permanganate are required.

Then, x cc. permanganate ≡ 0·90866 gm. Sb

1 cc. permanganate ≡ $\frac{0{\cdot}90866}{x}$ gm. Sb

or, having determined the factor for, say, iron, the factor for antimony, CaO, etc. may be worked out from the ratios:

	$(COONa)_2$	$KMnO_4$	Fe^{++}	Sb^{+++}	CaO	Mn^{++} (bismuthate)	Mn^{++} (Volhard)
	670·00	316·12	558·40	608·80	280·35	109·90	164·85
Sol. No.	(i).	1 cc. $KMnO_4$ ≡	0·005584 gm.	0·006088 gm.	0·002803 gm.	0·001099 gm.	0·001648 gm.
„	(ii).	„ ≡	0·003049 gm.	0·003325 gm.	0·001529 gm.	0·00060 gm.	0·00090 gm.
„	(iii).	„ ≡	0·009959 gm.	0·01086 gm.	0·00500 gm.	0·001959 gm.	0·002939 gm.

Sodium oxalate is the best general reagent for standardising permanganate, but in view of the slightly different end-points obtained in different assays it is always best to standardise under conditions as closely resembling the actual conditions of the assay as possible. Thus:

1. *Solutions for titrating oxalic acid and oxalates*: standardise against sodium oxalate.

2. *Solutions for titrating iron:* (*a*) in H_2SO_4 solution. Standardise against pure ferrous ammonium sulphate, or (but not so good) against a known weight of Armco iron (= 99·85 per cent. Fe) or electrolytic iron (99·9 per cent. Fe), dissolved in H_2SO_4 in an atmosphere of CO_2 or hydrogen. (*b*) In HCl solution. Weigh out a suitable amount of iron as above ; dissolve in HCl without taking any special precautions against oxidation. Add a drop or two of $SnCl_2$, destroy the excess with $HgCl_2$ as usual, and titrate (but see under Iron, for necessary precautions).

3. *Solutions for antimony.*—Standardise against 0·25 gm. pure antimony powder, or, if antimony is not available pure, against tartar emetic

taken to fumes with H_2SO_4, or against oxalate. *Note.*—Antimony is dissolved in hot conc. H_2SO_4, the solution boiled until all SO_2 and liberated sulphur are expelled, and then diluted to 100 cc. with cold water. Two to five grams of tartaric acid are added, the solution cooled rapidly under the tap and titrated. If a white precipitate of basic antimony salt comes down, the process must be repeated. Five cc. of conc. HCl will keep the basic salts in solution, but the end-point will be transitory. The end is taken at the first tinge of pink that colours the whole volume of the solution.

4. *Solutions for Mn*: Volhard or Bismuthate method.—The best way is to standardise against a steel containing a known percentage of manganese, treating the standard in exactly the same way as the samples for titration. For Volhard's reaction, when used to determine manganese in, *e.g.*, an ore, use a known weight of pure $MnSO_4$ as the standard.

Preparation of the $KMnO_4$ Solutions.—Weigh out slightly more than the calculated amount of the crystals into a small beaker, add water and shake for a minute or so ; pour the solution into the measuring flask. Add more water and repeat the procedure until all the crystals are dissolved. This method is quicker than dissolving the crystals in 800 cc. or so of water and then making up to bulk ; also, in the case of permanganate, which gives a solution so dark as to be opaque, it is an advantage to be able to *see* whether all the salt is dissolved. Make the solution up to the mark and mix thoroughly by pouring it to and from a clean beaker several times. It is then ready for immediate use. It is much better, however, to proceed as follows, as the solution is then more permanent, though the above method will serve if the analyst is in a hurry to use the solution.

Transfer to a large beaker and boil for 10-15 minutes (covered). Allow to cool overnight and then filter the solution through a small asbestos pad into the bottle in which it is to be kept. The reasons for this treatment are as follows:—$KMnO_4$ can be bought sufficiently pure to weigh out the exact amount (as for dichromate), but unless water that has been recently distilled from $KMnO_4 + KOH$ in an all-glass still is used for making up the solution, the permanganate will react with dust and traces of soluble organic matter in the water and so lose strength. Moreover, the first product of the decomposition is MnO_2, and this catalyses the decomposition of the permanganate, so that the solution, unless made up with specially prepared water, should never be kept in the vessel in which it was made up. The object of boiling is to destroy the organic matter, and the filtration is to remove the MnO_2 that is formed. Thus prepared, $KMnO_4$ solution retains its " strength " almost indefinitely, though it is always advisable to re-standardise occasionally. In a commercial laboratory it is routine to weigh out a standard steel with each batch of bismuthate assays, and any variation in the factor of the principal solution is noted on the label of the bottle.

Apropos of the " personal equation " in volumetric analysis, it may be of interest to record that the author and a former colleague, using the same solutions, always worked with (slightly) different factors, the results of personal standardisations. In spite of this, closely agreeing results were obtained when duplicate samples of steel were analysed.

Summary of $KMnO_4$ Factors and Data.

$KMnO_4$. Molecular weight 158·03.

No. 1 Solution: (0·1 *N*)—3·1612 gms. per litre. Weigh out 3·162 gms.

No. 2 Solution: (for Fe, Sb, Mn)—3·452 gms. per litre. Weigh out 3·453 gms.

No. 3 Solution: (for CaO, Oxalates)—5·639 gms. per litre. Weigh out 5·646 gms.

Oxalate Standardisation.

No. 1 Solution: 1 gm. sodium oxalate requires 149·25 cc. $KMnO_4$ solution.

No. 2 Solution: 1 gm. ,, ,, 136·64 cc. $KMnO_4$ solution.

No. 3 Solution: 1 gm. ,, ,, 83·67 cc. $KMnO_4$ solution.

Ferrous Ammonium Sulphate Standardisation.

No. 1 Solution: 1 gm. ferrous ammonium sulphate requires 46·62 cc. $KMnO_4$ solution.

No. 2 Solution: 1 gm. ferrous ammonium sulphate requires 25·50 cc. $KMnO_4$ solution.

No. 3 Solution: 1 gm. ferrous ammonium sulphate requires 14·27 cc. $KMnO_4$ solution.

Standardisation by Pure Iron, Pure Antimony or a Standard Steel.

No remarks are necessary, as the calculation is simple and direct.

Ratios:

	$(COONa)_2$	$KMnO_4$	Fe^{++}	Sb^{+++}	CaO	Mn^{++} (bismuthate)	Mn^{++} (Volhard)
	670·00	316·12	558·40	608·80	280·35	109·90	164·85
No. 1 Solution.		1 cc.	≡ 0·005584 gm.	0·006088 gm.	0·00280 gm.	0·001099 gm.	0·00165 gm.
No. 2	,,	,,	≡ 0·00305 gm.	0·003325 gm.	0·001529 gm.	0·00060 gm.	0·00090 gm.
No. 3	,,	,,	≡ 0·009959 gm.	0·01086 gm.	0·0050 gm.	0·00196 gm.	0·002939 gm.

1 cc. of 0·1 N $KMnO_4$ is equivalent to:

0·005584 gm. Fe
0·007184 gm. FeO
0·007984 gm. Fe_2O_3
0·001099 gm. Mn (bismuthate)
0·001648 gm. Mn (Volhard)
0·004501 gm. Oxalic acid (anhy.)
0·006303 gm. Oxalic acid ($2H_2O$)
0·006700 gm. Sodium oxalate
0·006403 gm. Calcium oxalate
0·002803 gm. CaO
0·002004 gm. Ca
0·03428 gm. Pb_3O_4
0·001701 gm. H_2O_2
0·001269 gm. I_2
0·001581 gm. $Na_2S_2O_3$ (anhy.)
0·002482 gm. $Na_2S_2O_3$, $5H_2O$
0·006088 gm. Sb.
0·002350 gm. HNO_2
0·001900 gm. "N_2O_3"
0·004104 gm. H_2SO_3
0·002303 gm. SO_2

Potassium Dichromate.

$K_2Cr_2O_7$. Molecular Weight 294·3.

As in the case of potassium permanganate, it is useful to formulate this salt on the lines of the dualistic theory, and write K_2O, 2 CrO_3. This enables one to visualise its reactions and materially assists in the calculation of results.

When potassium dichromate acts as an oxidising agent it is itself reduced (in the presence of an acid) to a mixture of potassium and chromic salts, CrO_3 being reduced to Cr_2O_3, so that each molecule of dichromate is capable of yielding three atoms of oxygen.

$$K_2O, 2\,CrO_3 \rightarrow K_2O + Cr_2O_3 + 3\,O.$$

Potassium dichromate is a less powerful oxidising agent than potassium permanganate, and its great advantage for volumetric work lies in this fact; $K_2Cr_2O_7$ in cold acid solution does not react with Cl^- as $KMnO_4$ does, so that it can be used for titrations in the presence of Cl^-, a fact of great importance, as HCl is the chief solvent acid from the analytical point of view.

Dichromate solution has one other great advantage, which also is connected with its less energetic oxidising power, and that is it does not react with organic matter in the cold, and as $K_2Cr_2O_7$ can be obtained in a state of considerable purity, its solutions can be made up to exact volumetric "strength" by weighing out an exact quantity of the dry crystals and dissolving them in a known volume of water; in fact dichromate solutions are in themselves used as volumetric standards. They retain their "strength" indefinitely in the absence of evaporation.

The fact that the analyst is able to make up a dichromate solution of exact strength (1 cc. ≡ 0·01 gm. Fe, etc.) in one weighing, without standardising, coupled with the facts that the solution retains its strength, and can be used in the presence of Cl^-, results in its almost universal application in commercial laboratories as the standard reagent for the determination of iron, to the almost complete exclusion of $KMnO_4$. The easy standardisation is a minor point; the actual weighing of a standard salt and its titration is a matter of five minutes, the great point in favour of dichromate from the professional point of view being that the analyst's iron assays can be reduced with $SnCl_2$, instantly and quantitatively; there is no trouble in eliminating the excess of the reducer, and the solution is ready for titration in a few seconds, whereas if permanganate is used, unless the iron be originally in the ferrous state (which is practically never the case), reduction with H_2S, SO_2, or zinc and acid, takes time, and without testing, the analyst can never be certain that the excess of the reducing agent has been eliminated.

The chief disadvantages of dichromate solution are: (1) The green coloured reduction product (Cr^{+++}), (2), the fact that the progress of the titration has to be followed on a spot plate. It cannot be denied that these are important objections, and make the detection of the end-point slow and often uncertain in inexperienced hands, but with practice and experience this difficulty becomes of less and less importance; also

it must be remembered that the commercial analyst usually has a very good approximate idea as to how much iron he has in his "unknown" solution, which considerably simplifies matters.

Practically the only important application of dichromate solutions is in the determination of iron, but a method for the estimation of manganese using dichromate will also be given, in addition to precipitation methods for lead and barium. The student is also referred to the use of standard Fe^{++} solutions for the estimation of Cr^{++++++}, which estimation is the converse of the former mentioned.

Factors and Data.—$K_2Cr_2O_7$. Molecular Weight 294·3.

294·3 gms. $K_2Cr_2O_7 \equiv$ 200·0 gms. $CrO_3 \equiv$ 152·1 gms. $Cr_2O_3 \equiv$ 104·1 gms. $Cr \equiv 3\,O$.

Two solutions are usual (but the 0·1 N solution is given for completeness,) viz.:

No. 1. (Weak). Weigh 2·635 gms. $K_2Cr_2O_7$ and dissolve in water; make up to 1 litre.

No. 2 (Strong). Weigh 8·785 gms. $K_2Cr_2O_7$ and dissolve in water; make up to 1 litre.

[No. 3 (0·1 N). Weigh 4·905 gms. $K_2Cr_2O_7$ and dissolve in water; make up to 1 litre.]

No. 1—1 cc. $\equiv$ 0·00300 gm. Fe.
No. 2—1 cc. $\equiv$ 0·01000 gm. Fe.
No. 3—1 cc. $\equiv$ 0·005584 gm. Fe.

Titrations with $K_2Cr_2O_7$—1. *Potassium Dichromate/Iron.*—This has been fully described under Iron (*q.v.*).

2. *Potassium Dichromate/Manganese.*—Manganese is precipitated as MnO_2 by any of the following methods:

(*a*) Add solid $KClO_3$ to a solution of manganese in conc. HNO_3. Wash with conc. HNO_3.

(*b*) Add a suspension of bleaching powder in water to the manganese solution. Filter, and wash well with water.

(*c*) Saturate the solution with bromine, add ammonia and boil.

In any case the washed precipitate is rinsed into a clean beaker and excess of the usual acid ferrous sulphate solution is added. The mixture is stirred until the MnO_2 is dissolved, and the excess of ferrous sulphate titrated with the standard dichromate. This is an excellent method for estimating manganese in alloy steels, in spiegeleisen, in ferromanganese and in manganese ores.

Reduction (*a*), $2\,CrO_3 - 3\,O = Cr_2O_3$
Reduction (*b*), $MnO_2 - O = MnO$
Oxidation: $2\,FeO + O = Fe_2O_3$.

Whence: 2 atoms Fe are equivalent to 1 atom oxygen or 1 atom Mn or $\frac{1}{3}$ mol. $K_2Cr_2O_7$.

i.e. $2 \times 55{\cdot}84$ parts Fe $\equiv$ 54·95 parts Mn or $\frac{294{\cdot}3}{3}$ parts $K_2Cr_2O_7$.

Calculation:

Suppose x cc. $FeSO_4$ solution were used and y cc. $K_2Cr_2O_7$ solution were required to titrate the excess; also, by actual titration, z cc. $K_2Cr_2O_7$, are equivalent to x cc. $FeSO_4$.

Then: $(z - y)$ cc. $K_2Cr_2O_7$ solution are equivalent to the manganese reduction (*b*), and knowing the "iron factor" of the dichromate, the "manganese factor" follows from the relation:

$2 \times 55{\cdot}84$ gms. Fe $\equiv 54{\cdot}95$ gms. Mn (at least as far as these particular reactions are concerned).

Note that it is not necessary to know the actual concentration of the ferrous sulphate solution. All that is required is to know the dichromate equivalent of 1 cc. of $FeSO_4$ $\left(i.e.\text{ the ratio } \frac{x}{z}\right)$; this is obtained once and for all with each batch of titrations, and it is of course not necessary to use exactly x cc. of ferrous sulphate for the cross titration; any volume will do provided that it is not too small (it should be at least 20 cc.). This is an exact parallel to the method of calculating results in the bismuthate method.

3. *Potassium Dichromate/Lead or Barium.*—(*a*) Precipitate barium or lead chromate with excess of dichromate solution, filter and wash. Transfer the precipitate and paper to a beaker and add excess of $FeSO_4$ solution, stirring until all the chromate has been converted into sulphate. Titrate the excess Fe^{++} with dichromate. There are numerous variations possible.

(*b*) If a solution of dichromate be added to a solution containing lead or barium, $PbCrO_4$ or $BaCrO_4$ is precipitated. If the precipitate be filtered off and washed, and then dissolved in a little warm HCl, the solution contains CrO_3 in equivalent amount to the lead or barium. After titration with standardised $FeSO_4$ solution, the weight of lead or barium can be calculated.

(*c*) Precipitate with a known volume of standard dichromate, filter, and titrate the excess CrO_3 in the filtrate with $FeSO_4$.

(*d*) In either of the above cases excess of $FeSO_4$ may be added and the excess titrated with standard dichromate (*cf.* above, for manganese).

Method (*a*) is to be preferred.

Calculation.

1. *Reduction*: $2\,PbCrO_4\,(= 2\,PbO,\ 2\,CrO_3) - 3\,O = 2\,PbO + Cr_2O_3$,
2. *Oxidation*: $2\,FeO + O = Fe_2O_3$.
3. *Reduction*: $K_2Cr_2O_7\,(= K_2O,\ 2\,CrO_3) - 3\,O = K_2O + Cr_2O_3$.

Titrate the $FeSO_4$ against the dichromate to obtain the relation:

$$1 \text{ cc. } FeSO_4 \equiv x \text{ cc. } K_2Cr_2O_7.$$

Then, if a cc. $FeSO_4$ $(= a\,x$ cc. $K_2Cr_2O_7)$ were added to the chromate precipitate, and b cc. $K_2Cr_2O_7$ were added to titrate the excess of Fe^{++}, the chromate precipitate is equivalent to $(a\,x - b)$ cc. of dichromate.

Knowing the "iron factor" of the dichromate, the lead or barium factor follows from the relation:

$$2\ Pb \text{ or } 2\ Ba \equiv 3\ O \equiv 6\ Fe^{++} \equiv K_2Cr_2O_7.$$

Whence:

207·2 × 2 gms. Pb or 137·36 × 2 gms. Ba ≡ 6 × 55·84 gms. Fe^{++}

i.e. 414·4 gms. Pb or 274·72 gms. Ba ≡ 335·04 gms. Fe^{++}

i.e. 1·2369 gms. Pb or 0·8199 gm. Ba ≡ 1·00 gm. Fe^{++}.

4. *Potassium Dichromate/Iodine, etc.* See Iodimetry.

Ferrous Sulphate Solution.—This solution is complementary to the two oxidising solutions, $KMnO_4$ and $K_2Cr_2O_7$. The writer prefers solutions such that 1 cc. ≡ 0·01 gm. Cr. (approx.) since, when the exact strength is required to be known (which is rare), the solution is almost exclusively used in conjunction with dichromate. In most cases, however, $FeSO_4$ is used as an "intermediate" solution, and all that is required to be known about it is its equivalent in terms of standard permanganate or dichromate solution.

Preparation of the Solution.—Weigh out 22·6 gms. of $FeSO_4$, $7\ H_2O$. Pour (carefully) 50 cc. conc. H_2SO_4, with constant stirring, into 150 cc. of water, and at once add the ferrous sulphate crystals. Stir until dissolved, cool, and dilute to 1 litre.

Note.—It does not matter if the crystals are somewhat oxidised.

Standardisation.—Against Pure $K_2Cr_2O_7$.—Weigh out 0·2000 gm. of recrystallised potassium dichromate that has previously been dried at 140° C. into a beaker. Dissolve in 200 cc. of water and titrate with the ferrous sulphate solution.

A ferrous sulphate solution of which 1 cc. ≡ 0·01 gm. Cr will give a titre of 70·75 cc. with the above amount of potassium dichromate, and the "chromium factor" of the freshly prepared solution may be calculated from this relation.

Ferrous sulphate solution gradually oxidises, and it is essential that its strength be frequently checked, either against a weighed amount of pure dichromate, as described, or against standard permanganate or dichromate solution. As has been mentioned, it is rarely necessary to know the actual chromium or manganese equivalent of the solution; the ratio between the solutions is all that is usually required.

Note that this solution contains H_2SO_4, so that it may be titrated against either of the oxidising solutions without further addition of acid.

Even in the estimation of chromium in steels (*e.g.*) it is not essential to know the "chromium factor" of the solution, though it is convenient, and the previously given method of direct standardisation will give the chromium value at once if it is preferred to work with the ferrous solution only. As a rule, however, the analyst works with two burettes, one filled with the ferrous solution and the other with standard dichromate.

The chromium assay, with 6-valent Cr, is first treated with the ferrous sulphate solution, run in rapidly, say 5 cc. at a time, until the spot reaction shows a decidedly blue colour. The excess of Fe^{++} is then titrated with the standard dichromate until the spot test gives a null reaction. The two burette solutions are then titrated one against the other. The calculation is simple:

Suppose a cc. of $FeSO_4$ solution are used for the assay, and that the back titration takes b cc. of dichromate. Also let 1 cc. $FeSO_4$ solution $\equiv x$ cc. dichromate. Then the net addition of ferrous sulphate solution is $\left(a - \frac{b}{x}\right)$ cc., which is equivalent to $x\left(a - \frac{b}{x}\right)$ cc. of dichromate. The chromium content of the dichromate solution is known, and the chromium in the assay follows.

IODIMETRY.

Two solutions are required, standard iodine and standard thiosulphate, of which the relative and individual equivalents are known.

Iodimetry is applicable both to reduction and oxidation reactions; for instance, antimony may be estimated when in the pentavalent state by the addition of excess of KI and titration of the liberated iodine, or, if in the trivalent condition, it may be estimated by titration with the standard iodine solution. The reaction which is fundamental in iodimetry is:

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

This involves a colour change, it is true, since iodine solution is yellow or brown, but the yellow colour is so faint in dilute solution, and is, moreover, so easily masked, that it cannot be used for the exact detection of the end-point; for this purpose a solution of starch is employed. Note, however, in this connection, that the colour is destroyed by heating the solution, and that other substances besides iodine can give a blue colour with starch.

Iodometric reactions may be grouped under two headings, corresponding to the two methods of attack mentioned above: (*a*) Cases in which the substance to be determined is allowed to react with an excess of KI, the liberated iodine being titrated with standard thiosulphate; examples of this are the well-known copper assay, the estimation of free chlorine and bromine, of oxidising agents such as MnO_2, $K_2Cr_2O_7$, etc.; (*b*) which consists of those estimations which involve direct titration with a standard iodine solution. Examples of this are the tin assay, assay of antimony, sulphides, etc.

Note that practically in every case in iodimetry, as in the other sections of volumetric analysis, two solutions, opposite and complementary, are used. In very few cases is it really necessary to proceed very cautiously towards the end-point, as that point, if overshot, may be "brought back" by adding sufficient of the complementary solution, and again titrating, this time more cautiously. If the exact equivalence of the two solutions be known, and it is easily determined, this overshooting and bringing back does not involve any additional calculations beyond a simple subtraction. Note also, that in certain cases it is more

accurate to approach the end-point from one particular direction. A notable example of this is the titration of permanganate against Fe^{++}; the best end-point is "first pink" and not "last pink," and the end-point should always be taken after adding permanganate, not ferrous sulphate. Thus, in, *e.g.* bismuthate titrations, add excess of ferrous sulphate from the burette and bring the colour back to faint pink with the standard permanganate. Similarly, in iodimetry, it is easier to detect the *first* sign of blue than the completion of the discharge of this colour, especially when working with dilute solutions. The proper procedure, therefore, is to over-titrate with the thiosulphate and then just restore the colour with a drop or two of iodine.

Preparation of Solutions.

(1) *THIOSULPHATE SOLUTION.*—Sodium thiosulphate is hygroscopic and the crystals cannot be dried without decomposition, so that an approximate solution must be made up and then standardised. When made up, thiosulphate solution resembles permanganate in that it reacts with impurities associated with itself and with the water, but, unlike permanganate, when it has completed these reactions and deposited a certain amount of sulphur, it does not further decompose, so that thiosulphate solutions maintain their strength almost indefinitely after standing a week or so.

For practical work, the writer uses two solutions, a strong, "even number" factor solution for copper assays, of which 1 cc. $\equiv$ 0·01 gm. Cu, and a 0·1 N solution to accompany the 0·1 N iodine. Conversely, an "even number" iodine solution for tin, antimony and arsenic determinations, and 0·1 N iodine to use with the thiosulphate. A very dilute solution, approximately 0·02 N, is used for titrating As^{+++} derived from copper alloys and steels.

$$CuSO_4 + 2\,KI = CuI + I + K_2SO_4$$

whence: 1 atom of copper is equivalent to 1 atom of iodine or 1 mol. of sodium thiosulphate.

i.e. 63·55 gms. Cu $\equiv$ 126·93 gms. I $\equiv$ 248·32 gms. $Na_2S_2O_3 \cdot 5H_2O$

1·0 gm. Cu $\equiv$ 3·907 gms. $Na_2S_2O_3 \cdot 5H_2O$

Weigh out 40–41 gms. of the moist thiosulphate crystals and dissolve them in water. Make the solution up to 1 litre, and allow it to "mature" for a fortnight. It is of course not necessary to "mature" a solution that is required for immediate use as the strength does not alter rapidly, but it is an advantage to have a solution that does not require continual re-standardisation. If many copper assays are to be made, make up 5 or 10 litres of thiosulphate solution and standardise only after it has stood undisturbed for a fortnight. Make up to the exact factor. Properly stored, the solution should not alter in titre for at least 3 months.

This "strong" solution, required for copper, is always standardised against pure electrolytic copper, 0·8 or 0·9 gm. of pure copper being accurately weighed and titrated exactly as was described under the estimation of copper.

0·1 *N Thiosulphate Solution.*—One molecule of sodium thiosulphate is equivalent to 1 atom iodine or 1 atom of hydrogen. Hence: $\frac{248{\cdot}32}{10}$ gms. of thiosulphate per litre will give a decinormal solution. Weigh out 25 gms. of the commercial salt, and dissolve in a litre of water.

Standardisation.—(1) *Against Pure Iodine.*—Grind up 3 to 4 gms. of iodine with 1 or 2 gms. of KI and transfer the mixture to a lipless beaker, in the mouth of which is fitted a small round-bottomed flask, as shown in fig. 23. Start the water flowing in the flask, and place the whole upon a hot plate (a sheet of asbestos over a small Bunsen flame). The iodine will sublime and condense as a crust upon the bottom of the flask. Detach the sublimed crust and catch it on a clean watch glass which is then placed in a desiccator (ungreased) and stood over $CaCl_2$ overnight. [*Note.*—Iodine becomes contaminated with HI or H_2SO_4 respectively if left in proximity with grease (hydrocarbons) or H_2SO_4.]

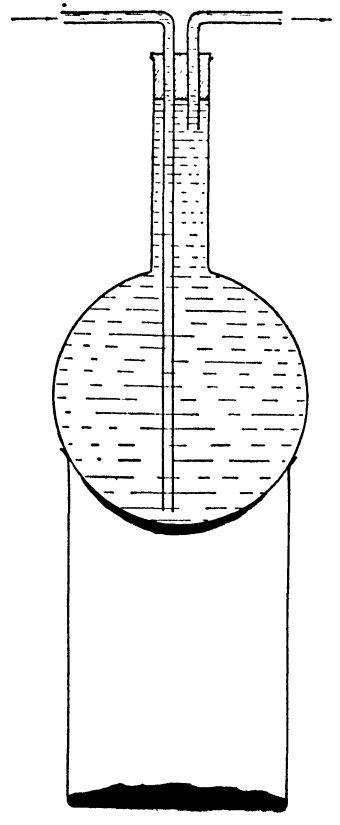


Fig. 23.—Apparatus for Sublimation of Iodine.

Place approximately 2 gms. of KI in a small weighing bottle and add about 0·5 cc. of water; stopper the bottle and weigh it accurately. Now add about 0·3 gm. of the sublimed and dried iodine quickly, and re-stopper the bottle. Re-weigh accurately. Having obtained the exact weight of iodine, make the solution up as follows: Place 150 cc. of cold water in a flask and add about 2 gms. of solid KI. Unstopper the weighing bottle and quickly slide it and its contents into the flask. The iodine will dissolve in the concentrated KI solution in the weighing bottle (as KI_3, which reacts like a solution of free iodine) and on dropping into the water the dilute solution is formed at once. Note that it would take a very long time to dissolve 0·3 gm. of dry iodine in 150 cc. of water, even though the latter did contain KI, and probably quite an appreciable amount would be lost by volatilisation during the process. The above method ensures, firstly, weighing the iodine out exactly, and secondly, that none of this volatile solid is lost prior to titration.

Titrate directly with the thiosulphate until the yellow colour is very faint. Then add 2 or 3 cc. of fresh starch solution and continue until the colour is exactly discharged.

Calculation.—This is simple if the "*iodine factor*" only is required, as

pure iodine was used for the standardisation. To calculate the "*normality*": Suppose a gms. iodine are equivalent to b cc. thiosulphate, then:

$$12{\cdot}693 \text{ gms. iodine} \equiv 12{\cdot}693 \times \frac{b}{a} \text{ cc. of thiosulphate solution.}$$

With exactly 0·1 N solutions this expression should work out to exactly 1,000. If it is not exactly 1,000, the normality factor may then be calculated, remembering that a solution is below or above correct strength according as more or less than that volume is used for a titration.

(2) *Against Copper.*—A standard copper solution or a weighed amount of pure copper may be used for standardisation. For the method, see under Copper.

6·355 gms. Cu are equivalent to 1,000 cc. 0·1 N thiosulphate solution. Weight out exactly 0·3178 gm. of pure copper foil. This should require exactly 50 cc. of the thiosulphate for its titration.

Note on weighing out metal foil. With a pair of sharp scissors cut a rectangle of the foil, judging the weight as closely as possible. Place weights to the correct amount on the right-hand pan of the balance. Test the weight by lowering the suspension. If the metal be too light, cut another small strip from the main piece and add it to the left hand pan; try the weight again, repeating until a little too much has been added. Now remove the last strip added and cut it in halves; replace one-half and again try the weight. If too heavy, again halve the last piece added and repeat the halving until the pans nearly balance. At this point thin shavings from the edge of the foil are cut off with the scissors, either from the last piece added (to lighten) or from the last piece removed (to be added to the left hand side); with a thin curling sliver available it is easy to make the final adjustment if the scissors are sharp.

If the original piece of foil was too heavy, clip a small strip from the edge and test the weight. If still to heavy, remove another strip and so on until the left-hand pan is outweighed. Then cut the last strip removed into halves and add one-half, finishing as before. In weighing foil it is important to have a regular system.

(3) *Against Dichromate.*—The reaction is:

$$K_2Cr_2O_7 + 6\,KI + 14\,HCl = 2\,CrCl_3 + 8\,KCl + 7\,H_2O + 6\,I$$

and:

$$6\,I \equiv 6\,Na_2S_2O_3.$$

Whence: $6 \times 248{\cdot}32$ gms. $Na_2S_2O_3 \equiv 294{\cdot}3$ gms. $K_2Cr_2O_7$.

Or: 1,000 cc. 0·1 N $Na_2S_2O_3$ solution $\equiv \frac{29{\cdot}43}{6}$ gms. $K_2Cr_2O_7$

$= 4{\cdot}9050$ gms.

Weigh out 0·2452 gm. of pure $K_2Cr_2O_7$ into a 600 cc. beaker, dissolve the salt in 100 cc. of water, and add 10–12 cc. conc. HCl, followed by 3–4 gms. of KI. Mix the solution by swirling gently, wait a minute or two, dilute to 350 cc. and titrate the liberated iodine with the thiosulphate solution until the colour approaches the pure green of the

Cr^{+++} ion. Add starch at this point and continue the titration until the deep blue changes into pure green. The end-point is quite definite.

This is quite a good method for standardising thiosulphate solution.

(4) *With* 0·1 *N Iodine Solution.*—If a standard iodine solution is available, the thiosulphate may be checked against this. This is the simplest method of all.

Thiosulphate may be standardised against iodine the exact strength of which is not at first known, in fact this is quite usual. The two solutions, iodine and thiosulphate, are made up at the same time, and either the iodine or the thiosulphate is standardised. The other solution is then checked against its complementary solution.

2. *IODINE SOLUTION.*

Iodine solution *may* be made up to known strength by dissolving an accurately weighed amount of pure iodine in the calculated volume of water, but there is no permanent advantage in this, as iodine solution always loses strength slowly and progressively, so that it requires constant re-standardisation.

Accordingly, an approximate weight of iodine is roughly weighed out and dissolved in a saturated solution of KI (use about twice as much KI as iodine). The solution is diluted to 1 litre. The more concentrated the KI solution, the more easily does the iodine dissolve.

No. 1 *Solution.*—For the assay of tin (antimony, arsenic).

The author uses this solution made up so that 1 cc. ≡ 0·005 gm. tin, but if antimony or arsenic titrations predominate, slightly different strengths of solution are advised, such that the factors may be "even number" with regard to the metal which is most frequently encountered. In what follows it is assumed that the chief assay for which the iodine is required is Pierce's, for the estimation of tin.

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

Whence: 118·70 gms. tin ≡ 2 × 126·93 gms. iodine.

0·005 gm. tin ≡ 0·010693 gm. iodine.

To make up the solution weigh out 10·7 gms. iodine to the nearest 0·01 gm. and transfer to a small beaker containing 20-25 gms. of KI dissolved in 10-15 cc. of water. When the iodine is dissolved, dilute the solution to 1 litre. Just as in the case of thiosulphate for the estimation of copper, which is best standardised against pure copper, this solution is best standardised against pure tin, which is carried through the same cycle of manipulations as the actual assays are, thus to a large extent neutralising any "blanks" or other errors, always provided that the burette readings are approximately the same. If the solution is to be used for the estimations of antimony or arsenic, standardise it against pure antimony or As_4O_6.

The reactions are, respectively:

$$SbCl_3 + 2\,HCl + I_2 = SbCl_5 + 2\,HI$$

and:

$$AsCl_3 + 2\,HCl + I_2 = AsCl_5 + 2\,HI.$$

Whence: 2 atoms Iodine are equivalent to 1 atom Antimony or 1 atom Arsenic or 1 atom Tin.

Or: 2 × 126·93 gms. Iodine ≡ 121·77 gms. Antimony or 74·93 gms. Arsenic or 118·70 gms. Tin.

Or: 0·10693 gm. Iodine ≡ 0·005130 gm. Antimony or 0·003157 gm. Arsenic or 0·005000 gm. Tin.

From this the factor for any of these metals can be calculated if any one factor be known.

No. 2 *Solution.*—0·1 *N* Iodine. To accompany the 0·1 *N* thiosulphate.

12·7 gms. of iodine are weighed out to the nearest 0·01 gm. and dissolved in a solution of 25 gms. KI in 12 cc. of water, and the solution diluted to 1 litre.

Standardisation.—(May also be applied to No. 1 Solution.)

(1) *Against Thiosulphate.*—If a standardised, approximately 0·1 *N* solution of thiosulphate is available, the easiest way to check the strength of the iodine solution is to titrate one against the other. It is, however, always better to obtain an independent check when standardising a complementary pair of reagents. For this purpose pure $BaS_2O_3.H_2O$ is now available; this salt, not being hygroscopic, can be weighed out exactly for standardisation purposes. Weigh out 0·6688 gm. of $BaS_2O_3.H_2O$ and dissolve in about 300 cc. of water. This weight of thiosulphate is equivalent accurately to 25 cc. of exactly 0·1 *N* iodine.

(2) *Against Pure* As_4O_6.—Another very convenient reagent for the standardisation of iodine solutions is arsenious oxide, especially for arsenic estimations. Weigh out 0·2473 gm. of the pure, resublimed oxide and transfer it to a small beaker, in which it is dissolved in a little conc. NaOH solution to form sodium arsenite. Dilute the arsenite solution to about 100 cc. and add 2 drops of phenolphthalein solution. Make just acid with HCl and then add about 2 gms. of solid $NaHCO_3$. Titrate the solution with the iodine until the yellow drops disappear but slowly in the colourless solution; then add the starch and continue until one drop produces a deep blue coloration.

The above weight of arsenious oxide should require exactly 50 cc. of exactly 0·1 *N* iodine solution.

Note.—As arsenious acid solution retains its strength very well (though it slowly oxidises) it may be useful to make up a litre or two of arsenious acid for standardisation purposes. 4·946 gms. of oxide in 1,000 cc. of solution make a decinormal solution.

(3) *Against Potassium Antimony Tartrate* or *Potassium Bi-iodate*, both of which can be obtained pure.

No. 3 *Iodine Solution.*—For the titration of arsenic solutions derived from iron and steel, and copper alloys.

This solution is approximately 0·01 *N*. It is made up by first checking either the 0·1 *N* or the "tin" iodine against 0·2473 gm. of arsenious oxide and calculating out the "arsenic value" of the solution. The standardised solution is then diluted suitably. Or, it may be checked

against barium thiosulphate, of which 0·1337 gm. ≡ 50 cc. of 0·01 N iodine.

Suppose 1 cc. of the "tin" iodine is equivalent to 0·00316 gm. arsenic; remove 100 cc. with a pipette and dilute to $\frac{3,160}{3}$ cc. (= 1,053 cc.). Then 1 cc. ≡ 0·0003 gm. As. The "tin" iodine (1 cc. ≡ 0·005 gm. Sn) when so diluted will be found to give the same factor for arsenic, viz: 1 cc. ≡ 0 0003 gm. As.

(See note concerning the indicator and the end-point, which refers especially to this dilute solution, pp. 221 and 222.)

Starch Solution.—Take as much starch as will cover a sixpence and make it into a paste with cold water, grinding it free from lumps with the rounded end of a glass rod. Boil about 100 cc. of water in a small beaker and, while this is still boiling, slowly add the starch emulsion. Continue boiling for a minute or two and cool under the tap. Use 2 or 3 cc. of this for each iodine estimation. The solution does not keep for more than a day or two if left exposed to the air. Sterile starch may of course be kept indefinitely in full, close-stoppered bottles, but it is not worth the trouble to do this.

"Soluble" starch is obtainable. This gives a solution more quickly, but has no other advantage over the ordinary indicator.

The actual end-point with 0·1 N or stronger solutions is very sharp under almost all conditions. With weaker solutions the end-point is not so definite, and depends on: (i.) temperature, (ii.) concentration of KI or HI, and (iii.) volume of solution. It is, therefore, essential to run a standard along with each batch of assays, carefully keeping conditions as similar as possible to those that obtain in the assays. If this is done, the "blank" will cancel itself, provided that the volume of iodine used for the standard is within a cc. or two of that required for the assays, and the titrated solutions are 'matched' for colour at the end-point.

Summary of Iodometric Factors and Data.

Special Solutions.

1. "Copper" thiosulphate, 39·07 gms. per litre (theory)
= 40·0 gms. per litre (practical).

1 cc. ≡ 0·01 gm. Cu.

2. "Tin" iodine, 10·693 gms. per litre (theory)
= 10·7 gms. per litre (practical).

1 cc. ≡ 0·005 gm. Sn ≡ 0·003157 gm. As ≡ 0·00513 gm. Sb.
≡ 0·00135 gm. S.

3. "Arsenic and Sulphur" iodine, 100 cc. of "tin" iodine diluted to 1 litre.

1 cc. ≡ 0·000315 gm. As ≡ 0·000135 gm. S.

0·1 *N Thiosulphate.*—24·83 gms. per litre (theory) = 25 gms. (practical).
0·1 *N Iodine.*—12·692 gms. per litre (theory) = 12·7 gms. (practical).

1 cc. ≡ 0·012693 gm. Iodine
≡ 0·02483 gm. Sodium Thiosulphate
≡ 0·003546 gm. Chlorine
≡ 0·007992 gm. Bromine
≡ 0·004347 gm. Manganese Dioxide
≡ 0·002043 gm. Potassium Chlorate
≡ 0·004903 gm. Potassium Dichromate

1 cc. ≡ 0·002400 gm. Ozone
≡ 0·006355 gm. Copper.
≡ 0·003748 gm. Arsenic
≡ 0·004946 gm. Arsenious Oxide
≡ 0·006010 gm. Antimony
≡ 0·007210 gm. Antimony Trioxide
≡ 0·005933 gm. Tin
≡ 0·001600 gm. Sulphur (S^{-})

PRECIPITATION.

Silver Nitrate Solution.

Four solutions of silver nitrate are commonly used, viz:

No. 1. Containing 5·000 gms. Ag per litre.
No. 2. 0·1 *N*, containing 10·79 gms. Ag per litre.
No. 3. 'Dilute,' of which 1 cc. ≡ 0·001 gm. Cl^{-}.
No. 4. A dilute solution used in the volumetric estimation of nickel (*q.v.*).

Preparation of Solutions.—Nos. 1 and 2. Weigh out respectively 5·000 gms. and 10·79 gms. of pure assay silver; transfer to a small conical flask and dissolve the metal in a slight excess of 1 : 1 HNO_3. Boil to expel "N_2O_3," cool and dilute to 1 litre in each case.

No. 3. Weigh out 4·791 gms. of pure $AgNO_3$, dissolve and make up to 1 litre; 1 cc. ≡ 0·001 gm. Cl^{-}.

No. 4. See under Nickel.

Solutions 1 and 2 are used in conjunction with equivalent solutions of NaCl and KCNS (or NH_4CNS). Since both pure NaCl and pure Ag are readily obtainable either solution may be the standard, but it is usual to make up both solutions accurately and so have a double check as to strength. Both solutions are quite permanent.

In Mint assays of silver bullion, etc. the 0·005 gm. per cc. $AgNO_3$ (No. 1) is used to standardise a NaCl solution which is designedly made slightly too dilute to be equivalent; some operators indeed make it up to 99 per cent. of its true strength. This solution is supplemented by a second NaCl solution of one-tenth the strength of the more concentrated solution; this is prepared by removing 100 cc. of the "strong" NaCl and diluting to 1 litre; 1 cc. of this solution is approximately equivalent to 0·1 cc. of the $AgNO_3$ solution.

Gay Lussac's Method (outline).—The percentage of silver is first determined approximately either by a rough titration or a cupellation. For the estimation proper, weigh out such quantity of the sample as will

contain 0·5 gm. silver as nearly as possible. Dissolve it in 10 cc. of 1 : 2 HNO_3, boil off "N_2O_3," cool and dilute slightly. Add 100 cc. of the "strong" solution of NaCl. This will precipitate practically all the silver as AgCl. Shake vigorously to coagulate the precipitate, and finish with the dilute solution, of which about 10 cc. will be required. Shake the assay flask after the addition of each 5 drops of the NaCl solution; allow the precipitate to settle, and make the next addition of NaCl into the clear solution. When a drop fails to produce a cloudiness, the titration is complete. The true titre $= \left(100 \text{ cc.} + \frac{\text{burette reading}}{10}\right)$ of the concentrated solution.

The concentrated NaCl solution is standardised against 100 cc. of the No. 1 $AgNO_3$ solution, and also by the original weighing out of the pure salt.

2·709 gms. NaCl ≡ 5 gms. Ag

and 2·682 gms. NaCl ≡ 99 per cent. of 5 gms. Ag,

but 2·700 gms. do very well in practice.

No. 2 *$AgNO_3$*.—This is 0·1 *N* solution. Weigh out exactly 10·79 gms. of Ag; dissolve, and make up to 1 litre. The corresponding solutions are:

0·1 *N* NaCl, 5·846 gms. per litre.
0·1 *N* KCNS, 9·718 gms. per litre (use 10 gms. in practice).
0·1 *N* NH_4CNS, 7·612 gms. per litre (use 8 gms. in practice).

For the two latter solutions, use a saturated solution of ferric alum as indicator, the alum being treated with conc. HNO_3 until the colour fades. Use 2 cc. of this for each titration, measuring the reagent with a pipette, as its volume has an effect on the end-point.

No. 3 *Solution.*—1 cc. ≡ 0·001 gm. Cl^-. This solution is used, with K_2CrO_4 as indicator, for the estimation of Cl^- in very dilute solutions such as natural waters.

The solution is not standardised; the correct amount of $AgNO_3$ (4·791 gms.) is weighed out and made up to exactly 1 litre.

Summary of Factors and Data.

No. 1 *Solution.*—5 gms. Ag per litre ≡ 2·709 gms. NaCl per litre.
No. 2 *Solution.*—10·79 gms. Ag per litre ≡ 5·846 gms. NaCl per litre.
No. 3 *Solution.*—3·043 gms. Ag per litre ≡ 1·000 gm. Cl^- per litre.

No. 1.—1 cc. contains 0·00500 gm. Ag ≡ 0·002709 gm. NaCl.
No. 2.—1 cc. contains 0·01079 gm. Ag ≡ 0·005846 gm. NaCl.
≡ 0·003546 gm. Cl^-.
No. 3.—1 cc. contains 0·003043 gm. Ag ≡ 0·00100 gm. Cl^-.

1 *cc. of* 0·1 *N $AgNO_3$*

≡ 0·005846 gm. NaCl
≡ 0·003546 gm. Cl^-
≡ 0·007992 gm. Br^-
≡ 0·012693 gm. I^-
≡ 0·006512 gm. KCN (Volhard).
≡ 0·002601 gm. CN^- (Volhard).
≡ 0·01302 gm. KCN (Liebig).
≡ 0·005202 gm. CN^- (Liebig).

MISCELLANEOUS VOLUMETRIC DATA.

POTASSIUM BROMATE. $KBrO_3$.

0·1 N solution contains 2·784 gms. $KBrO_3$ per litre.

1 cc. ≡ 0·004946 gm. As_4O_6
≡ 0·006010 gm. Sb
≡ 0·005935 gm. Sn
≡ 0·0009847 gm. HCNS.

SODIUM ARSENITE. Na_2HAsO_4.

0·1 N solution contains 4·946 gms. As_4O_6 per litre.

1 cc. ≡ 0·003546 gm. Cl^- (available chlorine in bleaching powder)
≡ 0·012692 gm. I^- (standardisation of iodine solution).

POTASSIUM CYANIDE. KCN.

Used for titration of copper solutions.

20 gms. KCN per litre is suitable. Standardise against pure copper dissolved in HNO_3 and treated like the assay.

AMMONIUM MOLYBDATE.

For the titration of lead solutions.

Use a solution containing 4·3 gms. per litre. 1 cc. ≡ (approx.) 0·0005 gm. Pb. Standardise against pure, precipitated $PbSO_4$. 0·300 gm. $PbSO_4$ requires approx. 41 cc. of this molybdate.

POTASSIUM FERROCYANIDE. $K_4Fe(CN)_6$.

For the titration of zinc solutions.

Use a solution containing 43·2 gms. per litre. 1 cc. of this ≡ 0·0100 gm. Zn (approx.). Standardise against pure zinc: 0·4 gm. is a suitable quantity, and will require 40 cc. of the ferrocyanide.

SECTION VI.

SEPARATIONS.

THE foregoing Sections contain a sort of catalogue of the chief methods for estimation of all the commoner metals and acids, the estimation being conducted on a *pure* solution, *i.e.* one containing no other metal. In most cases in the examination room and in all cases in a commercial laboratory, however, pure solutions are not the rule, and before any metal can be estimated it usually has to be isolated from others. The separation of metal from metal is so bound up with the scheme of analysis that although in the preceding sections an attempt has been made to catalogue the methods of estimation of the metals from simple solutions only, it has not always been found possible to ignore the fact that in the very great majority of cases separation must necessarily precede estimation ; in some few cases actual separations have been outlined, while in practically all the fact that separations will be required has never been forgotten. This may explain why at times one method of estimation has been mentioned as being preferable to others, while at other times another method is preferred.

It is impossible to give a complete catalogue, cross-indexed, of separation methods that shall apply in all possible circumstances, nor is it particularly desirable. In special cases the student must rely upon his theoretical knowledge of the reactions of Inorganic Chemistry, aided by reference to Physico-Chemical Tables, to devise methods suited to the individual problem. It cannot be too strongly emphasised that Analytical Chemistry is not a matter of routine or the blind following-out of " Methods " detailed in a text-book ; a Chemist is one who is capable of working out methods for himself.

Separations vary in character and degree. The isolation of a group of metals might well be called a Primary Separation, while the isolation of the individual sought from its group-mates might similarly be styled a Secondary Separation. This double process will always result in the isolation of the desired metal ready for estimation, but it is often a lengthy and cumbersome business. In a great many cases, however, short cuts are available, while in a few cases only, the individual metal may be picked out from a complex mixture by one simple operation. Primary separation is of universal application ; thus, (whatever the original mixture) if, for example, we desire to separate zinc, we may do so by separating Groups I, II, and III as usual, discarding the precipitates. Group IV is then isolated by precipitation with H_2S in alkaline solution, and finally, zinc is separated by (1) extracting with dil. HCl, which gives zinc and manganese in the filtrate, (2) by treating this filtrate with $Br_2 + NH_3$, which precipitates the manganese and leaves the zinc—altogether, a lengthy process. On the other hand it may be possible

to take a short cut to the zinc, but the possibility of this will depend upon the nature of the mixture. As an example, suppose the mixture consists of Ag, Pb, Fe, Al, Ni, Mn and Zn, *i.e.* a representative of every group. Here, the separation can be simplified to:

(1) Add excess of HCl and filter off AgCl.
(2) Add excess of H_2SO_4, evaporate to fumes, dilute, and filter off $PbSO_4$.
(3) Add ammonia until a slight, but definite precipitate forms. Dissolve this in H_2SO_4, and add a definite, slight, excess of acid (see under Zinc).
(4) Pass H_2S to saturation ; zinc is completely precipitated, while iron, aluminium, manganese and nickel remain in solution.

As examples of " short cuts " two or three cases may be mentioned:

1. Arsenic in many alloys and mixtures may be separated as $AsCl_3$ by the evolution method.
2. Chromium evolved as CrOCl represents a separation from all other metals ; the reaction is unique.
3. Mercury, heated with iron and quicklime, is distilled.
4. Silver is separated by cupellation, but this may involve a subsequent separation from the other noble metals.

The foregoing considerations apply to actual separations. In many cases, however, actual separation is unnecessary, as there are many Volumetric methods which give accurate results when metals which interfere Gravimetrically are present. Examples of this are tin by iodine in the presence of all other Group II metals, and iron by dichromate in the presence of almost any metal. Also, it must not be forgotten that some gravimetric methods are in themselves separations. These need not be detailed here, but two examples may be quoted:

1. Copper by the CuCNS method.
2. Pb as $PbSO_4$ in the presence of all other metals except Ba, Sr, and Ca.

After Group IV, separations are less clean-cut and the choice of methods is more limited. Where Groups V and VI are concerned, therefore, very great care is required, and it must be remembered that all errors due to impure reagents, splashing, etc. tend to accumulate towards the end of the analysis, and the Analyst is usually unable to fall back upon any method of checking. This is the region of " difference methods " with all their inherent errors, and the Chemist may very well be thankful that these metals only rarely enter into alloys, and not very frequently into ores. Of course, in a mixture of salts given for analysis in an Honours examination, anything may occur, but it will be rare that a very difficult separation will be required, if only on account of the time limitation. This practically precludes such mixtures as barium with strontium and/or calcium, Group V metals with Group VI metals, or any mixture containing traces of potassium or sodium. Separations of potassium from sodium or from ammonium are possible, but if they are given, there will be little time for anything else.

The first step when confronted by a sample for analysis is to obtain a solution. It is naturally impossible to give "Cookery Book" recipes that will meet all cases, but the main lines of attack can be indicated. These are:

I. *Solution in Water.*— Solution in water, aided, if necessary, by heating, requires no explanation or amplification, except the remark that the fact that the sample is soluble in water automatically excludes a host of ions and combinations of ions from consideration.

II. *Dilute Hydrochloric Acid.*—Use 25 per cent. HCl first. This will bring into solution such substances as carbonates, hydroxides, some oxides, phosphates, arsenates, and cyanides. Note, of course, if any gas is evolved.

If the sample refuses to dissolve in the dilute acid, even on heating, but shows signs of attack, add an equal volume of

III. *Concentrated Hydrochloric Acid* to the dilute acid and allow the mixture to digest, under cover, on the hotplate for an hour. This will dissolve most sulphides and oxides, but for the former, HNO_3 (*q.v.*) is the best solvent. Conc. HCl attack is valuable for many ores, and here again, commonsense should be exercised. Almost all ores contain silica, either combined or free ; a silicate ore will rarely be completely broken up by acids, but with experience it is usually possible to tell whether the attack is effective or not. Free silica is, of course, insoluble in HCl, and is left behind as a white, sandy residue after digestion ; if nothing but silica remains, it may be filtered off after dilution, and weighed, the filtrate being used for the rest of the analysis.

In the case of metals, the following are quickly dissolved by HCl: Cd, Sn, Fe, Al, Ni, Co, Zn, (Cr and Mn), and of course the metals of Groups V and VI, and for these HCl is the best solvent. Tin is included in this list, though the action is slow, especially with the pure metal, because the HCl attack on tin is very common in practice. Copper, lead and mercury can also be dissolved in HCl, but the attack is never used in practice.

Alloys dissolving in HCl are relatively few, apart from iron and steel. The chief are: Tin alloys, aluminium alloys, magnesium alloys, iron-chromium alloys (stainless steel), nickel-chromium alloys, cobalt-chromium alloys and other "acid-resisting" alloys, together with some electrical resistance wire alloys. To this list may be added copper alloys, but only for the estimation of arsenic by evolution.

IV. *Sulphuric Acid.*—This acid is generally very similar to HCl in its effect and range of application. It is not often used as a solvent, at least not as an attacking solvent, except in the few cases where its higher boiling-point makes it useful. H_2SO_4 is used in conjunction with HF in the attack of certain silicious materials, and by itself at the boiling-point for the opening up of some alloys for the estimation of antimony. Its chief use in analysis is to get rid of unwanted HCl or HNO_3, taking advantage of its high boiling-point.

V. *Nitric Acid.*—HNO_3 is, perhaps, the most important solvent for metals and alloys. It readily attacks: Ag, Hg, Cu, Pb, Bi, Cd, As, Sb, Sn, Fe, Al, Ni, Co, Mn, Zn, Mg, etc., but it should be noted (1) that many metals have nitrates which are insoluble in conc. HNO_3 (*e.g.* Pb) and in the conc. acid a protective coating soon forms which

stops further action. (2) Antimony and tin are oxidised, not dissolved to form nitrates, the products being, respectively, antimonic acid, $Sb_2O_5.xH_2O$, and, on boiling, metastannic acid, $SnO_2.xH_2O$. (3) Iron, chromium and nickel are made " passive " by immersion in conc. HNO_3, though all dissolve readily enough in the more dilute acid. (4) Aluminium is scarcely attacked by conc. HNO_3 and only slowly by the dilute acid when the metal is pure.

HNO_3 is used for opening up the following alloys:

Silver alloys (Coinage, jewellery, etc.).
Mercury alloys (Dental alloys).
Lead alloys (Bearing metals, solders, hard lead, etc.).
Copper alloys (Brass, bronze, gunmetal, etc., etc.).
Bismuth alloys (Fusible alloys).
Tin alloys (Whitemetals, pewter, etc.).
Iron and steel (for most estimations).
Aluminium alloys.
Nickel alloys (Nickel silver, Monel metal, resistance alloys, etc.; but HNO_3 is *useless* for opening up " Stainless ", or acid-resisting alloys).

Nitric acid, though a very important solvent, especially in metal analysis, is often a nuisance on account of its oxidising properties, which make it impossible to use H_2S as a reagent and prevent the immediate application of any Volumetric method depending on oxidation-reduction reactions. Fortunately, however, it is always possible to get rid of HNO_3 by " taking to fumes " with H_2SO_4, using sufficient of the latter acid to combine with all the bases and leave a small excess. This method is very frequently adopted in practice. (See p. 59.)

VI. *Aqua Regia.*—This compound solvent acts like HNO_3 alone in that it is an oxidising agent, but it is more intense in its action than HNO_3; the nascent chlorine that is produced by the interaction of the two acids ($HNO_3 + HCl$) is capable of bringing nearly anything into solution except silicates and some iron-nickel-chromium alloys.

Aqua regia is well suited for the attack by oxidation of sulphide minerals, but it is safest to allow the HNO_3 to act alone for a minute or two, adding the HCl slowly and a little at a time. As regards metals and alloys, gold and platinum may be added to the HNO_3 list, and it must be remembered that tin and antimony are not left insoluble as oxides, but are brought into solution as chlorides by the Cl^- present. In practice, aqua regia attack is generally only used in the following cases:

Iron and steel (for silicon, sulphur, phosphorus, etc. estimations).
Phosphor bronze (for phosphorus).
Certain lead alloys.
Certain tin alloys.

VII. *Hydrofluoric Acid.* This (+ H_2SO_4) is sometimes used to open up materials containing much free silica, and certain ores containing silica. It is useful in saying a fusion in the case of silica brick and ganister.

VIII. *NaOH and KOH Solutions.*—These are sometimes used to

bring aluminium and zinc alloys into solution, and for the attack of ferrosilicons containing much silicon.

IX. *Fused NaOH (KOH).*—Attacks ferrosilicon (medium silicon), and certain metallic oxides, *e.g.* SnO_2 and Sb_2O_5.

X. *Fused* Na_2O_2.—Acts similarly to fused NaOH, but with the addition of a powerful oxidising action. This is used for the attack of certain ores, notably chromite.

XI. *Fused* Na_2CO_3.—This important attacking agent is chiefly used for breaking up silicates which resist the action of acids. The fusion is also employed (sometimes with the addition of a little KNO_3) to bring certain metallic oxides, such as Cr_2O_3, Al_2O_3, WO_3, into a state suitable for analysis. In short, alkaline fusion is used to deal with those weakly acidic oxides which are insoluble in acids.

The success of the fusion depends upon Mass Action, and a considerable excess of the carbonate must, therefore, be used ; the usual proportions are 5 to 10 times the weight of the sample to be decomposed.

As this fusion is of the utmost importance, the procedure will be described in some detail:

The sample must be in an extremely finely divided condition, and every additional minute spent in grinding most materials in the agate mortar will save many minutes in the long run. The fine powder is placed in a platinum crucible and 5 to 10 times its weight of pure anhydrous sodium carbonate is roughly weighed out on to a watch glass. A quantity of the carbonate is then placed into the crucible and the two powders are thoroughly mixed with a stiff platinum wire. A little more carbonate is then added and the mixing process is continued, adding a little of the reagent at a time, each time stirring well with the wire. When about three-quarters of the sodium carbonate have been added, the remainder is poured into the crucible, without mixing, to act as a ' cover ' ; the crucible is tapped on the bench once or twice to settle and compact the mixture, which is then ready for fusion.

An alternative method is to mix the sample and three-quarters of the carbonate upon a piece of glazed paper by tilting first one corner and then the other, finally pouring the mixture into the crucible, brushing the paper over with a stiff feather and adding the rest of the carbonate as a cover. This method requires careful brushing of the paper after transference. There should be at least 5 mm. clear space at the top of the crucible.

The crucible and contents are then carefully placed in the muffle furnace (uncovered) and pushed to the back in the region of greatest heat. The door of the furnace is closed to allow the temperature to attain its maximum ; at least 900° C. is required ; this is a bright yellow heat. After 20 minutes' heating the crucible is removed to inspect its contents. It is usually possible to detect whether any of the sample remains unattacked, as although most metallic oxides will not be in solution, they will be seen as floating, flocculent particles which are quite unlike the original powder. If necessary, the fusion is continued for a further period, at the end of which the melt is again removed for inspection. When the sample is completely decomposed, the fusion is finally removed from the furnace and allowed to solidify in the crucible on a piece of clean asbestos sheet with a piece of stout platinum wire

dipping into the centre. When the mass is quite solid, the crucible is replaced in the muffle for a minute or two in order to remelt the layer that is next to the metal of the crucible. At this point a gentle pull on the wire will remove practically the whole of the mass.

Extraction with water is the next procedure. A suitable volume of water is placed in a tall beaker and the crucible is carefully dropped in so that it lies on its side. The mass adhering to the wire is then suspended so that it hangs just below the surface of the water ; (bending the end of the wire and hooking it over the edge of the beaker is the usual method). The whole is then placed (covered) on the hotplate in order to extract. By suspending the melt, solution is much more rapidly effected, as the solution, as it forms, falls to the bottom of the beaker and fresh solvent is always in contact with the solid mass.

When solution is complete, the next procedure depends upon the nature of the analysis. In some cases the solution is filtered at once, *e.g.* in separating P_2O_5 or WO_3 from Fe_2O_3, or in breaking up $BaSO_4$; in other cases the extract is acidified and then filtered, *e.g.* in the analysis of a silicious material.

After the extraction it is easy to see whether the fusion has been complete. If any undecomposed sample remains, it must be filtered off (if other insolubles are present it does not matter) and re-fused with five times its weight of carbonate ; the filtrate from the second extraction is combined with the filtrate from the first.

The writer does not recommend the use of so-called " fusion mixture," which is, approximately, $NaKCO_3$, and which melts at a considerably lower temperature than Na_2CO_3 alone does. Pure sodium carbonate melts at about 850° C., but the attack is not rapidly effective at temperatures much below 900° C.; this being so, there is no point in using a lower-melting mixture, and there are the active disadvantages that, (1), K_2CO_3 is hygroscopic and spatters in the muffle unless previously dried, and, (2), K^+ is much more prone to be adsorbed than is Na^+. The muffle is always to be preferred to a blowpipe or blast lamp for fusions, as not only is it more convenient (the operator can go away and leave the fusion), but a naked flame is apt to harm platinum.

As the result of an alkaline fusion, the ' insolubles ' consist of the oxides (or carbonates) of the metals in the sample ; these are Fe, Cr, W, Mn, Ni, Co, Ba, Sr, Ca, Mg. (*Note.*—Fusions in platinum should only be attempted when no easily reducible metal is present.) The ' solubles ' consist of the excess of Na_2CO_3 and the sodium salts of the ' acids ' originally present in the sample. These are: SiO_2, CrO_3, WO_3, Mn_2O_7, P_2O_5, etc. and of course *any* acid that is not decomposed by the fusion ; *e.g.* if $BaSO_4$ is in the sample, the products are $BaCO_3$ and Na_2SO_4.

Note that chromium and manganese may appear either in the soluble part or the insoluble ; a pinch of KNO_3 in the fusion brings all the chromium into the soluble portion.

XII. *Fused $KHSO_4$.*—This is the acid fusion corresponding in importance to the alkaline fusion just described. It brings the bases into solution as sulphates and leaves the acids and SiO_2 insoluble. The following procedure should be adopted:

Set a clean platinum crucible upon a triangle and incline it slightly

to one side. Drop a lump of the fused salt into the crucible and apply a small Bunsen flame held in the hand. The salt fuses at about 200° C., and as water is usually present, there is always a certain amount of spattering ; this is the reason for heating cautiously and for commencing the fusion without adding the sample. When the first lump is in a state of quiet fusion, add a second, heating the rim of the crucible rather than the base, and continue in this manner until a suitable amount of quietly molten bisulphate has been obtained. *Note* that in this fusion, mass is not so important, as the reaction is not reversible.

Remove the flame and introduce the sample from a piece of glazed paper or from the weighing scoop of the balance. Replace the flame and gradually increase the temperature so that fumes of SO_3 begin to make their appearance. This denotes that the $KHSO_4$ is being converted into $K_2S_2O_7$ by the reaction:

$$2\,KHSO_4 = K_2S_2O_7 + H_2O.$$

The $K_2S_2O_7$ in turn decomposes:

$$K_2S_2O_7 = K_2SO_4 + SO_3.$$

Thus, at high temperatures, the fusion liquid behaves like H_2SO_4, all basic oxides being converted into sulphates.

As the SO_3 is expelled, the melting-point of the mass rises, until sufficient K_2SO_4 (M.P. 1,070° C.) has accumulated to cause some of the melt to solidify. If by that time the whole of the sample is not opened out, more fused $KHSO_4$ must be added ; needless to say, this should *not* be added in the lump form or a dangerous spurting of the molten mass will result, but it should be fused in a separate crucible and only added when all its water has been expelled.

The mass is extracted as was described under the alkaline fusion, but in this case, it is better to use water containing a little H_2SO_4. The chief insolubles after an acid fusion are: $BaSO_4$, $SrSO_4$, $CaSO_4$ and SiO_2. The soluble matter includes the sulphates of the common metals.

This is the method used in opening out certain ores and in bringing ignited Fe_2O_3 and Al_2O_3 into solution, and it is used particularly in the analysis of samples containing titanium.

The best way to clean a platinum crucible that has become stained is to fuse about a gram of $KHSO_4$ in it.

It is of the greatest importance to exercise the utmost care when carrying out a bisulphate fusion as the early stages must not be hurried. The spatterings that are always liable to occur until the water has been driven out are not only liable to cause loss of sample, but are a possible source of danger to the analyst. The sample itself must, of course, be dry.

GROUP I.

Silver, Mercury (ous), Lead.

A sample containing these metals, especially silver, will obviously not dissolve in HCl directly. It is dissolved in water, HNO_3 or H_2SO_4, the solution nearly neutralised, and HCl added, drop by drop, until no further precipitation takes place. Five cc. excess are added for

every 100 cc. of solution, the solution stirred well, and brought just to the boil. If Hg^+ is present the solution is not actually boiled or some mercury may be volatilised ; the solution is allowed to settle a moment and the clear liquid is then decanted through an asbestos Gooch crucible, using slight suction. 20 cc. of hot water containing 2 per cent. of HCl are added to the precipitate in the beaker, the mixture is stirred, allowed to settle and again decanted through the crucible. This is repeated five or six times with hot water only, finally washing with boiling water until the runnings are free from Cl^-.

The precipitate consists of AgCl and Hg_2Cl_2 ; the filtrate contains the metals of Groups II to VI, including lead.

Note, here, that Hg^+ is never met with in commercial products (except in mercury ores and amalgamation process products) and is not likely to be given in an examination. If Hg^+ should be present in a mixture, it is unlikely that the candidate will be expected to estimate Hg (-ous) and Hg (-ic) separately, but only total mercury, in which case the -ous compound is oxidised with chlorine gas or HNO_3, so that the metal will be found in Group II.

It is, of course, possible that mercurous nitrate or chloride may be given for analysis, but it is not probable that silver will be co-present. The estimation of these salts singly is not difficult, and it must be left to the candidate's commonsense and experience to devise a method. In the case of the nitrate the following is suggested: Precipitate with $(NH_4)_2CrO_4$ solution as Hg_2CrO_4, filter and ignite ; weigh as Cr_2O_3, calculating the equivalent weight of mercury. Estimate NO_3^- in a separate sample. In the case of Hg_2Cl_2, boil with a large excess of Na_2CO_3 in saturated solution, filter, wash with hot water containing Na_2CO_3, and estimate Cl^- in the filtrate. Estimate mercury in a separate portion of the sample.

Hg_2Cl_2 and AgCl may be separated by pouring successive small quantities of conc. NH_4OH through the Gooch crucible. The mercurous compound is blackened and the AgCl can be re-precipitated in the filtrate by just acidifying with HNO_3. This sort of separation is never required in practice, however.

SILVER.

As a rule silver is separated in a condition for direct weighing by the addition of HCl, as described, the $PbCl_2$ which is co-precipitated being extracted with hot water.

Short Cut.—If a silver alloy is cupelled on an absorbent support in the open muffle with, say, 10 times its weight of pure lead, the button finally remaining consists of silver (plus the noble metals, of course). In the absence of gold, etc. this is not only a complete separation for silver, but is an accurate quantitative method for its estimation. The methods of dry assaying are, however, too complex a matter to be considered in an elementary text-book, and the student is referred to a text-book on Assaying.

MERCURY (-ous).

As has been mentioned already, it is not usual to estimate mercurous mercury as such, in the same sense as ferrous and ferric iron would be

separately determined if co-present in a solution. The proper procedure is to estimate (1) total mercury, (2) total acid or acids, and to calculate, from these, the relative percentages of -ous and -ic mercury.

Mercury, if present, is *not* separated as Hg_2Cl_2, but as HgS, the metal being previously oxidised; or it may be estimated as metal; mercury comes, therefore, into Group II, and the same remark applies to lead, but for a different reason.

LEAD.

Lead is classified with Group I because of the very slight solubility of $PbCl_2$ in dilute HCl.

SOLUBILITY OF $PbCl_2$.

In Water.	*At* 0° *C.*	*At* 15° *C.*	*At* 100° *C.*
(Gms. $PbCl_2$ in 100 cc.)	0·583 gm.	0·907 gm.	3·208 gms.

In Dil. HCl at 0° *C.*:

Gms. HCl per litre.	*Wt. of $PbCl_2$ dissolved in* 100 *cc. of the acid.*
Nil,	0·583 gm.
0·5,	0·45 gm.
1·0,	0·36 gm.
3·0,	0·16 gm.
6	0·14 gm.
10	0·12 gm.
100 (2·8 N),	0·12 gm.
200 (5·5 N),	0·52 gm.
300 (8·2 N),	1·75 gms.
400 (11 N, *conc. acid*),	4·00 gms.

In alcohol. Insoluble.

It will be seen from this table that lead, even under conditions that are most favourable to its precipitation by HCl is nevertheless perceptibly soluble in water, and more or less lead will always pass on to Group II. It may, however, be remarked that $PbCl_2$ is almost completely insoluble in alcohol, and this fact is made use of in the analysis of certain alloys, as by a fortunate chance the chlorides of copper, tin and antimony are quite soluble in alcohol, a fact which considerably simplifies the necessary separations.

GROUP II.

Mercury (ic), Lead, Copper, Bismuth, Cadmium, Antimony, Arsenic, Tin.

The essential fact to be grasped in dealing with these metals is that their sulphides are very differently affected by acids. Some of the sulphides, *e.g.* those of arsenic, copper and bismuth, are quite stable in the presence of fairly large amounts of acid, while others, notably

PbS and CdS, are very easily redissolved, and may indeed never be precipitated if the concentration of H^+ exceeds quite a small amount. The following is a rough scale giving the metals in order of their sulphide 'sensitiveness' to H^+, As_2S_3 being the least soluble, and MnS the most easily soluble, in acid solutions:

As, (Ag), Cu, Bi, Hg, Sb, Sn, Cd, Pb, Zn, Fe^{++}, Ni, Co, Mn.

In many cases the actual details have been worked out, notably by Strell, Scharrer, Vestner, Brauner and Tomicek, and others. A practical summary of selected results is tabulated under the headings of the respective metals in question, but two facts may be mentioned here: 1. The sulphides tend to dissolve more easily the higher the temperature. 2. The rate of supply of the H_2S has an important influence on the precipitation. To these may be added a third fact, by way of a note: (3) The very process of precipitation by H_2S involves an increase in acidity, and in the case of the more soluble sulphides this fact must be borne in mind. Thus: $CdCl_2 + H_2S = CdS + 2\,HCl$, so that for every 56 gms. of Cd in the solution, 1 gm.-mol. of HCl is formed. In practice, the calculation might be made on the following lines:

Suppose in 1 gm. of alloy there is 56 per cent. of Cd; this is equal to 0·56 gm. If the solution is originally neutral, and its bulk 100 cc., by the time all the Cd is precipitated by the H_2S, 0·365 gm. of HCl will have been formed, and this will be equivalent to 0·1 N HCl. If, however, as is invariably the case, the solution is acid at the outset, it is obvious that it may be necessary to allow for this generation of HCl during the precipitation. CdS is not entirely precipitated from hot 0·1 N HCl solution, and if, as is usual, the solution is originally about 0·3 N as regards HCl, the acidity at the end of the reaction will be nearly 0·5 N, so that even a slight elevation of the temperature will result in incomplete precipitation of Cd as CdS. Similar remarks apply to PbS, and with special force to ZnS (see under Zinc for this).

The above fact, while it must be kept in mind, need not cause trouble, as the analyst can either add an alkali to reduce the H^+ concentration, or, more simply, he can dilute his solution, thereby at once lowering H^+ concentration and increasing the mass of H_2S present.

Methods for the separation of the Group II sulphides depending on the group tables will be indicated.

GROUP SEPARATION.

The acidity should be about 0·3 N HCl (= 3 per cent. by volume of the conc. acid, approx.). It is essential to know exactly how much HCl is present. If the solution is originally neutral, it is easy to add 3 cc. of HCl to every 100 cc. of solution, but if HCl has been added to bring the sample into solution the matter is not quite so straightforward. The acid added for the purpose should, therefore, always be measured by volume, then, assuming that it was allowed to attack the sample at boiling-point, the acid actually remaining in the beaker will be of Const. B.Pt. strength, *i.e.* approximately 6 N. A simple calculation will show how much water to add to bring it to 0·3 N concentration. (In diluting, the beaker may often be used as a measuring cylinder;

to reduce the concentration from 6 N to 0·3 N, a dilution of 18 times is required. Note the depth of the acid, and add water to bring the depth to 18-20 times this.) *Note*, however, that trouble may be experienced by zinc, if present in large quantities, precipitating as ZnS, especially if the bulk of the sulphides is also large.

Removal of Excess Nitric Acid.—If HNO_3 was used for the original attack of the sample, conditions become more complicated. Nitric acid, except when cold and dilute (approx. 0·5 N) rapidly oxidises H_2S, sulphur being precipitated and not sulphides, so that, except in special cases, it is best to remove the excess of HNO_3. This is effected—

1. *By Adding H_2SO_4 and Evaporating to Fumes.*—In this, the quickest method, the excess of H_2SO_4 is known with fair accuracy. Add 5 cc. of the conc. acid and evaporate to copious fumes ; dilute to 100 cc. and cool.

We may assume that 1 cc. of conc. H_2SO_4 is approximately equivalent to the metals in 1 gm. of sample ; 1 or 2 cc. will have been driven off as fumes, leaving 2 or 3 cc. remaining as excess. Dilution to 100 cc. will, therefore, give an approximately N solution. This is usually a suitable and safe concentration for H_2SO_4, for the following reasons:—

(*a*) Lead, the sulphide of which is one of the most soluble, will be out of consideration as it will have been precipitated as $PbSO_4$.

(*b*) The sulphides are less ' sensitive ' to H_2SO_4 acidity than to HCl, and N H_2SO_4 is reasonably safe, even for CdS. (Cadmium is fortunately rare in alloys.)

2. *By Evaporating to Dryness*, adding 20 cc. HCl to dissolve the residue, re-evaporating to dryness, and yet again evaporating with 25 cc. HCl.

This process will expel all the HNO_3, even that combined with the metals, in spite of the fact that HNO_3 boils at a higher temperature than HCl does. The first evaporation removes all the excess HNO_3, and in taking dry, a good deal of ' N_2O_5 ' will be expelled, leaving basic oxides in the beaker. Evaporation with HCl then causes the following reaction to take place:

$$HNO_3 + 3\,HCl = NOCl + 2\,H_2O + Cl_2$$

and, as all compounds on the right hand side of the equation are volatile, the HNO_3 is first decomposed and the products then driven off by boiling. On the whole, Method 2 is preferable unless lead is to be separated.

Note.—If mercury is present, it will be largely expelled during this evaporation, and must be estimated on a separate portion of the sample.

Having diluted to the correct volume, pass a rapid stream of H_2S through the solution until the precipitate coagulates into large flakes and shows signs of settling well. When this is achieved, stop the flow of gas and allow the precipitate to settle completely. Raise the delivery tube slightly and pass H_2S gently through the clear liquid to see if the precipitation is complete. If complete, rinse the tube inside and out, then the sides of the beaker, and filter immediately. Wash with 0·1 N HCl saturated with H_2S.

MERCURY.

HgS is separated from the other sulphides of Group II by digestion with 1·2 sp. gr. HNO_3, in which it alone is insoluble.

Method of Estimation.—The precipitated sulphides are filtered off on a smooth surfaced paper (non-ashless) and washed first with dil. HCl which has been saturated with H_2S and then twice with H_2S-water. The paper is then opened out in the funnel and the precipitate rinsed into a 250 cc. dish with the minimum amount of water. Conc. HNO_3 is added with constant stirring in amount equal to the volume of the water, and a jet of hot 1·2 sp. gr. HNO_3 is applied from a small wash-bottle to the paper, followed by a rinse with water, catching both in the dish.

The contents of the dish are warmed on the hotplate, covering it to minimise evaporation ; after 20 minutes' digestion the dish is rinsed out into the original precipitation beaker and the rinse diluted with at least an equal volume of water, the whole cooled, and filtered through a pulp filter. The residue on the filter consists of sulphur, a little $PbSO_4$ if the mixture contained lead, and all the mercury as HgS, except that still adhering to the original filter paper. This residue is treated with a wash of hot 1 : 1 HCl followed by a quick wash with saturated $KClO_3$ solution to bring it into solution, and then, immediately, the filter is thoroughly washed with cold water. The cycle is repeated if necessary. The filter is washed thoroughly and the mercury estimated in the filtrate. Aqua regia may be used instead of HCl + $KClO_3$ to effect solution of the HgS.

If mercury alone of Group II*a* is present, the HNO_3 digestion may be substituted by digestion with yellow ammonium sulphide, which also leaves HgS insoluble.

Short Cut.—Mercury (except in the form of iodide) can always be estimated by the distillation method described under Mercury on p. 51.

LEAD.

Conditions for Separation as PbS.

Precipitation of Lead as PbS.

It is assumed that there is 0·2 gm. of lead in each 100 cc. of solution, containing HCl as indicated.

DILUTION.*	SEPARATION OF $PbCl_2$.	COMPLETE PRECIPITATION OF PbS.	ALL LEAD IN SOLUTION.
Inf. (no HCl)	Nil	At all temps.	..
1/120	Nil	Up to 80° C.	..
1/50	$PbCl_2$ precipitated below 20° C.	Up to 70° C.	..
1/25	,, ,,	Up to 50° C.	At B. Pt.
1/15	,, ,,	Up to 30° C.	At B. Pt.
1/12	,, ,,	At no temp.	Above 80° C.
1/5	$PbCl_2$ precipitated below 40° C.	,,	Above 40° C.

* Dilution means, here, parts conc. HCl (sp. gr. 1·20) by volume.

Note that the above table is approximate only, erring on the side of "safety" from the analyst's point of view. Thus, in line 4, where it

is stated that lead is completely precipitated as PbS up to 50° C. from a concentration of HCl of 1 in 25, the precipitation will actually be complete at temperatures slightly above 50° C. and at acid concentrations slightly greater than 1 in 25.

Lead is best separated before the precipitation of Group II sulphides by the addition of 5 cc. (per gram of lead) of conc. H_2SO_4 and evaporation to fumes. On diluting so that the acid remaining represents 5 to 15 per cent. by volume of the solution, $PbSO_4$ will be left insoluble and may be filtered off from the other metals the sulphates of which are soluble. The $PbSO_4$ is washed with cold 5 per cent. H_2SO_4.

Note.—The addition of HCl in Group I will show whether lead is present in notable quantities or not. $PbCl_2$ is quite distinctive in appearance and is easily recognised even when the amorphous chlorides are co-precipitated. If $PbCl_2$ alone separates (but beware of confusing this with NaCl or $BaCl_2$, both of which may be thrown down from moderately concentrated solutions by conc. HCl), lead may be ignored as a member of Group I ; H_2SO_4 is added and the solution taken to fumes ; all $PbCl_2$ will be converted into $PbSO_4$. Similarly also, $PbCl_2$ will be completely converted into PbS by H_2S.

This separation is satisfactory from mercury (some of this will be lost during fuming), from copper, cadmium, arsenic and the metals of later groups (except barium, calcium, etc.), but is not satisfactory when bismuth is present, or in the presence of relatively large percentages of antimony and/or tin, since these metals are very prone to the formation of basic salts which are insoluble in acids of moderate dilution. If antimony and tin are present the dilution should not be too great and rather more than 5 per cent. of H_2SO_4 should be present ; 10 per cent. is not too much in cold solution, and this will keep all ordinary amounts of these metals in solution ; more than 15 per cent. will dissolve serious amounts of $PbSO_4$.

Special Separations—*From Mercury.*—1. Evaporate the chloride solution to dryness several times under a hood in a good draught. Mercury is completely volatilised.

2. Take the solution to dryness, mix with Na_2CO_3 and heat. Metallic mercury is expelled and the PbO may subsequently be boiled with dil. H_2SO_4 and so converted into sulphate for weighing.

3. The mixed sulphides, as obtained in the course of the Group separation, are separated as described under Mercury by digestion in 1·2 sp. gr. HNO_3.

From Copper.—1. The best separation by far is electrolysis of the HNO_3 solution. Copper is deposited quantitatively on the kathode and PbO_2 on the anode.

2. Evaporation to fumes with H_2SO_4 gives a perfect separation.

3. Evaporation to bare dryness with excess of HCl, followed by the addition of 95 per cent. alcohol leaves $PbCl_2$ insoluble, while $CuCl_2$ dissolves. Wash with 95 per cent. alcohol.

4. Precipitation of the copper as CuCNS gives separation.

5. Adjust the HCl acidity to exactly 20 per cent. by volume, heat to 80° C. and saturate with H_2S. CuS alone is precipitated. If the bulk of the CuS is great it should be dissolved in a little hot conc. HCl,

the solution diluted to the above concentration of acid, and H_2S again passed. Combine the filtrates, which will contain all the lead. Wash with acid of the same concentration, saturated with H_2S.

From Bismuth.—This is one of the most difficult of separations as the H_2SO_4 method fails to give complete separation.

1. From small amounts of lead, the electrolytic method is best.
2. Perhaps the best general method is the precipitation of bismuth as BiOCl (see under Bismuth).
3. Precipitation of bismuth as metal with formaldehyde (etc.) is also good.
4. Basic nitrate method (see under Bismuth).
5. Basic formate method:

Nearly neutralise the HNO_3 solution with NaOH or Na_2CO_3; clear up any permanent precipitate with a few drops of 1·20 sp. gr. formic acid. Add 20 cc. of 10 per cent. sodium formate solution and 3 or 4 cc. of 50 per cent. formic acid. Boil until the white granular precipitate settles out well, filter and wash with hot water. Redissolve in a little conc. HCl and re-precipitate as before, combining the filtrates. The precipitate is basic bismuth formate; estimate the bismuth by any of the usual methods (the precipitate dissolves in all acids). This is an excellent method for the separation of bismuth from lead.

From Cadmium.

1. Sulphate method.
2. The electrolytic method is satisfactory for small amounts of lead.

From Antimony, Arsenic, Tin.

1. Digestion with NaOH, Na_2S or $(NH_4)_2S$ dissolves the sulphides of antimony, arsenic and tin and leaves PbS insoluble.

2. The sulphate method, using up to 15 per cent. of H_2SO_4, is effective, but if much antimony is present (10–20 per cent.), its basic sulphate will be slowly precipitated on standing. The method is quite effective for such alloys as lead-base bearing metals, solders, hard lead, etc., but the solution should not be allowed to stand longer than necessary. A turbidity in the supernatant liquid means that antimony is beginning to separate.

3. In cases where the amount of lead is not great, *e.g.* in white metals, the separation is conducted as follows: Dissolve the alloy in HCl, aided by a pinch or two of $KClO_3$. Boil off Cl_2 and ClO_2, and dilute somewhat. Add at least 10 gms. of tartaric acid and warm until the crystals dissolve, then add a concentrated solution of NaOH (fresh) until the solution is just alkaline. (If a precipitate forms here, there is not enough tartaric acid present.) Now make the solution decidedly alkaline with NaOH (5 cc. of the 25 per cent. solution in 100 cc.), and saturate with H_2S.

PbS, CuS, CdS and Bi_2S_3 are precipitated (also FeS, ZnS, NiS, CoS, MnS), while the sulphides of antimony, arsenic and tin remain in solution as thio-compounds. Filter, and wash with very dilute Na_2S solution. (See White Metal analyses.)

4. Quite a good separation for small amounts of antimony and arsenic

from larger amounts of lead is to adjust the acidity to 20 per cent. by volume of HCl, heat to 80° C. and saturate with H_2S. No PbS is precipitated though the separation of Sb_2S_3 is complete.

5. For small amounts of Sb, As, Sn, and larger amounts of lead, the $PbCl_2$-alcohol method is excellent. (See Copper, Method 3.)

From Metals of Group III, et seq.

1. The ordinary Group II separation with H_2S.
2. From all except barium, strontium and calcium, the sulphate method is excellent.

COPPER.

Conditions for Separation as CuS.

Precipitation of Copper as CuS.

It is assumed that there is 0·3 gm. copper in each 100 cc. solution, containing HCl as indicated. A brisk current of H_2S is employed.

DILUTION.*	COMPLETE PRECIPITATION OF CuS.	ALL COPPER IN SOLUTION.
Less than 1/12	At all temperatures.	..
1/5	Traces unprecipitated at B. Pt.	..
1/3	At all temps. up to 60° C.	..
1/2	At all temps. up to 40° C.	..
1/1·5 (2/3)	Traces unprecipitated at 20° C.	..
1/1	Incomplete at all temps.	At B. Pt.

* Parts conc. HCl (sp. gr. 1·20) by volume.

Separation from All Other Metals:

Method 1.—Electrolysis of strongly acid (HNO_3) solutions using a rotating kathode. The separation is generally good, but silver, arsenic and antimony are liable to be deposited with the copper if conditions are incorrect. A double electrolysis, dissolving off the impure copper first deposited and re-electrolysing, effects a perfect separation.

Method 2.—Estimation as thiocyanate.

Separation from Mercury.—1. Mercury is separated as described under Lead.

Separation from Lead.—1. See Separation of Lead from Copper.

Separation from Bismuth.—1. The acid solution is made ammoniacal, sufficient excess of ammonia being added to convert the original pale blue solution into the dark blue cuprammonium solution. $(NH_4)_2CO_3$ is added, the mixture digested, filtered, and washed with dil. $(NH_4)_2CO_3$ solution. Bismuth remains insoluble as carbonate.

2. Thiocyanate method.

3. Precipitation of the bismuth as BiOCl is the best method of separating large amounts of bismuth from smaller amounts of copper. A double precipitation may be necessary.

4. Precipitation of bismuth as metal.

Separation from Cadmium.—1. Adjust the acidity of the H_2SO_4 solution to 1 in 4 and saturate with H_2S. Dissolve the precipitate in a little conc. HNO_3, evaporate to fumes with 10 cc. H_2SO_4 and dilute to 400 cc. Add 10 gms. of NH_4Cl and again saturate with H_2S. The copper will remain as sulphide, and the cadmium can be estimated in the filtrate.

2. Similarly with HCl acidity, following the method given for the separation of Copper from Lead. A double precipitation is necessary in both cases if there is much CuS precipitated.

3. Another method which is sometimes useful is to take advantage of the fact that H_2S does not decompose the double cyanide of copper (also zinc), whereas it does that of cadmium. To the mixture add 10 per cent. KCN solution until the precipitate first thrown down is just re-dissolved. Saturate the solution with H_2S, when CdS is alone precipitated. This method is useful in the estimation of cadmium in Brass (*q.v.*).

Separation from Later Groups.—1. If copper alone of Group II is present, its precipitation as CuS, or as Cu_2S with sodium thiosulphate (see Copper) is the ideal method.

2. Electrolysis.

Separation from Iron and Aluminium.—Excess of ammonia is added and solution filtered. The copper passes into the filtrate as a cuprammonium compound.

Separation from Manganese (or from Iron and Manganese ; *e.g.* in Steel Analysis, or if the electrolysis for copper has not been complete in a Brass or Bronze Analysis) :

Add Br_2 to saturation, followed by excess of ammonia.

Separation from Chromium, Aluminium, Manganese, Nickel, Cobalt, Zinc and later groups can be effected by " *Cupferron* " ; see under Iron.

CADMIUM.

Cadmium is not often met with in important amounts.

Separations.

From Mercury, Copper, Bismuth, Antimony, Arsenic, Tin.—Adjust the acidity to 15 per cent. by volume of HCl, heat to 80° C. and saturate with H_2S. The sulphides of the above metals are precipitated ; cadmium and lead remain in solution. A double precipitation is usually necessary, the precipitated sulphides being re-dissolved in HCl + $KClO_3$.

From Lead.—Sulphate method.

From Copper.—1. Electrolysis.
2. Thiocyanate method
3. Double cyanide method.
4. H_2S passed through a solution of adjusted acidity.

} For details see Copper (separations).

From Metals of Later Groups.—Cadmium is associated, metallurgically, with zinc, and is an invariable impurity in that metal and its alloys.

In the analysis of Brass, it is usual to work with solutions of such acidity that CdS is not precipitated in Group II even if the H_2S method of removing the copper is used. Moreover, $Cd(OH)_2$ is instantly soluble in excess of ammonia, so that cadmium will reappear in the analysis only when Group IV is reached. It is usually separated and estimated in a separate portion of the sample, but this is not essential ; the weighing out of a separate sample is usual on account of the very small percentages of the metal that are likely to be present ; the detection of cadmium in a 1 gm. sample, to say nothing of the estimation, would be a very difficult matter.

Method.—Remove copper, tin and lead, by solution in HNO_3 followed by electrolysis. Remove iron and aluminium by ammonia. The solution now contains only cadmium and zinc, the latter in large excess. Make the solution just acid and saturate with H_2S. Now add dilute ammonia, drop by drop, with constant shaking or stirring, until a small permanent precipitate is formed ; this will be ZnS and will contain all the cadmium as CdS. Decant the clear solution through a filter, rinse the precipitate on and allow it to drain completely. Dissolve the precipitate off the paper with dil. HCl, make the solution neutral to methyl orange and then add 3 cc. of conc. HCl for every 100 cc. of solution. Saturate with H_2S, digest until the precipitate settles out well, and filter off the CdS, containing traces of ZnS and possibly CuS ; wash with water containing H_2S and made slightly acid with HCl.

Make the final separation by redissolving in HCl, neutralising with Na_2CO_3 solution, and adding an excess of KCN, after which again pass H_2S. CdS alone is precipitated. Weigh as $CdSO_4$. See under Cadmium and also under Brass.

GROUP II B.

Antimony, Arsenic, Tin.

The sulphides are precipitated as has been described under the Group separation. The sub-group separation is carried out as follows:

The sulphides are washed back into the beaker in which they were precipitated and there digested with excess of rather concentrated NaOH, KOH, Na_2S, or $(NH_4)_2S$ for half an hour at a moderate temperature. The mixture is then filtered and washed with the dilute reagent. The thio-salts of antimony, arsenic, tin (-ous and/or -ic) are found in the filtrate.

Note as to Choice of Reagent.—1. Na_2S dissolves HgS as well as the sulphides of Group II*b*, but in the absence of mercury, the separation is neater and cleaner than with $(NH_4)_2S$.

2. $(NH_4)_2S$ partially dissolves CuS owing to the formation of ammonium complexes.

3. SnS is not dissolved by Na_2S, but it is dissolved if the sulphide contains polysulphides (*i.e.*, thiostannites are not formed). As, however, SnS is practically never met with in analysis, this point is of minor importance.

4. As_2S_3 is soluble in $(NH_4)_2CO_3$ solution, a fact which is sometimes useful. It is obvious that a reagent free from polysulphides is an advantage, as it saves messing up the solution with precipitated sulphur, to say nothing of accelerating filtration.

The metals of Group II*b* can each exist in two states of oxidation, and each state has its sulphide, so that six sulphides are to be considered. All these except SnS dissolve as thio-salts in the reagents mentioned in the foregoing.

Antimony, arsenic and tin are somewhat alike in their reactions ; especially is this the case with antimony and arsenic, and as they frequently occur together in alloys and ores, much ingenuity has been expended in devising methods for their separation. They are easily separated as a group, so that the only difficulty lies in effecting their mutual separation. For this reason they will first be considered together, separations from one another come next, and finally a few strictly individual separations will be mentioned.

Separation of Group IIb Metals from Group I.—This separation will have been effected as a preliminary, as it is assumed that the solution is acid with HCl.

Precipitation with the Metals of Group IIa.—As for the Group separation, except that if antimony, arsenic and tin are the only metals of Group II present, a 10 per cent. or even 15 per cent. solution of HCl can be used for the precipitation. This strength interferes with the precipitation of cadmium and lead, but does not, in the cold, affect the separation of any of the other sulphides.

Properties of Group IIb Sulphides.—The physical natures of Group II*b* sulphides are described below:

Sb_2S_3—A flocculent, orange precipitate, passing by stages through red to black crystalline. The actual colour depends on the temperature and acidity ; an elevated temperature and high acidity favours a compact, dark coloured form.

Sb_2S_5—A flocculent, orange precipitate ; indistinguishable from one form of Sb_2S_3. Sb_2S_5 has some tendency to be reduced by H_2S to Sb_2S_3 and S.

As_2S_3—A lemon yellow, flocculent precipitate.

As_2S_5—The same, but slightly lighter in colour. These two sulphides have a tendency to form colloidal solutions ; high acidity and prolonged gassing are necessary for their complete and satisfactory precipitation. They are hydrolysed to the respective acids and H_2S on boiling with water.

SnS—Black or very dark brown ; flocculent. Not often met with in analysis. This is the only sulphide of the six which is not dissolved by Na_2S, as tin does not form sodium thiostannite.

SnS_2—Dirty yellowish-brown ; flocculent.

All of the above (except SnS) are soluble in any of the reagents

NaOH, KOH, Na_2S, $(NH_4)_2S$, NaHS, Na_2S_x, $(NH_4)_2S_x$; As_2S_3 and As_2S_5 are soluble in $(NH_4)_2CO_3$, while the sulphides of Group II*a* are not affected. Exceptions to this statement are: 1. HgS is soluble in Na_2S (NaHS); 2. CuS is slightly soluble in $(NH_4)_2S$.

Separation from Group IIa.—Rinse the sulphides back into the precipitation beaker and add excess of moderately conc. Na_2S solution. Digest the mixture for half an hour on the edge of the hotplate, under cover, and then filter, washing with dilute Na_2S. The sulphides of antimony, arsenic and tin are in the filtrate and may be recovered by acidifying.

Note that if mercury is in the mixture it will be found with the antimony, etc.; SnS will not be found. If mercury is in the original mixture it is best removed by distillation before analysing for the rest of the metals. Sn^{++} should be oxidised to Sn^{++++}. Or, if copper is absent, use $(NH_4)_2S_x$ as separating reagent, when mercury and tin will come into their proper places. A good method in this case is to remove copper as CuCNS (or by electrolysis) before precipitating the sulphides.

Separation from Lead.—Separation of small amounts of antimony, arsenic and tin from large amounts of lead, as in the case of lead-base bearing metals:

Method 1.—Fume with excess of H_2SO_4; lead remains as sulphate.

Method 2.—Dissolve the sulphides in HCl + $KClO_3$ or in HCl and a little HNO_3. Take to dryness and extract with alcohol. All the chlorides except $PbCl_2$ are soluble.

Method 3.—Adjust the acidity to 12 per cent. by volume of conc. HCl, heat to 50° C. and pass a rapid stream of H_2S. No PbS is thrown down.

Separation of Arsenic from Antimony and Tin.—(*a*) The metals are assumed to have been separated as their thio-salts. Oxidise the metals to their -ic condition and the polysulphides to sulphates by adding H_2O_2 until the yellow polysulphide colour fades to a pale straw, boil for a minute or two to destroy the excess of peroxide, cool completely and pour the mixture with constant stirring into twice its volume of cold conc. HCl. Cool and saturate with H_2S, passing the gas for 20 minutes at a brisk rate. The precipitate consists of As_2S_5 (with possibly a little sulphur). Wash with 2:1 HCl.

The filtrate may be suitably diluted and again treated with H_2S for the precipitation of the animony (see under separation of Tin from Antimony).

(*b*) Distillation Method.—Transfer the solution of the chlorides of arsenic, antimony and tin (*Note.*—Any other metal may be present; this method separates arsenic and antimony from all others) to a small distillation flask fitted with condenser, tap-funnel and thermometer dipping *into* the liquid. Add about 5 gms. of $FeCl_3$, 2 gms. of Cu_2Cl_2 and considerable conc. HCl. Add a piece of porous pot and distil slowly, keeping the temperature of the liquid below 110° C. If much arsenic is present, add a further 50 cc. of conc. HCl through the tap-funnel and again distil until the temperature commences to rise above 110° C. All the arsenic will be found in the distillate as $AsCl_3$ which may be titrated

directly with standard iodine, or may be estimated gravimetrically as As_2S_3. (See Arsenic and Antimony, pp. 78 *et seq.*)

(*c*) Precipitate the sulphides from the thio-solution by adding excess of HCl, if necessary previously oxidising polysulphides, etc. with a little H_2O_2. Filter, and dissolve the precipitate in conc. HCl aided by a little $KClO_3$. Boil off Cl_2 and ClO_2, dilute, and add 5 gms. of tartaric acid followed by ammonia until decidedly alkaline. (No precipitate should form here ; if the solution does throw down a precipitate, more tartaric acid is necessary.) Add excess of magnesia mixture and stand the beaker in a warm place, overnight if possible. Dissolve the precipitate in a little dil. HCl and re-precipitate, adding a few ccs. of magnesia mixture. The precipitate is $MgNH_4AsO_4$. (See Arsenic.)

Antimony from Tin.—(*a*) In HCl solution. A rough method which is interesting theoretically, is to pass H_2S through a 15 per cent. (by volume) HCl solution (Panajotov). (15 per cent. corresponds to 1·075 sp. gr. at 60° F., or to 1 part of 1·120 sp. gr. acid in 2 parts of water.) At this concentration no SnS_2 will be precipitated, but if much antimony is present, the precipitate should be redissolved in HCl and re-precipitated from a solution of the same concentration of acid in order to recover the SnS_2 that is adsorbed by the Sb_2S_3. The temperature must not rise above 20° C. or the antimony will not be quantitatively precipitated.

Conditions for the Precipitation of Sb_2S_3 by H_2S from HCl Solution.

It is assumed that not more than 0·4 gm. Sb is present in 100 cc. of solution and that a rapid stream of H_2S is maintained (1 litre per minute).

Dilution.*	Complete Precipitation of Sb_2S_3.	All Antimony in Solution.
Inf.	At all temperatures.	..
1/12	„ „	..
1/5	At all temperatures up to 80° C.	..
1/3	At all temperatures up to 40° C.	..
1/2	Up to 20° C.	At B. Pt.
1/1·4	At 0° C.	Above 80° C.
1/1	No complete precipitation.	Above 60° C.
4/3	„ „	Above 20° C.
2/1	No precipitation at any temperature.	..

* See under Lead for a note on this.

With a slow stream of H_2S, antimony is not so well nor so completely precipitated at higher temperatures. To be on the safe side, if a slow stream of gas is used, take 10° C. off all the above temperatures for complete precipitation and add 10° C. to the temperatures at which all the antimony remains in solution.

Conditions for the Precipitation of SnS_2 from HCl Solutions.

It is assumed that not more than 0·3 gm. of Sn^{++++} is present in each 100 cc. of solution, and that a rapid stream of H_2S is maintained.

DILUTION.*	COMPLETE PRECIPITATION OF SnS_2.	ALL TIN IN SOLUTION.
Inf.	At all temperatures.	..
1/12	Up to 80° C.	..
1/5	Up to 40° C.	..
1/3	At 0° C.	At B. Pt.
1/2	No complete precipitation.	Above 20 °C.
1/1·4	No precipitation at any temperature.	..

* See under Lead for a note on this.

With a slow stream of gas the same remarks as apply to antimony hold, but to a greater degree ; to be on the safe side, subtract 20° C. for temperatures of complete precipitation, and add 20° C. to the temperatures at which no precipitate occurs, if using a slow stream of H_2S.

(*b*) A much better method, and the standard one for this troublesome separation, is that of Clarke and Henz, who precipitate Sb_2S_3 from an oxalic acid solution. This method is very important, and as the success depends upon an exact adjustment of concentrations throughout, it will be described in some detail.

The tin and antimony are assumed to be present as their thio-salts, as is generally the case in analysis after the primary separation from lead and copper. The total weight of the two metals should not exceed 0·3 gm., and the solution (about 100 cc.) should be in a large beaker of 600–700 cc. capacity. To the mixed thio-salts, add 6 gms. of KOH, dissolved in about 30 cc. of water, followed by 3 gms. of tartaric acid, also in concentrated solution. Add hydrogen peroxide drop by drop until the deep yellow colour of the polysulphide ion fades to a pale straw colour by reason of the oxidation of $S_x^=$, $S_2O_3^=$ and the thionic acid radicles, to $SO_4^=$. Boil for a minute or two, first to accelerate the oxidation and then to decompose the excess of peroxide. To the hot, but not quite boiling, solution, add cautiously a hot, saturated solution of 15 gms. of oxalic acid. Considerable heat is produced and CO_2 comes off in large quantities. Boil vigorously for several minutes to complete the expulsion of gas, and especially to remove all available oxygen. After, say, ten minutes' boiling, commence the introduction of washed H_2S gas in a rapid stream.

Usually, no precipitate forms for some minutes, but on continuing the gassing, large flocks of red Sb_2S_5 suddenly make their appearance and settle out well. After 10–15 minutes' gassing, dilute to 250 cc. with hot water and continue passing H_2S until the mixture is nearly cold. Settle and decant through a weighed Gooch crucible, washing with hot 3 per cent. oxalic acid that has been saturated with H_2S. Wash finally with hot, very dilute acetic acid, also saturated with H_2S. Dry

in an atmosphere of CO_2 and heat (still in CO_2) to 300° C. to constant weight.

From the filtrate, separate tin by acidifying with HCl (after boiling off H_2S) and precipitating as metal on a strip of pure zinc foil. Filter off on a small paper, taking care to keep excess of zinc always in the solution both in the beaker and in the funnel, in order to prevent re-solution of tin. Wash with hot water and dissolve in HCl in an atmosphere of CO_2, cool the solution (still in CO_2), dilute so that the acid represents about one-fourth of the bulk of the solution, and titrate with standard iodine. See under Tin. This method is very accurate. The author does not like the electrolytic method.

Note.—The foregoing weights and proportions are taken from Treadwell's treatise and embody Henz's modification of Clarke's method. The weights are calculated on the assumption that 0·3 gm. Sn + Sb is present. The method is unsatisfactory for larger amounts of metal; for smaller quantities than 0·3 gm. the appropriate weights of reagents may be calculated from the relations:

If weight of Sb + Sn = 1, then KOH = 20, tartaric acid = 10 and oxalic acid = 50. The volume at the commencement of gassing should be about 30 cc. per 0·1 gm. of metal, and at the end 80 cc. per 0·1 gm. of metal. It is important that these weights and volumes be strictly adhered to, because the separation depends upon the concentration of H^+.

(*c*) Another variant of this separation employs phosphoric acid, but it possesses no particular advantages.

(*d*) Distillation Method.—This is really in continuation of the distillation method for arsenic ; see pp. 78 and 249. If $ZnCl_2$, $CaCl_2$, or more $FeCl_3$, be added to the distillation flask and the temperature of the liquid be taken up to 130° C. or even higher, repeating the distillation at least once with more HCl, the antimony is quantitatively distilled as $SbCl_3$ (see under Antimony). In this manner antimony can be separated from all other metals, but the method is only really suitable for the determination of small amounts of antimony such as are found in Brass, Bronze, etc. No tin will be distilled provided that (1) a reducing agent is present, and (2) the temperature is not allowed to rise beyond, say, 200° C.

(*e*) In strongly acid solution, all the antimony (and some arsenic) will be precipitated upon clean iron rod or sheet suspended in the solution. This is a convenient rough separation from tin. Use the purest iron. (Armco.)

(*f*) A very approximate method is to separate Sb + Sn as "mixed oxides" by treatment with HNO_3. The oxides are weighed, and then either the tin or the antimony is estimated volumetrically in a separate solution, the other metal being determined by difference. Needless to say, this only gives very approximate results.

For a further separation of arsenic, antimony and tin from copper alloys, see under Copper Alloys.

It is important to remember that in most cases separations are quite unnecessary. For most work, the following three methods are standard, others being only adopted in special circumstances.

1. Estimate antimony in one portion by attack with H_2SO_4 followed by titration with $MKnO_4$.

2. Estimate tin in a separate portion of sample by attack with HCl and titration with standard iodine.

3. Arsenic, which only occurs in small amounts, is separated by the distillation method and the solution titrated directly with dilute iodine.

It is interesting to note that there are many alloys of the greatest commercial importance which are made up entirely of the metals of Group II.

**Bearing metals*	(*a*) Tin base.	Sn, Sb, Cu, . . . Pb.	The last-mentioned metals are not always present.
	(*b*) Lead base.	Pb, Sb, . . . Cu, Sn.	
	(*c*) Copper base.	Cu, Pb, . . . Sn.	
**Solders*		Sn, Pb, . . . Sb, . . . Cd.	
**Pewter,*		Sn, Pb, Sb, . . . Cu.	
**Fusible Metals,*		Sn, Pb, Bi, . . . Cd, . . . Hg.	
**Typemetal,*		Pb, Sn, Sb, . . . Cu, . . . Bi.	

GROUP III.

Iron, Aluminium, Chromium.

The metals of Groups III and IV are closely related ; indeed, in some systems they are classified as one group, with ammonium sulphide as group reagent, while in others they are called Groups III*a* and III*b*. The writer prefers to number them III and IV.

The group reagent for Group III is *ammonia in the presence of ammonium salts*, the hydroxides of Fe (-ic), Al and Cr (-ic) being precipitated by this combination. Ammonia, alone, only partially precipitates the hydroxides of Group IV, starting from an acid solution, as these are soluble in the presence of ammonium salts, and the very addition of ammonia will, of course, introduce the NH_4^+ ion. Actually, the separation is not so simple a matter as would appear from the foregoing, and, in practice, the efficient separation of Group III from Group IV may be one of the most difficult problems in Analysis.

As in the case of the earlier groups, a brief note on the nature, appearance, and chemical properties of the precipitates produced by the group reagent(s) will precede consideration of the separations.

Fe (-ous) . . More properly belongs to Group IV.
NH_4OH precipitates (incompletely) white, flocculent $Fe(OH)_2$, soluble in ammonium salts. The precipitate rapidly absorbs oxygen from the air and changes colour, through dirty green to black, and finally to the red-brown of $Fe(OH)_3$.
NaOH acts similarly, but the precipitation is complete in the absence of NH_4^+. The oxidation to $Fe(OH)_3$ is more rapid.

* The metals first given are the usual constituents ; metals occasionally added are mentioned at three dots interval ; metals still more rarely added, after a second interval.

Fe (-ous) . . *H_2S (acid)*. No effect.
(Continued) *H_2S (alk.)*. Precipitates black FeS, which has a strong tendency to 'go colloidal' and pass through the filter, and is easily oxidised to (basic) ferric sulphate.

Fe (-ic), . . *NH_4OH* precipitates red-brown, gelatinous $Fe(OH)_3$; insoluble in excess and in presence of NH_4^+.
$NaOH$ acts similarly.
H_2S (acid). Fe^{+++} is reduced to Fe^{++} with deposition of sulphur. No precipitate.
H_2S (alk.). Precipitates a black mixture of FeS and Fe_2S_3.

Al, . . *NH_4OH* precipitates white, gelatinous $Al(OH)_3$, slightly soluble in water but insoluble in the presence of ammonium salts. Slightly soluble in excess of ammonia.
$NaOH$ precipitates the same compound; easily soluble in excess, forming $NaAlO_2$, which is decomposed by acids.
H_2S (acid). No effect.
H_2S (alk.). $Al(OH)_3$ is precipitated. Al_2S_3 is not formed in solution.

Cr (-ous), . . *NH_4OH* precipitates $Cr(OH)_2$, but Cr^{++} is never met with in analysis.

Cr (-ic), . . *NH_4OH* precipitates grey-green gelatinous $Cr(OH)_3$, somewhat soluble in excess, yielding a pink or a violet solution. $Cr(OH)_3$ is re-precipitated on boiling the solution sufficiently to remove the excess of NH_4OH. Insoluble in the presence of ammonium salts.
$NaOH$ acts similarly, but the precipitate is easily soluble in excess, forming a chromite, $NaCrO_2$, decomposable by acids and by boiling. Note that the precipitate thrown down by ammonia or an alkali *may* contain chromites of other metals such as Mg, Fe or Zn, making it almost impossible to separate Cr^{+++} from the metals of later groups. Complete separation may, of course, be effected after oxidising Cr^{+++} to Cr^{++++++}.
H_2S (acid). No effect.
H_2S (alk.). No sulphide, but $Cr(OH)_3$ is precipitated.

Chromate, . *NH_4OH* / *$NaOH$* } No effect.
H_2S (acid). Reduces Cr^{++++++} to Cr^{+++}.
H_2S (alk.). Reduces Cr^{++++++} and then $Cr(OH)_3$ is precipitated.

Mn (-ous), . *NH_4OH* precipitates white $Mn(OH)_2$ incompletely. Soluble in ammonium salts. Slowly oxidised by air to MnO_2, H_2O (manganous acid); this is precipitated as dark brown flakes.
NH_4OH + oxidising agent. MnO_2, H_2O is immediately precipitated.

Mn (*-ous*), (*Continued*)

NaOH similar to NH_4OH, but the oxidation is more rapid (*cf.* Fe).

NaOH + *oxidising agent.* $MnO_4^{=}$ or MnO_4^{-} is formed, some of which may decompose, yielding MnO_2. A complete yield of MnO_2 may be obtained by boiling the alkaline solution with alcohol.

H_2S (*acid*). No effect.

H_2S (*alk.*). Precipitates flesh-pink MnS. In the presence of a large excess of reagent and in hot solution, *green*, hydrated MnS is formed. Both are easily soluble in dilute acids, even in acetic acid.

Permanganate, Stable in acid solution. In alkaline solution is reduced to $MnO_4^{=}$ and/or MnO_2, H_2O.

H_2S reduces $Mn^{+++++++}$ to Mn^{++}.

Ni (*-ous*), NH_4OH precipitates a green basic salt, soluble in excess to form a deep blue solution containing nickel-ammonium ions. No precipitate in presence of ammonium salts.

NaOH precipitates apple-green $Ni(OH)_2$, insoluble in excess and not oxidised by air (*cf.* Co). Oxidised by Cl_2, Br_2, ClO^- to black $Ni(OH)_3$, insoluble in excess of alkali.

H_2S (*acid*). No precipitate.

H_2S (*alk.*). Black NiS precipitated ; insoluble in dilute acids when once precipitated ; soluble in hot 1 : 1 HNO_3 and in dilute aqua regia.

Co (*-ous*), NH_4OH precipitates a blue basic salt, not completely soluble in excess. Not precipitated in presence of ammonium salts, but the solution is oxidised in air and changes colour. No precipitate of $Co(OH)_3$ is formed in the presence of ammonium salts.

NaOH precipitates a blue, basic salt, passing, on digestion, into pink $Co(OH)_2$, which is then oxidised to black, flocculent $Co(OH)_3$ (*cf.* Ni, Mn, Fe^{++}). No precipitate is given in the presence of ammonium salts. Co is more easily oxidised than Ni ; in addition to Cl_2, Br_2, and ClO^-, H_2O_2 will oxidise Co, as also will atmospheric oxygen.

H_2S (*acid*) } Similar to Ni.
H_2S (*alk.*) }

Zn, NH_4OH precipitates white $Zn(OH)_2$ incompletely. Soluble in excess. Soluble in ammonium salts and not precipitated in their presence.

NaOH precipitates $Zn(OH)_2$, which is easily soluble in excess, forming Na_2ZnO_2, decomposed by dilute acids.

H_2S (*acid*). Precipitates white, compact ZnS if the concentration of H^+ is low (acetic acid + acetate, very dil. H_2SO_4, etc.). The precipitate is stable and not liable to ' go colloidal.'

Zn, *(Continued)*	. .	H_2S *(alk.)*. Precipitates white ZnS, which is liable to ' go colloidal ' and pass the filter ; *cf.* MnS NiS and CoS (and FeS).

Group III consists of the three metals iron (ferric), aluminium and chromium (all valencies, but the metal is separated as -ic compound) The group reagent is Ammonia, which being added to the filtrate from the acid H_2S group (after boiling off excess of the gas and re-oxidising any Fe^{++}), precipitates those three metals as insoluble hydroxides.

The actual facts are, however, not quite so simple as might be assumed from the foregoing ; apart from the fact that these hydroxides are extremely adsorptive, and almost invariably carry down with them amounts of the metals of subsequent groups which may be by no means negligible, ammonia, especially in the presence of the hydroxides in question, tends also to precipitate the hydroxides of nickel, cobalt manganese and zinc, since these metals also have insoluble hydroxides which may be thrown down in varying amounts unless the concentration of OH^- in the solution be kept below a certain very low value. In practice, this is effected by the addition of a considerable amount of ammonium chloride before the addition of the ammonia ; *any* ammonium salt will do, provided it is well ionised in solution, but NH_4Cl is most effective and is usually employed.

Note.—If the solution is moderately acid, containing *e.g.* 10 gms. or even less of acid before the addition of ammonia, it is, of course, unnecessary to add ammonium chloride, on account of this (or another) ammonium salt being formed by the neutralisation of the acid with the group reagent, ammonia.

The way in which the ammonium salt functions in reducing the concentration of OH^- may briefly be explained thus:

Ammonia solution consists of a mixture of free NH_3 (relatively great) some hydrated NH_3, (NH_3, H_2O), and some (relatively little) NH_4OH which ionises into NH_4^+ and OH^-. These are in equilibrium with one another, and the concentration of one cannot be altered without the equilibria being disturbed. We may imagine that the actual precipitant is the NH_4OH ; this, in the first place, is at quite a low concentration in the reagent, and secondly, is so weak a base that only very few OH^- ions are present. The concentration of OH^- is, however, sufficient to effect the precipitation of the hydroxides of iron (ferric), aluminium and chromium (-ic), though ordinarily not sufficient to bring down the hydroxides of the metals of Group IV anything like completely. In order to prevent these latter being precipitated at all, we add a well ionised ammonium salt, usually NH_4Cl, the addition of large amounts of NH^+ ion having the effect of so throwing back the reaction

$$NH_4OH \rightleftarrows NH_4^+ + OH^-$$

that the concentration of OH^- falls almost to the vanishing point ; certainly it is reduced sufficiently to prevent the precipitation of nickel, manganese, etc. though the Group III metals are still completely precipitated.

Apart from actual co-precipitation, the question of adsorption is of primary importance in the separation of the metals of Group III. The hydroxides are voluminous, amorphous, and for a small weight present a very large surface. Adsorption is a surface phenomenon, and the amount of a soluble substance adsorbed in practice is greatly influenced by the physical condition of the adsorbent. In this particular separation the concentration of H^+ in the solution is of the utmost importance ; it is even possible to " extract " most of the adsorbed kations from the Group III precipitate by making the solution very slightly acid, but not sufficiently so to " re-dissolve " the hydroxides to any appreciable extent.

In order to enable the student to form a rough mental picture of the possibilities of adsorption in this separation, it may be remarked that if a 90 : 10 Fe : Ni mixture is precipitated with ammonia only, only 8 per cent. of the total nickel will be found in the filtrate, and even in the presence of so large an amount as 50 gms. of NH_4Cl, about one-third of the nickel is still found with the iron in the precipitate. If, however, the solution is faintly acid, the separation is quantitative.

It is interesting to note that the hydroxides only adsorb kations strongly, so that if, *e.g.* sufficient KCN is added to form $K_2Ni(CN)_4$, a quantitative separation of the nickel may be effected with ammonia, as $Ni(CN)_4^=$ is not seriously adsorbed ; it is probable, therefore, that the formation of ammonium complexes is at least partly responsible for the effect that ammonium salts have upon the completeness of the separation of Group III from Group IV. In practice, however, if the amount of metals of Group III is relatively great, precipitation in slightly acid solution is adopted. This gives a quantitative separation in all cases.

Separation.

Two main cases must be considered—(i.), where a large amount of Group III metals is to be separated from a relatively small amount of Group IV metals, and (ii.), the converse of this. Of these, the former is the more common, and, analytically speaking, by far the more important. Before considering the separation in detail, three points must be noted.

(*a*) The metals in Group IV tend to come down with the metals of Group III in the following order :—Ni, Co, Zn, Mn ; *i.e.*, Ni is the most strongly adsorbed and Mn the least. (*b*) Manganese in solutions containing OH^- ions takes up oxygen from the air and $Mn(OH)_4$ is slowly precipitated. This occurs even if much NH_4^+ is present, so that in alkaline solution, the separation of manganese can never be perfect, except when conducted in a non-oxidising atmosphere. Cobalt behaves similarly. (*c*) Fe^{++} behaves as a Group IV metal. Thus : FeS is precipitated by H_2S in alkaline solution, and ferric and ferrous ions can be separated by means of their hydroxides in exactly the same manner as, *e.g.*, Fe^{+++} can be separated from Ni^{++}. This fact is occasionally made use of ; thus, one separation of iron from aluminium consists in reducing the iron to the ferrous condition and then precipitating the aluminium as hydroxide by means of a thiosulphate (which also reduces the Fe^{+++}). It is important to remember that alkaline ferrous

solutions rapidly take up oxygen from the air and deposit a slimy film of (basic) ferric salt.

Case 1. Separation of Much Iron (etc.) from Relatively Little Nickel (etc.)—(i.) *Barium Carbonate Separation.*—As has been pointed out already, the salts of Al, Fe^{+++} and Cr^{+++} with strong acids are very considerably hydrolysed in solution, thus: (*e.g.*)

$$AlCl_3 + 3\,HOH \rightleftarrows Al(OH)_3 + 3\,HCl,$$

the solution containing hydrated alumina and HCl in equivalent amounts, the former being at first in solution as the hydrosol. On standing, however, the ultra-microscopic particles tend to coalesce, and, owing to the well-known fact that the 'aged' hydroxides are less 'soluble' in acids than they are when first formed, a precipitate will slowly appear; this usually contains considerable amounts of the acids, owing to partial hydrolyses such as

$$AlCl_3 + HOH \rightleftarrows AlCl_2(OH) + HCl$$
$$AlCl_3 + 2\,HOH \rightleftarrows AlCl(OH)_2 + 2\,HCl,$$

so that the hydrolysed hydroxide is usually referred to as a 'basic chloride' (sulphate, etc.). As hydrolysis proceeds, acid accumulates, so that long before the whole of the base is thrown down, the left to right action ceases to predominate; if, however, the acid produced could be progressively removed, the left to right reaction (hydrolysis) would proceed to completion, and, if no OH^- is introduced in the process, there is very little tendency for the hydroxides of nickel, manganese, etc. to be precipitated, especially if the reaction is performed,

1. In dilute solution,
2. In cold solution,
3. In the presence of a high concentration of NH_4^+.

This is the theory of the barium carbonate separation.

Procedure.—Carefully neutralise the acid mixture, containing only Cl^- and/or NO_3^- (not $SO_4^=$ for obvious reasons), and not more than 2 gms. of the metals, with dilute ammonia until the precipitate which forms dissolves but slowly; add a drop or two of HCl in the case of a permanent precipitate being formed. Transfer the solution to a large flask (1,000 cc.) and dilute it to 400–500 cc. with cold water; add 10 gms. of NH_4Cl and shake until this is dissolved (if much nickel is present, add more NH_4Cl). Then add a creamy emulsion of barium carbonate, a little at a time, shaking the flask well after each addition until a small excess has been added. Allow the mixture to stand in a cool place for 4 or 5 hours, shaking it every 10 or 15 minutes, each time examining the precipitate to make sure that excess of barium carbonate is present. It is easy to be sure of this, as if the mixture be swirled, the heavy $BaCO_3$ settles out first, as a small white cone in the centre of the bottom of the flask. After the hydrolysis has had ample time to complete itself, allow the precipitate to settle and decant the clear solution through a large filter. Rinse the precipitate on to the paper and wash with cold water containing 2 per cent. of NH_4Cl.

The precipitate consists of the hydroxides of Fe (-ic), Al, and Cr

(-ic) plus the excess of $BaCO_3$, and the filtrate contains the chlorides of the metals of the later groups plus $BaCl_2$. Of course if barium is present in the original mixture under analysis it will have to be determined on a separate sample ; fortunately this is a simple matter, as $BaSO_4$ is the only common insoluble sulphate after lead has been removed.

In steel analysis, where the iron is not to be estimated, considerable time may be saved by making the mixture up to a definite volume and filtering off an aliquot part, thus avoiding the tedious washing of the precipitate. If, however, the precipitate is to be further analysed, it is dissolved in HCl and treated with dil. H_2SO_4 until no more $BaSO_4$ is formed. The latter is allowed to settle and the solution, containing iron, etc. is filtered off ; barium in the filtrate does not interfere, of course, if only metals in Group IV are to be estimated.

(ii.) *Zinc Oxide Separation.*—This is exactly the same in principle as the foregoing, the acid remover in this case being ZnO. The method is used chiefly in the estimation of manganese, in which connection see Volhard's Method (p. 127). The excess of zinc is removed as sulphide, but metals of Group IV obviously interfere here. The method is only mentioned for the sake of completeness.

The foregoing methods are simple, but are usually considered to take too much time to be of much use in practice. A better method of separating large amounts of the metals of Group III is the following well-known procedure.

(iii.) *BASIC ACETATE SEPARATION.*—This method is of the greatest technical importance, and will therefore be discussed in considerable detail. The method is, however, not easy to control unless considerable iron is present, although, theoretically, it can be used in the absence of iron.

Theory.—If a solution of $FeCl_3$ is progressively " neutralised " by the addition of an alkali, its hydrolysis proceeds to completion. If, however, the ' neutralising ' alkali be added slowly, no precipitate is formed for some time, as the $Fe(OH)_3$ dissolves in the residual $FeCl_3$, forming a clear (colloidal ?) solution, the colour of which becomes darker and darker, through purplish-brown to almost black, before a precipitate forms. It is possible to convert about 90 per cent. of the $FeCl_3$ into $Fe(OH)_3$ before the solution is saturated with the hydroxide, and in the case of the nitrate the ' neutralisation ' can proceed still further before the solution shows a precipitate.

At the point at which a slight permanent precipitate remains, therefore, not more than about one-tenth of the iron is in a permanently soluble form, the hydrolysed portion being precipitable by simple boiling. If, now, sufficient neutral or slightly acid (acetic) ammonium acetate be added, the unhydrolysed ferric salt will react as follows:

1. $FeCl_3 + 3\,CH_3COONH_4 \rightleftarrows (CH_3COO)_3Fe + 3\,NH_4Cl.$
2. $(CH_3COO)_3Fe + HOH = (CH_3COO)_2Fe(OH)^* + CH_3COOH.$
3. $(CH_3COO)_2Fe(OH) + HOH = (CH_3COO)Fe(OH)_2^* + CH_3COOH.$

The asterisked (*) compounds (basic acetates) are insoluble both in

water and in dilute acetic acid, so that reactions 2 and 3 will proceed to completion as shown, if hydrolysis is accelerated by boiling the solution.

Boiling subsequent to the addition of ammonium acetate has the effect of producing a complete precipitation of the iron (etc.), firstly by breaking up the unstable supersaturated solution of $Fe(OH)_3$ in $FeCl_3$, and secondly, by hydrolysing every molecule of ferric acetate as it is formed to an insoluble basic compound plus acetic acid. From the foregoing it will be noted that it is incorrect to call the precipitate a ' basic acetate ' ; actually, it is about 90 per cent. hydroxide, containing only about 10 per cent. of basic acetate.

The free acetic acid, while not interfering with the precipitation of the metals of Group III, effectively prevents the precipitation of the nickel, etc., and also reduces the adsorption of the kations to a negligible amount, so that the separation, if properly conducted, is always complete and quantitative.

Method.—The solution, containing chlorides (nitrates do not interfere), is transferred to a 1,000 cc. flask and treated with dilute ammonia, 2 or 3 cc. at a time, until either a slight precipitate remains or the precipitate redissolves but slowly ; in the former case, clear by *quickly* adding a few drops of HCl (*i.e.* before the hydroxide has time to ' age ' ; after standing, the precipitate will require more than a drop or two of HCl to dissolve it). The solution is then diluted to 300–400 cc. and a saturated solution of ammonium carbonate is added, 1 or 2 cc. at a time. Ammonia will serve, but the carbonate is preferable, as the CO_2 liberated when this alkali mixes with the acid solution breaks up and disperses the precipitate, enabling it to dissolve more readily. After each addition of the carbonate the flask is vigorously shaken and the solution allowed to stand for a minute or two to give the precipitate time to dissolve. The colour of the mixture deepens rapidly ; the volumes of alkali added should be made less and less as the ' neutralisation ' proceeds, and the periods of swirling longer and longer, until the solution becomes almost black, so that the flask must be held up to a powerful light to be sure that no precipitate is present.

Great care is necessary here, as it will be necessary to add HCl and start all over again if the end of the ' neutralisation ' is seriously overshot ; the student is advised to go slowly and deliberately until he is accustomed to the appearance of the ' neutralised ' solution, when he will be able to work with more speed and certainty. The appearance of a permanent precipitate is indicated by a quite characteristic ' muddiness ' of the dark solution ; when this point is reached, the solution is cleared *quickly* with the minimum amount of dilute (1 : 2) acetic acid, which should be at hand, ready measured in a small cylinder, in order to avoid ' ageing ' of the precipitate. Not more than 20 cc. of the 1 : 2 acetic acid may be used ; if the precipitate is heavy, it will be necessary to clear with HCl and start the neutralisation again, as the addition of too much acetic acid renders the separation incomplete. (See note.) The solution ought to clear on the addition of 5 or 10 cc. of the acid, followed by a minute or two of shaking. If 20 cc. of acetic acid fail to clear the solution, too much alkali has been added and some of the metals of Group IV will come down with Group III (especi-

ally nickel). The remedy is to add HCl and re-neutralise, this time taking extra care to observe the exact end-point, as acetates are present already ; in the case of the separation of nickel it is doubtful whether this is a satisfactory procedure, though the sharp separation of manganese may be ensured.

The clear solution, containing $Fe(OH)_3$ to saturation, and not more than 20 cc. of the 1 : 2 acetic acid, is placed on a gas ring and rapidly heated to boiling. It should remain practically clear up to about 75° C. ; if much precipitate forms before this, too much alkali (or too much acetic acid) has been added. (Note that the latter may be, but is not necessarily, a consequence of the former.) If not much precipitate forms on boiling, the neutralisation has not been taken far enough (*or*, too much acetic acid has been added). In a properly conducted estimation, most of the iron comes down as a dark, granular precipitate at about 75°–80° C. The mixture is allowed to boil, 10 cc. of dilute ammonium acetate solution are added, the solution boiled for exactly one minute, the precipitate allowed to settle, decanted as far as possible, and then filtered and washed with boiling water containing 1 or 2 cc. of acetic acid per litre.

Note 1.—The success of the separation depends upon the amount of ammonium acetate present. This reagent influences the hydrolysis of the metallic acetates, and if an undue excess be present, ferric acetate may begin to be hydrolysed at quite low temperatures (*i.e.* below 70° C.), and the acetates of nickel, etc. at the boiling-point, whereas if the excess be such that the hydrolysis of the ferric acetate does not commence much below 75° C., the acetates of the Group IV metals will not be affected at the boiling-point of the solution. From this it follows that the critical stage of the separation is the end-point of the ' neutralisation ' ; if this be overshot, too much acetic acid will have to be added to clear the solution, thereby forming too much ammonium acetate ; the ferric acetate will be hydrolysed at too low a temperature, and at the boiling-point some of the Group IV metal acetates may also be hydrolysed. If the end of the neutralisation is overshot, and a heavy precipitate is formed, it is better to clear the solution with HCl and start afresh, rather than to risk spoiling the whole estimation by adding too much acetic acid.

Note 2.—The ammonium acetate reagent is made by neutralising conc. (0·880) ammonia with 1 : 2 (B.P.) acetic acid. The final solution may be faintly acid. The dilute solution used in the foregoing separation is made by diluting 100 cc. of the strong solution to 1,000 cc.

Note 3.—Ten cc. of the dilute solution contain about 0·25 cc. of conc. acetic acid, and 6–7 cc. of conc. acid (≡ 20 cc. of 1 : 2 acid) are all that may be added to clear the solution. If less than 6 cc. conc. acid (20 cc. dilute acid) are required to clear the solution, more than 10 cc. of ammonium acetate solution may be added to the boiling solution with impunity, provided that the *total* acetic acid, whether as acid or as acetate, is less than 6–7 cc. of the conc. acid.

Note 4.—Nickel is the metal that is most prone to come down with the metals of Group III ; manganese is the least. In the case of nickel great care must be taken not to exceed the limits in the addition of acetates, but with manganese even 30 cc. of the conc. acid (or its equi-

valent) may be added without spoiling the sepaartion. Cobalt and zinc are intermediate.

Note 5.—The guide to the neutralisation is the colour of the solution of $Fe(OH)_3$ in the $FeCl_3$. Theoretically, aluminium and chromium might be separated by this method, but, in the absence of a guide to the end-point of the neutralisation the whole process would become guess-work, and the $BaCO_3$ method would be preferred.

Note 6.—$Cr(OH)_3$ is a very slimy precipitate, and if much chromium is present the filtration becomes a very slow and tedious process.

Note 7.—In steel analysis, where it is only required to estimate the metals of Group IV, it is best to avoid washing altogether by making the solution up to a known volume and filtering off an aliquot part.

Thus: (i.) The boiling solution is poured out into a 500 cc. measuring flask which has previously been heated to 100° C. on the water-bath, and the mixture made up to the mark with boiling water, adding an additional 2 cc. per gram of iron to allow for the volume of the precipitate. The temperature of the solution is observed and the solution re-transferred to the original flask, thereby mixing it thoroughly. The precipitate is allowed to settle and 250 cc. of the clear solution are decanted off through a dry filter paper, catching the filtrate in a warmed 250 cc. measuring flask. When 250 cc. have been collected, the flask is heated up to the same temperature as that at which the original bulk was measured, and the excess pipetted out ; the solution will then contain exactly half the original weight of the metals of Group IV. If desired, a further portion of 125 cc. may be filtered off and used for the estimation of nickel, manganese being estimated in the larger volume.

(ii.) The boiling solution is poured into a warmed 500 cc. measuring cylinder ; the volume is read and the temperature taken. The precipitate is allowed to settle in the cylinder. When settled, the clear liquid is decanted through a filter and an aliquot part of the original volume collected in a dry beaker. The filtrate is warmed to the temperature at which the original volume was measured, and the excess pipetted out. Method (i.) is the more accurate ; method (ii.) is slightly quicker. The choice depends upon the nature of the mixture under separation.

Case 2. Separation of Small Amounts of Metals of Group III from Relatively Large Amounts of Group IV Metals.—This is a simpler matter and bears out the general rule that it is always best to arrange matters so that the smaller constituent is precipitated. The barium carbonate method may be used, but it takes too long a time ; the acetate separation is not suitable, as there is, by hypothesis, insufficient iron present to act as indicator to the ' neutralisation.'

Method.—Add 10 gms. of NH_4Cl to the mixture, dissolve it, and add a drop of methyl orange, followed by ammonia, drop by drop, until the colour changes. Boil, settle, filter, and wash five times with boiling water containing 2 per cent. of NH_4Cl. Open out the filter paper and rinse the precipitate back into the precipitation beaker ; redissolve in HCl, add 3 gms. of NH_4Cl, and again precipitate with ammonia. Filter and wash as before, combining the filtrates.

If necessary, a third or even a fourth precipitation may be made. This may be necessary if manganese is present, owing to the tendency

for Mn^{++} to become oxidised to Mn^{++++} and precipitate as perhydroxide. A complete separation of 20 per cent. iron from 80 per cent. manganese may be made by four such precipitations.

Separation by Direct Precipitation of the Metals of Group IV.—This should more correctly come under the heading of Special Separations, and the methods will be more fully discussed there. At this point, however, it may be observed that in the presence of tartaric acid, citric acid, some sugars, malic acid, and similar organic compounds containing both OH and COOH groups, the metals of Group III are not precipitated by ammonia, a fact which occasionally makes it possible to pass over Group III and estimate one or more metals of Group IV without having to make any separation at all.

General Note.—It should be noted that on occasions manganese is treated as if it belonged to Group III, the precipitation with ammonia being performed after saturating the solution with bromine, so that MnO_2, H_2O is precipitated. Also, sometimes it is convenient to consider iron as belonging to Group IV, handling it in the ferrous instead of the ferric condition. Methods involving these re-arrangements of the regular group system will occasionally be detailed ; see pp. 269 and 273.

Group Separations in the Presence of Phosphates.—A further complication that occurs in the group separations at this point is caused by the possible presence of phosphates in the solution under analysis. If the solution contains $PO_4^{\equiv}$ this will be found in the Group III ammonia precipitate combined with Fe^{+++}, Al and Cr^{+++} as phosphate, and should the amount of iron, aluminium and chromium be insufficient to combine with all the $PO_4^{\equiv}$, the excess of the latter combines with the metals of Groups IV and V, with the result that their phosphates, being insoluble in neutral or weakly alkaline solutions, are precipitated with the metals of Group III. Any excess of $PO_4^{\equiv}$ beyond that which is required for combination with the metals of Groups III, IV and V, will then remain in solution, presumably combined with the alkali metals.

It is easy to see, therefore, that the composition of the ammonia precipitate in the presence of $PO_4^{\equiv}$ depends upon the amount of this ion relative to the amounts of the metals having insoluble phosphates, and the precipitate may include any or all of the metals of the later groups, more or less completely precipitated, so that the separation of Group III from the later groups is only complete if there is enough iron, etc., to unite with all the $PO_4^{\equiv}$.

Unless, therefore, the composition of the mixture under analysis is known within narrow limits, it is unsafe to assume that a proper separation has been made ; in any case, it will be necessary to remove $PO_4^{\equiv}$ from the ammonia precipitate, as the latter otherwise would no longer ignite to a mixture of oxides, but would result in a mixture of oxides and phosphates.

Three cases may occur:

1. There is sufficient of the metals of Group III to combine with all the $PO_4^{\equiv}$.

In this case:

Filtrate contains: Metals of Groups IV, V and VI.
Precipitate contains: Phosphates and hydroxides of the metals of Group III.

2. The $PO_4^{\equiv}$ is in excess of that required by the metals of Group III, but is insufficient to combine with the whole of the metals of Groups IV and V.

In this case:

Filtrate contains: The rest of the metals of Groups IV and V plus the metals of Group VI.
Precipitate contains: Phosphates of the metals of Group III plus variable amounts of the phosphates of Groups IV and V.

3. There is excess of $PO_4^{\equiv}$.

In this case:

Filtrate contains: The alkali metals, plus the excess of the $PO_4^{\equiv}$.
Precipitate contains: The phosphates of the metals of Groups III, IV and V.

In Qualitative Analysis, phosphoric acid is removed by adding iron to the solution in sufficient amount to combine with the whole of the acid, so that when NH_4OH is added, all the phosphate ions are removed in combination with the metals of Group III. Unfortunately, however, for Quantitative purposes, this method entails the addition of an excess of iron, which not only makes it necessary to estimate the iron and its group-mates in a separate portion of the sample, but involves the removal of the superfluous iron before the analysis of the later groups can be proceeded with. For some purposes, however, *e.g.* when the amount of $PO_4^{\equiv}$ is small, the method can be usefully adapted to Quantitative work.

Method 1. (General).—To the solution from Group II, after boiling off H_2S and re-oxidising with HNO_3, add a 10 per cent. solution of $FeCl_3$ until there is sufficient Fe^{+++} present to combine with all the $PO_4^{\equiv}$ and leave a slight excess. Unfortunately, there is no means of knowing exactly when the proper amount of $FeCl_3$ has been added unless the composition of the mixture is known; it is advisable, therefore, to estimate the $PO_4^{\equiv}$ by the molybdate method before carrying the estimation of the bases beyond Group II. Then, knowing the amount of $PO_4^{\equiv}$ that is present, it is easy to calculate the amount of $FeCl_3$ to be added in order to confine the excess to within moderate limits, from the relations:

	P	:	$\frac{1}{2}(P_2O_5)$	:	$PO_4^{\equiv}$	:	Fe	:	$FeCl_3$
=	31	:	71	:	95	:	56	:	163

Or:—

0·1 gm. P is equivalent to 0·53 gm. $FeCl_3$ and requires 5·5 cc. of 10 per cent. $FeCl_3$ solution.
0·1 gm. P_2O_5 is equivalent to 0·23 gm. $FeCl_3$ and requires 2·5 cc. of 10 per cent. $FeCl_3$ solution.
0·1 gm. $PO_4^{\equiv}$ is equivalent to 0·17 gm. $FeCl_3$ and requires 2·0 cc. of 10 per cent. $FeCl_3$ solution.

Note.—It is assumed that the $FeCl_3$ solution is made up from the anhydrous salt. The volumes given represent a slight excess of the reagent.

Having added the $FeCl_3$ in slight excess, as determined from the result of the phosphate estimation, the phosphoric ions are removed, together with the metals of Group III originally present and the excess of iron that has been added, by carrying out a basic acetate separation if the amount of total iron is greater than about 0·5 gm. If, however, the amount of phosphorus be small, so that relatively little iron has to be added, the separation may be effected by a double precipitation with NH_4OH, the filtrates being combined for the subsequent analysis.

This method is of general application ; two others follow, Method 3 being of special application only.

Method 2 (General).—The usual procedure is followed as far as the removal of the metals of Group II as sulphides from dilute HCl solution. The filtrate from the sulphide precipitate containing the metals of Groups III–VI and all the $PO_4^{\equiv}$ is then evaporated to dryness in a porcelain dish. To the dry residue, 50 cc. of HNO_3 are added and the whole again taken to dryness and baked. The treatment with HNO_3 is repeated in order to remove the last traces of Cl^- (which would injure platinum), and the cake of dry oxides (nitrates, basic nitrates) is carefully detached from the dish with a glass or porcelain spatula, broken up, and transferred to a platinum crucible, using a brush to transfer the fine dust that remains. The oxides are then gently crushed to powder with the flattened end of a glass rod, after which a mixture of 4 parts of Na_2CO_3 and 1 part of precipitated SiO_2 is added (at least 6 times the weight of the dried oxides), and carefully mixed by stirring with a stout platinum wire.

The mixture is fused at bright redness (800°-900° C.) in the muffle for at least twenty minutes, the melt extracted with hot water containing a little $(NH_4)_2CO_3$, and the solution filtered through an open-textured paper (41). The filter is washed well with hot, dilute $(NH_4)_2CO_3$ solution.

The *precipitate* consists of the oxides or carbonates of the metals of Groups III, IV and V, plus some SiO_2.

The *filtrate* contains the alkali metals, the excess of sodium carbonate and silicate and all the $PO_4^{\equiv}$ as sodium phosphate.*

The precipitate is dissolved in a little dilute HCl and the usual analytical separations proceeded with ; any silica which may be present remains insoluble in the acid.

Method 3.—NH_4OH (and NH_4Cl if necessary) is added to the rather dilute solution obtained after boiling off H_2S (not less than 400 cc.), until it is just alkaline, and the solution boiled under a cover glass until the precipitate becomes ' granular,' avoiding expelling the slight excess of ammonia. The precipitate is allowed to settle out completely by standing the beaker on the corner of the hotplate, and is filtered off on an open-textured paper (41), decanting as far as possible, and washing *well* with very hot water. The filtrate is at once available for the estimations of Groups IV-VI.

The precipitate is dissolved in a small quantity of 1 : 1 HNO_3 (hot) and the solution diluted to 50-75 cc. 10 cc. of HNO_3 are added and

* Also, possibly, some Na_2CrO_4 and Na_2MnO_4.

10 gms. of NH_4NO_3 dissolved in a little water, for every 0·1 gm. of $PO_4^{\equiv}$, and the solution heated until N_2O begins to come off. Meanwhile 30 cc. of 10 per cent. ammonium molybdate solution are measured out for each 0·1 gm. of $PO_4^{\equiv}$, and, having heated this solution to boiling, it is poured into the phosphate solution in a thin stream with constant stirring, the stirring being continued for about one minute after the last of the molybdate has been added. The precipitate is allowed to settle in a warm place until the liquid is quite clear ; the latter is decanted as far as possible and the remainder filtered through a hardened paper (50). The precipitate is washed with 5 per cent. NH_4NO_3 solution, using the pump if necessary.

The molybdate precipitate contains all the $PO_4^{\equiv}$, and this may be estimated directly by weighing after drying at 100° C. or by titrating with standard alkali ; but the best method, if the precipitate is at all bulky, is to dissolve it in ammonia and re-precipitate the $PO_4^{\equiv}$ with magnesia mixture. (See under estimation of Phosphoric Acid.)

The solution contains the metals of Group III plus molybdenum. Before proceeding with the analysis, the latter must be removed.

Removal of Excess Molybdenum.—Evaporate the solution to fumes with a bare (known) excess of sulphuric acid. When cool, dilute so that the solution contains 5 per cent. of H_2SO_4. Transfer it to a stout stoppered bottle and saturate in the cold with H_2S. Tie the stopper firmly into place with wire or string and place the bottle, weighted if necessary, in a large beaker of water or a water-bath, which is then heated to 80–90° C. for an hour.

When the precipitate of molybdenum sulphide has settled out well, open the bottle and filter the solution through an open paper. Wash with H_2S water slightly acidified with H_2SO_4.

The filtrate is used for the usual analytical separation of the metals of Group III.

IRON.

Separations.—*From Group I Metals.*—Precipitation with HCl. (See Group I, p. 237.)

From Group II Metals.—Precipitation with H_2S from HCl solution. (See p. 240.)

From Metals of Groups IV–VI:

(*a*) Precipitation with NH_4OH + NH_4Cl. (See p. 262.)
(*b*) Precipitation with $BaCO_3$. (See p. 258.)
(*c*) " Basic Acetate Method." (See p. 259.)

From All Metals except Molybdenum.—Rothe's Ether Method.

ROTHE'S ETHER METHOD.—This method is of great importance in Steel Analysis, and as it introduces a fresh principle, the separation of compounds by distribution between two solvents, it will be described in some detail.

Theory.—Ferric chloride is extremely soluble in ether that has been saturated with HCl, whereas the chlorides of all other metals (except $MoCl_3$) are not soluble. It is necessary, however, that the solution

for separation shall contain a definite concentration of HCl. If, therefore, a solution of the mixed chlorides, acidified with HCl of the proper concentration, is shaken up with ether, practically the whole of the $FeCl_3$ will be found in the ethereal layer, which can easily be separated mechanically.

It is found that from an aqueous solution of $FeCl_3$ very little of the chloride is transferred to the ether, and the same is true of a very concentrated HCl solution, The transference of the iron is, however, almost 100 per cent. complete from solutions containing 20 per cent. by weight of HCl. This corresponds to a sp. gr. of 1·10, and (very conveniently) to the constant B.Pt. acid. The writer found that less than 0·2 mgm. of iron remained in the acid layer after two ether separations had been made on a 2 gm. sample of steel.

Procedure.—Evaporate the chloride solution * to a syrup in a small beaker. Dilute to not more than 15 cc. with HCl of 1·10 sp. gr. and rinse the solution into a conical or cylindrical 250 cc. separating funnel with the least possible quantity of the same 1·10 acid. The acid must be *cold* or Fe^{+++} may be reduced by the ether, and $FeCl_2$ will remain in the acid layer with the other metals.

Add 75 cc. of ether which has previously been shaken up with conc. HCl and separated ; agitate the two liquids vigorously together for a minute or so. To do this, the safest method is to invert the separating cylinder so that the liquids are in contact with the stopper. (Note that a perfect fit is essential, and that no grease may be used.) The stopper is held firmly in position with the left hand, the fingers encircling the neck of the funnel, whilst the right hand holds the other end, near the stop-cock. Shake once or twice only at first, and then *cautiously* open the cock. Considerable excess pressure relieves itself, and if care is not taken some liquid may be lost as spray. Close the cock and again shake the mixture, always with the stop-cock end inclined upwards. This time the shaking may be longer and more vigorous, but it will still be necessary to ease the internal pressure by momentarily opening the cock.

Repeat this procedure until the shaking has lasted a full minute, releasing the pressure due to the ether vapour at intervals, and finally re-invert the cylinder and allow its contents to separate out completely. Two sharply defined layers are formed, the upper golden-yellow and containing practically all the $FeCl_3$, while the lower (acid) layer is usually green, being coloured by nickel and/or chromium chlorides.

While the solutions are separating out, 50 cc. of fresh ether are placed in a second similar funnel. As soon as the two liquids in No. 1 funnel have separated reasonably completely, the lower layer is carefully transferred to funnel No. 2, the cock of No. 1 being closed at the instant that the separating line between the two liquids reaches it ; the hole in the stop-cock should contain the lower solution only, no ether should be allowed to escape.

Replace funnel No. 1 in its clamp for further settling and shake funnel No. 2 as already described. Set it in its clamp to settle, and if any more acid has separated out in No. 1, it is transferred to No. 2.

* If the usual small amount of HNO_3 has been added to oxidise Fe^{++}, it is advisable to evaporate to syrup, add 10 cc. HCl, and re-evaporate to syrup. This removes NO_3^-, which interferes.

While the liquids in No. 2 are settling out, add 25–30 cc. of 1·10 sp. gr. HCl to No. 1 and shake this up with the ether in order to wash the ethereal $FeCl_3$, allowing the funnel to stand in an erect position until the two layers have settled out. Meanwhile, the acid layer in No. 2 will have separated well ; it is run out into the original beaker, again carefully avoiding the escape of any ether.

The 25 cc. of wash HCl in funnel No. 1 are then run into funnel No. 2 and the second ether solution is in its turn washed with the acid by shaking the funnel as described ; finally, the acid wash having been shaken up with both ether solutions, is run out into the main acid solution ; this time, however, the ether is allowed to run out into the bore of the stop-cock, which is turned just as the ether is about to run down into the stem.

The lower acid layer plus washings contains the chlorides of all metals except iron (and molybdenum), together with all $SO_4^{=}$, if in small amounts, while the ether contains all but traces of the iron.

To recover the iron, transfer the ethereal solution to a conical flask and distil off the ether from the water-bath. Take the residue up in HCl. Or, if preferred, but this is wasteful of ether, shake the ether with a large excess of water, when the iron will return to the aqueous layer, leaving the ether perfectly colourless. One repetition of this, washing the separated colourless ether with another 50 cc. of water, will extract all the iron and leave the ether ready for use again, of course after re-saturating with HCl. Some ether is lost by this method, but much time is saved ; a drawback is that the iron is recovered in rather dilute solution.

The importance of the " Ether Separation " in steel analysis can hardly be over-emphasised ; it is the sovereign test-analysis method, applied in cases of doubt, or when the conditions lead the analyst to suspect interference. An alleged objection is the length of time taken to carry the separation through, but this is not so long as the time required for an acetate separation, for example. In nearly every case where an occasional analysis of a special alloy steel such as a cobalt-chrome, chrome-vanadium, high-speed or similar steel, is required, the writer would always commence operations by performing an Ether Separation, if only for the increased ease and certainty in handling accruing from the removal of the iron ; it is a tremendous asset to be freed at once from the bugbear of adsorption.

Individual Separations—*From Aluminium.*—1. Pour the acid solution from Group II, after boiling off H_2S and re-oxidising the Fe^{++}, into boiling 10 per cent. NaOH solution. Boil for a minute to coagulate the precipitate, and filter. The precipitate is $Fe(OH)_3$. Redissolve this in HCl after thoroughly washing with hot water, add NH_4Cl and reprecipitate with the minimum amount of NH_4OH. The second precipitate contains the iron free from adsorbed alkali. Acidify the filtrate with HCl, add NH_4Cl, and precipitate aluminium as $Al(OH)_3$ by the addition of the minimum amount of NH_4OH ; a reprecipitation may be necessary.

2. *Ether Method.*—$FeCl_3$ is soluble and $AlCl_3$ insoluble in anhydrous ether saturated with HCl gas. The chlorides are evaporated to dryness

in an Erlenmeyer flask and moistened with a *few* drops of conc. HCl. Ether, which has been saturated with HCl gas, is then added (50 cc. for each 0·2 gm. of the mixed chlorides) and the mixture thoroughly shaken, all the time cooling the flask under the tap. The yellow solution is decanted through a filter (a Gooch crucible is preferable), and the residue shaken with at least two further portions (25 cc. each) of the ether-HCl. Finally the crystalline $AlCl_3$ is rinsed into the crucible and washed once or twice with the same reagent, a few drops at a time, each time sucking the Gooch as dry as possible.

The filtrate is transferred to a distilling flask and the ether gently distilled off from a hot water-bath. The ether-free residue is dissolved in a little very dilute HCl and the iron estimated by any convenient

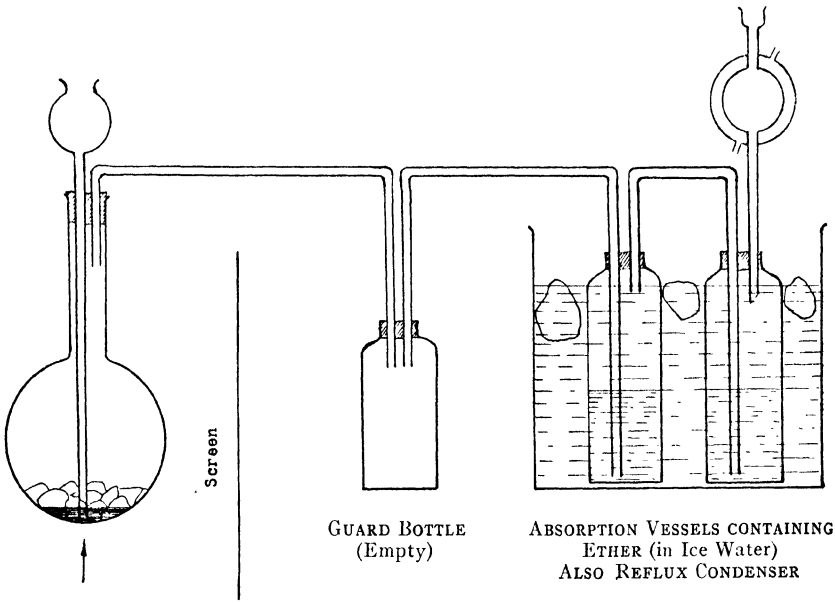


Fig. 24.—Preparation of Ethereal Hydrochloric Acid.

method. The original residue of $AlCl_3$ is also dissolved in water and the aluminium estimated as phosphate.

Preparation of Ether-HCl.—Sufficient of this reagent for one estimation may be prepared in a very short time by the use of the apparatus shown in fig. 24. Note that 100 gms. of ether dissolve 25–30 gms. of HCl gas (20 litres at laboratory temperatures).

3. *Thiosulphate Method.*—The mixture, containing only sulphates, is almost neutralised with ammonia ; a solution of 5 gms. of sodium thiosulphate in water (5 gms. for every 0·1 gm. Al) is then added, and the mixture boiled until it ceases to smell of SO_2, which may take an hour or more. Aluminium salts are completely hydrolysed by this

means, Al_2O_3 being a weak base, while the thiosulphate breaks down into sulphur, sodium sulphate, sulphite, tetrathionate, pentathionate, etc. ; the sulphite further decomposes under the action of the acid liberated by the hydrolysis into sulphur dioxide and the sodium salt of the sulphuric acid which was originally combined with the aluminium. The SO_2, in neutral solution, reduces the iron to the ferrous state, and, ferrous iron being a much stronger base than aluminium, the iron is not hydrolysed sufficiently to be precipitated with the $Al(OH)_3$. The sulphur which forms during the breakdown of the thiosulphate provides nuclei for the separation of the $Al(OH)_3$, which comes down in a more compact and more easily filtered form than when precipitated by ammonia only.

This is an excellent method for the separation of the aluminium, *e.g.* in the analysis of Aluminium Bronze.

4. *Rothe's Ether Separation.*

5. *Fusion* of, *e.g.*, an ore, or the ignited mixed oxides of iron and aluminium with Na_2CO_3 results in the aluminium being converted into a soluble aluminate, while the ferric oxide remains insoluble on extraction with water.

6. *Without Separation.*—In some analyses it is usual to precipitate the iron and aluminium together by NH_4OH in the presence of NH_4Cl ; the precipitate is washed, filtered, and ignited to $Fe_2O_3 + Al_2O_3$ at as low a temperature as possible. These oxides are weighed. They are then dissolved in a little conc. HCl, the $FeCl_3$ reduced with $SnCl_2$, and the Fe^{++} titrated with standard dichromate solution. The weight of iron is then calculated to its equivalent weight of Fe_2O_3 ; this is subtracted from the total of the mixed oxides, and the weight of the aluminium obtained by difference.

From Chromium.—1. The acid solution, saturated with Br_2, is poured into excess of boiling NaOH solution (10 per cent.). $Fe(OH)_3$ remains insoluble, but chromium and aluminium pass into solution as chromate and aluminate respectively. The ferric hydroxide should be reprecipitated with ammonia in order to eliminate the adsorbed alkali. Chromium is estimated in the filtrate by acidifying, and after vigorous boiling to decompose NaBrO and $NaBrO_3$, titrating the cold solution with standard ferrous sulphate solution.

2. Precipitate the hydroxides with NH_4Cl and NH_4OH, filter and wash as usual. Rinse the precipitate into a beaker and add several small quantities of solid Na_2O_2, agitating well after each addition. Dilute the solution and boil it for ten minutes to destroy peroxides and coagulate the precipitate. Filter off the ferric hydroxide, wash it well with hot water, redissolve, and re-precipitate with NH_4OH, combining the filtrates. Estimate the iron either by weighing as ferric oxide or by reducing and titrating. Aluminium may be recovered both here and in the previous method by just acidifying and adding a bare excess of ammonia ; the chromium as chromate will then be in the filtrate, in which it may be estimated by acidifying and boiling to break up peroxides. The solution is then cooled and titrated with standard ferrous sulphate solution.

3. After a fusion with Na_2CO_3 plus a pinch of KNO_3, or with Na_2O_2, ferric oxide is left insoluble ; aluminium passes into solution as aluminate

(acidify and precipitate with ammonia), and chromium is left in solution as chromate (acidify, boil, cool, and titrate with ferrous sulphate solution).

4. *Rothe's Ether Method.*

5. It is usually not necessary to separate iron and chromium, *e.g.* in the analysis of a chromium steel or ferro-chromium as Volumetric methods may be used. Dissolve the alloy in dilute H_2SO_4, just oxidise with HNO_3, and make up to a known bulk, taking aliquot parts for estimating the constituents. One part is reduced with H_2S or SO_2, etc., and titrated with standard permanganate (this gives iron) ; another part is oxidised hot with $KMnO_4$, cooled, and titrated with ferrous sulphate (this gives chromium). See under the metals for details.

From Manganese.—(1) $Mn(OH)_2$ is not precipitated in the presence of ammonium salts by NH_4OH, but the solution, unless kept in a neutral or reducing atmosphere, absorbs oxygen from the air and insoluble MnO_2, H_2O is slowly thrown down, so that manganese is almost invariably found in the ferric hydroxide precipitated by the usual methods. To avoid this trouble and to obtain definite conditions, it is quite common, in the absence of chromium, to precipitate Group III with NH_4OH and Br_2. This results in a mixed precipitate of $Fe(OH)_3$, $Al(OH)_3$, and MnO_2, H_2O. This is redissolved in HCl and a quick acetate separation is made ; this separates the iron and aluminium from manganese completely, as in the slightly *acid* solution (acetic), the Mn^{++} is not oxidised. (Also, of course, the flask is more or less filled with CO_2 from the ammonium carbonate.)

2. It may not be necessary to separate the two metals if Cl^- is absent. Redissolve the precipitate in H_2SO_4 and divide the solution into two equal parts. In one, estimate the iron by reduction and titration with $KMnO_4$. To the other add HNO_3 and estimate the manganese by the bismuthate method.

From Zinc.—Precipitate ZnS from slightly acid solution (see pp. 133 and 310). FeS is not precipitated.

From Phosphoric Acid.—See p. 264.

General Note.—1. Rothe's ether separation is the universal separation for iron, as it removes $FeCl_3$ quantitatively from all other metals (except molybdenum).

2. For substances soluble in HCl (*e.g.* oxides ore), the HCl solution is concentrated, reduced with $SnCl_2$, and the Fe^{++} titrated with standard dichromate.

3. For substances insoluble in HCl (*e.g.* silicate ores, etc.), the sample is fused with Na_2CO_3 and the melt extracted with water and filtered. The insoluble ferric oxide is dissolved in HCl and titrated as before ; *or* the fusion may be extracted with HCl, concentrated, reduced and titrated. By methods 2 and 3, iron can be accurately estimated in the presence of nearly all the common metals.

From Aluminium, Chromium, and the Metals of Later Groups:

"*Cupferron*" *Method.*—Baudisch's reagent, aminonitrosophenylhydroxylamine, is an interesting 'specific' reagent for copper and ferric iron, in consequence of which it is commonly known as "cupferron." Besides copper and iron, silver, lead, mercury, bismuth and tin are partially precipitated under the conditions laid down, and as there is no need

for a new reagent for copper (the electrolytic method is not easily improved upon), it is usual to consider cupferron as a reagent for iron only, using it only after the Group II metals have been removed by passing H_2S. As the precipitation is made in a decidedly acid solution, there is no tendency for manganese or nickel to be co-precipitated, though of course adsorption effects will not be eliminated.

Procedure.—To the solution, containing not more than 0·3 gm. of Fe^{+++} in 100 cc., 20 cc. of conc. (1·2 sp. gr.) HCl are added for every 100 cc. of solution, thus producing an approximately 2 N concentration of acid. The mixture is cooled completely, and the reagent is added slowly and with stirring until the red-brown precipitate of the ferric compound ceases to come down and the dirty grey crystals of the free base are noticed instead. Excess of the reagent is now added to the extent of about one-fifth of the total volume of the solution and the precipitate allowed to settle out completely in the cold. The precipitate is filtered off, washed first with 2 N HCl (20 cc. conc. acid in 100 cc. water), then with water to remove the acid. Two washes with dil. NH_4OH follow (to remove the free base as its soluble ammonium salt), and the precipitate is then freed from ammonium salts by again washing with water. The precipitate is dried and ignited carefully to Fe_2O_3.

Note.—The copper compound is a dirty grey colour ; it is, like the iron compound, 'insoluble' in 2 N HCl (cold), but differs from the latter in that it is decomposed by ammonia. Copper and iron may, therefore, be separated after co-precipitation by washing with NH_4OH.

Reagent.—Six grams of the compound are dissolved in 100 cc. of water. It does not keep in solution.

ALUMINIUM.

Separations.

Aluminium from Chromium.—This separation has been outlined in the foregoing. Cr_2O_3 is oxidised to CrO_3 by NaOH + Br_2 or by Na_2O_2 ; the solution is acidified with H_2SO_4 and made just ammoniacal. $Al(OH)_3$ is precipitated. The hydroxide is redissolved in HCl and re-precipitated with ammonia in order to eliminate adsorbed alkali ; the chromium is estimated in the boiled and cooled filtrate by titration with ferrous sulphate.

CHROMIUM.

Separations.

From Later Groups.—The acetate and $BaCO_3$ methods work well with small amounts of chromium, but with samples containing much of this metal the precipitate becomes very difficult to handle owing to its sliminess. Fortunately, it is not very often necessary to effect an actual separation, as chromium, manganese and nickel can all be estimated in the presence of one another by volumetric methods.

From Nickel and Cobalt.—Saturate the solution with Br_2 and pour it in a slow stream into excess of 10 per cent. boiling NaOH solution. Nickel and cobalt are precipitated as -ic hydroxides, which filter well, while chromium passes into solution as chromate.

Iron and Chromium from Nickel.—The dimethylglyoxime method may be used if sufficient citric acid be added to keep the Group III metals in solution when the ammonia is added.

* * * * * * * * *

Special Note.—It sometimes happens that in routine analysis of copper alloys the solution is removed from the electrolysis bench before all the copper has been deposited. If, then, on adding ammonia, the solution becomes blue owing to the presence of copper, the following procedure is to be adopted:

1. Filter off the iron (+ aluminium) and estimate them as usual.
2. Just acidify.
3. Pass H_2S and filter off CuS; ignite to CuO and add the copper found to the weight of copper by electrolysis.
4. Make the filtrate ammoniacal ; ZnS is precipitated.

This procedure saves time. If the residual copper is removed *before* iron, the operations are considerably complicated ; *e.g.*, on making ammoniacal the solution is found to be blue. To re-acidify (HNO_3) and continue the electrolysis is the logical procedure, but it immobilises the electrodes, which will probably be wanted for other analyses, and the determinations of iron and zinc are delayed. The alternative is:

1. Re-acidify (HCl).
2. Pass H_2S, filter off CuS, roast, and weigh the CuO.
3. Boil off H_2S.
4. Re-oxidise the Fe^{++}.
5. Precipitate iron with ammonia.
6. Pass H_2S and filter off ZnS.

It will be noted that two additional operations are necessary, and one of these, namely the boiling off of the H_2S, is a lengthy business.

GROUP IV.

Manganese, Zinc, Nickel, Cobalt.

Group Separation.—It is an interesting fact that in commercial analysis, except in the examination of ores, it is very rarely necessary to make both of the two separations Group III from Group IV and Group IV from Group V. In the analysis of metals and alloys it is rare indeed to meet with any metal belonging to a group later than the fourth, though there are alloys containing calcium, barium or sodium, whilst magnesium enters into light metals occasionally ; on the other hand, products such as sands, cements, refractories, slags, etc. rarely contain any of the Group IV metals, so that the analyst passes directly on to Group V. Note, however, that manganese is occasionally found in slags, but it is usual to separate it along with iron and aluminium by precipitating these from a brominated solution.

The practical result of the foregoing is that an elaborate separation of Group IV from V is rarely necessary. It is not a pleasant separation, as the sulphides are rather slow filtering, and also possess a strong tendency to return to the 'sol' condition, passing through the filter as soon as washing has removed the bulk of the electrolytes which coagulated them ; and there are other complications.

Nominally, the separation is straightforward. We are told in qualitative analysis to " add ammonium sulphide and filter off the sulphides that are precipitated." In practice, however, it is essential to proceed deliberately, as follows:

Re-acidify with HCl and boil the solution for 10 minutes with one or two pieces of porous pot in the beaker. This treatment will decompose any carbonates that are present and expel dissolved CO_2 (derived by the absorption of CO_2 from the air by the previously alkaline solution). Cool, and transfer to a flask. Make the solution just ammoniacal and pass H_2S until the precipitate coagulates into large flocks which settle well. If necessary, add more ammonia. Note that the ammonia used here should be from a freshly opened bottle, or at least one the contents of which have not been exposed to the air or to CO_2. Stopper the flask and allow the mixture to stand for some hours, finally decanting the clear liquid off through a filter. Cover the precipitate in the flask with dilute ammonium acetate solution containing a little ammonium sulphide, allow it to settle, and again decant ; finally, transfer the clear solution to the filter and wash it free from Cl^- with very dilute ammonium sulphide water.

If considerable amounts of Group V metals are present, the sulphides must be re-precipitated. If the precipitate is *light* in colour (absence of nickel and cobalt) this is effected by treating on the filter with a little 1 : 1 HCl (hot), and, after making the solution ammoniacal, re-precipitating with H_2S. The filtrates are combined for Group V. Unfortunately, NiS and CoS, although not precipitated from acid solutions, when once they are precipitated do not dissolve in dilute acids. If, therefore, the precipitate is dark-coloured, it must be transferred to a crucible, with the paper, and, after drying, the sulphides roasted to oxides. These are then dissolved in a little dil. HCl, and the re-precipitation conducted as already explained.

The following points should be noted:

1. It is advisable to change the receiver when washing ' alkaline sulphide ' precipitates after the first decantation. This will save much time in the filtration in case the sulphides do come through the filter, as only a small bulk will require to be re-filtered.

2. NiS and CoS tend to dissolve in excess of ammonium sulphide forming (probably) complexes. In the presence of these metals, therefore, it is essential to use no more than the barest excess of the group reagent, and it is advisable to precipitate with a solution made by halving a definite bulk of dilute ammonia, saturating one-half with H_2S, and then adding the remaining half. This is preferable to passing H_2S even through a weakly ammoniacal solution, as in the latter case there is bound to be a greater or less excess of ammonium sulphide present. The " solution " of NiS (CoS) in ammonium sulphide is dark brown in colour, almost black ; if, therefore, the solution passing through the filter is seen to be dark in colour, it must be re-acidified and again made *just* ammoniacal. Then, on digestion for a short time, the NiS (CoS) will separate out and may be filtered off on to a separate small pulp filter.

3. The possibilities of removing nickel and cobalt by electrolysis, or as -ic hydroxides, or as the dimethylglyoxime compound (Ni) or the α-nitroso-β-napthol compound (Co), should not be overlooked.

4. If barium is the only Group V metal present it is far simpler to separate it from Group IV than to perform the reverse operation. The solution from Group III is merely poured into excess of boiling dilute sulphuric acid, and the $BaSO_4$, after proper digestion and settling, filtered off and weighed.

MANGANESE.

Separation from Nickel, Cobalt and Zinc.—1. *As Dioxide.* Make the filtrate from Group III very slightly acid and add one or two drops of bromine. Stir the solution with a glass rod until it is saturated with the halogen. (Note that Br_2 attacks rubber, so do not use a rubber-tipped rod.) When the solution is deep orange in colour, add a bare excess of ammonia, stirring constantly, and set the ammoniacal solution to boil on the hotplate, covering the beaker with a clock-glass. The Mn^{++} is oxidised to Mn^{++++} and black flakes of MnO_2, H_2O separate out. Filter, wash well with hot water and finally ignite to Mn_3O_4, or estimate the manganese volumetrically by treating the precipitate with an excess of standard ferrous sulphate solution.

2. *As Sulphide.* Adjust the acidity as explained under Zinc, and precipitate the zinc as ZnS ; filter, and wash well. Make the filtrate just ammoniacal by the addition of a few drops of ammonia and again saturate with H_2S ; digest the precipitate until it settles out well, and filter. After one wash (no more) rinse it back into the beaker and treat it with warm 5 per cent. HCl, washing the opened-out paper with the same acid. After digesting the precipitate in the acid for 10 minutes, filter off the undissolved NiS and CoS through a small pulp filter, and wash with cold dilute HCl containing some H_2S. Manganese may be estimated in the filtrate: (*a*) By making ammoniacal and re-precipitating the MnS. Filter, wash, and burn off the paper in a weighed porcelain or platinum crucible. Moisten the ash with conc. H_2SO_4 and finally weigh the manganese as $MnSO_4$. (*b*) Boil off H_2S and precipitate MnO_2, H_2O with Br_2 and NH_4OH. (*c*) Boil off H_2S and precipitate the manganese as phosphate. The last method is the best for large amounts of manganese.

Estimation without Separation. (*a*) Evaporate to fumes with H_2SO_4 ; dilute and add 7 per cent. by volume of HNO_3 ; cool, and estimate the manganese by the bismuthate or Volhard's method. (*b*) Colorimetric Method. [*Note* that the bismuthate method fails in the presence of cobalt owing (1) to the formation of cobaltic compounds and (2) to the colour of Co^{++} compounds.]

From Nickel and Cobalt.—1. Precipitate the sulphides from a slightly ammoniacal solution ; filter, and wash once ; extract with warm 5 per cent. HCl. NiS and CoS are insoluble, while manganese dissolves. Estimate manganese in the filtrate by any convenient means.

2. Electrolysis. Nickel and cobalt are deposited from sulphate solutions.

From Nickel.—1. As above.

2. Make ammoniacal and precipitate the nickel with dimethylglyoxime ; but note that manganese tends to oxidise in alkaline solution.

From Cobalt.—1. As from Nickel and Cobalt.

2. Precipitate the cobalt with α-nitroso-β-naphthol.

From Zinc.—1. Precipitate the zinc as sulphide from acid solution. (Best method.)

2. Precipitate manganese as MnO_2, H_2O with Br_2 and NH_4OH.

3. Bismuthate method.

4. Colorimetric method.

From Metals of the Later Groups.—1. As MnO_2, H_2O.

2. As MnS.

ZINC.

Separation from Group III Metals.—The usual methods, plus precipitation of zinc from slightly acid solution.

From Manganese, Nickel and Cobalt.—Precipitation of ZnS from slightly acid solution.

From Manganese.—Precipitate manganese as MnO_2, H_2O.

From Nickel.—Precipitate nickel as dimethylglyoxime compound.

From Cobalt.—Precipitate cobalt as α-nitroso-β-naphthol compound.

Or electrolysis.

Or precipitation of the -ic hydroxides.

Or by precipitation of ZnS from slightly acid solution.

The choice of method depends upon the relative proportions of the metals to be separated. As always, it is best to select a method in which the minority constituent is precipitated. Thus, to separate traces of zinc from much nickel, precipitate the zinc as ZnS ; but for traces of nickel and much zinc, use the glyoxime method.

NICKEL AND COBALT.

Separation from Manganese and Zinc.—1. Precipitate all the sulphides from an ammoniacal solution and extract with warm 5 per cent. HCl. NiS and CoS are not dissolved.

2. Electrolysis.

From Manganese.—1. As above.

2. Precipitate the manganese as MnO_2, H_2O.

From Zinc.—1. As from manganese and zinc.

2. Precipitate the zinc as ZnS from slightly acid solution.

3. As -ic hydroxides. Ammonia must be absent. Saturate with Br_2 and pour the solution into excess of boiling KOH or NaOH.

Separation of Nickel from Cobalt and vice versa.—Divalent nickel resembles divalent cobalt so closely that there is no method for their separation. Cobalt, however, is readily oxidised to the trivalent state, and the separation is then a simple matter. All methods of separating these two metals depend upon a preliminary oxidation of Co^{++} to Co^{+++}, while the nickel remains divalent.

1. *Separation by Dimethylglyoxime.*—See under Nickel, pp. 115 *et seq.* This is the best method for separating small quantities of nickel from excess of cobalt. The nickel compound is a non-electrolyte, being fully

co-ordinated within the molecule ; cobalt might be expected to form a fully co-ordinated -ic glyoxime, which would undoubtedly be insoluble, but, up to the present at least, this has not been prepared, the Co^{+++} ions appearing to prefer to become co-ordinated with simpler radicles than " glyoxime," *e.g.* with NH_3.

2. *By α-Nitroso-β-Naphthol.*—See under Cobalt, p. 121. In neutral solution the precipitate is brownish-red, and the cobalt is divalent ; in acid solution, however, Co^{++} is oxidised to Co^{+++} by the atmosphere (and, possibly, by water), and the -ous compound is converted into the insoluble -ic compound. Nickel forms an -ous compound with this reagent, insoluble in water and acetic acid, but strong acids decompose it, and nickel is not precipitated from HCl and H_2SO_4 solutions. This is the best method for separating small amounts of cobalt from excess of nickel.

3. *By the Cobaltinitrite Reaction.*—This at one time held the field for the nickel-cobalt separation, and it is still useful. The drawbacks are: 1. It takes a long time to carry through. 2. The cobalt in the precipitate is not in a convenient form for estimation. 3. Another metallic salt (KNO_2) has to be added.

Procedure.—As a rule, nickel and cobalt are first separated from the other metals of the sample by (i.), electrolysis ; (ii.), precipitation as sulphides; or (iii.), precipitation as -ic hydroxides. Whichever method is adopted, the mixed metals (as sulphides, hydroxides, oxides) are dissolved in aqua regia and the solution taken to dryness in a porcelain basin, taking care not to overheat the dry nitrates. This is in order to remove " strong " acids, which decompose nitrites.

The nearly neutral residue is taken up in the minimum amount of water, and, after cooling completely, 5 gms. of KNO_2 for every 0·25 gm. of mixed metals in cold saturated aqueous solution, are added, followed by acetic acid until the nitrites just begin to decompose. The mixture is stirred well, and the dish set, covered with a glass plate, in a warm place for at least 12 hours. The yellow compound, consisting essentially of $K_3Co(NO_2)_6$, crystallises out well, and may be separated almost completely by decantation. It is washed with dil. (say, 5 per cent.) KNO_2 solution that has been made faintly acid with acetic acid, until free from nickel. The two metals may then be estimated by any convenient method, first decomposing the nitrites by boiling the solution or the precipitate with 1 : 4 HCl.

Note 1.—It is necessary to allow the solution to stand for a long time in order to complete the atmospheric oxidation of the cobalt ; 12 hours is the minimum and 24 hours is not excessive ; it is also as well to test the clear solution before filtering for the completeness or otherwise of the precipitation by pouring off a few cc. and warming with a little fresh KNO_2.

4. *Liebig's Method.*—This method is quite reliable and rapid ; it is the best method of separating nickel-cobalt if the special reagents are not available. The drawback to the method is that if cobalt is to be estimated, large amounts of highly poisonous cyanogen compounds have to be destroyed before the metal can be recovered from the complex.

The method depends upon the fact that on adding KCN to a solution containing Ni^{++} and Co^{++}, the $Ni(CN)_2$ and $Co(CN)_2$ which are first formed dissolve in excess of the reagent to form soluble nickelo- and

cobalto-cyanides. The cobalt compound, however, is oxidised to the stable -icyanide, whereas nickel forms no such compound. On treating the solution with Br_2 and alkali, therefore, $Ni(OH)_3$ is precipitated, while cobalt remains in solution as part of the anion of a complex.

Procedure.—Obtain a neutral solution of the two metals as already described under Method 3 ; dilute it to about 100 cc. for each 0·25 gm. of the two metals. Add a dilute solution of KCN slowly and with stirring until the precipitate which first forms just redissolves in excess, and add a slight excess of the reagent. Now make the solution decidedly alkaline with KOH, and add about 1 cc. of a conc. solution of Br_2 in KBr (*cf.* I_2 in KI), drop by drop, still stirring, until no more $Ni(OH)_3$ is precipitated. Filter the latter off through a non-ashless paper, and when it has drained completely, wash the precipitate with hot water. Estimate the nickel by any convenient method.

It is not easy to " get at " the cobalt in the filtrate. The best method is to acidify with H_2SO_4 and evaporate the solution to dryness in a porcelain basin. The dry residue is then moistened with excess of 1 : 1 H_2SO_4 and the mixture heated under a hood in a good draught until fumes are evolved. This treatment decomposes the cyanide complex and leaves a mixture of $CoSO_4$ and K_2SO_4, in which the cobalt may be estimated by any of the ordinary methods.

Note 1.—" Non-ashless paper." The solution is too alkaline for ashless paper, which would probably collapse in the funnel. If ashless paper is used, the solution must be diluted considerably before filtering.

Note 2.—Treatment with H_2SO_4 involves the evolution of CO and possibly of $(CN)_2$ and HCN from the cyanide. The operation *must*, therefore, be conducted under a hood in a good draught.

5. There are other special reagents for nickel, but they are of no great practical importance.

GROUP V.

Barium, Strontium, Calcium, (Magnesium).

Magnesium is included in this group for convenience. Strontium need hardly be considered at length, since, commercially, it is only met with as a constituent of a few rather uncommon ores, and, if it is given for analysis in an artificial mixture, it is most unlikely that the other metals of its group will accompany it, on account of the difficulty of effecting their separation in a limited time.

In the course of the usual qualitative separations the above metals are found in the solution after filtering off the sulphides of nickel, cobalt, manganese and zinc. They are then precipitated as carbonates by the addition of ammonium carbonate to the ammoniacal solution, the carbonates of magnesium, sodium and potassium being left in solution ; magnesium carbonate, though insoluble in water, is not precipitated in the presence of the ammonium salts which have at this stage accumulated in the solution.

Note.—In any case, it would be a basic carbonate of magnesium that would be precipitated, its composition depending upon conditions.

For the purposes of quantitative analysis the separation is, however, not quite so simple. The alkaline earth metals are characterised by the

small solubilities of their sulphates ($BaSO_4$, 0·0002 gm., $SrSO_4$, 0·11 gm., $CaSO_4$, 0·20 gm., per 100 cc. water at ordinary temperature), and this fact introduces complications which may not at first sight be suspected. The chief obstacles to the regular separation as carbonates are tabulated and explained below:

1. In the presence of oxidising agents such as $MnO_4^{=}$, MnO_4^{-}, $CrO_4^{=}$, Fe^{+++}, Co^{+++}, $S_2O_8^{=}$ and even atmospheric oxygen, the H_2S used in Group II is oxidised to H_2SO_4 (among other sulphur compounds), with the result that barium and more or less strontium and calcium are liable to be precipitated quite early in the routine.

2. HNO_3 is generally used to oxidise any Fe^{++} that has been reduced by the H_2S of the second group. This, when boiled (as NH_4NO_3) with the sulphide used in Group IV, also oxidises some of the $S^{=}$ to $SO_4^{=}$, with the same result.

3. If $PO_4^{\equiv}$ is present when the solution is made alkaline at Group III the phosphates of Fe, Al, Cr, Ni, Co, Mn, Zn, Ba, Sr, Ca and Mg are precipitated to an extent which depends upon the relative proportions of $PO_4^{\equiv}$ and the metallic ions in the solution. Thus, all or any of these metals are liable to be precipitated in Group III along with iron, aluminium and chromium.

4. $Fe(OH)_3$, $Al(OH)_3$ and $Cr(OH)_3$ tend to adsorb salts of the alkaline earths (*cf.* remarks on Group III).

5. In the presence of large quantities of ammonium salts the alkaline earth metals are only partially precipitated by any reagent, if at all.

6. Ammonia and the alkalies absorb CO_2 from the air, forming carbonates, so that $BaCO_3$, etc. may be precipitated to some extent along with the hydroxides in Group III when ammonia is added.

This being the case, it is usually the best practice to estimate the metals of Groups V and VI in a separate portion of the sample, at least if the sample be at all complex, an ore, for example.

Phosphates and the complications they introduce have already been discussed; see under Group III. Leaving these out of the question for the moment, it may be noted that in many cases it is possible to attack the problem of the estimation of the alkaline earth metals by special methods, especially when it is known that only barium or calcium is present. In the former case it is quite easy to estimate barium as $BaSO_4$ in the original solution, or in the solution after removing lead as $PbSO_4$ should this metal be present, no other metals having insoluble sulphates.

Again, if calcium is present it is easy to avoid serious difficulty by care in the earlier group separations. $CaSO_4$ is appreciably soluble in water (1 in 500, about, at ordinary temperatures; less at higher temperatures), so that the $SO_4^{=}$ produced by the oxidation of sulphides should not cause precipitation of $CaSO_4$. Then, if the amount of acid added and hence the amount of ammonium salts formed, be carefully watched, so that lavish excesses are avoided, there will be no difficulty in precipitating calcium as oxalate in the filtrate from Group IV.

If it be decided that the preliminary operations up to the separation of the metals of Group IV (phosphates being absent) have made the quantitative separation of the alkaline earths a matter of uncertainty, a separate sample should be taken and handled as follows:

Obtain the solution as usual, adding 3 per cent. excess HCl by

volume in a bulk of 400 cc. or thereabouts. The presence of oxidising compounds can usually be detected before proceeding any further, since the chief oxidising anions are coloured characteristically, as is also the ferric ion, which is the most common cause of oxidation of H_2S. In any case, the analysis of the first four groups will have shown the operator what sort of a mixture he is handling. If any oxidising agents are present, they may be reduced by treating the solutions with a strong reducing agent, such as $SnCl_2$, before diluting to pass H_2S.

Pass H_2S to saturation, raising the solution to near boiling-point and then allowing it to cool completely, still passing the gas. If there is very much precipitate it may be safer to cork the precipitation flask and digest its contents under pressure for an hour on the water-bath before filtering. Filter and wash thoroughly with slightly acid (HCl) H_2S water. Make the filtrate just ammoniacal and again pass H_2S for a minute or two, adding more ammonia, a little at a time, if the solution becomes acid owing to a reaction such as $ZnCl_2 + H_2S = ZnS + 2\ HCl$. Digest, settle and filter, washing with very dilute ammonia through which H_2S has been passed for a few minutes. The filtrate now contains only the metals of the alkaline earth group and the alkalies (and ammonium, of course).

To separate the metals of Group V it is preferable to precipitate them as oxalates or as sulphates instead of carbonates, as follows:

'*Oxalate Separation.*—NH_4Cl must be present to the amount of at least 10 times the weight of magnesium present. If the foregoing separation has been carried out carefully, the amount of HCl present is known, and the weight of NH_4Cl that will result from its neutralisation can easily be calculated; as a rule no additional NH_4Cl need be added. The total weight of barium, calcium (strontium) should not be more than about 0·75 gm., and the bulk of the solution should be 300–350 cc.

Add sufficient solid oxalic acid, $(COOH)_2, 2\ H_2O$ (molecular weight 126), to combine with all the barium, strontium and calcium present (At. wts. 137, 88 and 40 respectively). When this is dissolved, add 2 or 3 drops of methyl orange and slowly run in dilute ammonia until the colour turns. Add a further 0·5 gm. of oxalic acid, followed by dilute ammonia (1 : 3) until the colour again changes.

Place the beaker on the edge of the hotplate under a glass cover for at least an hour, or until the precipitate settles out well. The precipitate consists of all the calcium, and practically all the barium and strontium as oxalates. Filter and wash with 1 per cent. ammonium oxalate solution to which a few drops of ammonia have been added.

Note.—If magnesium is present in large quantities (*e.g.* 5 times the total amount of the alkaline earths) some will be precipitated as oxalate in spite of the presence of the ammonium salts. In this case:

Filter as before and wash. Wash the precipitate back with hot water and rinse the paper with successive washes of 1 : 1 HCl and cold water. Then dissolve the precipitate in the acid and re-precipitate the metals of Group V exactly as before, the two filtrates being combined.

Alternative Separation (*Sulphate Method*).—Evaporate the solution from Group IV to dryness and add 5 cc. of H_2SO_4. Heat until fumes are evolved, cool, and disintegrate the precipitate with a glass rod. Add 50 cc. of " rectified spirit " (at least 95 per cent. alcohol) and stir well.

Settle, and filter through a compact filter, washing with the alcohol until free from magnesium. $MgSO_4$ is not very soluble in anhydrous alcohol, and if more than about 0·5 gm. is present the precipitate should be treated first with 10-15 cc. of water and then with the alcohol before filtering. The insoluble residue is $BaSO_4 + SrSO_4 + CaSO_4$. The anhydrous alcohol is only necessary when calcium is present. With barium alone, no alcohol need be used ; with strontium in the mixture, a 1 : 1 water-alcohol mixture is sufficient, but the more soluble calcium requires almost anhydrous spirit. Note that practically all sulphates are insoluble in absolute alcohol.

SOLUBILITIES OF GROUP V SALTS.

	BARIUM.	STRONTIUM.	CALCIUM.	MAGNESIUM.
Bicarbonate, (Solution saturated with CO_2 at 1 atmos.)	1·2/1000 at 10° C.	1·2/1000 (cold)	0·38/1000 at 15° C.	26/1000 at 20° C.
Carbonate, (Contact with air.)	0·02/1000 at 18° C.	0·01/1000 at 24° C.	0·06/1000 at 20° C. (Carbonates are more soluble in presence of ammonium ion.)	0·19/1000 at 15° C. (Very soluble in presence of ammonium ion.)
Chromate,	0·0037/1000 at 20° C.	0·12/100 at at 15° C.	2·27/100 at 18° C.	72/100 at 18° C.
Hydroxide,	3·9/100 at 20° C.	1·71/100 at 20° C.	0·16/100 at 20° C.	0·009/1000 at 18° C. (Completely in presence of ammonium ion.)
Oxalate,	0·11/1000 at 18° C.	0·046/1000 at 18° C.	0·006/1000 at 18° C.	0·3/1000 at 18° C. (Completely in presence of ammonium ion.)
Sulphate,	0·0024/1000 at 20° C. 0·016/100 at 25° C. in 20 per cent. ammonium acetate.	0·11/100 at 17° C. (More soluble in presence of ammonium ion.)	0·20/100 at 20° C.	35/100 at 20° C.

The above figures represent grams dissolved in 100 or 1,000 gms. of solvent. Most of the figures were determined by the conductivity method.

Separation of Barium, Strontium and Calcium from Magnesium and the Alkali Metals.—This is the nearest approach to a regular group separation that is available. The alkaline earths are precipitated as oxalates in the presence of NH_4Cl (see Separation of Calcium from Magnesium, below). Some barium will remain in solution. This is recovered as $BaSO_4$ by treating the acidified (HCl) boiling solution with a little dilute H_2SO_4. See also under Separation of Barium from Strontium and Calcium, Note 1, which indicates a method for isolating the alkaline earths as sulphates (p. 283).

Calcium and/or Strontium from Magnesium.—This is the most important separation ; certainly it is the one that is most frequently required.

Theory.—Magnesium oxalate is by no means easily soluble in water, and, in pure solutions (*i.e.* those containing neither excess of oxalate nor ammonium salts), the separation would be impracticable. Calcium oxalate is, in any case, liable to carry down with it serious proportions of magnesium oxalate, the degree of adsorption depending upon the concentration of the undissociated oxalate, being increased by increasing concentration. On the other hand, in the presence of excess of ammonium oxalate, magnesium oxalate is much more soluble, as it forms complexes, a process which is assisted by the addition of ammonium salts, usually NH_4Cl. The presence of a somewhat high concentration of NH_4^+ is beneficial in spite of the fact that this increased concentration reduces the ionisation of ammonium oxalate (common ion). In any case a considerable excess of oxalate ion must be present in order to render the calcium oxalate sufficiently " insoluble " for quantitative work.

Method.—The solution should have a volume of not less than 100 cc. for each 0·1 gm. of calcium plus magnesium. Make the solution acid with 3–5 cc. of HCl for every 100 cc., boil and add excess of a saturated ammonium oxalate solution (1 cc. will precipitate 0·01 gm. of CaO) ; colour the solution with one or two drops of methyl orange. Carefully add dilute ammonia, drop by drop, with constant and vigorous stirring, until the colour of the indicator changes to full yellow, the solution being held near the boiling-point the whole time.

Digest the precipitate near the boiling-point until it separates out well as a compact, crystalline mass ; filter, and wash with cold water. The precipitate contains all the calcium and practically all the strontium as oxalates, and if the magnesium in the original solution represented more than about one-quarter of the total weight of the metals, some magnesium oxalate as well. In this case, wash it back into the beaker and dissolve in HCl, dilute as before and re-precipitate, combining the filtrates for the magnesium estimation.

If strontium is present, traces of this metal may be found in the filtrate, especially if the concentration of NH_4^+ is high. To recover it, add excess of HNO_3 and evaporate slowly to dryness in a wide beaker, adding more HNO_3, if necessary, to complete the decomposition of the ammonium salts. Finally, add 1 or 2 cc. of H_2SO_4 to the dry residue and heat until the acid fumes strongly. Dilute (after cooling) with 50 per cent. alcohol, allow to settle for several hours and filter off the $SrSO_4$, washing with 50 per cent. alcohol.

Estimate calcium either by titration with $KMnO_4$ or gravimetrically. Estimate magnesium in the filtrate as phosphate, either with or without

a preliminary removal of NH_4^+. If strontium is present, the oxalates must be separated as described below, always remembering that traces of strontium will have to be recovered from the filtrate.

Barium from Strontium and/or Calcium. Chromate Method.—The neutral solution, which should not contain abnormal amounts of ammonium salts (*Note* 1), and not more than 0·5 gm. of the metals of Group V, is diluted to 200–300 cc. and 3 or 4 drops (no more) of acetic acid are added. The solution is brought to the boil and a solution of $(NH_4)_2CrO_4$ (*Note* 2) is added in a thin stream until no more precipitation takes place and the supernatant liquid is coloured decidedly yellow. The solution is then cooled and filtered through a weighed asbestos Gooch crucible, washing four times with dilute $(NH_4)_2CrO_4$ solution (very pale yellow) to remove calcium and strontium, and then with cold water until the runnings fail to give a coloration with $AgNO_3$. The crucible is then placed on a pad of soft asbestos sheet and heated at dull redness in the muffle until the precipitate is a clear golden yellow (*Note* 3). It is then cooled in the desiccator and the precipitate weighed as $BaCrO_4$. Or, the precipitate may be shaken out into excess of the standard $FeSO_4$ solution and the barium determined volumetrically.

If there is but little barium and considerable calcium and strontium, it is advisable to redissolve the chromate and re-precipitate it as follows.

The receiver under the Gooch is changed and a little (about 1·5 to 2 cc. is usually sufficient) hot. 1·2 sp. gr. HNO_3 is run through it drop by drop until the precipitate is all dissolved. The solution is then diluted to about 200 cc. and boiled. 2 or 3 cc. of ammonium acetate solution are added in order to immobilise the H^+ ions, and then, since this addition produces an undesirable concentration of acetic acid, a decided excess of the 10 per cent. $(NH_4)_2CrO_4$ reagent (say, 10 cc.) is added, so that the solubility of the $BaCrO_4$ may be sufficiently reduced by the common ion effect. The precipitate is filtered off and washed as above.

Note 1.—If previous operations have resulted in the accumulation of ammonium salts to the amount of more than about 1 or 2 per cent., *e.g.* after a basic acetate separation, or as the result of a double precipitation of the Group III metals, it is best to isolate barium, strontium and calcium as sulphates before separating them individually. (See p. 280 for the method.) After separation, the mixed sulphates are fused in a platinum crucible with six times their weight of Na_2CO_3 and the fluid melt is extracted with hot water. The alkali salts are filtered off and the solution discarded. The alkaline earth carbonates are then rinsed back into the beaker and there dissolved in the minimum amount of hot 1·2 sp. gr. HNO_3. The solution is gently evaporated on the hotplate until the residue is pasty, in order to expel the bulk of the acid ; the residue is then dissolved in a little hot water and the solution diluted to 200–300 cc., when it is carefully neutralised with a few drops of NH_4OH (using an indicator).

Note 2.—$(NH_4)_2CrO_4$ is prepared by adding NH_4OH to a solution of $(NH_4)_2Cr_2O_7$ until the latter turns yellow. The final solution should be slightly acid rather than alkaline.

Note 3.—Occasionally there is a slight reduction of CrO_3 to Cr_2O_3, and the precipitate turns green at the edges. Prolonged roasting in air will restore the proper golden yellow colour.

Barium from Small Amounts of Calcium.—Precipitation with H_2SO_4 may be used.

Calcium from Small Amounts of Barium.—Precipitation of calcium oxalate affords a fairly complete separation. Re-precipitation will certainly be necessary.

Barium from Magnesium and the Alkalis.—Make the solution just acid with HCl and boil. Add dilute H_2SO_4 drop by drop until no more precipitate is produced. Filter, and wash well with hot water. Ignite, and weigh as $BaSO_4$. Note, however, that if the precipitate is large, and especially if the solution contains much Cl^-, it should be ignited in a

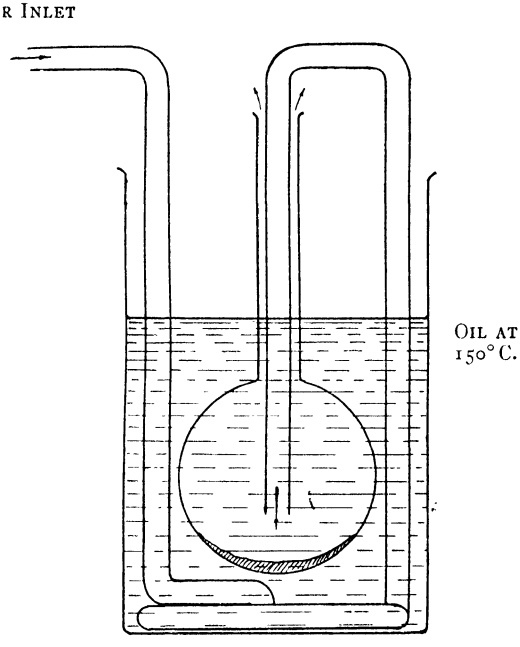


Fig. 25.—Apparatus for Calcium from Strontium and Barium Separation.

weighed crucible and treated with a drop or two of H_2SO_4 to expel adsorbed Cl^-. After driving off the excess of acid, re-ignite and weigh as $BaSO_4$.

Calcium from Strontium and Barium.—This is given for the sake of completeness, but it is not a pleasant separation. Fortunately, it is extremely rare to find the three alkaline earth metals present together in a sample for analysis.

It is supposed that the alkaline earth metals have been separated as oxalates. Rinse the precipitate into a 250 cc. flask and dissolve it in hot 1 : 3 HNO_3, rinsing the opened-out paper with the acid in order to remove any adhering precipitate. Evaporate to as low bulk as possible on the water-bath and finally expel the excess of HNO_3 by heating in an oil-bath at 150° C. and blowing a stream of hot air through the

flask (see fig. 25). When the crystals are quite dry, add 100 cc. of a 1 : 1 mixture of alcohol and ether, and after shaking and stirring to break up the crystals, allow the mixture to stand in a cool place, shaking at intervals ; finally stand over night. Decant the clear solution through a dry filter. Wash the residue with small doses of the alcohol-ether mixture until no more $Ca(NO_3)_2$ is extracted.

The residue consists of barium and strontium nitrates ; dissolve in water and separate by the chromate method. The solution contains the calcium ; evaporate off the solvent and precipitate the calcium as oxalate.

General Note.—A wave-length spectrometer for arc and/or spark spectra is a wonderful time saver when an unknown mixture of alkaline earths is to be analysed. The information obtained in a few seconds saves literally hours of work, as the analyst can at once select the correct method of separation.

GROUP VI.

The separations of Mg, Na, K and (NH_4), are individual, and are considered under the respective metals.

SECTION VII.

SEPARATIONS OF THE ANIONS.

In the great majority of cases there is no need for an actual separation of the anions as is necessary in the case of the metals. The reason for this is that in most cases the methods of estimation of the anions are specific, and even when they are not, it is usually possible to determine any particular anion in the presence of nearly any other without separation.

In the Quantitative analysis of the acidic constituents of a mixture, two principal cases occur.

1. *The Acids are from Different Groups, e.g.* a sulphur acid mixed with a halogen acid ; a nitrogen acid mixed with a phosphate, etc. In this case, of course, it is a perfectly simple matter to estimate each by the fundamental method for the group ; that is to say, in the cases mentioned, it would be sufficient to estimate the sulphur acid as $BaSO_4$ (whatever the actual acid), and the halogen acid as silver salt. In the second case, the nitrogen acid could be estimated as ammonia gas by reduction with Devarda's alloy, and the phosphate estimated in a separate portion of the sample by any ordinary method.

2. *The Acids are from the Same Group, e.g.* a sulphide and a sulphate ; a chloride and a bromide ; a nitrite and a nitrate ; chloride and chlorate ; etc.

In this case it is usual to proceed as follows: (*a*) Estimate the total sulphur (halogen, nitrogen, etc.) by the fundamental method for the group. (*b*) Estimate either of the constituents individually, and so obtain a figure for the other by difference. Thus, in the nitrate-nitrite mixture, estimate (*a*) total nitrogen by Devarda's method, and (*b*) nitrite by titration with permanganate.

Case I requires no comment. The analyst usually has a choice of several methods, and he must make his own selection according to the nature of the mixture with which he is dealing, basing his choice upon his knowledge of the reactions of the respective anions, and being on his guard against complications arising from unsuspected interfering reactions.

Case II.—In most cases it will be unnecessary to give details, for which see under the individual acids. The following catalogue is not intended to be by any means exhaustive.

GROUP I.—THE SULPHUR ACIDS.

A. Sulphide and Sulphite.—1. Estimate *total sulphur* by oxidising the weighed solid sample with either conc. or fuming HNO_3, or, if in solution, with a large excess of Br_2 or with ammoniacal H_2O_2.

2. Estimate *sulphide sulphur* by adding excess of acid (HCl), cupric chloride solution, and then boiling until SO_2 is expelled, after which the copper sulphide is estimated as Cu_2S by ignition in hydrogen.

3. Estimate *sulphide sulphur* by the Evolution Method, p. 293.

4. *Sulphite sulphur* is obtained by difference.

B. Sulphide and Sulphate.—1. Weigh the sample into a flask fitted with a three-holed stopper carrying entry and exit tubes for bubbling CO_2 through the solution and a tap-funnel. Fill the flask with CO_2 and then admit excess of 1 : 5 HCl *via* the funnel. Start passing the CO_2, and slowly heat the mixture to boiling. When all the H_2S has been expelled, rinse the contents of the flask out into a beaker and estimate the *sulphate sulphur* as $BaSO_4$. If desired, the issuing gases may be passed through a solution of lead acetate, and the *sulphide sulphur* estimated as described on p. 154. This serves as a check on the difference methods.

2. Treat the sample with considerable excess of Br_2 or $Br_2 + NHO_3$ if the sulphide is insoluble in water, and after boiling off the excess, estimate the *total sulphur*. The difference between 1 and 2 represents the *sulphide sulphur*. Alternatively, oxidise the solid sample with conc. $HNO_3 + Br_2$ or with fuming NHO_3; but it will then be necessary to expel the NO_3^- by evaporating several times with HCl before precipitating with $BaCl_2$.

C. Sulphite and Sulphate.—1. Estimate the *total sulphur* as $BaSO_4$ after oxidising the sulphite with Br_2 in dilute acid solution.

2. Titrate the *sulphite* with iodine or permanganate.

D. Sulphate and Thiosulphate.—1. Estimate total sulphur after oxidising the hot solution with Br_2.

2. Titrate the thiosulphate with standard iodine.

3. Add excess of 1 : 5 HCl and boil the solution in a flask in an atmosphere of CO_2. When all the SO_2 has been removed, estimate the SO_4^- directly as $BaSO_4$.

E. Sulphate and Persulphate.—1. Estimate the total sulphur after reducing $S_2O_8^-$ to SO_4^- by treatment with pure iron sheet in HCl solution, and gently warming.

2. Estimate 'sulphate' separately by precipitation with $BaCl_2$ in dilute HCl solution.

3. Estimate 'persulphate' separately, by treating the solution with excess of standardised acid $FeSO_4$ solution in the cold. After well mixing the solutions in a flask (preferably filled with CO_2), titrate the excess of Fe^{++} with $KMnO_4$.

GROUP II.—THE HALOGEN ACIDS.

A. Chloride and Bromide.—1. Precipitate the total halogens as AgCl and AgBr by adding excess of $AgNO_3$ to the dilute HNO_3 solution and wash the precipitate twice with hot very dilute HNO_3 and then with hot water. Dry the precipitate and paper and carefully brush the precipitate off the filter on to a piece of smooth paper; cover it with an inverted beaker. Then transfer the filter to a weighed porcelain boat and burn in the muffle, after which treat the residue with a drop of HNO_3 to dissolve any reduced silver, followed by a drop of HCl. Dry the boat and contents on the hotplate. Now add the main precipitate

and dry the whole carefully on the centre of the hotplate at 200° C. Weigh boat plus precipitate (= AgCl + AgBr).

2. Now place the boat in a combustion tube and while passing a slow stream of chlorine through the tube, heat it gently with a small flame, taking care the precipitate does not fuse. Cool, and re-weigh. The precipitate is now all AgCl, according to the reaction:

$$AgBr + Cl = AgCl + Br.$$

Calculation.

Let a = weight of AgCl + AgBr.
b = ,, total AgCl.
x = ,, AgCl originally present.
y = ,, AgBr ,, ,,

Then:

$$x + y = a, \text{ and } x + \frac{AgCl}{AgBr} y = b.$$

If these simultaneous equations are solved for x and y the amounts of Cl and Br originally present are obtained.

B. Chloride and Iodide.—The method is exactly similar to the foregoing.

C. Bromide and Iodide.—1. Weigh AgBr + AgI as above (= a gms.).

2. Convert both salts into AgCl using the above method (= b gms.). Similar equations can be obtained to the above.

D. Chloride, Bromide and Iodide.—This case is slightly more complicated, but the method is similar. (*a*) 1. Weigh AgCl + AgBr + AgI.

2. Weigh total AgCl, after converting the mixed precipitate entirely to chloride by heating in a stream of chlorine.

3. Estimate the iodide separately as PdI_2.

(*b*) Alternatively, (Baubigny's Method): AgCl and AgBr react with sulphuric acid and potassium dichromate to form Ag_2SO_4, the halogen being set free; AgI, however, is converted into $Ag_2SO_4 + HIO_3$.

Method:

1. Precipitate and weigh AgCl + AgBr + AgI from one portion of the sample (= a gms.).

2. Precipitate the same compounds from a separate portion of the sample, and after filtering them off and washing them well on an asbestos pulp filter, transfer them, pulp and all, to a conical flask. To 0·25 gm. of the halide salts add 2 gms. of solid potassium dichromate and 25 cc. of conc. H_2SO_4, and digest the mixture at about 100° C. for at least two hours. Bubble a rapid stream of air through the solution for ten minutes in order to remove the last traces of Cl_2 and Br_2.

Dilute the cooled mixture to at least 250 cc. and filter off the strands of asbestos pulp. The filtrate contains Ag_2SO_4, representing the Ag originally combined with the Cl, Br and I, plus HIO_3, representing the iodine. Now add, drop by drop, a bare excess of a concentrated solution of a bisulphite, whereby HIO_3 is reduced to HI and AgI is precipitated. The latter is then filtered off and weighed (= b gms.).

To the filtrate, containing the Ag^+ originally combined with the

Cl^- and Br^-, add excess of KI and filter off; wash and weigh the resulting AgI (= *c* gms.).

Simultaneous equations can be made up whose solutions give the original weights of Cl, Br and I. There are, of course, *three* simultaneous equations, corresponding to the three unknowns.

E. Chloride and Hypochlorite.—See Analysis of Bleaching Powder.

F. Chloride and Chlorate.—1. Estimate the *chloride* as AgCl.

2. Reduce the chlorate to chloride with SO_2 or Fe^{++} and precipitate and weigh *total chlorine*. *Chlorate chlorine* follows by difference.

G. Chloride and Perchlorate.—1. This is similar to **F.** The perchlorate is reduced as explained on p. 172.

H. Chlorate and Perchlorate.—1. Estimate *total chloride* after heating with NH_4Cl (p. 172).

2. Reduce with SO_2 or Fe^{++} and again estimate chloride. This corresponds to *chlorate chlorine ; perchlorate chlorine* follows by difference.

I. Chloride, Chlorate and Perchlorate.—1. Estimate *chloride chlorine* by precipitating with $AgNO_3$ solution.

2. Reduce a separate portion of the sample with SO_2 or Fe^{++} and again estimate chloride. The difference between 1 and 2 represents *chlorate chlorine.*

3. Treat the solid mixture with NH_4Cl and again estimate chlorides. The difference between 3 and (1 + 2) represents *perchlorate chlorine.*

GROUP III.—THE NITROGEN ACIDS.

A. Nitrate and Nitrite.—1. Estimate *total nitrogen* by Devarda's or Kjeldahl's method.

2. Estimate *nitrite nitrogen* by titration with $KMnO_4$.

GROUP IV.—THE CARBON ACIDS.

A. Carbide and Carbonate.—Two cases arise:

(*a*) The carbide is decomposed by water. This becomes a matter for Gas Analysis and is outside the scope of this book.

(*b*) The carbide is stable in water:

1. Estimate *total carbon* as CO_2 by heating the sample in oxygen in a carbon combustion furnace. (See p. 181.) Most carbonates (except $BaCO_3$, $MgCO_3$, and the alkali carbonates) are decomposed at 1,000° C.

2. Estimate *carbonate carbon* by any convenient method.

B. Carbonate and Bicarbonate.—The only important case, the analysis of mixtures of the alkali compounds, has been fully discussed under Alkalimetry.

SECTION VIII.

ALLOYS AND OTHER INDUSTRIAL PRODUCTS.

A. FERROUS ALLOYS.

STEEL.

UNHARDENED " carbon " steel consists essentially of a physical mixture of iron and iron carbide (Fe_3C). The " iron," metallurgically known as " ferrite," is, however, never pure, as it invariably contains in solid solution small percentages of manganese, phosphorus (as Fe_3P), arsenic (as arsenide), and silicon (as silicide) ; in addition to these it also contains small amounts of mechanically admixed sulphides (FeS and MnS), also silicates (ferrous and manganous). Hardened steel is similar except in the disposition of the carbide, which in this case is more or less in solid solution in the excess of iron ; there is no analytical distinction possible between hardened and annealed steel.

In the ordinary chemical analysis of steel it is usual to estimate carbon, manganese, silicon, sulphur and phosphorus, while for specially important work the following may be added: copper, arsenic, oxygen, carbon monoxide and nitrogen.

Estimation of Carbon.—This has been discussed on p. 181.

Estimation of Manganese:

(i) *Bismuthate Method.*—Weigh 1 gm. of drillings into a 300 cc. beaker and add 20–30 cc. of 1·2 sp. gr. HNO_3. Cover the beaker with a clock-glass and gently heat on the hotplate until all the metal has dissolved.

Note.—Occasionally it happens that for some unexplained reason, one or more of the drillings " goes passive " and remains unattacked by the acid. If this should occur, decant the solution into a clean beaker and add a few drops of HCl + 1·2 sp. gr. HNO_3 to the obstinate metal, which will have the effect of bringing it into immediate solution. Evaporate until the salts commence to separate out ; add 20 cc. of conc. HNO_3 and continue evaporating rapidly until crystallisation again sets in. Now re-transfer the decanted solution and continue as directed. In some cases it is quicker to re-weigh the sample and start over again.

Boil the solution for a minute to expel nitrous fumes and then add about 0.5 gm. of solid sodium bismuthate, which will oxidise the carbonaceous compounds that remain in solution in the nitric acid, a procedure which is necessary, as they will otherwise reduce the permanganic acid subsequently produced. If necessary, add more bismuthate ; the completion of the preliminary oxidation is shown either by a permanent residue of insoluble bismuthate or by a MnO_4^- coloration which persists on boiling for a short time.

Reduce the excess of bismuthate (or MnO_4^-) with a drop of NH_4HSO_3 solution or a crystal of Na_2SO_3 or $FeSO_4$; boil off the SO_2 and nitrous fumes and set the beaker in the cooling trough to cool to air temperature. Meanwhile, set up burettes containing the ferrous sulphate and the No. 2 $KMnO_4$ solutions, and prepare a quick-running asbestos pulp filter. A wash-bottle containing 3–5 per cent. HNO_3 is also necessary.

Remove the cold assay solution from the cooling trough and add about 0·5 gm. of bismuthate. Swirl the beaker steadily for one minute and then hold it up to the light to see if an excess of bismuthate remains ; if this is not the case, add a little more bismuthate. If no colour develops it is probable that insufficient HNO_3 is present, either because too much reducing agent has been used or because too much acid has been boiled away in driving out the SO_2. Try adding 5–10 cc. of conc. HNO_3. If this fails to produce a deep purple colour after agitating the solution for one minute, it is probable that the sample is very low in manganese. In either case it is advisable to weigh out a fresh sample as a check against error.

Assuming that the oxidation of the manganese has proceeded correctly, the next step is to filter off the excess of bismuthate, and wash with the dilute HNO_3 until the runnings are colourless. The filtrate must be cold (say, below 20° C.), and should not contain more than 7.5 per cent. by volume of conc. HNO_3, or Fe^{++} may be oxidised by the acid.

The filtration and washing should be conducted without undue delay, as there is a tendency for MnO_2, H_2O to separate out, and, if chromium and/or vanadium be present, these metals tend to oxidise in addition to the manganese. Titrate the solution rapidly with the $FeSO_4$, adding at least 2 cc. in excess ; bring the end-point back to "just pink" with the $KMnO_4$. The calculation is made as described on p. 126.

Other methods for the estimation of Mn in steel are:

(ii) *Colorimetric.*

(iii) *Oxidation to MnO_4^- with persulphate in presence of $AgNO_3$ and titration with a standard solution of sodium arsenite.*

(iv) *Volhard's method.*

(v) *The "basic acetate" separation.* This is the method adopted when all others fail. See under Separations, p. 259.

Estimation of Silicon:

Weigh out 5 gms. of the drillings into a wide 600 cc. beaker. Add 15 cc. of HNO_3, followed by 20 cc. of HCl, added a little at a time, or the reaction may become unduly violent. When the reaction subsides, set the beaker to evaporate on the hotplate. Great care is necessary when the salts begin to separate out, as the residue has a great tendency to spurt violently, throwing splashes of the ferric compounds out of the beaker. During the latter stages, constant attention is necessary to prevent loss in this manner, and if results are required in a hurry, considerable experience is necessary to be able to push the evaporation forward rapidly and yet safely. Also note that just at the end of the evaporation, when parts of the bottom of the beaker are wet and parts dry, the beaker is liable to crack if heating be too rapid, owing to moisture being driven over on to the dry portions.

When the residue is quite dry, push the beaker into the centre of the plate and " bake " for 20 minutes to expel the bulk of the NO_3. Cool, add 20 cc. of HCl, cover, and set the beaker on the edge of the hot-plate to allow the acid to act without evaporation. Note that if the baking is unduly prolonged or conducted at too high a temperature, the Fe_2O_3 will be very slow in passing into solution. On the other hand, if the baking is insufficient, the silicic acid will not be properly dehydrated, and some, remaining in the " sol " state, will pass into solution again and be lost.

When the iron is all in solution, if silicon alone is to be estimated, hot water is added and the insoluble SiO_2 filtered off. Usually, however, sulphur is estimated in the filtrate, and as the acidity of the solution requires control (see Sulphur), the following procedure is adopted: Remove the cover-glass and allow the acid to evaporate until a scum of $FeCl_3$ just forms on the surface. Remove the beaker, cool somewhat, and add 7 cc. of conc. HCl. Dilute to 100 cc. with boiling water and filter through a small pulp filter, washing once with cold water. The filtrate is then removed for the precipitation of the sulphur. The SiO_2 on the filter is usually contaminated with a little iron. Wash it alternately with hot 50 per cent. HCl and cold water until it is absolutely white (or slightly grey ; not yellow or brown). Transfer the silica and paper to a crucible and ignite at the full temperature of the muffle. Weigh as SiO_2.

Note 1.—A temperature of at least 900° C. is necessary to dehydrate silicic acid completely. Also, unless strongly ignited, silica is hygroscopic and difficult to weigh.

Note 2.—The silica should be pure white. If reddish in colour, brush it out into a platinum crucible and weigh. Add 1 drop of H_2SO_4 and 2 or 3 cc. of HF ; evaporate dry in the front of the muffle ; ignite at redness and re-weigh. The loss is SiO_2. See also the note on the Estimation of Silicon in Cast Iron.

Estimation of Sulphur:

The filtrate, which will measure about 300 cc., is brought to the boil and 10 cc. of 10 per cent. $BaCl_2$ solution is added in a slow stream. The beaker is covered and the solution kept at or near the boiling-point until the precipitate settles out well. The latter is filtered off hot through a close-textured pulp and washed with cold water until the washings are free from Cl^-, ignited, and weighed as $BaSO_4$.

Note 1.—Acids usually contain traces of $SO_4^=$, so that a blank estimation is necessary. See under Sulphur, p. 160.

Note 2.—The beaker containing the solution in which sulphur is being estimated should be kept away from SO_3 fumes, beakers evolving SO_2, H_2S, etc., for obvious reasons.

Note 3.—The digestion should not be carried out with the solution vigorously boiling. If the liquid is allowed to bump at all, splashes of $FeCl_3$ will dry on the sides of the beaker and become converted into a difficultly soluble basic compound. Later, when pouring the solution through the filter, these are liable to be transferred also, with the result that the precipitate is contaminated with iron in a form which cannot

be removed by washing. Very often a little care in pouring the solution will prevent this trouble, but it is better avoided altogether.

Note 4.—If the foregoing directions are followed carefully the results will be satisfactory; but see under Sulphur for remarks on the subject of adsorption by $BaSO_4$, action of HCl on $BaSO_4$, etc. If the final ignited precipitate is found to be reddish in colour, Fe is present ; this may be due either to adsorption or to the reason mentioned in Note 3. Iron could, of course, be removed by washing the precipitate with HCl, but some $BaSO_4$ would also be dissolved ; washing with a mixture of $BaCl_2$ and HCl has been recommended, but it is of doubtful efficacy ; the best and safest method to follow if the precipitate is contaminated with Fe is to brush it out into a small (100 cc.) beaker and digest it with

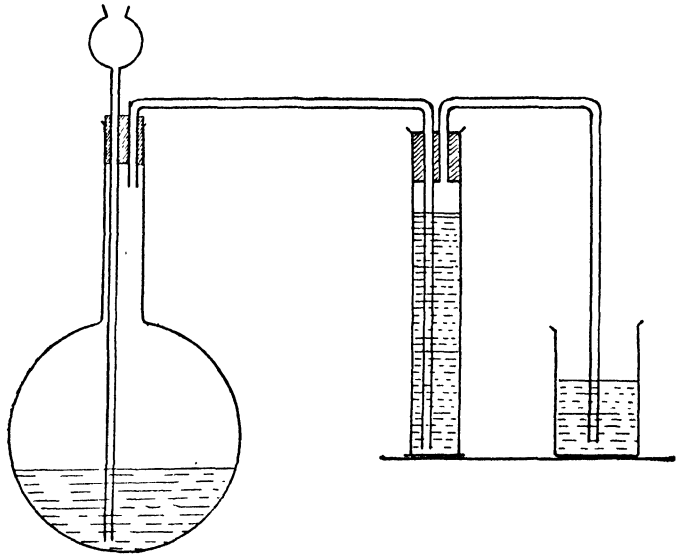


Fig. 26.—Apparatus for Evolution Method for Sulphur in Steel.

conc. HCl until the residue is quite white, then dilute to about 50 cc., boil, and add 2 or 3 cc. of $BaCl_2$ solution to furnish the proper excess of Ba^{++} ions and to re-precipitate the dissolved $BaSO_4$. Digest as before and refilter for weighing. This method completely neutralises all adsorption of iron, and minimises the effect of Cl^- and of Ba^{++} adsorption.

Note 5.—The foregoing gravimetric method is the most accurate method and has the advantage of being universally applicable. A more rapid method is the evolution method, but this is apt to give low results in certain circumstances. It is, nevertheless, an excellent method r routine work provided that the reagents used are standardised against a steel of known sulphur content and similar in character to that under analysis.

The Evolution Method.—Weigh 5 gms. of the steel into a 500 cc. flask fitted with a well-fitting two-holed stopper carrying a tap (or thistle)

funnel and a delivery tube, the latter preferably fitted with a splash-head (see fig. 26).

Connect the delivery tube to a tall, narrow gas washing bottle containing 50 cc. of an ammoniacal cadmium chloride solution (120 gms. $CdCl_2$ in 1,500 cc. of water containing 600 cc. of 0·90 sp. gr. ammonia. Take 20 cc. of this and dilute to 100 cc., using 75 cc. in the wash-bottle and 25 cc. in the beaker). The exit tube is further connected to a fine pointed delivery tube dipping below the surface of a few cc. of the same reagent contained in a small beaker ; this is to ensure the capture of all the H_2S.

When the apparatus is ready, and proved gas-tight, pour 100 cc. of 1 : 1 HCl into the flask. H_2S will be evolved from the FeS and the MnS that are present, along with considerable excess of hydrogen and hydrocarbons. The issuing gas bubbles through the $CdCl_2$ in the wash-bottle and CdS is precipitated. When the evolution of the gas slackens, a small flame is placed under the flask and the acid heated to nearly boiling, which has the effect of completing the solution of the metal and also of expelling dissolved H_2S from the acid. When all the sample has disappeared (ignore traces of insoluble carbides), introduce a small crystal of sodium carbonate and quickly recork the flask. CO_2 will be generated where this meets the acid, thereby (1) mechanically removing traces of residual dissolved H_2S from solution, and (2) pushing the light H_2–H_2S mixture that fills the flask over into the absorption vessel.

While the evolution is proceeding (it takes 30–45 minutes), fit up two burettes containing respectively No. 3 sodium thiosulphate and No. 3 iodine and prepare the starch indicator. The evolution being finished, remove the wash-bottle and pour its contents into a tall 400 cc. beaker. Add sufficient of the iodine solution to produce a decidedly yellow colour and then 10–15 cc. of conc. HCl, stirring well. Rinse the wash-bottle out with this solution, which will dissolve off any CdS that has formed inside the delivery tube ; re-transfer the solution to the beaker and rinse the bottle once or twice with cold water.

Titrate the cold solution with No. 3 sodium thiosulphate, adding about 2 cc. of the fresh starch solution, and bring the end-point back to the " just blue " stage by means of the iodine. The reactions are:

Solution: $MnS\ (FeS) + 2\,HCl = MnCl_2\ (FeCl_2) + H_2S.$
Absorption: $H_2S + CdCl_2 + 2\,NH_4OH = CdS + 2\,NH_4Cl + 2\,H_2O.$
Re-liberation of H_2S: $CdS + 2\,HCl = CdCl_2 + H_2S.$
Titration (*a*): $H_2S + I_2 = 2\,HI + S.$
Titration (*b*): $I_2 + 2\,Na_2S_2O_3 = 2\,NaI + Na_2S_4O_6.$

The iodine and the thiosulphate are then checked one against the other to evaluate the equivalent in iodine of 1 cc. of thiosulphate solution. For this at least 20 cc. of the iodine solution must be used. Suppose that 1 cc. thiosulphate $\equiv x$ cc. of iodine, the net volume of iodine added is then:

(Iodine burette reading) $- x$ (thiosulphate burette reading).

The best way of standardising the solutions is, as has been observed, to carry through the foregoing analysis upon a steel of known sulphur

content. If the net volume of the iodine used in this case is *a* cc. and the net volume used in the assay sample is *b* cc., then:

$$\frac{\text{Per cent. of Sulphur in the Assay}}{\text{Per cent. of Sulphur in the Sample}} = \frac{b}{a}$$

(always understood, of course, that equal weights of steel are used for the two operations). The calculation of the results from an independent standardisation of the solutions, *e.g.* against copper, As_4O_6 or BaS_2O_3, H_2O, has been explained under Iodimetry (p. 226). Note here, however, that two atoms of iodine are equivalent to one atom of sulphur.

Estimation of Phosphorus:

Weigh 2 gms. of the steel into a tall 300 cc. beaker and dissolve in 10 cc. of HNO_3 + 15 cc. of HCl, adding the latter a little at a time on account of the violence of the reaction. When the reaction slackens, place the beaker on the hotplate and evaporate the solution to dryness, taking the same precautions as have been mentioned under sulphur. When dry, bake the residue for 30 minutes and take it up in 15 cc. of conc. HCl, digesting under a cover until the solution is clear. Dilute to 50 cc. with hot water and filter through a pulp to remove silica ; wash once or twice with cold water. Set the filtrate on the edge of the hotplate and introduce a small piece of zinc (about 1 gm.). Hydrogen is vigorously evolved and the arsenic in the steel will thereby be reduced and expelled as AsH_3. When the zinc has disappeared, push the beaker towards the centre of the hotplate and evaporate until crystallisation commences ; the bulk will be very small, 3 or 4 cc. at the most, and the amount of Cl^- present will not be sufficient to affect the result. Remove the beaker, cool somewhat, and dilute to 20–30 cc.

Meanwhile, prepare two large burettes, one filled with conc. ammonia and the other with conc. HNO_3. To each assay add 8 cc. of NH_4OH, followed by exactly 12 cc. of conc. HNO_3 ; then add NH_4OH from the burette until a slight permanent precipitate forms, persisting on boiling. It is needless to observe that this operation requires care, as there is not only great danger of loss by spurting, but the operator may himself be burnt by splashing acid. The secret is to incline the mouth of the beaker away from the operator's face and to keep the contents rotating. The addition of conc. NH_4OH to the acid will heat the solution to near boiling-point, so that the final neutralisation is easily followed. With experience, it is easy to see when enough NH_4OH has been added from the appearance of the precipitate. The solution should always be actually boiled, and a slight precipitate should remain before proceeding to the next step. It is advisable to work near a hotplate or else to have a burner and gauze close at hand. If a number of assays are being made it is best to set them on the hotplate and to add a few drops of NH_4OH to each in turn, replacing the beakers on the hotplate. By the time the last of the series has been treated, the first will probably be boiling, and it will at once be apparent whether more NH_4OH is to be added or not.

When the solution has been neutralised, and a small precipitate remains on boiling, add exactly 2 cc. of HNO_3 from the burette and swirl the solution to dissolve the precipitate and any hydroxide that

adheres to the sides of the beaker. To the hot, slightly acid solution, which must be vigorously swirled, add 10 cc. of filtered 10 per cent. ammonium molybdate solution in a steady stream ; adding it from a burette is a very good plan, and the reagent should be directed at a point about midway between the centre and the edge of the rotating solution. When the molybdate has been added, quickly add 2 cc. more of HNO_3, still swirling, and continue the agitation for another minute to start the precipitation. This done, cover the beaker and set it on the hotplate or on the top of the steam-bath.

The molybdate reagent should not be added too slowly nor too rapidly, or molybdic acid (hydrated MoO_3), or a crystallising insoluble molybdate may be thrown down, and as both are slow to dissolve in HNO_3, the estimation will be spoiled. It is certain that this will occur if the solution be too weakly acid or, what is the same thing, too dilute. The precipitation of these contaminating compounds may be detected by (1) an unnaturally pale colour of the precipitate ; (2) a voluminous precipitate ; (3) a chalky appearance. If such precipitation occurs, the remedy is to allow the precipitate to settle, decant off the clear solution and discard it, and then dissolve the residue in 10 cc. of NH_4OH + 20 cc. water. When the solution is clear, heat it to boiling and quickly add 12 cc. of HNO_3, which will re-precipitate the phosphomolybdate, now free, in all probability, from contamination.

After half an hour or so of digestion, the precipitate settles out completely. Then carefully decant the clear solution into a clean beaker (in case of accidents) and allow the precipitate to run out on to a smooth surfaced filter-paper (No. 50). Rinse the rest of the precipitate on to the filter with a *few* drops of 3 per cent. HNO_3. Note that the wash liquid should never be allowed to fill more than the apex of the filter; it may be even necessary to apply the wash solution five or six times before the precipitate is wholly transferred, but the saving of time in the long run is considerable. With the dilute acid carefully collect the precipitate in the apex of the funnel, allow it to drain completely (test the runnings with NH_4CNS for Fe^{+++}) and then open out the paper upon a clean, glazed tile and dry it at 100° C. in the air oven. Thus handled, the precipitate comes away intact from the paper (use a spatula and a feather tip to transfer it). Weigh the yellow precipitate to the nearest mgm.

Note 1.—With Whatman's No. 50 paper, the phosphomolybdate can be filtered off with the aid of the water pump if desired. This paper stands the pressure well.

Note 2.—Alternatively, the precipitate may be filtered off on a pulp filter and washed with dilute KNO_3 until free from iron and acid. The pulp and precipitate are then transferred to a 250 cc. Erlenmeyer flask, excess of N NaOH solution is added, and the mixture well shaken to dissolve the precipitate. The excess of alkali is titrated with standard acid. In this method, 1 atom P is equivalent to 12 mols. MoO_3 and to 23 mols. NaOH ; whence 31 gms. P ≡ 920 gms. NaOH ; or 1 cc. N NaOH ≡ 0·00135 gm. P. It is, however, better to standardise the NaOH solution directly against a steel of known phosphorus content.

Note 3.—Again, alternatively, dissolve the precipitate in excess of NH_4OH and re-precipitate the phosphorus as $MgNH_4PO_4$, weighing

as pyrophosphate. This method is to be preferred where high percentages of phosphorus are concerned.

Note 4.—The foregoing method is very satisfactory for routine work and gives perfectly satisfactory results. The fastidious may prefer the method indicated under phosphoric acid, in which graduated amounts of molybdate, ammonium nitrate and nitric acid are added, the actual amount depending on the percentage of phosphorus ; see p. 196.

Estimation of Arsenic.

See under Arsenic, p. 84. For As in steel, take 5 gms. of sample. Titrate finally with " tin " iodine diluted 10 times ; the As factor is 0·0003 gm. per cc. approx.

Estimation of Copper.

Small amounts of copper are almost invariably found in steel. Weigh at least 10 gms. of the metal into a large beaker (800 cc., tall) and dissolve in 1 : 3 HCl, adding the acid a little at a time and ignoring traces of insoluble matter (SiO_2, carbides, etc.). 10 gms. will require approximately 150-160 cc. of the 1 : 3 acid. When all is dissolved, dilute to 500 cc. and add 20-30 cc. of conc. HCl as excess, heat to near the boiling-point and saturate with H_2S. Filter, and wash free from Fe^{++} with cold 5 per cent. HCl that has been saturated with H_2S. Transfer the precipitate and paper to a small crucible and roast the copper to oxide, after drying and charring the paper in the mouth of the muffle. Brush the precipitate out into a small beaker and treat it with a few drops of HNO_3. Dilute, filter, and estimate the copper by any suitable means.

WROUGHT IRON.

The analysis is similar in every respect to that of steel except that the carbon content is always very low, and a large sample will probably be required for the estimation. The manganese is also usually lower than in steel, but a 1 gm. sample will serve. Phosphorus may be high, and a 1 gm. sample is usually enough.

CAST IRON, PIG IRON.

Cast iron and pig iron consist essentially of small flakes of graphite dispersed throughout a matrix of rather impure steel. In their analysis one additional estimation, viz. that of **Graphite,** is necessary (see Carbon, p. 190).

Cast iron may contain 3 or 4 per cent. of impurities, and in all cases the estimations are conducted on smaller samples than in the case of steel, thus:

Carbon, Total (i.e. *Graphite* + *Carbide Carbon*),	1 *gm. sample.*
Carbon, Graphitic,	1 *gm. sample.*
Carbon, Carbide,	*always estimated by difference.*
Silicon,	2·5 *to* 3 *gms.*
Sulphur,	,,
Phosphorus,	0·5 *gm. is usually ample.*
Manganese,	1 *gm. sample.*

Note that large quantities of silica and graphite separate out when cast iron is attacked with acids. This is a considerable help in the Si, S and P evaporations, as spitting is largely prevented. On the other hand more, and more careful, washing is required. A few special points of difference as compared with steel will now be noted

Silicon.—The precipitate *must* be treated with HF in platinum, as it is impossible to free it from impurities. On a 2·5 gm. sample the silica may amount to 0·1 gm.

Method.—Burn the filter and precipitate in platinum ; ignite at 900° C. for 20 minutes to dehydrate the silica. Cool in the desiccator and weigh as quickly as possible (crucible + precipitate). Add 5 drops of H_2SO_4 and then almost fill the crucible with HF, adding this latter acid cautiously. Evaporate the contents in the mouth of the muffle and finally raise the temperature so that all acid fumes are expelled. Again ignite at 900° C., cool, and re-weigh ; the difference represents SiO_2.

Note 1.—H_2SO_4 is added, firstly, to convert Fe_2O_3 into the sulphate, so that it may re-form the oxide without loss after the re-ignition, and secondly, to prevent loss of titanium as TiF_4. Titanium is often present in cast iron, and most of it is associated with the SiO_2 precipitate. For the estimation of this metal, see a text-book on steel analysis.

Note 2.—Long and strong ignition of the SiO_2 precipitate is necessary, firstly, to expel water, and secondly, to render the SiO_2 less hygroscopic after heating. SiO_2 is more hygroscopic than is usually realised ; it will even gain in weight when left in a desiccator over H_2SO_4, removing traces of water from the acid.

Sulphur and Phosphorus.—These are always present in considerable quantities in commercial cast iron and pig iron, but there are certain grades of special metal which may contain only very small amounts of these elements.

Manganese.—This is present in quantities similar to those obtaining in steel. It is always estimated in the filtrate from the Graphite estimation.

SPECIAL STEELS.

In a book such as this it is not proposed to enter into a complete discussion of the very complicated and by no means easy methods and manipulations necessary for the analysis of modern alloy steels, which are matters for the specialist. As, however, some few methods are not by any means difficult, and, moreover, give opportunity for practising certain characteristic analytical methods, a few alloy steel methods will be given. " Alloy Steels " may contain combinations of the following elements, added intentionally, in addition to the invariable Fe, C, Mn, Si, S and P:

Alloying elements: Ni, Cr, V, W, Mo, Co, Ti, Cu, B, Zr, Al and the rare earths.

Estimation of Nickel.

1. *Volumetric Estimation.*—Weigh 0·5 gm. of the steel into a tall 300 cc. beaker. Add the minimum amount of HCl and gently warm until dissolved. When nothing but carbides remain, add conc. HNO_3, drop

by drop, until the Fe^{++} is just oxidised (the reaction itself indicates its end-point), and evaporate carefully until the solution is nearly dry, but not sufficiently dry to prevent all the salts from passing into solution on simple dilution. If taken too low, so that on dilution a muddy suspension remains, the assay must be re-evaporated with 1 or 2 cc. of HCl.

Dilute to 50 cc. and add 8 gms. of citric acid, followed (when the acid has dissolved) by dilute NH_4OH, added drop by drop until the solution is very slightly ammoniacal. During the neutralisation the colour changes characteristically, first darkening, then passing through very dark brown, olive green, emerald green, and finally becoming reddish-brown. The solution is sufficiently ammoniacal when, after blowing NH_3 out of the beaker, the analyst can just detect the smell of the gas coming from the solution. An excess of ammonia must be avoided ; if too much be added, throw the assay away and start again. For the titration details, see under Nickel, p. 118.

2. *Gravimetric.*—Weigh 1 gm. of sample for low nickel content and 0·5 gm. for 5 per cent. Ni and over. Place the drillings in a tall 600 cc. beaker and dissolve them in 10 cc. HCl, using gentle heat. When the reaction is complete, add HNO_3, drop by drop, until all the Fe^{++} is oxidised. Boil to expel " nitrous fumes " and dilute to 300 cc. Add 10 gms. of citric or tartaric acid for every 1 gm. of steel. When this has dissolved, make the solution slightly ammoniacal and add dimethylglyoxime until no more precipitation takes place. To ensure complete precipitation, stand the solution on the hotplate, covered, until the red mass settles out well and leaves a clear solution at the top of the beaker. To this add one or two drops of the precipitating reagent ; if further precipitation results, more dimethylglyoxime must be added.

Cover the beaker and boil for a minute or two ; allow the precipitate to settle, decant the clear liquid through a weighed Gooch crucible, and finally transfer the precipitate. Wash free from Cl^- with hot water, suck as dry as possible on the pump and dry to constant weight at 110° C. in the air oven. Weigh as nickel dimethylglyoxime.

Estimation of Chromium.

For steels containing less than 1 per cent. Cr, weigh 2 gms.
For steels containing 2 to 4 per cent. Cr, weigh 1 gm.
For steels containing over 4 per cent. Cr, weigh 0·5 gm.
For ferro-chromium (60 per cent. Cr) weigh 1 gm. and take an aliquot part of the solution, representing 0·2 or 0·1 gm. of alloy.

(i) Place the weighed sample in a tall 600 cc. beaker and dissolve it in 30–40 cc. of 10 per cent. H_2SO_4, setting the beaker on the edge of the hotplate, covered, to allow solution to become complete. When the reaction ceases and nothing remains but traces of carbides, add HNO_3, drop by drop, to oxidise the iron. This procedure usually brings the carbides into solution, but if black flakes persist on boiling, they should be filtered off on a small pulp, and after a gentle roasting in a crucible, brought into a soluble form by fusion either with $Na_2CO_3 + KNO_3$, followed by extraction with dil. H_2SO_4, or with $KHSO_4$ and extraction with water. In either case combine the extract with the main solution.

Dilute to 400 cc., add one or two small pieces of broken porcelain and bring the solution to a vigorous boil. When boiling, add a concentrated solution of $KMnO_4$ a few drops at a time until a precipitate of MnO_2,H_2O is formed and remains after 10 minutes' boiling. Allow this precipitate to settle in a warm place and filter the solution through an asbestos pad. Wash the manganous acid well with hot water until the liquid in the stem of the funnel is no longer coloured yellow ; if a reddish colour is seen it indicates that either too much permanganate has been added or that the boiling was insufficient. During the oxidation a moderate excess of MnO_4^- is decomposed by boiling, but if too much has been added, 10 minutes will prove insufficient. It is usually advisable to examine the solution before filtering by holding it up aslant against the light and looking through the edges of the liquid. The presence of the pink colour of excess MnO_4^- can thus be detected and the ion decomposed before filtration by adding a few cc. of $MnSO_4$ solution and continuing the boiling for a minute or two longer. MnO_2,H_2O is precipitated as in Volhard's manganese method. At one time it was considered necessary to continue the addition of permanganate until the pink colour persisted. This has now been shown to be unnecessary, as MnO_2 is able to oxidise the chromic ion ; furthermore, it is not only unnecessary but harmful, as the manganous acid strongly adsorbs chromates.

The chromate filtrate is evaporated down to a suitable bulk ; too dilute a solution means that the end-point will be ill-defined ; on the other hand, if the solution be too concentrated with respect to chromium, the deep green colour of the Cr^{+++} ion masks the blue on the spot-plate ; for a chromium steel, about 100 cc. bulk is convenient. Titrate the solution with $FeSO_4$ to a decided blue and then bring the spot test back to null with standard dichromate (or permanganate). See Volumetric Analysis.

(ii) *Oxidation with Bismuthate.*—In moderately concentrated HNO_3 solution (20–30 per cent. by volume) sodium bismuthate oxidises MnO to Mn_2O_7 in the cold, but Cr_2O_3 is only oxidised very slowly. In boiling solution, however, Cr_2O_3 is oxidised to CrO_3, while Mn_2O_7 is reduced to MnO_2. If, therefore, the solution be boiled with excess of bismuthate, the chromium is fully oxidised as above while the manganese is precipitated as MnO_2, which may be filtered off on asbestos.

Weigh the sample (2 gms.) into a tall beaker and dissolve it in 30 cc. of 1·2 sp. gr. HNO_3. Bring any refractory carbides into solution as already described, boil, and treat the solution with excess of sodium bismuthate, added a little at a time. When the solution, on being held to the light, shows the deep orange of the chromate ion unmixed with any tinge of purple due to MnO_4^-, allow the precipitate to settle and decant the clear liquid through a quick-running asbestos pulp filter. Dilute the filtrate to 100 cc. (or evaporate to that bulk, as the case may be), cool, and titrate with $FeSO_4$.

Analysis of Nichrome.

This, strictly speaking, is not a ferrous alloy, but is usually classed as such, being considered as the limiting case of a nickel-chrome steel when the alloying elements are present in such quantity as to reduce

the iron to a very low percentage of the whole. Nichrome is of growing importance industrially. The composition varies, but it is essentially an alloy of Ni–Cr–Fe with minor amounts of C, Mn, S, P, Si, etc.

Weigh 1 gm. of fine drillings and digest them in conc. HCl until all is in solution. Oxidise Fe^{++} with a drop or two of HNO_3 as already described. If carbides remain, filter them off and bring them into solution by means of a fusion with $Na_2CO_3 + KNO_3$, or with $KHSO_4$. Acidify the aqueous extract of the melt with HCl and add the resulting solution to the main filtrate. Make the bulk up to 200 cc. in a measuring flask.

Iron.—Pipette out 50 cc. and saturate with bromine. Pour the solution slowly, and in a steady stream, with constant stirring, into excess of boiling 10 per cent. NaOH. Boil for a moment and filter. Wash with hot water once or twice ; redissolve the precipitate in HCl, boil vigorously for 15 minutes to expel Cl^-, etc. and estimate the iron by titration with dichromate after reducing with $SnCl_2$.

Nickel.—Take 25 or 50 cc., and after adding 10 gms. of citric acid and stirring until dissolved, make the solution just ammoniacal and precipitate the nickel with dimethylglyoxime.

Chromium.—Take 25–50 cc. and estimate the chromium volumetrically as described for chrome steel.

Manganese.—(*a*) Take a separate 1 gm. sample and dissolve it in 30 cc. of 1 : 1 H_2SO_4. Evaporate the solution to copious fumes, which will usually bring the carbides into solution ; if they prove obstinate, however, a fusion is necessary. Extract the solution with 50 cc. of hot water and boil until the sulphates are dissolved, which may take an hour or more. Add 20 cc. of HNO_3 to the boiling solution, boil for a minute longer to expel any nitric oxide and cool completely. Attempt the estimation by the bismuthate method using (1) a very cold solution, (2) only a minute's contact with the bismuthate, and (3) a very free-running filter in order to prevent the oxidation of Cr^{+++}. Titrate the solution as quickly as possible. If, however, the runnings show a yellowish tinge on filtration, the bismuthate method will not work ; in this case it is necessary to re-weigh the sample and try the following:

(*b*) Oxidise with HNO_3 and saturate the cold solution with bromine. Add, slowly, and with stirring, a bare excess of ammonia, and boil. Filter off the ferric hydroxide and manganous acid, washing with water, which should be as hot as possible, at least six times, after which redissolve the precipitate in HCl. Cool, and make an acetate separation. Precipitate the manganese in the filtrate as MnO_2,H_2O with bromine and ammonia ; ignite and weigh as Mn_3O_4. *Or*, and possibly preferably, redissolve the precipitate containing Fe + Mn in HCl, fume with 1 or 2 cc. of H_2SO_4, add HNO_3, cool, and estimate the manganese by the bismuthate method.

Carbon, Sulphur, Silicon, Phosphorus.—Estimated as described under Steel. For carbon, the furnace temperatures will have to be higher than for steel ; at least 1,100° C. is advisable, and an oxidiser such as red lead or Mn_3O_4 should be sprinkled over the sample in the boat.

Estimation of Tungsten.

No account has previously been given of the estimation of tungsten, but a method for its estimation in steel is included here, partly because the manipulation is not difficult, but chiefly because it affords practice in a slightly different type of procedure.

Weigh out 2 gms. of the steel and attack with conc. HCl (20 cc.) in a tall 400 cc. beaker. When the reaction ceases, add 10 cc. of conc. HNO_3 and digest the insoluble residue until the tungsten is converted into the golden-yellow oxide, WO_3. Evaporate just to dryness and take the mixture up in 10 cc. of HCl. Dilute to 100 cc. and boil. Filter off the $WO_3 + SiO_2$ on a paper pulp filter and wash well with hot 5 per cent. HCl, six times. Transfer the oxides and paper to a platinum crucible, char off the paper and ignite the oxides at redness for a minute or two. Weigh crucible $+ WO_3 + SiO_2$. Treat the contents of the crucible with two drops of H_2SO_4 followed by 5 cc. of HF ; evaporate gently to dryness and again ignite in the muffle. Weigh crucible $+ WO_3$. (Note that if tungsten only is required to be estimated, the first weighing is unnecessary.)

Add 5 gms. of dry Na_2CO_3 and fuse the mixture at full redness for 20 minutes. Cool the melt and extract it with hot water. Filter, and wash any residue with hot water six or eight times ; reserve the filtrate, which contains tungsten as sodium tungstate. Transfer the filter plus the insoluble matter to the original platinum crucible and after burning off the paper and again igniting, re-weigh. The difference between the last two weighings represents WO_3.

Note 1.—In transferring the WO_3 to the filter, it will often be found that some adheres very obstinately to the sides of the beaker, defying the " policeman." This is probably due to a sort of pseudo-combination of the originally colloidal WO_3 with the bases in the glass (the same thing happens in the case of SnO_2 and Sb_2O_5 when produced by oxidation of the metals with HNO_3). To remove the WO_3 a small piece of folded filter-paper, moistened with conc. NH_4OH, should be rubbed over the deposit with the aid of the " policeman." The paper is then transferred to the crucible with the main deposit. NH_4OH, of course, dissolves WO_3 as ammonium tungstate.

Note 2.—If the filtrate is yellow, it denotes that some chromium which has escaped the original washing has become oxidised to CrO_3. In this case, acidify with H_2SO_4, cool, and titrate the solution with standard $FeSO_4$. Calculate the chromium found to Cr_2O_3, and deduct this weight from the weight of the WO_3 found.

Note 3.—WO_3 adsorbs some ferric and chromic oxides ; these, except the little chromium which is oxidised to chromate (see Note 2), are recovered by the fusion, being left insoluble in the fused carbonate.

The estimation of the other alloying elements found in steels is not a matter for an elementary text-book, and so will not be discussed here. Those interested should refer to a text-book specialising on iron and steel analysis, such as that by Hall and Williams, Blair, or Brearley and Ibbotson.

B. NON-FERROUS ALLOYS.

COPPER ALLOYS.

BRASS.

Brass is essentially an alloy of copper and zinc, and many brasses contain no more than traces of other metals. Copper and zinc may be present in various proportions, of which the most important are 70: 30, 60: 40 and 55: 45. The chief constituents to be looked for in brass analysis are: Cu, Zn, Pb*, Cd, Sn*, As, Fe*, Ni*, Mn*. The asterisked metals are occasionally added intentionally in proportions as high as 1 or 2 per cent. Besides the above, in special cases it is necessary to test for: Ag, Bi, Sb, Al, Mg, S, O, P, Si.

Method.—Weigh out 1 gm. of the drillings and attack them with 20 cc. of 1 : 1 HNO_3 in a small, wide beaker. When the reaction is over (cover the beaker at first, as there is a tendency to spray and spit), carefully evaporate the solution until nearly dry, or until the copper nitrate is of a syrupy consistency. Add 5 cc. more of the HNO_3 and dilute to 75 cc. If a precipitate forms, (SnO_2), boil for a minute to complete the separation and filter it off on a small, compact pulp, washing with hot 5 per cent. HNO_3 five or six times. Transfer the precipitate to a porcelain crucible and after charring off the paper, ignite to SnO_2, in which form the tin is weighed. (See p. 92.)

If no precipitate forms, as is more usual, electrolyse the solution at once for copper and lead (see p. 62). If tin has been separated, the solution should be cooled before electrolysing.

After the electrolysis is complete, add two drops of methyl orange and make the solution just ammoniacal. Cover the beaker and boil for a minute to collect the slight precipitate of $Fe(OH)_3$ which almost invariably forms at this stage ; filter it off, and wash thoroughly with hot water. Usually the precipitate is small and may be ignited to oxide and the iron estimated in that form. If, however, there is more than a trace of $Fe(OH)_3$ present (*e.g.* in Delta metal), it should be dissolved in HCl and reprecipitated, combining the filtrates for the estimation of zinc. The iron in this case should be estimated by the dichromate titration. (See p. 273 for a note on the procedure in the case of all the copper not having been removed.)

The ammoniacal filtrate is then tested for nickel by adding 5 cc. of the glyoxime reagent and boiling. If a precipitate forms, excess of dimethylglyoxime must be added and the resulting precipitate filtered off, washed with hot water, and filtered off through a Gooch crucible for weighing. Note, however, that HNO_3 interferes somewhat by decomposing the reagent, but the difficulty is not serious with the traces of nickel found in brasses and bronzes.

Zinc is estimated in the filtrate. It is best to separate the zinc first as ZnS, which is accomplished by saturating the solution with H_2S and filtering after digestion on the hotplate. Do not attempt to wash the precipitate or it will become slimy and will be liable to pass through the paper ; in any case, it is very slow filtering. Wash the dirty white

precipitate off the opened-out paper and dissolve it in a little hot dilute HCl, pouring the acid over the paper to remove adhering sulphide and then rinsing once or twice with cold water. Boil the solution to expel H_2S and dilute to 100 cc. Estimate the zinc as phosphate (see p. 133), or by titration (p. 136).

Manganese, if present, will probably show itself during the electrolysis by producing the pink coloration of MnO_4^-, and some MnO_2 may be deposited on the anode with the PbO_2. If the deposit is heavy, it is advisable, after weighing, to dissolve it in dilute HNO_3 to which a small crystal of Na_2SO_3 has been added, and then, after boiling off SO_2, to test the solution with a little sodium bismuthate. If no pink coloration is produced it is almost certain that no manganese is present in the alloy. If manganese is found, the iron should be thrown down only after saturating the solution with bromine, in order to bring the manganese down with the Group III metals. The precipitate is redissolved in HCl and an acetate separation is performed ; the iron is estimated as usual, and the manganese in the filtrate by re-precipitation with Br_2 and NH_4OH. The traces of MnO_2 from the anode may usually be ignored ; if, however, the colour produced by the bismuthate is deep, titrate the solution with $FeSO_4$ and add the result to the main manganese result. Note, here, that *manganese* " *bronzes* " are really 60 : 40 *brasses* with some of the zinc replaced by manganese.

Cadmium is estimated in a separate sample, taking 5 gms. at least as the amount of this constituent is usually very small. Dissolve the alloy in HNO_3, boil off fumes, and dilute somewhat ; filter off any SnO_2. Electrolyse to remove copper and lead. Add 10 cc. of H_2SO_4 and evaporate to fumes. Cool, and take up the residue in water ; dilute to 500 cc. and saturate with H_2S. Now add dilute ammonia with constant stirring until a precipitate *begins* to form ; allow this to settle, and decant, discarding the clear solution. Dissolve the precipitate in HCl, and after diluting suitably, again saturate with H_2S. Once more decant off the solution, this time filtering through a pulp. The precipitate contains CdS, contaminated probably with a little CuS and some ZnS. Digest it in a little hot 10 per cent. HCl and filter if necessary (this removes any CuS). Add sodium carbonate solution until a precipitate forms, and then 10–20 cc. of saturated KCN solution until the precipitate re-dissolves. Pass H_2S again, when CdS alone is precipitated, Cu and Zn being in the form of complexes undecomposed by H_2S. Estimate the cadmium as sulphate (p. 71).

BRONZE.

Bronze is an alloy of copper and tin, the usual proportions being approximately 90 : 10, but alloys with more tin are used, viz. *bell-metal* (80 : 20) and *speculum metal* (70 : 30). *Gunmetal* is a variety of bronze containing up to 1 per cent. of lead and about 2 per cent. of zinc. *Phosphor bronze* contains up to about 1 per cent. phosphorus. Other " bronzes " are *aluminium bronze*, in which aluminium replaces tin, and *manganese* " *bronze*," which is not a true bronze at all, but a brass containing 2 or 3 per cent. manganese.

Analysis (Bronze, Gunmetal, Phosphor-bronze).—Weigh 1 gm. of the drillings into a small, wide beaker and attack with 20 cc. of 1 : 1 HNO_3, taking care that nothing is lost by spraying. When the action ceases, remove the cover and evaporate the solution to low bulk (syrupy consistency) ; add 5 cc. of HNO_3, dilute to 25 cc. and boil for 5 minutes, then digest for one hour on the hotplate, covering the beaker. The residue usually remains as compact pseudo-morphs of the original drillings, and consists of metastannic acid. Decant the clear solution through a compact pulp, avoiding the transference of the residue as far as possible. Break up and crush the particles of metastannic acid with the tip of a glass rod, add 5 cc. of HNO_3 and 20 cc. of water and again boil, under a cover-glass. Decant the clear solution through the filter and then rinse the insolubles out of the beaker with a jet of hot 5 per cent. HNO_3 from a special wash-bottle. Wash the residue thoroughly with hot dilute nitric acid, dilute the filtrate to 100–120 cc., and electrolyse it for copper and lead. Meanwhile, transfer the residue to a porcelain crucible, char off the paper and finally ignite to SnO_2, which is weighed.

Note that this residue adsorbs rather badly, and that it will always include traces of copper, lead, and especially iron, particularly if much of that metal be present ; fortunately, however, this is not generally the case. If the double acid treatment following the crushing of the coarser particles of residue be followed out, the adsorption will be small, and may be ignored for ordinary purposes when the tin present is under 12 per cent. (*i.e.* for ordinary bronzes). For special work, however, the residue must be " purified " after weighing, as follows:

Mix the residue with 5 times its weight of 1 : 1 Na_2CO_3 + sulphur mixture in the porcelain crucible in which the ignition was carried out. Cover the crucible and fuse the mass over a Meker or blast Bunsen, continuing the heating until the flame of burning sulphur just expires. Allow the crucible to cool, still covered, and then extract the thiostannate with hot water. A deep brown or yellow solution results, the colour being due to the presence of poly-sulphides ; the tin is present in solution as Na_2SnS_3, with Fe, Cu and Pb as insoluble sulphides. Cover the beaker and heat the solution on the hotplate, adding a concentrated solution of Na_2SO_3 drop by drop to the hot solution until the colour fades to a pale straw. This addition converts polysulphides into thio-sulphates and sulphates, and tends to prevent the insoluble sulphides, especially FeS and ZnS, from ' going colloidal ' and passing through the paper. Filter off through a small, compact pulp, changing the receiver before venturing to wash the precipitate, as a precaution against FeS and ZnS passing through. If the filtrate is seen to be dark and/or muddy, passing through has taken place and the filtrate must be re-filtered. A slight dark coloration is not serious, although it means that some iron is being lost.

Wash once or twice with very dilute Na_2S solution and once with cold water, allowing the pulp to drain completely each time. Transfer the precipitate and pulp to a porcelain crucible and, after charring off the paper, gently roast the sulphides to oxides, which are then weighed. Subtract this weight from the original weight of SnO_2. Treat the oxides, in the crucible, with a few drops of HNO_3, (1 : 1) ; filter, if

necessary, through another small pulp, and transfer the runnings to the main solution for electrolysis. Note how much Cu, Pb, etc. is retained by the SnO_2 precipitate ; if it amounts to more than about ·2 mgms. there is something wrong with the manipulation.

Iron.—Add excess of NH_4OH to the solution after electrolysis, boil, and filter. Dissolve the precipitate in a few drops of HCl, reduce with $SnCl_2$ and titrate with dichromate solution ; or, if the precipitate is small, weigh as Fe_2O_3.

Zinc.—Pass H_2S through the filtrate from the iron determination and bring the zinc down as ZnS, which should be a dirty grey at the worst. Wash once only, as there are no other metals to be separated. If the precipitate is small (Zn below 2 per cent.) it may be ignited and roasted to ZnO in the mouth of the muffle. If, as is sometimes the case, the zinc is considerable (5 per cent. and over), it should be estimated as phosphate, or titrated if the ferrocyanide solution has recently been standardised. It is not worth while standardising for an occasional titration.

PHOSPHOR-BRONZE.

This introduces a complication. Treatment with HNO_3 or aqua regia oxidises phosphorus to P_2O_5, and this will all be found in the SnO_2 residue as tin phosphate. On attacking a phosphor-bronze with HNO_3, the SnO_2 will be found to be grey in colour, owing to the incomplete oxidation of the phosphorus during the brief contact with the acid ; in order to obtain quantitative conditions, therefore, it is essential to digest the residue in conc. HNO_3 (the fuming acid is best) until the grey becomes white ; also, the particles must be crushed in the beaker so that the oxidising agent may act properly. Otherwise, the main analysis is as already described, except that it must be remembered that the phosphorus will be weighed with the stannic oxide precipitate.

Phosphorus.—Weigh 0·5 gm of the alloy into a 250 cc. Erlenmeyer flask and attack it with conc. HNO_3 (dens. 1·42) plus bromine ; or, and possibly preferably, with fuming HNO_3 (dens. 1·50). Digest the metastannic acid at the boiling-point until the residue is pure white, breaking up the pieces with the rounded end of a glass rod. When this is achieved, add an equal volume of conc. HCl and boil, adding more HCl if necessary, *i.e.* if the metastannic acid shows any reluctance to dissolve. When the solution is quite clear (dark green), add 3 cc. of 10 per cent. $FeCl_3$ solution from a pipette, dilute to 100 cc., cool somewhat, and carefully add excess of NH_4OH. Boil for a moment to collect the precipitate consisting of $Sn(OH)_4$, $Pb(OH)_2$ and $Fe(OH)_3$, plus P_2O_5 ; allow it to settle as far as possible and then filter it off on a non-ashless paper. Wash once or twice with water containing a little NH_4OH until the bulk of the copper has been removed, then open out the paper and wash the precipitate back into the flask. Pour a little 1 : 1 HCl over the paper to remove adhering precipitate, and wash again with water. Heat the contents of the flask until the solution is clear, adding more HCl if necessary, but do not overdo the addition of the acid, or it may be necessary to dilute considerably if tin is to be completely precipitated by H_2S. The tin is then separated by one of the following methods:

(*a*) Dilute so that the solution contains not more than 10 per cent. of HCl by volume and saturate with H_2S. When all the SnS_2 is down, warm the mixture gently on the hotplate to coagulate the precipitate, and decant the clear liquid through a non-ashless paper ; wash the precipitate on to the paper with water and allow the filter to drain completely. Wash free from Cl^- with cold water. The SnS_2 may be used for a direct estimation of tin (see p. 91), but remember that it will contain traces of lead and copper. Boil the filtrate until H_2S is expelled ; add a few drops of HNO_3 to re-oxidise the iron (*), followed by a bare excess of NH_4OH added to precipitate the phosphorus as $FePO_4$ together with the excess of iron as hydroxide. Boil for a minute or two and filter hot through a non-ashless paper. Wash once with hot water to remove the bulk of the Cl^-, which interferes somewhat with the precipitation of the phosphomolybdate ; open out the paper and wash the precipitate back into the beaker, taking care that the volume does not exceed 25 cc., including a wash with hot 1 : 2 HNO_3 to remove adhering precipitate from the paper. Now add 8 cc. of NH_4OH and 12 cc. of HNO_3 and complete the precipitation and estimation of the phosphorus exactly as described on p. 295.

(*b*) A rather concentrated solution is best. Introduce a strip of pure zinc foil and set the beaker (covered) on the hotplate in such a position that a rapid evolution of hydrogen is obtained. Metallic tin is precipitated on the zinc. At the end of ten minutes or less, pour the solution through a small free-running pulp filter upon which a scrap of zinc foil has been placed in order to preserve reducing conditions and so prevent re-solution of the tin while filtering and washing. Wash well with hot water to which a little HCl has been added in order to maintain the evolution of hydrogen. Re-oxidise the hot filtrate with a few cc. of HNO_3 and complete the estimation as before [from the mark (*)].

Note 1.—It is essential to maintain an excess of zinc and to keep the hydrogen coming off at a brisk rate. It may be necessary to add more acid, but it is advisable to keep the acid content as low as possible, as if undue amounts of zinc are brought into solution, there will be trouble in precipitating the iron with NH_4OH, owing to the co-precipitation of $Zn(OH)_2$.

Note 2.—The precipitated tin may conveniently be dissolved in HCl (in an atmosphere of CO_2) preparatory to its titration with standard iodine. Use a 250 cc. Erlenmeyer flask and hook the CO_2 delivery tube over its lip. The flocculent precipitate dissolves very readily in 40 cc. of 2 : 1 HCl, aided by gentle heating. When the metal is all in solution (ignore traces of insolubles, which are probably small amount of metallic copper and lead, and will not affect the result), the flask and its contents are cooled under the tap with the CO_2 still passing 100 cc. of cold recently boiled (*i.e.* air-free) water are then added and the solution titrated at once with the standard iodine. The results are excellent.

Note 3.—If the tin is not directly estimated after separation from phosphorus as described, the phosphorus found is calculated to P_2O_5 and the result is subtracted from the weight of the " SnO_2 " precipitate For high phosphorus bronzes and for accurate work, method (*b*) and the procedure indicated in *Note* 2 should be adopted.

ALUMINIUM BRONZE.

This alloy usually contains no tin, this being replaced by up to 10 per cent. of aluminium. The method of analysis is as described under Brass as regards attack and the removal of copper and lead. After electrolysis, the solution is transferred to a wide 400 cc. beaker and 5 cc. of H_2SO_4 are added ; the solution is then evaporated to fumes, care being taken to avoid spurting as the solids begin to separate. The residue is taken up in 50 cc. of water, boiling if necessary. If a slight, white, gelatinous precipitate remains at this stage, it should be filtered off, well washed with dilute acid (HCl or H_2SO_4) and weighed, after ignition, as SiO_2. (Most aluminium contains silicon.)

To the main filtrate 2 gms. of ammonium phosphate are added, followed by dilute ammonia until a slight permanent precipitate forms. This is cleared with a drop or two of HCl, and about 5 cc. excess acid are added. The neutralisation and re-acidification must be carefully carried out, as the amount of free acid present is important. The solution is diluted to at least 250 cc. and 5 gms. of sodium thiosulphate in saturated aqueous solution are added. The solution is boiled, 25 cc. of 1 : 3 acetic acid are added, and boiling is continued until the precipitated sulphur coagulates well ; the cake of coagulated sulphur should be removed separately, if possible.

The solution is decanted carefully through a free-running pulp filter and the precipitate washed free from Cl^- with hot water, ignited at redness until pure white, and weighed as $AlPO_4$.

The filtrate contains the iron that was originally present. To estimate it, re-oxidise Fe^{++} in the hot solution with a few cc. of HNO_3 and add excess of NH_4OH ; boil, and filter off the $FePO_4$. Wash well, redissolve in HCl, and estimate iron by reducing and titrating with standard dichromate. Note that the precipitate is *not* hydroxide but phosphate.

LEADED BRONZE.

Occasionally lead is added to copper in quantities up to 30 per cent. or 40 per cent., and to bronzes up to 15 per cent. for use in bearings. These alloys usually contain tin, and occasionally nickel also, as these metals are supposed to have the effect of increasing the solubility of lead in copper, a solubility which, normally, is nearly zero. The proportions of lead render the ordinary electrolytic method of estimation impracticable, and for the analysis the following method is used:

Weigh 1 gm. into a wide 400 cc. beaker. Attack the alloy with HNO_3 as usual. If, on slight dilution and boiling, no SnO_2 separates, add 10 cc. H_2SO_4 and evaporate to fumes. If SnO_2 does separate it is essential to treat it as described under Bronzes, after which the evaporation with H_2SO_4 is performed.

Dilute to 100 cc., heating, if necessary, to dissolve the anhydrous $CuSO_4$, and allow the beaker to stand in a cool place until the $PbSO_4$ has settled out well. Filter through a weighed asbestos Gooch, and complete the estimation of the lead as described on p. 46.

The filtrate, with or without the addition of 5 cc. of HNO_3, is then

electrolysed for copper, and Fe, Ni and Zn are estimated in the solution after electrolysis, for which, see under Bronze, p. 305.

BISMUTH, ARSENIC AND ANTIMONY.

These three metals are usually found in traces in copper alloys, and arsenic is an essential constituent of copper used for certain purposes. As far as the analytical estimation of As, Bi and Sb is concerned, the same methods can be used whatever the nature of the alloy.

Bismuth.

Weigh 5 gms. into a 400 cc. beaker and dissolve in 30 cc. of 1 : 1 HNO_3. Evaporate the solution to a syrupy consistency, dilute, boil, and filter off any SnO_2 that separates, washing with hot 5 per cent. HNO_3. Make the filtrate strongly ammoniacal and add 10 cc. of a saturated solution of Na_2HPO_4. Stir well, and allow the beaker to stand overnight. Filter through a small pulp, wash with dilute NH_4OH until the bulk of the copper has been removed ; then dissolve the precipitate, which consists of lead, bismuth and ferric phosphates, off the paper by running a little hot dil. HCl through the filter, followed by cold water, catching the solution in a small, wide beaker. Add 2 cc. of H_2SO_4 (more if there is much Pb) and evaporate to fumes. Filter off $PbSO_4$ and wash once or twice with cold 5 per cent. acid. To the filtrate, which contains traces of copper, together with all the bismuth and the iron, add $NH_4OH + (NH_4)_2CO_3$ and boil ; bismuth and iron are precipitated, copper remains in solution. Filter on a small pulp and wash with water. Again dissolve the precipitate off the filter, this time with a few drops of hot dil. H_2SO_4 ; add a crystal of Na_2SO_3 and boil until Fe^{+++} is reduced and all the SO_2 expelled. Then add a single crystal of KI ; a vivid yellow coloration indicates the presence of bismuth. Estimate the bismuth colorimetrically, as described on p. 70.

Note 1.—$BiPO_4$ is insoluble in ammonia.

Note 2.—It is necessary to remove lead, as PbI_2 is yellow.

Note 3.—Fe^{+++} must be reduced or iodine will be liberated from KI and this might be mistaken for the coloration due to bismuth iodide.

Arsenic and Antimony.

These are separated by the distillation method. See Separations, p. 249, also pp. 78 *et seq.* under the respective metals.

NICKEL ALLOYS.

(*CUPRO-NICKEL* and *NICKEL-SILVER*, *CROWN METAL* and various electrical resistance alloys.)

Cupro-nickel is met with in the form of 85 : 15, 80 : 20, 70 : 30 and 60 : 40 alloys, which usually also contain considerable amounts of iron and sometimes manganese. Nickel-silvers are ternary alloys of Cu-Ni-Zn with, usually, small percentages of iron and lead; their composition

varies, the best qualities being those with the highest percentages of nickel, and these are also the whitest in colour. The ordinary analysis lies between the following limits: Cu = 65–40 per cent., Zn = 30–15 per cent., Ni = 6–35 per cent.

Cupro-Nickel.—Weigh 1 gm. of the drillings into a small, wide beaker and attack with 10 cc. of HNO_3 diluted somewhat with water. Evaporate the solution to a syrupy consistency, dilute slightly, and boil. Filter off any SnO_2 and weigh it after ignition. Electrolyse the filtrate for Cu + Pb. To the solution after electrolysis, add H_2SO_4* and evaporate to fumes. Make ammoniacal and boil ; filter off and wash the $Fe(OH)_3$ with boiling water, ignite to Fe_2O_3 and weigh. If the precipitate is considerable, redissolve it in hot 10 per cent. H_2SO_4 and re-precipitate, the filtrate being added to the main solution containing the nickel.

Estimate the nickel in the main filtrate by electrolysis (see p. 116); or the metal may be precipitated from an aliquot part of the solution (not over 0·1 gm. Ni) as the dimethylglyoxime compound.

If manganese is present, it will be found in the solution after the nickel has been removed (but note the possibility of MnO_2 being precipitated as an anodic deposit if lead be present). The manganese may be recovered and estimated (1) by re-acidifying, and after saturating the solution with Br_2, adding a bare excess of NH_4OH and boiling ; it is weighed as Mn_3O_4.

Nickel-Silver.—Weigh 0·5 gm of the drillings into a small, wide beaker and dissolve in 15 cc. of 1 : 1 HNO_3. Evaporate to syrup, dilute and boil ; filter off any SnO_2 and weigh. Electrolyse the filtrate for Cu + Pb. Add 5 cc. H_2SO_4 and evaporate to fumes in order to remove NO_3^- ; dilute to 50 cc. and add NaOH solution cautiously until nearly neutral (use methyl orange to show this). Complete the neutralisation by adding saturated $NaHCO_3$ solution until the indicator becomes decidely yellow, and a slight turbidity remains. Transfer the solution to a stout flask and re-acidify by adding 1·12 sp. gr. formic acid until the pink colour is restored ; then dilute the solution so that there is 0·15–0·20 gm. Zn per 100 cc. Add 0·5 cc. per cent. excess of the acid and heat to 80° C. Precipitate the zinc from the acid solution using a rapid current of H_2S. When the ZnS has settled completely, cork the flask securely and stand in a warm place for an hour. The precipitate filters well and shows no tendency to " go colloidal " on washing. Iron and nickel will remain unprecipitated.

Note that ZnS may also be separated from H_2SO_4 solution. Dithionic acid, $H_2S_2O_6$, has also been used to obtain a solution containing $[H^+]$ between 10^{-2} and 10^{-3}.

The nickel is estimated in the filtrate by electrolysis after boiling off the H_2S (see p. 116).

Iron is best estimated in a separate sample as follows: Weigh 1 gm. and attack it as already described. Add 5 gms. of NH_4Cl and make the solution ammoniacal ; boil, and filter off $Fe(OH)_3$, which will contain the lead and some copper, nickel and zinc, even after washing with hot, very dilute NH_4OH. Dissolve the precipitate in a little HCl, reduce the

* See Estimation of Nickel by Electrolysis (p. 116) for information as to how much H_2SO_4 is required here.

Fe^{+++}, and titrate with dichromate. Note that if a considerable amount of lead is present the results may be slightly high, though there should be no precipitation of lead chromate in the acid solution. The lead will have already been estimated so that the analyst will know whether or not there is likely to be interference. If the lead amounts to more than about 0·003 gm., it will have to be removed by evaporating to fumes with .5 cc. of H_2SO_4 and filtering, before precipitating the iron.

Another method is: Weigh 0·25 gm. of the alloy and attack as already described.

Electrolyse for Cu + Pb.

Add 2 gms of NH_4Cl followed by excess of NH_4OH, boil, and filter off iron. Redissolve in HCl and re-precipitate, combining the filtrates. Estimate the iron by titration.

Add 100 per cent. excess of dimethylglyoxime, boil for a minute and estimate the nickel by filtering off through a weighed Gooch.

In the filtrate, precipitate the zinc as ZnS, redissolve in HCl and estimate as phosphate, or by titration.

For details of the respective estimations see under the individual metals.

General Note on the Analysis of Alloys containing Copper as a Major Constituent.

It may happen that electrolytic apparatus is not available. In this case, the analysis of all copper alloys will be considerably lengthened and complicated. A method for their analysis without the use of electrolytic methods is as follows:

Weigh 1 gm. of alloy and attack it with HNO_3 as usual, removing any SnO_2 as described under Bronze. Add 10 cc. of H_2SO_4 and evaporate to copious fumes, dilute to 100 cc. and transfer the solution to a tall 600 cc. beaker. When all the sulphates are in solution (boil if necessary), filter off $PbSO_4$ from the cold solution, and weigh. Dilute further to 250 cc. and boil ; meanwhile prepare a saturated solution of 10 gms. sodium thiosulphate in water and add this slowly to the boiling assay solution. At first sulphur alone will be precipitated as a white cloudiness, but suddenly the whole mass will become dark brown in colour, and then black, as Cu_2S separates. Cuprous sulphide settles out very well and filters and washes without any of the difficulties associated with CuS. When the addition of the thiosulphate no longer produces a precipitate, allow the solution to stand for a short time and then filter, washing the Cu_2S with hot water.

Copper is then estimated either gravimetrically as Cu_2S in a Rose crucible or the sulphide is roasted to oxide, this dissolved in HNO_3 and the copper estimated by titration with thiosulphate after adding excess of KI ; both methods are accurate enough, but if a number of estimations have to be made, the volumetric method is to be preferred.

The filtrate from the Cu_2S is well boiled to expel SO_2, and the iron, which has been reduced, is re-oxidised by the addition of several cc. of HNO_3 and continuing the boiling. The rest of the analysis is as

usual, but note that considerable Na^+ has to be washed out of each precipitate.

TIN ALLOYS.

The chief alloys in which tin figures as the main constituent are tin-base bearing metals (Babbitt metal) and solder. Bearing metals contain: Sn, 60–90 per cent. ; Sb, 3–20 per cent. ; Pb, nil–20 per cent. ; Cu, 1–6 per cent., with the occasional addition of Ni.

These alloys are extremely susceptible to segregation and special care must be taken in sampling them. Two methods are good:

(*a*) In the case of an ingot, drillings should be taken from a number of points on both sides. The drillings are placed in an iron crucible and a drop or two of heavy oil added. The alloy is then melted over a small flame, and when the oil is just burnt out, the molten alloy is poured into a basin of water from a height of about 4 feet in a steady stream. The thin-walled granulations are then dried in the air oven.

(*b*) In the case of a smaller sample, the best way is to make several saw-cuts right through the specimen with a coarse-toothed hacksaw, catching the sawings on a piece of clean paper.

Analysis.

Tin.—Weigh out such quantity of the sample as shall contain about 0·4 to 0·45 gm. of the metal (*i.e.* 0·5 gm. of an 80 per cent. alloy, etc.) and dissolve in 50 cc. of 1 : 1 HCl in a covered 300 cc. tall beaker. Place the beaker on the edge of the hotplate until the action slackens and most of the metal is in solution ; Cu, Pb and Sb do not dissolve readily in HCl and will be left as a dark, somewhat flocculent residue, containing, however, some tin. To bring this into solution, add an occasional pinch of $KClO_3$, continuing the gentle digestion, but avoid boiling the solution, as $SnCl_4$ is volatile. Estimate the tin by titration with iodine as described on p. 94. A "standard," using 0·4–0·45 gm. of pure tin must be carried through with each batch of assays.

Antimony.—Weigh 1 gm. of the alloy into a dry 250 cc. Erlenmeyer flask and attack it with 20 cc. of conc. H_2SO_4. Heat the flask over a small Bunsen flame, gripping the neck with a pair of bow tongs and swirling the contents steadily the whole time. The reaction starts suddenly and is rather violent, but is not dangerous. When the reaction is over, boil the acid until the line of condensed acid droplets on the sides of the flask is driven right up into the neck and the interior space is quite free from visible fumes. Set the flask on a piece of asbestos sheet to cool. When sufficiently cool to bear handling, *quickly* pour about 100 cc. of cold water into the flask. This *must* be done quickly and steadily, or there will be a loss of solution by spurting, and the operation is not without danger to the operator's eyes ; if, however the dilution be boldly performed, there is no danger at all. Add 5 cc of conc. HCl to the hot mixture and cool the flask under the tap as quickly as possible.

When quite cold, titrate the solution with standard $KMnO_4$, taking as end-point that point at which a pink colour just '*fills*' the solution the colour fades rapidly in the presence of HCl. Occasionally this

method fails, the solution becoming muddy brown, probably owing to the separation of MnO_2, H_2O. When this occurs there is no remedy, and the estimation should be repeated.

The bromate titration is preferred by some workers, but the writer obtains the most consistent results by the use of the foregoing method.

Lead, Copper, Iron and Nickel.—Weigh 1 gm. into a wide 400 cc. beaker and dissolve it in HCl as far as possible ; bring the insolubles into solution by pouring off the clear liquid into a separate beaker and treating the residue with a *few* drops of HNO_3 followed by the addition of 10 cc. of HCl and boiling. Evaporate this portion nearly dry to expel most of the NO_3^- and then add the decanted portion. *Note*: A little tin may be lost during the evaporation of the oxidised solution owing to the volatility of $SnCl_4$; this does not matter, as tin is not being estimated in this portion of the sample. (The -ic chlorides of the other metals are not volatile at low temperatures.)

Dilute the solution to 250 cc. and add 5 gms. of tartaric acid, followed by conc. NaOH solution until the mixture is decidedly alkaline (say, 10 cc. of 10 per cent. NaOH in excess). If a white precipitate forms here, insufficient tartaric acid has been added. Pass H_2S through the hot solution, or, add 3 gms. of solid Na_2S and digest the mixture until the precipitate settles well.

The precipitate consists of CuS, PbS, FeS, and NiS. Filter through a double non-ashless paper (the caustic will break an ashless paper), and wash not more than twice with cold water, catching the washings in a clean beaker in case the precipitate passes through, as it is apt to do. Open out the paper and wash the precipitate back into the beaker with hot water ; pour 20 cc. of hot 1 : 2 HNO_3 over the paper to dissolve any adhering precipitates and rinse with water several times. Evaporate the solution to low bulk, dilute somewhat, and filter off any oxidised Sn + Sb that may separate. To the filtrate add 5 cc. H_2SO_4 and evaporate to fumes, filtering off the $PbSO_4$, which is weighed for the estimation of lead. Electrolyse the filtrate for copper ; or, if the copper content is low, pass H_2S and roast the CuS to CuO, in which form the copper may be weighed. As an alternative to electrolysis for copper in quantities above about 2 per cent., the separation as CuS followed by estimation by a volumetric method may be adopted.

Iron.—Make the solution from the electrolysis just ammoniacal, boil and filter. As the precipitate of $Fe(OH)_3$ is usually very small, and there are usually no other metals to be separated, it is sufficient to ignite to oxide and weigh.

Nickel.—Test the filtrate from the iron estimation for nickel by adding a little dimethylglyoxime solution and boiling. If a precipitate settles out, add excess of the reagent and estimate the Ni as usual (see p. 116).

It is advisable to test the filtrate from the nickel for other metals by passing H_2S through the ammoniacal solution. Occasionally a slight precipitate of ZnS is obtained.

Note.—The $PbSO_4$ left insoluble in the course of the estimation of the antimony may be employed for a check estimation of the lead, if required, but note: (1) It must be filtered off immediately, as basic antimony sulphate may be precipitated on standing, and (2) the results are liable to be a trifle low on account of the solubility of $PbSO_4$ in HCl.

SOLDER.

Solder is essentially a mixture of tin and lead, but antimony is occasionally added. Common proportions are: Sn, 50 to 30 per cent. ; Pb, balance ; Sb, if present, about 2 per cent.

Analysis :

Tin.—Tin is estimated as described on p. 312 for bearing metals.

Lead.—In the absence of antimony, attack the alloy (1 gm.) with a little aqua regia. When all is dissolved, add 10 cc. of H_2SO_4 and evaporate to fumes. Estimate the lead as $PbSO_4$, but do not unduly prolong the filtration or some tin may separate as a basic compound.

Antimony.—As described for Bearing Metals. If antimony is present, the lead must either be estimated in the solution remaining after the antimony titration, or else the longer method described under Bearing Metals must be adopted. This is rarely necessary in practice, as the amount of antimony put in solders is so small that there is very little tendency for basic salts to precipitate on standing.

LEAD ALLOYS.

The most important lead alloys are the numerous lead-base bearing metals. These are, essentially, lead and antimony, but tin and copper are usually added to confer additional hardness and stiffness. Lead will represent at least 80 per cent. of the alloy in most cases. " Hard lead " is Pb + Sb up to about 20 per cent. Lead is also hardened by the addition of arsenic (shot) ; also by the addition of barium and/or calcium, or even sodium, these being introduced electrolytically. Alloys containing copper plus barium and calcium present a very pretty problem in analytical manipulation.

Analysis :

Lead-Antimony Alloys (*i.e.* " Hard lead ").

(*a*) Weigh 1 gm. of sawings or granulations into a wide 400 cc. beaker and attack with aqua regia. When all is in solution, add 10 cc. of H_2SO_4 and evaporate to copious fumes. Cool, and dilute with about 100 cc. of water, boil, if necessary, to dissolve soluble sulphates, and then allow the $PbSO_4$ to settle out in a cool place. When filtering, examine the solution to make sure that no antimony compounds have separated. In mild cases, the precipitation of basic antimony is marked by an opalescence in the liquid, but if the trouble is serious and an actual precipitate has come down on standing, it is best detected by swirling the beaker and noticing the manner in which the precipitate settles down again. $PbSO_4$ is very dense and crystalline, and settles characteristically as a sort of cone in the centre of the beaker. Antimony compounds will be found to take much longer in settling and to be of a different nature physically, being lighter and more flocculent. If the precipitate is seen to be non-homogeneous, suspect the separation of basic antimony compounds.

If antimony separates, the straightforward method of analysis is unsuitable for the alloy in question, and must be abandoned ; usually,

however, the solution prepared as described remains perfectly clear. If no antimony separates, estimate the lead as before as $PbSO_4$. To the filtrate add excess of NH_4OH and note whether the solution turns blue as a sign of the presence of copper.

(*b*) Antimony is estimated by the H_2SO_4 attack and $KMnO_4$ titration, as described under Tin Alloys (p. 312).

(*c*) If copper is found (this is rather unlikely unless the alloy has been made from scrap) the method given below must be used.

Lead-Antimony-Tin-Copper Alloys (*i.e.* Bearing metals, but with high Pb content instead of Sn content).

(*a*) The methods given for the analysis of Tin Base Bearing Metals may be used.

(*b*) Alternative (preferable for high lead content alloys):

Weigh 0·5 gm. into a wide beaker and attack it with the least possible quantity of aqua regia. Ignore the separation of $PbCl_2$ needles, but make sure, by prodding the sample with a rounded glass rod, that no particles of undissolved metal remain. Evaporate carefully just to dryness ; moisten the crystals with HCl (5 cc.) and again take to dryness ; add 3 cc. of conc. HCl followed by 30–40 cc. of 1 : 1 alcohol and cool completely, constantly stirring the solution. Filter through a weighed Gooch crucible and wash with HCl-alcohol mixture (1 : 10) 5 or 6 times, sucking the crucible quite dry each time. Finally, wash once with a crucible-full of alcohol and dry the crucible and contents at 100° C. in the air oven. Weigh as $PbCl_2$.

Transfer the filtrate containing alcohol and a little HCl to a small flask and distil off the alcohol from a water-bath. Keep the distillate for similar estimations only, as it will be contaminated with a small amount of ethyl chloride. Continue the distillation to near dryness ; rinse the solution out into a beaker and continue the evaporation to complete dryness. Take the residue up in a few cc. of HCl and make a Clarke and Henz separation, by which copper and antimony will be precipitated as sulphides and tin will be present in the filtrate (see p. 251).

Note.—There is no need to oxidise polysulphides here ; simply add the oxalic acid and pass H_2S.

Filter off the CuS + Sb_2S_3 and wash three times with a solution of oxalic acid saturated with H_2S, then with cold water twice. Rinse the precipitate back into the beaker and treat it with a little KOH solution (2 gms. in 10 cc. of water) ; boil for a minute, dilute slightly and filter through a small pulp, washing the CuS with very dilute KOH solution through which H_2S has been passed for a minute or two. Roast the residue (CuS) to CuO and estimate the copper by electrolysis or by the cyanide or thiosulphate titration. It cannot be weighed as CuO on account of the alkali present.

Re-precipitate the Sb_2S_3 in the filtrate by making the solution just acid with HCl. Filter and wash with dilute HCl containing H_2S, estimating the antimony gravimetrically as sulphide. Or, the sulphide may be dissolved in conc. HCl (avoiding boiling, which would volatilise the antimony as $SbCl_3$) and the metal estimated iodometrically (see p. 77).

In the original filtrate, containing the tin in oxalic acid solution, the tin may be estimated by electrolysis, but this is not to be recommended,

though good results can be obtained if great care be taken. It is preferable to acidify strongly with HCl and precipitate out the tin on a piece of zinc foil, finally redissolving the metal in HCl in a neutral atmosphere and titrating with iodine (see p. 307).

On the whole, it is best to use the first method if possible, viz.:

1. Estimate Pb as $PbSO_4$. (Method 1, Solder.)
2. Estimate Sn by titration with iodine.
3. Estimate Sb by solution in H_2SO_4 and titration with $KMnO_4$; if this fails, try the bromate method or titration with iodine.
4. Estimate Cu in the filtrate from the $PbSO_4$ by precipitating with H_2S, and, after one wash, digesting the precipitate in a little 20 per cent. KOH solution to extract Sb + Sn as thio-salts. Dilute somewhat, and filter, washing once or twice. Roast the CuS to CuO, dissolve this in HNO_3 and estimate the copper by any convenient method.

Note 1.—Although the separation of $PbCl_2$ with alcohol is a lengthy method of analysis, it is very useful in cases where Sb and Sn are found to precipitate out on diluting the H_2SO_4 solution in order to allow the $PbSO_4$ to settle out. These cases are, however, very rare, and the writer only uses the insolubility of $PbCl_2$ in alcohol in the analysis of certain bearing metals which contain barium and calcium dissolved in a lead base; with care and proper attention to manipulation, especially to acidity, there should be no trouble in separating lead as sulphate even from large amounts of tin and from up to 20 per cent. of antimony.

Note 2.—It may occasionally happen that a sample of hard lead bearing metal, which should normally contain, say, 10 per cent. antimony and a little copper, may be suspected of having picked up a little tin, owing to improper sorting of foundry scrap. It is by no means an easy matter to be sure whether small quantities of tin are present or not, especially as the whole of the alloy is made up of Group II metals and antimony is certainly present. If antimony were absent, it would, of course, be a simple matter to attack the alloy with HNO_3, when any tin would be left as insoluble SnO_2, but in the presence of antimony this reaction is masked.

In cases like this, weigh 1 gm. into a beaker and attack it with a solution containing 3 gms. of tartaric acid in 20 cc. of water to which 10 cc. HNO_3 have been added. When the reaction ceases, concentrate to a low bulk, dilute to 50 cc. and boil. If nothing separates out, tin may be presumed to be absent, as the tartaric acid will bring antimony into solution as a complex.

Lead-Arsenic Alloy (Lead shot).

Lead is estimated by attacking the sample with HNO_3 and then evaporating the solution to fumes with 5 cc. of H_2SO_4. (See Method 1 in the foregoing).

Arsenic is estimated in a 1 gm. sample as follows:

Dissolve 1 gm. of the alloy in HNO_3 and evaporate the solution to dryness. Treat the dry residue, which contains lead arsenate, with 20 cc. of HCl and again evaporate to dryness. Take up the chlorides in 50 cc. of 1 : 1 HCl and rinse the insoluble $PbCl_2$ two or three times with acid of the same strength, pouring the washings into a clean beaker; finally transfer the crystals to a Buchner funnel or Gooch crucible and

suck them quite dry on the water pump. Cool the acid filtrate in ice water, if necessary, and saturate with H_2S, passing the gas for at least an hour. Digest, with occasional shaking, until the precipitate settles out completely, and estimate the arsenic by any convenient means ; the author prefers to estimate it as magnesium pyroarsenate, thus: Filter off the precipitate, consisting of a mixture of As_2S_3 and As_2S_5, and wash it thoroughly with 1 : 1 HCl containing H_2S. Then wash back into the precipitation beaker and dissolve in a little strong ammonia or ammonium carbonate solution. Add 2 or 3 gms. of solid NH_4Cl and complete the precipitation of the arsenate as described on p. 82.

Alternatively, and if the arsenic is only present in small amounts, the filtrate from the $PbCl_2$ may be rinsed into a 250 cc. distilling flask, 5 gms. of a ferrous salt, preferably ferrous chloride (but sulphate will do) added, and the arsenic distilled over as $AsCl_3$, which may be titrated directly in the distillate as described on p. 85.

Lead-Barium-Calcium Alloy.

A method for the analysis of an alloy of this type is included, not because these alloys are of great industrial importance, but on account of the interesting problems in separation that are involved. An approximate analysis might be: Pb, 96-98 per cent. ; Cu, 1–1·5 per cent. ; Fe, traces ; Ca, about 1 per cent. ; Ba, about 1 per cent. ; Na, ? (Na is possible, but the writer has never met with Na when Ba is present). It will be noticed that three of the four metals with ' insoluble ' sulphates are present, and that barium and calcium are co-present.

Method :

The alloy should be sampled by sawing right through the sample with a coarse hack-saw, and weighings should be made quickly, as the sawings show a decided tendency to oxidise.

Weigh 1 gm. of the alloy into a wide, 400 cc. beaker, and attack it with 15 cc. of 1 : 2 HNO_3. A considerable amount of lead nitrate will separate out (Note [1]) but judicious agitation aided by prodding the sawings with the rounded end of a glass rod suffices to break up the protective coating of crystals and render the attack complete. Carefully evaporate the solution just to dryness ; cover the crystals with conc. HCl and again evaporate, repeating the process two or three times to convert the whole of the nitrates into chlorides.([2]) Finally, wash the crystals by decantation tion ([3]) five times with 10–15 cc. quantities of 1 : 4 HCl, pouring the washes into a tall 600 cc. beaker. There is no need for a filter here, as the crystals are dense and the decantation can be made without the transference of any of the solid. In this strength of hydrochloric acid, $CuCl_2$, $FeCl_3$ and $CaCl_2$ are quite soluble ([4]) and the small amount of $BaCl_2$ that is present dissolves sufficiently to enable the separation to be made complete, as $BaCl_2$, though almost insoluble in conc. HCl, is readily soluble in more dilute acid.

Carefully drain the $PbCl_2$ crystals as far as possible and set aside the beaker containing them for the moment ; dilute the solution to 500 cc., not less, or PbS will not be completely precipitated, and saturate with H_2S in the cold. The precipitate consists of PbS + CuS. Filter through a non-ashless paper and wash the precipitate with very dilute HCl containing H_2S.([5]) Set the filtrate on the hotplate to boil down,

adding a piece or two of broken pot to maintain a steady evolution of gas bubbles. Open out the paper and rinse the sulphides into the beaker containing the $PbCl_2$, dissolving adhering sulphides from the filter by means of a wash with warm 1 : 2 HNO_3 followed by one or two washes with water ; add 5 cc. of conc. H_2SO_4 to the contents of the beaker and evaporate to fumes. Cool, dilute to 50–75 cc., and allow the $PbSO_4$ to settle out in a cool place, finally filtering it off through a weighed Gooch crucible and estimating lead as described on p. 46.

Copper is estimated in the filtrate ([6]) by any of the following methods: (*a*) Electrolysis ; (*b*) precipitation as CuS with H_2S and roasting to CuO ; (*c*) precipitation as Cu_2S by adding thiosulphate ; (*d*) making ammoniacal and titrating with cyanide ; (*e*) neutralising the acid with carbonate, just acidifying with acetic acid and titrating with thiosulphate after addition of excess of KI.

In the meantime the main filtrate will have concentrated considerably and all the H_2S will have been expelled. Add a few cc. of bromine water ([7]) and boil until colourless, so that iron which has been reduced by the H_2S will be re-oxidised. Make the solution just ammoniacal and filter off any $Fe(OH)_3$; ignite and weigh as Fe_2O_3.

In view of the possibility of the presence of sodium, the chromate separation of barium from calcium is not recommended, as it introduces two alien metals. Instead, either of the following may be used: (*a*) To the boiling filtrate from the iron add dilute H_2SO_4 drop by drop until no further precipitation takes place. Digest the precipitate on the hotplate for at least an hour and filter off the $BaSO_4$ on a small pulp filter. With not more than 0·01 gm. of barium and calcium present, no $CaSO_4$ will be precipitated from a bulk of 300–400 cc.

Concentrate the filtrate to 200 cc. and precipitate the calcium by adding 5 cc. of saturated ammonium oxalate solution, followed by dilute ammonia until the solution is just alkaline to methyl orange.

(*b*) To the filtrate from the $Fe(OH)_3$ add 1 gm. of oxalic acid and two drops of methyl orange. Boil, and add dilute ammonia until the indicator *just* changes to full yellow. Digest on the hotplate for 15 minutes and then add 10 cc. of 1 : 3 NH_4OH in excess.([8]) Digest until the precipitate has settled out, filter, and wash with cold water. Estimate the calcium by titration with $KMnO_4$. In the filtrate, precipitate the barium as $BaSO_4$, as described above.([9])

The filtrate from the $BaSO_4$ must now be tested for sodium, though it is unlikely that alkali metals will be found if barium is present. Transfer the filtrate to a platinum dish and evaporate it to dryness on the edge of the hotplate. When salts begin to separate apply the heat very cautiously, as violent spurting is liable to occur ; copious fumes of decomposing ammonium salts are evolved, and finally, when only a slight residue remains, H_2SO_4 fumes come off. Continue heating until the dish is quite dry. If now no residue, or only a faint stain ([10]), be visible on the bright surface, and the rest of the analysis totals to within $\pm$ 0·2 per cent. of 100 per cent., it is safe to assume that no sodium is present. If, however, a noticeable stain remains, or a crystalline residue, take it up in a few cc. of hot water, rubbing the dish well with a rubber-tipped rod to loosen any insolubles. Add one drop of H_2SO_4 and three drops of ammonia ([11]) ; boil for a moment and filter through the smallest

possible pulp into a weighed platinum crucible or capsule. Wash with hot water, a few drops at a time, five or six times, and evaporate to dryness. Heat to expel all fumes and re-weigh. Consider the residue to be Na_2SO_4 (12).

Note 1.—Lead nitrate is nearly insoluble in conc. HNO_3. The addition of water would dissolve it, but would slow down the analysis, as not only would the attack be slower, but the water would have to be evaporated off before passing on to the second operation.

Note 2.—It is essential that no NO_3^- be left in the solution, (*a*) because it oxidises $S^=$ to $SO_4^=$ and $BaSO_4$ may be precipitated out of its place, and (*b*) because if NO_3^- and Cl^- be co-present, the platinum dish will be damaged during the evaporation.

Note 3.—The crystals may be drained quite dry with the exercise of a little care. Pour off as much acid as possible, then tilt the beaker and gently prod the $PbCl_2$ with a glass rod to press the acid out. No solid will be lost if care be taken. It would be possible, and possibly preferable, to do the washing in a Gooch crucible without a filter pad, sucking the crystals as dry as possible on the filter-pump between the washes, but the above method has been found to work well by the writer.

Note 4.—In 1 : 4 HCl, the solubility of $PbCl_2$ is 1·4 gms. per litre.

" " " $BaCl_2$ is about 200 gms. per litre.

In conc. HCl, " $PbCl_2$ is about 25 gms. per litre.

" " " $BaCl_2$ is 0·12 gm. per litre,

all measurements being taken at room temperature (say, 20° C.).

Note 5.—CuS oxidises to CuS_2O_3, thiosulphate-chloride complexes, and $CuSO_4$ under the action of air. This must be prevented at all costs, as, apart from loss of copper, the $CuSO_4$ will precipitate the barium as $BaSO_4$. A wash liquid containing H_2S will prevent this oxidation taking place.

Note 6.—Electrolysis is preferable, but any method will do.

Note 7.—Oxidise with bromine, *not* HNO_3 as usual, since NO_3^- must be kept out of the solution for two reasons, (*a*) the solubility of $BaSO_4$ in HNO_3 and (*b*) the certainty of corrosion of the platinum vessels used later.

Note 8.—This method of precipitation is adopted in order to sharpen the separation. If we approach the precipitation point from the *acid* side, *i.e.* from a state in which the precipitate tends to re-dissolve, the precipitation will be (at first) incomplete. The method has the two effects of (*a*) causing the crystals of the oxalate precipitate to separate out in a relatively large-grained condition, so that they are easier to wash and filter, and (*b*) reducing the tendency for barium to precipitate to a minimum. Later, when the main part of the calcium is precipitated in a form favourable for washing, excess of NH_4OH is added. This brings the remainder of the calcium oxalate down, this compound being almost insoluble in dilute ammonia, though not quite so in pure water.

Note 9.—The second method of separation theoretically is the better,

but both will be found to give identical results with the quantities of barium and calcium mentioned

Note 10.—Usually, of course, a residue is obtained. This is derived from (*a*) impurities in the reagents, (*b*) traces of organic matter charred and not completely oxidised by the H_2SO_4, (*c*) silica and alkalis from the glass ware, (*d*) faulty manipulation.

Note 11.—This serves to precipitate any stray lead, iron or barium that may have escaped separation. It should be possible to pronounce upon the nature of the residue by inspection, *i.e.* alkalis—white crystals which fuse at redness ; organic matter—black stain which burns on heating.

Note 12.—The ideal method of examining this (after weighing) is by the spectroscope. It would also be advisable to test the $PbSO_4$ and the $BaSO_4$ precipitates for impurities by this means.

ALUMINIUM ALLOYS.

Aluminium alloys are of growing industrial importance in these days ; indeed there would seem to be no group of non-ferrous alloys which have such possibilities. Aluminium itself is a soft, weak metal, but though it has important uses in the unalloyed condition, its future undoubtedly lies in its ternary alloys, some of which possess strength comparable to that of mild steel with but one-third of the weight.

Analytically, aluminium alloys resemble steels in one important respect, and that is that the main constituent is never (or very rarely) determined directly, but only by difference ; an important difference from steel is, that apart from the non-metals, the common alloying elements with steel are metals of Groups III and IV, whereas in the case of aluminium alloys they may be, and are, derived from any or all of the groups ; indeed, aluminium alloys are the only important ones which habitually contain a metal of the later groups—magnesium to wit—as an essential constituent.

The chief aluminium Alloys are:

1. Al-Cu, . Al, 97–88 per cent. ; balance Cu.
2. Al-Cu-Zn, . . Al, 83–93 per cent. ; Cu, 2–3 per cent. ; Zn, 5–14 per cent.
3. Al-Cu-Sn, . . Al, 89–92 per cent. ; Cu, 7–10 per cent. ; Sn, 1 per cent.
4. Any of the above alloys may contain up to 1 per cent. Mn or Ni.
5. Al-Cu-Mg, . Al, 94–95 per cent. ; Cu, 3–4 per cent. ; Mg, up to 1 per cent.
6. Al-Si, . . Al, 87–90 per cent. ; balance Si.
7. Al-Cu-Ni-Mg, . Cu, 4 per cent. ; Ni, 2 per cent. ; Mg, 1·5 per cent. ; balance Al.

The above represent the definitely added constituents ; besides these, aluminium alloys invariably contain silicon and iron in small amounts, occasionally lead, and varying amounts of sodium and calcium (derived from the raw materials during manufacture). Remelted aluminium

alloys will contain a certain amount of Al_2O_3. It is not usual to determine calcium, sodium and oxygen in commercial analysis.

As might be expected from the foregoing, there are a number of different methods for analysis of aluminium alloys, the choice of which must depend upon the nature of the alloy under analysis.

Method 1.—Weigh 1 gm. of the drillings into a wide 400 cc. beaker, add 20 cc. of water, followed by 10 cc. of HNO_3, and HCl a drop or two at a time (cautiously) until the alloy is all in solution. When the alloy is dissolved, add 5 cc. of H_2SO_4 and evaporate until fumes are freely evolved, taking all precautions against spurting when the solids begin to separate. Take the sulphates up in 100 cc. of hot water, boiling until all the $Al_2(SO_4)_3$ is in solution, a process which may take some time. If any lead is present in the alloy, it may be recognised by swirling the solution and holding the beaker up to the light, looking upwards through the bottom. $PbSO_4$ settles very rapidly and collects in a small, flat, circular heap in the centre of the beaker, which is readily distinguished from the gelatinous silica which is invariably present in small amounts.

As a rule lead will not be present in important amounts. If no $PbSO_4$ is observed, filter the solution through a small pulp and wash the SiO_2 thoroughly with slightly acidified (H_2SO_4) hot water. Ignite and weigh as SiO_2.

Note.—The SiO_2 is sometimes discoloured by the presence of the graphitic form of silicon. It is not usual to make any allowance for this, as the amount of unoxidised silicon is, in any case, very small.

Filtrate:

If the alloy is a *simple Al-Cu-Zn mixture*, or at least one which contains *no other metals of Group II*, the copper is removed by precipitation on aluminium foil, as follows:

A piece of pure strip aluminium foil, about $3'' \times \frac{1}{2}''$ and bent in the form of a triangle, is placed in the solution and the latter heated on the hotplate. Copper is deposited on the aluminium. After about ten minutes' boiling, the strip of foil is removed and washed down with a stream of H_2S water to remove most of the copper. The foil is then placed in a separate small beaker. The deposited copper is filtered off on a small paper pulp and washed thoroughly with H_2S water; finally a few drops of conc. HNO_3 are poured over the foil from a pipette, while holding it over the filter that carries the separated copper. The conc. acid will dissolve the copper, but will hardly affect the aluminium. The filter is washed free from copper and that metal estimated either by titration with cyanide or by electrolysis of the nitrate after a minute's boiling to expel nitrous fumes.

The solution from the copper is then boiled and poured slowly into a boiling solution of 200 cc. of 5 per cent. NaOH contained in a tall beaker, stirring the alkali constantly during the process. When the $Al(OH)_3$ precipitate has dissolved completely, the solution is boiled for a minute or two and filtered through a free-running pulp, washing the precipitate thoroughly with hot water. The $Fe(OH)_3$ is dissolved off the paper with a little HCl and reprecipitated with NH_4OH. The second precipitate is dissolved in HCl for the second time and iron

estimated volumetrically by titration with dichromate. The two filtrates should be combined for the zinc estimation.

H_2S is passed through the filtrate (or a gram of Na_2S crystals added) until no further precipitation takes place. The solution is digested until the precipitate settles out well, and the latter filtered off on a non-ashless paper, washing once only. The paper is opened out and the precipitate washed back into the beaker, dissolved in HCl, and the zinc estimated volumetrically by titration with ferrocyanide (see p. 136).

Variation (a).—Tin present. Weigh out 1 gm. and dissolve it in 30 cc. of 1·2 sp. gr. HNO_3. This will take considerable time, as Al is only very slowly soluble in HNO_3 ; the solution may be accelerated by the occasional addition of a *few* drops of HF, applied to the centre of the solution after having started the liquid rotating by swirling. By this means the HF is kept in contact with the metal without reaching the glass of the beaker. Evaporate the solution until salts begin to separate out, dilute to about 100 cc., boil for 5 minutes, and filter off through a small pulp filter. Ignite the precipitate in a porcelain crucible, and then brush it out into a weighed platinum crucible, where it is treated with a drop of H_2SO_4 followed by a few drops of HF. Gently drive off the acids by heating on the edge of the hotplate, and ignite at redness. Weigh as SnO_2. The treatment with HF is necessary as the SnO_2 is invariably contaminated with silica.

The solution may very conveniently be electrolysed for copper and lead, and iron and zinc may be estimated in the residual solution as described under Method 1.

Variation (b).—Manganese present. Proceed as described in Method 1 until after the separation of copper. At this point, add a drop or two of bromine to the solution and stir the mixture until it takes a deep yellow tint. Now pour the mixture into the boiling NaOH and add a few cc. of alcohol. $Fe(OH)_3 + MnO_2,H_2O$ is precipitated. The precipitate is filtered off and washed thoroughly with hot water ; it is then dissolved in HCl and re-precipitated with Br_2 and NH_4OH. The iron and manganese are separated by the "*acetate method*" (see p. 259) and separately estimated, the iron by titration with dichromate, and the manganese by re-precipitation with Br_2 and NH_4OH.

Note.—The alcohol is added to decompose any $MnO_4^=$ or MnO_4^- which might be formed in the oxidising alkaline solution.

Variation (c).—Nickel present. After the separation of the iron, make the solution nearly neutral with HCl and precipitate the nickel with dimethylglyoxime before proceeding with the separation of the zinc.

Variation (d).—Magnesium present. In Method 1 magnesium accompanies the aluminium and is found in the filtrate after pouring the solution into the NaOH. It is impracticable to separate these two metals from this solution, and, indeed, it is a difficult problem in analysis to separate magnesium from aluminium at all satisfactorily. In the analysis of an alloy containing magnesium (*Magnalium, Duralumin,* etc.) it is best to use the attack of Method 2.

Method 2.—The drillings (1 gm.) are attacked with 50 cc. of 10 per cent. NaOH. The reaction is rather vigorous, and the caustic solution heats up rapidly. In order to avoid loss of solution, therefore, it is

advisable to stand by with a beaker of cold water, ready to pour this into the reaction beaker in case of undue frothing. When the reaction is complete, dilute the solution to 200 cc. and boil for a minute or two. Filter off through a small pulp and wash with cold water five or six times. The solution contains (most of) the aluminium and zinc (and silicon), and the insoluble residue on the filter consists of metallic lead, copper, tin, iron, manganese, nickel, magnesium and some aluminium.

The insolubles are dissolved off the filter with a little warm 1·2 sp. gr. HNO_3, followed by several washes with hot dil. HNO_3. The filter is placed in a porcelain crucible and set aside for the moment while the solution is evaporated to low bulk. The solution is then diluted and the mixture boiled for five minutes ; it is then filtered, if necessary, owing to the separation of SnO_2, and after thorough washing with hot dil. (5 per cent.) HNO_3, the filter paper and precipitate are transferred to the porcelain crucible which contains the original filter, ignited and the SnO_2 weighed.

The filtrate is electrolysed to separate and estimate copper and lead. The solution remaining from the electrolysis is then treated with 2 gms. of NH_4Cl and made just ammoniacal ; it is then boiled, and the precipitate, containing iron and aluminium as hydroxides, is filtered off and well washed with boiling water. If the precipitate is bulky, it must be dissolved in HCl and re-precipitated with more NH_4Cl and NH_4OH, combining the filtrates. The iron is then estimated by titration with dichromate, as this conveniently avoids the necessity of separating the remaining aluminium.

Note.—If manganese be present (this may usually be recognised during the electrolysis) the Group III metals are precipitated with $Br_2 + NH_4OH$ instead of NH_4OH alone. An "*acetate*" separation of the iron and manganese is then necessary before the individual estimations are made.

The solution contains nickel, magnesium and traces of zinc. It is not convenient to separate the nickel with dimethylglyoxime in the presence of so much NO_3^-, and for this reason it is usual to precipitate nickel and zinc with H_2S or ammonium sulphide, filtering immediately and washing with dilute ammonium sulphide solution. The small amount of zinc is then separated from the nickel by extracting the precipitate with hot 5 per cent. HCl, in which NiS is insoluble. The HCl solution is reserved.(*) The NiS is then roasted to NiO which is dissolved in HCl and the nickel estimated by precipitation with excess of dimethylglyoxime and weighing in a Gooch crucible (see p. 116).

The filtrate from the alkaline sulphides is slightly acidified with HCl and boiled to expel H_2S, before precipitating the magnesium as phosphate.

The original solution, containing aluminium and zinc as aluminate and zincate, is then treated with H_2S or with a little solid Na_2S to precipitate the zinc ; the precipitate is digested until it settles out well, when it is filtered off through a non-ashless paper and washed once or twice with dilute Na_2S solution. The precipitate is then dissolved off the paper with HCl after washing as much as possible back into the beaker, and the small amount of aluminium that remains is separated by precipitation with NH_4Cl and NH_4OH, repeating the precipitation

if necessary. The solution (*) is then added to the filtrate and zinc is estimated either by precipitation as phosphate, or by titration with ferrocyanide.

This second method, though it appears rather complicated, is in reality shorter in practice than Method 1. The drawback is that the attack with NaOH does not give a perfectly quantitative separation of the aluminium and zinc from the other metals, and small amounts of copper, etc. are liable to pass into solution in the alkali. It is of course possible to detect whether this has taken place to a serious extent when the zinc is precipitated as ZnS. The precipitate should, of course, be pure white in colour ; as a rule, however, it is pinkish or brown, owing to the presence of small proportions of the metals the sulphides of which are dark in colour. If, however, the colour of the ZnS is not unduly dark the separation may be considered satisfactory.

The writer knows of no other method by which magnesium may be conveniently estimated.

Special Notes.—1. Direct estimation of manganese.

Manganese may be estimated directly (as a check) by attacking a separate weighing of the sample with HNO_3 and at once applying the bismuthate method. This gives perfectly accurate results.

2. Direct estimation of nickel.

Nickel may also be estimated separately in a separate solution by attack with HCl, followed by the addition of a few drops of HNO_3 to bring copper, lead, etc. into solution. Ten cc. of H_2SO_4 are added to the solution and the latter evaporated to fumes, cooled and the residue extracted with 100 cc. of hot water, boiling until all solubles are in solution. The solution is cooled under the tap and the $PbSO_4 + SiO_2$ filtered off. (Si may be estimated in this portion if preferred, as its separation is not quantitative from HNO_3 solution.) Ten gms. of citric or tartaric acid are added to the filtrate and the solution is made ammoniacal. Nickel is precipitated in this solution by the addition of a considerable excess of dimethylglyoxime solution and filtering through a weighed Gooch crucible.

C. MISCELLANEOUS ANALYSES.

SAND, CLAY, FIREBRICK, SILICA BRICK AND SIMILAR REFRACTORIES.

These materials are essentially alike, though they differ in composition. They are mentioned as examples of 'complete analyses' in which metals of Groups V and VI are found, because, in alloys, the analysis usually stops short at Group IV. It is worthy of note that in these analyses the metals of Groups I and II are hardly ever present, and rarely those of Group IV, of which manganese is normally the only metal to be expected. The analysis of sands and refractories, therefore, starts at Group III, skips Group IV (see the following) and finishes with Groups V and VI.

Method.—The material must be very finely powdered by grinding in an agate mortar. Weigh out 1 gm. into a platinum crucible. Heat the crucible and contents in the muffle at 800°–900° C. for half an hour ; cool it in the desiccator and reweigh. The loss of weight represents water, mechanically held plus combined, and CO_2 from $CaCO_3$; also, occasionally, SO_2 from pyrites. Report this as "*Loss on Ignition.*"

Note.—In some cases, as for example, the analysis of fireclay, it is usual to distinguish between mechanically held water and combined water by drying at 110° C. and weighing before proceeding to the ignition.

To the ignited residue add 5–7 gms. of anhydrous Na_2CO_3 and carry out a carbonate fusion ; extract the melt with hot water in a large porcelain dish (see p. 235). Make the extract just acid with HCl and evaporate it to dryness, taking due precautions against spurting when the salts begin to separate out. Bake the residue on the centre of the hotplate for at least half an hour ; cool, and moisten the residue with conc. HCl, rinse down the sides of the dish with hot water, add 5 cc. of HCl in excess, and filter through a free-running paper (No. 41). Wash the insolubles alternately with hot 5 per cent. HCl and cold water at least 6 or 8 times. Set the filtrate again to evaporate, and in the meantime transfer paper and precipitate to the platinum crucible ; dry carefully in the mouth of the muffle and after charring off the paper, ignite for twenty minutes at bright redness. Cool in the desiccator and weigh crucible + SiO_2.

The SiO_2 thereby obtained is never pure ; it always contains several mgms. of Na_2O as well as Fe_2O_3, Al_2O_3 and CaO. Treat it, therefore, as follows: Moisten the contents of the crucible with a little water and add 2 drops of H_2SO_4, followed by several cc. of HF, adding this latter reagent carefully as the reaction is apt to be violent. Carefully evaporate the contents of the crucible to dryness on the hotplate, expelling the last traces of the H_2SO_4 in the muffle. When dry, re-ignite the contents at redness, cool, and reweigh. The loss of weight is SiO_2. Usually quite a perceptible residue is left. This is extracted with a little HCl in the crucible and transferred to the main solution which is in the process of evaporation.

Take the second evaporation to complete dryness and again bake the residue for half an hour. As before, take up the residue in HCl and hot water, filtering off the secondary precipitate of silica through a small filter. Ignite at redness and weigh, adding the weight to that of the main SiO_2 determination. There is usually no need to treat this secondary precipitate with HF, as it should be too small to have adsorbed anything weighable. It is possible to obtain traces of silica from a third or even fourth evaporation, but this is not necessary except for very accurate work. Secondary silica is derived from the right to left reaction in the partly reversible equation

$$Na_2SiO_3 + 2HCl \rightleftarrows 2NaCl + H_2O + SiO_2.$$

The reversal of the usual reaction is especially prominent if the silicic acid is not thoroughly dehydrated by baking.

Filtrate:

Two cases arise:

(*a*) The original fusion was coloured green or blue, denoting the presence of manganese.

(*b*) The fusion was not coloured.

(*a*) *If manganese is present* it will be strongly adsorbed by the Group III precipitate and part will be found in Group III and part in Group IV. (Also, of course, the Mn tends to oxidise in alkaline solution and throw down a precipitate of hydrated MnO_2.) It is best, therefore, to keep all the manganese in the Group III precipitate by precipitating with Br_2 and NH_4OH instead of NH_4OH only :

Add 1 or 2 drops of bromine and stir well until the solution is strongly coloured. Then add NH_4OH until the solution is just alkaline and boil until the precipitate settles out well. (*Note.*—It is usually safest to add 1 or 2 gms. of solid NH_4Cl before proceeding with this precipitation, but if the solution was previously strongly acid, this will be unnecessary.) Filter through an open-textured paper and wash well with boiling water. Open out the paper and redissolve the precipitate in HCl ; add 1 gm. of NH_4Cl and re-precipitate with Br_2 and NH_4OH. Filter as before and combine the filtrates. Redissolve the precipitate in a little HCl and separate the manganese from Group III metals by the "*acetate method*," as follows: Measure out 10 cc. of neutral ammonium acetate solution and set it ready to hand for quick addition when required. Add 3 drops of methyl orange, and, holding the beaker in the right hand, keep the solution steadily swirling while dilute ammonia is added drop by drop with the left. Continue the addition of the ammonia until the colour of the indicator begins to turn to orange. At this point, add 2 cc. of acetic acid, quickly followed by the measured acetate. Cover the beaker and set the solution to boil on the hotplate. (*Note* that the addition of the neutral ammonium acetate will cause the colour of the indicator to change over to yellow, in spite of the presence of the free acetic acid ; the boiling will precipitate the iron and aluminium, while the manganese will pass into the solution.) Filter hot, and wash thoroughly with boiling water. Transfer the precipitate and paper to a crucible and after drying in the mouth of the muffle, ignite the hydroxides to oxides, which are weighed. Do not ignite at too high a temperature or the oxides will be refractory to HCl in the next operation.

Brush the oxides back into the beaker and digest them with conc. HCl under a cover until they are in solution, renewing the acid if necessary. Note that it does not matter if the Al_2O_3 refuses to redissolve. Reduce the hot HCl solution with a few drops of $SnCl_2$ solution, oxidise the excess of Sn^{++} with $HgCl_2$ and titrate the Fe^{++} with standard dichromate solution. Calculate the Fe to Fe_2O_3 and deduct this weight from the total of the mixed oxides ; the difference is Al_2O_3.

Manganese is estimated in the filtrate from the iron and aluminium by precipitation with Br_2 and NH_4OH, being weighed as Mn_3O_4.

The filtrates from the double Group III precipitation contain all the metals of Groups V and VI of which calcium and magnesium may

be expected to be present ; it is of course useless to test for the alkali metals after a carbonate fusion. To the faintly ammoniacal solution add 1 cc. of saturated ammonium oxalate solution for every 1 per cent. of CaO which is present and digest the mixture on the hotplate until the precipitate of calcium oxalate separates out well. If the precipitate is large, or if much magnesium be present, the special precautions mentioned on p. 282 under Separations, Group V, must be observed.

Filter the calcium oxalate off on to a small non-ashless paper and wash it well with cold water. Open out the paper and wash the precipitate back into the beaker. Add 20 cc. of 10 per cent. H_2SO_4, heat to 70°–80° C. and titrate with standard $KMnO_4$, using the " manganese " solution unless the precipitate is a heavy one, in which case the " CaO " solution is preferable. When the end-point is reached and the solution is coloured a permanent pink, drop the paper, to which some calcium oxalate still adheres, into the solution, and stir until the colour is discharged. Continue the titration, adding the $KMnO_4$ drop by drop, until the final end-point is attained. (*Note* that $KMnO_4$ will attack cellulose in hot, concentrated solution ; it is, therefore, essential to maintain a slow addition of the reagent in order to prevent a local concentration which might cause high results.)

Filtrate:

Add 5 or 6 cc. of a saturated solution of $(NH_4)_2HPO_4$, followed by one-third of the bulk of the solution of 0·90 sp. gr. NH_4OH. Stir well and digest on the hotplate for at least one hour. Filter off through a small pulp or, preferably, a weighed Gooch crucible ; wash with cold 2·5 per cent. NH_4OH. If the precipitate is bulky (this is unusual) it must be re-dissolved in HCl and re-precipitated by adding 1 cc. of the phosphate solution followed by excess of NH_4OH solution. Ignite to $Mg_2P_2O_7$ and weigh. (See, however, p. 141 for notes on the precipitation of Mg.)

It is usual in ordinary analysis to estimate the " *alkalis* " by difference, calling them " $K_2O + Na_2O$." If, however, the difference from 100 per cent. be greater than, say, 0·5 per cent., the alkalis must be determined in a separate portion of the sample, preferably by the " Lawrence Smith method " (p. 146). In very special cases, potassium and sodium are separated and separately estimated.

(*b*) *Manganese is absent* ; omit the treatment with bromine and the acetate separation. A double precipitation with NH_4OH is, of course necessary.

Alternative Method for refractories which contain a very high percentage of silica (*e.g.* silica sand, silica bricks, ganister and the like, which contain over 95 per cent. of SiO_2):

Weigh 1 gm. of the very finely powdered material into a platinum crucible and determine the " *Loss on Ignition* " ; this should be very small. Weigh the crucible + ignited sample. Add 5 to 10 drops of H_2SO_4 and then fill the crucible with HF and slowly evaporate to fumes. Drive off the last traces of acid at the lowest possible temperature, cool, add 1 cc. of HCl, 5 to 10 drops of H_2SO_4, and again fill the crucible with HF. Once more slowly evaporate off the acid mixture, and as before, expel the last traces of H_2SO_4 at the lowest possible temperature. When

quite dry, heat the crucible in the muffle to dull redness, cool, and re-weigh.

The crucible now contains oxides of iron, aluminium, calcium, and sulphates of sodium and magnesium, but these latter should be so small in quantity as to be negligible, and the loss in weight may safely be taken to be SiO_2.

The oxides are dissolved by extraction with HCl in the crucible, and the metals are estimated as before. This method is only satisfactory when the silica is almost all in the " free " state.

CEMENT.

Cement is one of the few silicious materials which are completely decomposed by acids.

Weigh 0·5 gm. of the cement into a dry 250 cc. platinum or porcelain dish and add sufficient water to moisten the sample without causing lumping. When the cement has been thoroughly broken up, add 10 cc. of HCl, stir well, and evaporate to dryness, taking care that no loss by spurting takes place. Bake the solid residue for half an hour on the hotplate, after which moisten the warm cake with a little HCl adding 10 cc. in all, followed by 50 cc. of hot water. When all the ferric oxide has passed back into solution (digest on the hotplate under a cover if necessary), filter the residual silica off through a No. 41 paper and wash it thoroughly with hot 1 : 1 HCl twice, then with cold water until the filtrate runs free from chlorides. Set the filtrate again to evaporate; when it is dry treat the second solid residue in the same way as the first and combine the two silica residues, drying them in a platinum crucible and finally igniting at the full temperature of the muffle (at least 900° C.). Cool in the desiccator and weigh the crucible plus silica. Moisten the silica with a few drops of water, add 3 drops of H_2SO_4, followed by several cc. of HF. Carefully evaporate the contents of the crucible to dryness and after driving off the last trace of acid fumes, re-ignite the crucible and contents in the muffle. Cool, and reweigh; the difference in weight respresents the SiO_2. *Note.*—This method of treating the SiO_2 precipitate may also be adopted in the analysis of Refractories.

Treat the slight residue of oxides in the crucible with about 10 cc. of HCl and warm the crucible on the hotplate until a clear solution is obtained. Then transfer this to the filtrate from the silica. Add 2 gms. of solid NH_4Cl and then NH_4OH, drop by drop, until the liquid is just alkaline. In this case it is best to use an indicator, as an excess must be avoided; litmus or methyl orange will serve. Bring the solution to the boil and digest the precipitate on the hotplate, until it settles out well. Decant the clear solution as completely as possible through a No. 41 paper, finally rinsing it on to the paper with boiling water. Wash with boiling water until the runnings are free from chlorides. In view of the relatively large amounts of calcium and magnesium that will be present, the Group III precipitate must be re-precipitated in order to counteract adsorption. Open out the paper and wash the precipitate back into the precipitation beaker, dissolving any residue

off the paper with a little hot dil. HCl. Add about 10 cc. of this acid to the contents of the beaker and warm until the hydroxides are completely in solution; add 2 gms. of NH_4Cl and re-precipitate; filter and wash exactly as described for the first precipitate. The hydroxides (which will also contain any phosphates and TiO_2 that were present in the original sample), are then ignited to oxides in the muffle, and these are cooled and weighed. Call this weight "*Alumina plus Ferric Oxide*" (P_2O_5 and TiO_2 may usually be neglected). Brush the oxides into a small beaker and digest them in conc. HCl under a cover until a clear solution is obtained. This may take some time, especially if the oxides were ignited at a high temperature; the alumina is more refractory than the ferric oxide, and it may be possible to obtain the latter in solution even though the former remains obstinate. As it is the iron which is required in solution, it may be possible to continue without necessarily getting a perfectly clear solution. The hot extract is treated with a solution of $SnCl_2$, added drop by drop until the deep colour of the ferric ion is just discharged; the solution is then diluted to 50 cc., 10 cc. of saturated $HgCl_2$ solution added, and the iron estimated by titration with standard dichromate. The iron is calculated to Fe_2O_3 and this deducted from the weight of the mixed oxides; the difference may be called *Alumina.*

Make the filtrate acid with HCl (5 cc.), and add 30 cc. of saturated ammonium oxalate solution; boil the solution, and add dilute (1 : 3) NH_4OH slowly, while stirring, until the indicator again turns colour. Add 5 cc. of the NH_4OH in excess. (*Note.*—The precipitation is approached from the *acid* side deliberately. The intention is to start the precipitation under conditions which are favourable to *solubility* of the precipitate so that the oxalate crystals may grow slowly and in the end become relatively large in size. This has two beneficial effects ; firstly, it renders the precipitate easier to handle and wash without passing through the paper, and secondly, the tendency for magnesium oxalate to be co-precipitated, either by adsorption or because its solubility product is attained, is very much reduced, so that a double precipitation of the calcium will usually be unnecessary.)

Filter off the calcium oxalate on a non-ashless paper and wash with cold water until free from excess of the reagent. Open out the paper and rinse the oxalate back into the beaker ; dissolve it in 50 cc. of 1 : 5 H_2SO_4 heated to 70°–80° C. and titrate at once with standard permanganate solution, adding the reagent slowly at first, but more boldly when the Mn^{++} ion has accumulated sufficiently to accelerate the reaction. When the end-point is reached, transfer the paper with the usual small amounts of adhering precipitate to the beaker and stir with a glass rod. The pink colour will be discharged by the added oxalate, and the end-point may once more be approached, this time adding the permanganate with the greatest care. The end-point is not permanent owing to the slow attack of the permanganate upon the cellulose of the paper.

Concentrate the filtrate from the calcium to about 150–200 cc. by evaporation and make slightly acid with HCl, after which add 10 cc. of 10 per cent. $(NH_4)_2HPO_4$, followed by NH_4OH, drop by drop, with stirring, until the precipitate of $MgNH_4PO_4$ comes down. Add one-

third of the bulk of the solution of 0·90 sp. gr. NH_4OH and digest on the hotplate until the precipitate settles out well ; filter off on a non-ashless paper and wash once with 2·5 per cent. NH_4OH. Open out the paper and rinse the precipitate back into its beaker, where it is dissolved in a little HCl (10 cc.). Dilute to not more than 50 cc. and add 1 cc. of the 10 per cent. phosphate reagent followed by 0·90 sp. gr. NH_4OH until the precipitate again forms. Add 15–20 cc. of the dilute NH_4OH in excess, and again digest the precipitate until it settles out in a compact, crystalline form. Filter it off through a weighed asbestos Gooch crucible and wash it thoroughly with 2·5 per cent. NH_4OH until free from Cl^-. Ignite it in the muffle until the pyrophosphate is pure white ; cool, and weigh.

Note.—The double precipitation is necessary on account of the accumulation of reagents in the solution by the time that the separation of magnesium is reached, a condition which, although it does not prevent the complete precipitation of the magnesium, nevertheless produces a precipitate of indefinite composition (see the discussion on p. 141). Re-precipitation under known conditions removes all uncertainty.

The filtrate contains the alkalis plus the excess of all the reagents used during the analysis, all their impurities and all the impurities they may have picked up during the analysis ; it is not suitable for alkali determination. Usually, alkalis are determined by difference if this be small ; if, however, a direct determination is required, the alkalis may be estimated either by the Lawrence Smith or the Gooch and Eddy method.

Estimation of SO_3.—One gm. is dissolved in dilute HCl as described. If this operation be properly conducted, no silica should separate. The solution is diluted to 250 cc. and brought to the boil, whereupon 20 cc. of 10 per cent. $BaCl_2$ solution are added with stirring. When the precipitate has settled out well, it is filtered off and washed with cold water preparatory to being ignited and weighed as $BaSO_4$. *Note.*—If a little SiO_2 should separate, the final precipitate may be ignited in a platinum crucible and treated with one drop of H_2SO_4 and 1 cc. of HF, after which it is re-ignited and again weighed.

Estimation of Total Sulphur.—Weigh 1 gm. of the cement into a platinum crucible and mix it well with 5 gms. of Na_2CO_3 with which is incorporated a pinch of KNO_3 to oxidise any pyritic sulphur. Fuse the mixture in the muffle and extract the melt with hot water. Acidify with HCl ; add 10 cc. excess acid, and dilute to 250 cc., again precipitating the $SO_4^=$ with 20 cc. of 10 per cent. $BaCl_2$ solution as described in the preceding paragraph

Loss on Ignition.—This is a rough measure of the "staleness," plus "insufficient burning" of the cement during manufacture. One gram of the cement is weighed out into a platinum crucible and ignited at the full heat of the muffle for half an hour, cooled in the desiccator, and re-weighed. The loss represents moisture plus carbon dioxide.

Insoluble Matter.—Weigh 1 gm. into a 250 cc. porcelain dish and cover it with 50 cc. of approx. 2 *N* HCl (say, 1 : 6 of the conc. acid). Digest on the edge of the hotplate until the sample is completely broken up. Filter off on a small pulp and wash until free from Cl^-. Then transfer precipitate and paper to the same dish and digest for half an hour in

a 5 per cent. solution of Na_2CO_3, after which filter and wash, first with hot water, then with dil. HCl, and finally with hot water. Ignite the residue and weigh. The weight is supposed to be a measure of the " free silica " in the cement.

Note.—The British Standard Specification for Cement is:

Insolubles, below 1·5 per cent.; SO_3, not over 2·75 per cent.; loss on ignition, not over 3 per cent.; MgO, not over 4 per cent. For the rest, calculate the weight of CaO necessary to combine with the SO_3 and deduct this from the total CaO found ; the remainder, in gram-equivalents (*i.e.* gms. CaO divided by 56), when divided by the sum of the gram-equivalents of the SiO_2 and Al_2O_3 found, shall give a factor lying between 2·0 and 2·9.

SLAG.

Slag, as a by-product in ferrous metallurgy, is ordinarily analysed by the same methods as have been outlined for Refractories and Cement. Some slags, notably blast furnace slag, are soluble in HCl ; these are attacked as below:

Place 1 gm., very finely divided, in a wide beaker, add 30 cc. of boiling water, and cover the beaker. Boil the mixture and add slowly 30 cc. of HCl, taking care that active ebullition does not cease at any time. Slowly evaporate the solution to low bulk and add 5 cc. of HNO_3 to oxidise Fe^{++}, continuing the evaporation until the solution is nearly dry. Take the residue up in HCl. The solution is then ready for analysis. Note that manganese is certain to be present.

Estimate SiO_2, FeO, Al_2O_3, MnO, CaO, MgO, (Na_2O), $S^{=}$, and P_2O_5.

Note.—Fe_2O_3 does not form a silicate and the iron may be regarded as being entirely in the ferrous condition. See Note on Basic Slag, however.

In cases where the slag is not completely attacked by HCl, fusion with sodium carbonate will be necessary.

Basic Slag.—In this case there is usually a considerable amount of phosphate in the sample, and a detailed scheme of analysis will therefore be given, as the process involves the separation of phosphoric acid. (See remarks under Group III, Separations.)

Method.—Weigh out 1 gm. of the sample and attack it as described before. Filter, wash thoroughly, and weigh the SiO_2 after strong ignition. Two evaporations are necessary, and the silica must be treated with HF and H_2SO_4.

Make a *basic acetate* separation on the combined filtrates, and filter off an aliquot part for the estimation of calcium, magnesium and manganese (*e.g.* dilute to 502 cc. and filter off 250 cc.). Normally, all the phosphoric acid will be in the precipitate as basic phosphates of iron and aluminium ; if, however, there is an excess of phosphoric acid over the amount that is necessary to form $FePO_4$ and $AlPO_4$, the phosphates of manganese, calcium and magnesium will contaminate the precipitate. In the rare cases of " excess phosphate " it is necessary to add a definite volume of a standard iron solution. This is conveniently prepared either

by weighing out a known amount of ferrous ammonium sulphate, and, after dissolving it in water, oxidising the Fe^{++} with a little Br_2 or HNO_3; or else, preferably, dissolving 1 gm. of electrolytic or Armco iron in aqua regia, evaporating dry, and, after taking the residue up in HCl, diluting to 1,000 cc., so that each cc. contains 0·001 gm. Fe^{+++}.

Note.—The impurities in the iron are negligible here; Armco iron contains less than 0·1 per cent. of manganese.

It will be easy to tell how much of the iron solution, if any, should be added to the assay solution after (1), estimating P_2O_5 in a separate portion of the sample, and (2), estimating iron and aluminium as below. If the amount of iron + aluminium be inadequate, the analysis must be restarted, this time adding such an amount of the standard Fe^{+++} solution as will give a suitable excess of bases.

Basic Acetate Precipitate.—This is dissolved in HCl and the solution made up to 150 cc. In 50 cc. of the solution iron is estimated by reduction with $SnCl_2$ and titration with dichromate. The other 100 cc. is treated as follows: Add 2 gms. of sodium or ammonium phosphate and precipitate the aluminium as $AlPO_4$ with thiosulphate as described on p. 107. The $AlPO_4$ must be redissolved in HCl and re-precipitated, after adding a further 1 gm. of phosphate reagent, in order to eliminate the Fe^{++}, (Ca, Mg), completely.

Note that the foregoing methods give true amounts of iron and aluminium, whether there is an excess of phosphate present or not. This part of the analysis, therefore, need not be repeated, although if P_2O_5 be in excess, it will be necessary to prepare a fresh solution and carry through an acetate separation in order to get at the manganese, calcium and magnesium.

Filtrate from the Basic Acetate Separation.—Separate manganese by making a double precipitation with Br_2 and NH_4OH. Estimate the manganese as Mn_3O_4.

In the combined filtrates, estimate calcium and magnesium as described under Cement.

Other estimations are made on separate portions of the sample.

Sulphur.—Slag contains sulphides (chiefly CaS). The sulphur is estimated as described under Steel (Gravimetric method). Take a 2 gm. sample.

Phosphates.—Attack a 0·5 gm. sample with HNO_3 + HF in a platinum dish. If platinum is not available, the attack may be conducted in a tall beaker, the HNO_3 being added first to the boiling suspension of the slag. HF is then added, drop by drop, to the swirling mixture, letting the acid fall into the centre of the liquid so that there is no excessive attack on the glass. Boil for 15 mins., uncovered; cool, and dilute to 100 cc. Pipette out 25 cc. (= 0·125 gms. sample) and precipitate the P_2O_5 as phosphomolybdate as usual, adding rather more than the usual quantity of the reagent.

Ferrous Oxide.—The iron is partly in the ferric condition owing to the formation of $FePO_4$. Weigh out 0·5 gm. of the finely powdered sample and attack it with HCl, digesting until the silica "cleans" well. Titrate the solution with dichromate without any further treatment except dilution. *Note.*—FeS and metallic Fe read as FeO; this is unavoidable.

WATER ANALYSIS.

The ordinary analysis of water is not a difficult matter. A simple method is given here for additional practice in the separation of the metals of Groups III, IV and V.

Results are commonly expressed in " parts per 100,000," " parts per million " or " grains per gallon," which is the same thing as parts per 70,000, there being 70,000 grains in an Imperial Gallon. In the case where decimal results are required, it is best to work with a 1 litre sample, but if the result is to be expressed in terms of grains per gallon take a 700 cc. sample, as the calculations are considerably simplified.

Measure out the sample to the nearest cc. and accurately weigh a 250 cc. platinum or porcelain dish. Fill this with the sample and set it on the hotplate to evaporate steadily, replacing evaporated water from the measured sample as required. When the last of the sample has been added, put the dish on a small piece of asbestos sheet so that the final drying may not be too severe ; or the water bath may be used. When the sample is quite dry, wipe the outside of the dish and re-weigh. Call this weight " **total solids at 100° C.**"

Place the dish inside the muffle and heat the residue to redness ; cool, and moisten the solids with a few drops of a saturated solution of ammonium carbonate in order to replace expelled CO_2 from the $CaCO_3$, etc. Again take to dryness on the water-bath, and re-weigh. The second weight represents **total inorganic solids.**

Note.—There is no very satisfactory general method for the weighing of total solids directly. For example, $CaSO_4$ behaves awkwardly as regards its water of hydration, $MgCl_2.6H_2O$ decomposes on heating into a basic chloride with loss of HCl, and other salts containing water of crystallisation, *e.g.* Na_2SO_4, $CaCl_2$ and Na_2CO_3, require heating to an accurately measured temperature if it is desired to obtain them in a known state of hydration. The weighing of " total solids " is, however, a useful guide.

Moisten the dry solids with a few drops of HCl and warm the dish until the ferric oxide is in solution. Add a little more HCl and 20–30 cc. of water, filter through a small pulp, and wash with hot water until free from Cl^-. Ignite the insoluble matter and weigh the residue. Call this **silica**, SiO_2.

Make the filtrate just ammoniacal and boil. Filter off any precipitated iron and aluminium hydroxides, wash with boiling water, dry, ignite to oxides, and weigh. Call this weighing **" ferric oxide plus alumina."** It is not usual in technical analysis to separate these oxides: they are almost always present in small amounts only and this being the case neither metal has any important effect upon the value of the water industrially. In certain cases, however, such as in the analysis of chalybeate water, the Fe should be separately estimated by dissolving the oxides in HCl and titrating the iron with dichromate solution.

Precipitate calcium in the filtrate from the Fe and Al as described under *Refractories* and estimate it by titration with dilute $KMnO_4$.

Set the filtrate from the calcium to evaporate in a 250 cc. porcelain dish. When the solids commence to separate, add 50 cc. of HNO_3 and

continue the evaporation slowly. This has the effect of decomposing and expelling ammonium salts, which by this time have accumulated in considerable amounts in the solution. Take the evaporation to complete dryness, and if the residue is considerable, add 20 cc. more HNO_3 and again evaporate. Finally, add a bare excess of H_2SO_4 and take to fumes. The amount of H_2SO_4 added will necessarily depend upon the amount of the residue. The analyst should attempt to gauge the minimum amount, but an excess is necessary or basic magnesium compounds will be left ; an undue excess prolongs the later stages of the manipulation.

Allow the fuming solution to cool ; dilute it with 3 or 4 cc. of water, boil, and filter through the smallest possible pulp filter into a weighed platinum crucible. (*Note.*—Filtration here removes stray silica derived from the ammonia and the glass-ware used.) Set the crucible to evaporate on the hotplate, meanwhile washing the filter with five or six *small* quantities of boiling water, catching the runnings in a small beaker. These runnings are added to the contents of the crucible as evaporation proceeds. When the acid in the crucible is again fuming, transfer to the mouth of the muffle and drive off the last traces of acid, finally heating the residue to dull redness. Cool and weigh. This weight represents **magnesium and alkali sulphates,** $MgSO_4 + Na_2SO_4 (+ K_2SO_4)$.

Dissolve the solids in a little water in the crucible and rinse the solution out into a small beaker. Add 2 gms. of solid NH_4Cl and 2 cc. of HCl, dilute to 50 cc. and add sufficient 10 per cent. solution of ammonium phosphate to precipitate the magnesium, avoiding unnecessary excess. Now add 1 : 3 NH_4OH drop by drop until the precipitation of the $MgNH_4PO_4$ is complete and an excess of 20 cc. of 0·90 sp. gr. NH_4OH. Digest near the boiling-point until the precipitate becomes crystalline and compact, and settles out well ; filter off through a weighed asbestos Gooch crucible and ignite at redness until the residue is pure white. Weigh as **magnesium pyrophosphate,** $Mg_2P_2O_7$. Calculate the Mg in this to $MgSO_4$ and deduct this weight from the weight of the mixed sulphates: the difference represents *alkali sulphates,* $Na_2SO_4 (+K_2SO_4)$. Calculate this to Na_2O. (Usually K_2O is reckoned as Na_2O.)

Estimation of Chloride (Cl^-).—Take 100 cc. for decimal results or 70 cc. for " grains per gallon." Measure the indicated amount into a 500 cc. porcelain dish and add 1 cc. of a 10 per cent. solution of K_2CrO_4 (measure this, as its volume has a slight effect on the end-point). Titrate with $AgNO_3$ solution of such strength that 1 cc. ≡ 0·001 gm. Cl^-.

Estimation of Sulphate ($SO_4^=$).—Take 250 cc. for decimal results or 350 cc. for " grains per gallon." Measure the indicated volume into a 600 cc. beaker ; acidify with 10 cc. of HCl and bring the solution to the boil. While boiling add 15 cc. of 10 per cent. $BaCl_2$ solution and digest the solution on the hotplate until the $BaSO_4$ has separated completely. Filter off through a small compact pulp, ignite, and weigh as $BaSO_4$.

Estimation of Carbonate ($CO_3^=$).—Take 250 cc. for decimal results or 350 cc. for " grains per gallon " of the sample and transfer it to a tall 600 cc. beaker. Add two drops of methyl orange, stand the beaker upon a white tile and titrate carefully with 0·1 N H_2SO_4 until the indicator is a full pink. One cc. of 0·1 N acid ≡ 0·0044 gm. CO_2 (as carbonate) or 0·0060 gm. $CO_3^=$.

Reporting Results.—It is very unscientific to report results in terms of actual salts, as it is of course perfectly obvious that all compounds in the original water will be almost completely ionised in solution. Two methods of reporting are correct, viz:

(*a*) KATIONS.	ANIONS.	OR: (*b*) BASES.	ACID RESIDUES.
Fe^{+++}	$SiO_3^{=}$	Fe_2O_3	SiO_2
Al^{+++}	$SO_4^{=}$	Al_2O_3	SO_3
Ca^{++}	Cl^{-}	CaO	Cl
Mg^{++}	CO_3^{-}	MgO	CO_2
Na^{+}	NO_3^{-}	Na_2O	N_2O_5
K^{+}		K_2O	

The latter is the more usual, and is one of the common survivals of the old dualistic theory ; the former is " scientific."

In a report for non-technical clients, however, it is usual to ' combine ' anions and kations according to an arbitrary system, although the chemist is perfectly well aware that in the actual water the percentage of associated molecules is very small indeed, and even if this were not so, it is obviously quite impossible to state which anion " belongs " to which kation. The system which is preferred by the writer if a " combined " report is demanded, has, however, in some measure a basis of practical truth. In this method the kations and anions are combined to make up those salts which are found in practice to separate out first from the solution on evaporation, and it is obvious that for the evaluation of a water for boiler purposes there is a good deal to be said for this method, as it gives a good idea of the nature of the scaling or corrosion that may be expected.

A summary of this method is appended.

A. (*i*). $SO_4^{=} + CO_3^{=}$ *are greater than* $Ca^{++} + Mg^{++}$.

Calculate:
1. MgO to $MgCO_3$.
2. Remaining CO_2 to $CaCO_3$.
3. Remaining CaO to $CaSO_4$.
4. Remaining SO_3 to Na_2SO_4.
5. Remaining Na_2O to NaCl. } These should balance.
6. Cl to NaCl. }

A. (*ii*). $CO_3^{=}$ *alone is greater than* $Ca^{++} + Mg^{++}$.

Calculate:
1. MgO to $MgCO_3$.
2. CaO to $CaCO_3$.
3. Remaining CO_2 to Na_2CO_3.
4. SO_3 to Na_2SO_4.
5. Remaining Na_2O to NaCl } These should balance.
6. Cl to NaCl. }

B. If $SO_4^{=} + CO_3^{=}$ are less than $Mg^{++} + Ca^{++}$.

(*a*) *All acids, calculated as Na salts, exceed the Total Mineral Residue.*

Calculate: 1. SO_3 to $CaSO_4$.
2. Remaining CaO to $CaCO_3$.
3. Remaining CO_2 to $MgCO_3$.
4. Remaining MgO to $MgCl_2$.
5. Remaining Cl to NaCl
6. All Na_2O to NaCl. } These should balance.

(*b*) *Total Mineral Residue exceeds all acid calculated as Na salts.*

Calculate: 1. All SO_3 to $CaSO_4$.
2. All MgO to $MgCO_3$.
3. Remaining CO_2 to $CaCO_3$.
4. Remaining CaO to $Ca(NO_3)_2$.*
5. Remaining NO_3 to $NaNO_3$.
6. All Cl to NaCl.
7. Remaining Na_2O to NaCl. } These should balance.

C. The water reacts acid.

Calculate CaO, MgO, Fe_2O_3, Al_2O_3 to the acid in excess ; the other bases in order.

Note 1.—No mention has been made of ferric oxide or alumina or silica. These are never present in serious quantities, and are reported first, uncombined.

Note 2.—The foregoing system has one serious defect, and that is, it makes no note of the possible presence of $Mg(OH)_2$. This compound is undoubtedly present in some samples of boiler-scale, and its solubility is very low.

Nitrates and *nitrites* are usually estimated by colorimetric methods:

Estimation of Nitrate.—Measure out 100 cc. (70 cc.†) of the sample into a clean porcelain dish ; add 2 cc. of 10 per cent. Na_2CO_3 solution and evaporate to dryness on the water-bath. Cool the dish and its contents and add, by means of a pipette, 2 cc. of phenolsulphonic acid and stir well. Take the mixture up in about 30 cc. of water and make the solution just ammoniacal. The presence of NO_3^- is indicated by a yellow coloration. Make the solution up to 100 cc. and compare the colour with that produced in a standard solution similarly treated.

Reagents:

Phenolsulphonic Acid.—Dissolve 25 gms. of phenol in 150 cc. of conc. H_2SO_4 ; add 75 cc. of the fuming acid and digest the mixture (covered) on the water-bath for 2 hours.

Standard Nitrate.—Weigh out 0·72 gm. of KNO_3 and dissolve this in 1 litre of water. Take 10 cc. of this solution and evaporate it to dryness on the water-bath with 2 cc. of the Na_2CO_3 solution. Dissolve the residue in 1 litre of water. 1 cc. of this = 0·001 mgm. of nitrogen.

Estimation of Nitrites. Take 100 cc. (70 cc.†) of the filtered sample

* The suggestion is that if the bases exceed the acids some of the acid has been lost; nitrates are decomposed during the treatment for Total Mineral Residue.

† The data in brackets indicates the amount to be taken for " grains per gallon."

of water and add 2 cc. of the sulphanilic reagent, followed by 2 cc. of α-naphthylamine acetate. Compare the colour with that generated in a standard solution of nitrite.

Reagents:

Sulphanilic Acid.—Dissolve 8 gms. of the acid in 1 litre of 30 per cent. acetic acid.

α-Naphthylamine Acetate.—Dissolve 5 gms. of α-naphthylamine in 1 litre of 30 per cent. acetic acid.

Standard Nitrite.—Dissolve 1·1 gms. of $AgNO_2$ in water and add excess of NaCl solution. Filter off the AgCl and dilute the filtrate to 1 litre. Pipette out 100 cc. of this solution and dilute it to 1 litre and then dilute 10 cc. of this second solution to one litre. One cc. of the resulting solution contains 0·0001 mgm. of nitrogen (as nitrite).

In cases where considerable NO_2^- (or NO_2^-) is present in water, this constituent is determined as below:—

(1) Distil the water (made alkaline with KOH) from Devarda's alloy into excess of standard 0·1 *N* acid.

(2) Titrate the excess acid with 0·1 *N* alkali. See under Ammonium, p. 151.

D. ORES.

COPPER.

(*a*) **Oxidised Ores** (*i.e.* Carbonates, hydroxides, basic carbonates).

Weigh 1 gm. of the finely divided ore into a 400 cc. beaker (more if the material is of very low grade). Attack it with 10 cc. of HNO_3 followed by 10 cc. of HCl and heat the mixture until no further action takes place (*). Carefully add 3 or 4 cc. of H_2SO_4 and evaporate the solution until copious fumes are evolved. Cool, add 20 cc. of water and boil until the sulphates are all in solution ; filter off any SiO_2, washing it with hot water. Finally, in a bulk of about 100 cc., add 10 cc. of HNO_3 and estimate the copper by the electrolytic method.

(*b*) **Sulphide Ores** (Pyrites).

Weigh 1 gm. as above and attack it with 10 cc. of HNO_3, adding an occasional pinch of $KClO_3$, and keeping the beaker covered until the ore is completely disintegrated (*). Evaporate and dry cautiously. Take the residue up in 10 cc. of HNO_3 and 30 cc. of water ; filter off any insoluble residue (silica, sulphur, etc.) and dilute to 100 cc. Electrolyse as usual. If the deposit is very dark in colour it is probable that some arsenic has been deposited with the copper. In this case, dissolve off the deposit in 15 cc. of HNO_3, boil for a minute or two to remove nitrous fumes, and after diluting to 100 cc., re-electrolyse ; the copper should now come down in a pure condition.

If desired, the copper may be estimated iodometrically. In this case, from the points marked *, continue thus:

Add 2 cc. of H_2SO_4 from a burette and evaporate to fumes, continuing the heating until the evolution of the fumes abates somewhat. Cool the beaker and add 20 cc. of water, warming if necessary until all soluble sulphates are in solution. Cool completely and add from a burette a saturated solution of Na_2CO_3, drop by drop, until a slight precipitate

is formed. Clear this with a drop or two of acetic acid, and complete the titration as described on p. 64.

LEAD.

Galena Ore.—Weigh out 0·5 gm. of the powdered ore and attack it with 20 cc. of HCl, heating until it is thoroughly decomposed and all the H_2S is driven out. Evaporate the solution to dryness and bake the residue to fix any silica. Dilute with hot water and filter rapidly through a small pulp filter, washing with hot water until the filter is free from lead. To the filtrate add 5 cc. of H_2SO_4 and evaporate to fumes ; dilute the solution to 100 cc., boil until all soluble sulphates are in solution and set the beaker aside to cool. When the precipitate has settled out completely, filter it off through a weighed Gooch crucible and complete the estimation as described on p. 47.

IRON.

All iron ores are oxides (some contain combined CO_2). The direct estimation of the iron is a simple matter.

Weigh 1 gm. of the finely powdered ore into a tall 400 cc. beaker and cover it with 15 cc. of conc. HCl. Cover the beaker, set it on the edge of the hotplate and digest until all the iron is in solution, leaving only a slight residue of colourless silica. At this point add a strong solution of $SnCl_2$ drop by drop until the deep colour of the ferric ion (Fe^{+++}) is destroyed, being careful to avoid any excess. Rinse down the sides of the beaker with a *little* hot water. ($FeCl_3$ is slightly volatile and some usually condenses on the sides ; this may escape reduction if the precaution described is not adopted at this point.) Dilute to 50 cc. with cold water and add 10 cc. of saturated $HgCl_2$ solution. Titrate with the "strong" dichromate (1 cc. ≡ 0·01 gm. Fe).

It is usually possible to estimate fairly accurately where the end-point is to be expected, as iron ores are generally fairly pure oxides (hydrated oxides), so that their iron content is known within somewhat narrow limits. This enables the analyst to obtain an accurate titration from the first assay. For the details of the titration, see p. 99.

MANGANESE.

Oxide Ores.—Weigh 0·5 gm. of the finely powdered ore into a tall 400 cc. beaker. The method of attack chosen depends upon the nature of the ore ; usually 20 cc. of HCl will suffice ; if this fails to "clean" the ore (*i.e.* give a colourless residue of silica) after one hour's digestion, add 10 cc. of HNO_3 and continue digestion until the gangue is cleaned. Finally add 5 cc. of H_2SO_4 and evaporate the solution to fumes. Cool, and take up the soluble salts in 100 cc. of water, boiling to accelerate solution if necessary. Cool again, and carry out the $BaCO_3$ separation as described on p. 258.

By this means, the chief impurity, iron, is removed, and any lead present will also be removed as $PbSO_4$ in the course of the subsequent filtration. Make the solution up to a definite bulk, filter off an aliquot part through a dry filter paper, and in the clear solution precipitate the manganese with Br_2 and NH_4OH. Weigh the manganese as Mn_3O_4.

ZINC.

Zinc Blende.—Weigh 0·5 gm. of the finely powdered ore (or concentrate) into a small conical flask (a Phillips' flask is suitable). Add 5 cc. of HNO_3 and heat until all nitrous fumes are expelled ; then add about as much $KClO_3$ as will cover a sixpence and evaporate the solution just to dryness.

Add 7 gms. of solid NH_4Cl (roughly weighed), 20 cc. of water, and 15 cc. of 0·90 sp. gr. NH_4OH. Boil ; filter off the insoluble matter through a small free-running pulp filter and wash it six times with boiling 2 per cent. NH_4Cl solution containing 50 cc. of 0·90 sp. gr. NH_4OH per litre. Add two drops of methyl orange to the filtrate and carefully neutralise with HCl, adding 10 cc. in excess. Pass one or two bubbles of H_2S gas through the clear solution ; if a precipitate forms (CuS, PbS) pass in H_2S to saturation, and if the precipitate be large, filter it off on a small pulp filter, washing with several small quantities of hot water. A small precipitate will not interfere and need not be filtered off. Dilute the solution (or filtrate) to 300 cc. and titrate the zinc with standard ferrocyanide solution. (See p. 136.)

Notes.—The ore usually contains SiO_2, Pb, Cu, Fe, Mn, and of course Zn and S. Sulphur is partly oxidised by the HNO_3 and partly precipitated as free sulphur, which, with the SiO_2, Pb, Fe and Mn is removed by the first filtration (the metals as hydroxides). Copper and traces of lead remain, and are either removed by filtration after passing H_2S or are left " immobilised " in the solution as insoluble sulphides. Copper salts affect the end-point by giving a coloured precipitate with ferrocyanide, but CuS is inert and is not decomposed, its solubility product being very small.

E. SPECIAL ALLOYS.

PHOSPHOR-COPPER.

Average analysis: P = 10–15 per cent. ; balance is Cu.

Weigh 1 gm. of the powdered material into a tall 400 cc. beaker and add either 15 cc. of 1·42 sp. gr. HNO_3 plus two or three drops of bromine, or 15 cc. of fuming HNO_3 (sp. gr. 1·5). Cover the beaker with a clock glass and set it aside until all the sample is in solution. When this is accomplished, rinse the sides of the beaker and the cover-glass with cold water and transfer the solution to a 500 cc. measuring flask, diluting it to the mark. Mix the solution thoroughly by pouring it out into a clean dry beaker and back into the flask.

As a working sample take 50 cc. of this solution (= 0·1 gm. of the solid phosphide). Pipette this volume out into a tall 300 cc. beaker and add 15 cc. of 1·42 HNO_3 from a burette followed by NH_4OH until a slight precipitate just forms (or just dissolves to a clear blue liquid). Now add 3 cc. of HNO_3 and bring the solution to the boil. Swirl the boiling solution vigorously with the right hand and add, in a steady stream, 20 cc. of clear 10 per cent. ammonium molybdate solution, continuing the swirling of the hot solution for at least 30 seconds after the addition of the last of the molybdate. Cover the beaker and place it on the edge

of the hotplate until the copious precipitate has settled out well. Carefully decant the clear solution as completely as possible into a clean beaker (in case of accident), taking care that no more than traces of the precipitate pass over. Dissolve the precipitate in the least possible quantity of 1 : 2 NH_4OH and dilute to 50 cc. Boil, add 3 cc. of ammonium molybdate solution, and then, while vigorously swirling the mixture, run in conc. HNO_3 from the burette until the yellow precipitate re-forms ; add 3 cc. HNO_3 in excess and continue the swirling of the solution for about half a minute. Again allow the precipitate to settle out as completely as possible, finally decanting the solution through a weighed Gooch crucible. The yellow phosphomolybdate is only transferred to the crucible filter when the decantation has been made as completely as possible, and then, owing to the small amounts of dissolved solids in the solution, very little washing will be necessary ; the wash liquid is 3 per cent. HNO_3, as cold as possible. Wash the contents of the crucible three or four times and finally suck crucible and precipitate as dry as possible on the pump. Wash once only with about 2 cc. of cold water in order to remove the bulk of the acid (which would otherwise attack the filter on heating in the oven), and again suck quite dry on the pump. Dry at 110° C. in the air-oven and weigh.

Note 1.—The double precipitation is desirable for accurate results.

Note 2.—The phosphomolybdate is somewhat soluble in water and, also, water tends to displace combined HNO_3 from the compound. A final washing with a little water is, however, necessary, firstly because HNO_3 remaining cannot be dried off at 110° C., and secondly because the hot acid is liable, as has been mentioned, to attack the filter.

Note 3.—The phosphomolybdate may also, of course, be estimated by the volumetric method described on p. 196. This method is, however, not recommended in a case where the precipitate is bulky, as here.

The Cu (and Pb) in the sample may be estimated by electrolysing 100 cc. of the solution, and any Fe in the residual solution after electrolysis as $FePO_4$. Note that the precipitate will *not* be $Fe(OH)_3$ when ammonia is added. It is not usual to estimate anything other than the phosphorus in commercial practice.

PHOSPHOR-TIN.

Usually contains about 5 per cent. phosphorus, but 10 per cent. is possible. The method of analysis of phosphor-tin is entirely different from that used for phosphor-copper, and the reason for this lies in the nature of the alloying metal. Copper is not seriously attacked in the ordinary way by HCl, but is by HNO_3 ; in the case of tin, however, HCl rapidly attacks it, while HNO_3 oxidises it to insoluble metastannic acid, in which residue practically the whole of the phosphorus will be found as tin phosphate.

It should be possible, theoretically, to estimate the phosphorus as described for its estimation in phosphor-bronze, but the method is not recommended ; the following is the best procedure:

Weigh out 1 gm. of the finely powered material and transfer it to a 250 cc. distilling flask fitted with a tap-funnel reaching to the bottom of the flask and drawn out to a somewhat fine point at the end. A

Meyer bulb is attached to the side tube as shown in the diagram, which also shows the method of working.

First seal the apparatus from the outside air by pouring in sufficient water to cover the bottom of the tap-funnel; then test for gas tightness, and attach the delivery tube of a CO_2 apparatus to the top of the tap-funnel. When ready, admit CO_2 until all air has been swept out of the apparatus, close the tap of the funnel, and for the moment, disconnect the CO_2 tube. Place 40 cc. of HCl in the bulb of the funnel and cautiously admit it into the flask, closing the tap before any air can enter; replace the CO_2 delivery tube.

The HCl attacks the phosphide, liberating hydrogen and phosphine, which in the neutral atmosphere is unable to oxidise. The gases bubble out through the bromine water in the Meyer bulbs, where

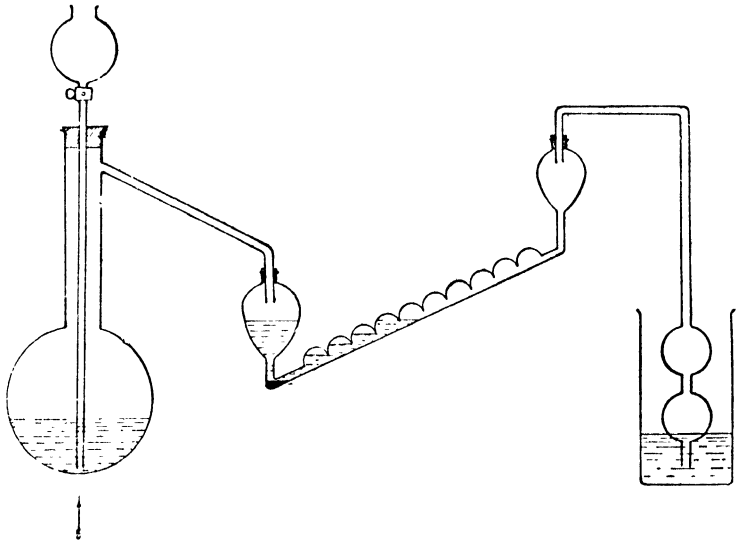


Fig. 28.

the PH_3 is oxidised to phosphoric acid. The attack of the sample is aided, if necessary, by gently heating the flask with a small Bunsen flame held in the hand, but great care must be taken that no sucking back takes place. When all the sample is in solution, again open the CO_2 tap and bubble the gas through the flask until all gaseous contents are again swept out into the bulb tube. This done, disconnect the apparatus and transfer the contents of the Meyer bulbs to a suitable beaker where the bromine is expelled by boiling; precipitate the phosphorus by the addition of magnesia mixture and ammonia. Weigh, finally, as $Mg_2P_2O_7$, as described on p. 195.

The tin may be estimated in an aliquot portion of the liquid in the flask by transferring to a tall beaker (still in CO_2) and titrating in the cold with standard iodine, as described on p. 95.

SECTION IX.

TABLES.

Notes on the Tables:

I. Atomic Weights, 1929.

II. Gravimetric Factors.

These factors have been taken out to 5 or 6 significant figures ; this does not mean that the student is supposed to use five-figure factors in his calculations. For Gravimetric purposes, four figures are enough, and three figures are often sufficient ; anything beyond this means that the calculations are being pushed to absurd lengths, beyond the accuracy of the ordinary analytical methods. It is obviously absurd to work with six-figure factors when most atomic weights are only known to three or four significant figures.

The " Direct " and " Reverse " factors explain themselves ; as an example of their use, however, to convert Al to Al_2O_3 multiply by 1·8899, and to perform the reverse operation of converting Al_2O_3 to Al, multiply by 0·5291.

III. Specific Gravity and Percentage Ionisation Tables.

These have been compiled for the common acids and alkalies. They are self-explanatory.

IV. Physical Properties of the Chief Inorganic Compounds.

Column 3 gives solubilities in water, usually at laboratory temperatures ; fuller data from an analytical point of view are given for the more important compounds. There are three chief methods of expressing solubilities, viz. :—

1. Grams of solute in grams of solvent. This method is the usual one here, and solubilities expressed in this way are denoted by " W," thus: " 0·02/100 gms. W at 20° " means, " 0·02 gm. of the substance dissolves in 100 gms. of water at 20° C."

2. Grams of solute in grams of saturated solution. This expression is occasionally adopted. An " S " denotes " saturated solution," thus: " 0·02/100 gms. S at 20° " means, " 0·02 gm. is contained in 100 gms. of the saturated solution at 20° C."

It should be observed that (1) can be converted into (2) by the use of elementary arithmetic, and that solubility in 100 gms. of solvent is always greater than solubility in 100 gms. of solution.

3. Grams of solute (cc. of solute, occasionally, in the case of gases), in 100 cc. of solvent. Gms. of solute in cc. of saturated solution is never used here, nor are solubilities ever expressed in terms of gm.-equivs., gm.-mols., or mgm.-equivs.

Other terms are self-explanatory in the main. It may, however, be noted that A denotes ethyl alcohol, and E ethyl ether in places where space forbids printing the complete word.

Column 4.—*Behaviour on heating*, does not pretend to be at all exhaustive, but the information there contained is occasionally very important. M. Pt. and B. Pt. denote Melting- and Boiling-Point respectively ; " dec." means " decomposes " and " subl." " sublimes."

In compiling these Tables, a number of works have been consulted, the chief of which are, van Nostrand's *Chemical Annual* (6th Edn.), Comey's *Dictionary of Solubilities*, Seidell's *Solubilities of Inorganic and Organic Compounds*, and *The Metallurgists' and Chemists' Handbook*.

V. Temperature Corrections for Volumetric Reagents.

TABLE I.—Atomic Weights, 1929.

Aluminium,	26·97	Molybdenum,	96·0
Antimony,	121·76	Neodymium,	144·25
Argon,	39·94	Neon,	20·18
Arsenic,	74·934	Nickel,	58·69
Barium,	137·36	Niobium,	93·3
Beryllium,	9·02	Nitrogen,	14·008
Bismuth,	209·00	Osmium,	191·0
Boron,	10·83	Oxygen,	16·000
Bromine,	79·915	Palladium,	106·7
Cadmium,	112·40	Phosphorus,	30·982
Caesium,	132·81	Platinum,	195·2
Calcium,	40·09	Polonium,	(210)
Carbon,	12·0036	Potassium,	39·105
Cerium,	140·2	Praseodymium,	140·9
Chlorine,	35·457	Radium,	225·95
Chromium,	52·04	Radon,	222
Cobalt,	58·95	Rhodium,	102·9
Copper,	63·55	Rubidium,	85·43
Dysprosium,	162·46	Ruthenium,	101·65
Erbium,	167·6	Samarium,	150·43
Europium,	152·0	Scandium,	45·15
Fluorine,	19·00	Selenium,	79·2
Gadolinium,	157·0	Silicon,	28·08
Gallium,	69·72	Silver,	107·880
Germanium,	72·60	Sodium,	23·000
Gold,	197·21	Strontium,	87·63
Hafnium,	178·6	Sulphur,	32·065
Helium,	4·0022	Tantalum,	181·3
Holmium,	163·5	Tellurium,	127·5
Hydrogen,	1·0078	Terbium,	159·2
Indium,	114·8	Thallium,	204·3
Iodine,	126·932	Thorium,	232·15
Iridium,	193·04	Thulium,	169·4
Iron,	55·84	Tin,	118·70
Krypton,	82·9	Titanium,	47·90
Lanthanum,	138·90	Tungsten,	184·1
Lead,	207·22	Uranium,	238·15
(Uranium Lead),	(206·02)	Vanadium,	50·95
Lithium,	6·940	Xenon,	130·2
Lutecium,	175·0	Ytterbium,	173·0
Magnesium,	24·30	Yttrium,	88·93
Manganese,	54·95	Zinc,	65·38
Mercury,	200·60	Zirconium,	91·2

The above are the values for 1929 as accepted by the Council of the Chemical Society.

TABLE II.—Gravimetric Factors.

Weighed.	Required.	Direct Factor.	Reverse Factor.
ALUMINIUM = 26·97, . .	..	..	..
Al_2O_3, ...	Al	0·52914	1·88986
$AlPO_4$, ...	Al	0·22114	4·52207
	Al_2O_3	0·41792	2·39278
AMMONIUM = 18·04 . .	..	..	..
NH_3, ...	NH_4	1·05918	0·94413
	NH_4OH	2·05777	0·48596
$(NH_4)_2PtCl_6$, ...	NH_3	0·07671	13·0353
	NH_4	0·08125	12·3076
	NH_4OH	0·15786	6·33464
Pt, ...	NH_3,	0·17450	5·73059
	NH_4	0·18482	5·41068
	NH_4OH	0·35909	2·78483
ANTIMONY = 121·76, . .	..	..	..
Sb, ...	Sb_2O_3	1·19711	0·83535
	Sb_2O_5	1·32851	0·75272
Sb_2O_4, ...	Sb	0·79198	1·26281
	Sb_2O_3	0·94797	1·05488
	Sb_2O_5	1·05203	0·95055
Sb_2S_3, ...	Sb	0·71684	1·39502
	Sb_2O_3	0·85815	1·16532
	Sb_2O_5	0·95235	1·05006
ARSENIC = 74·934, . . .	..	..	..
As_2O_3, ...	As	0·75741	1·32029
	As_2O_5	1·16172	0·86079
As_2S_3, ...	As	0·60906	1·64187
	As_2O_3	0·80414	1·24353
	As_2O_5	0·93414	1·07046
$Mg_2As_2O_7$, ...	As	0·48272	2·07160
	As_2O_3	0·63732	1·56908
	As_2O_5	0·74039	1·35064
BARIUM = 137·36, . . .	..	..	..
$BaCO_3$, ...	Ba	0·69586	1·43707
	BaO	0·77692	1·28714
$BaCrO_4$	Ba	0·54207	1·84479
	BaO	0·60521	1·65232
$BaSO_4$, ...	Ba	0·58854	1·69934
	BaO	0·65700	1·52207
	$BaCO_3$	0·84565	1·18252
BISMUTH = 209·0, . . .	..	..	..
Bi, ...	Bi_2O_3	1·11483	0·89700
Bi_2O_3, ...	Bi	0·89700	1·11483
BiOCl, ...	Bi	0·80244	1·24621
	Bi_2O_3	0·89457	1·11785
Bi_2S_3, ...	Bi	0·81294	1·23010
	Bi_2O_3	0·90630	1·10339
BROMINE = 79·915, . .	..	..	..
Ag, ...	Br	0·74080	1·34990
	HBr	0·75014	1·33309
AgBr, ...	Br	0·42555	2·34991
CADMIUM = 112·40, . .	..	..	..
$CdSO_4$, ...	Cd	0·54042	1·85040

TABLE II.—*Continued.*

Weighed.	Required.	Direct Factor.	Reverse Factor.
CALCIUM = 40·09, . . .	..	..	..
$CaCO_3$, ...	Ca	0·40050	2·49686
	CaO	0·56034	1·78463
	$CaSO_4$	1·36014	0·73522
	$Ca(HCO_3)_2$	1·61948	0·61748
CaO, ...	Ca	0·71457	1·39912
	$CaCO_3$	1·78469	0·56034
	$CaSO_4$	2·42735	0·41197
	$Ca(HCO_3)_2$	2·89017	0·34600
	CaF_2	1·39223	0·71827
CO_2, ...	CaO	1·27467	0·78452
	$CaCO_3$	2·27481	0·43960
MgO, ...	CaO	1·38861	0·71849
SO_3, ...	CaO	0·70056	1·42744
	$CaSO_4$	1·70049	0·58806
CARBON = 12·0036, . . .	..	..	..
$BaCO_3$, ...	C	0·06082	16·4420
	CO_2	0·22295	4·48517
	CO_3	0·30403	3·28919
BaO, ...	CO_2	0·28693	3·48517
CaO, ...	CO_2	0·78452	1·27467
CO_2, ...	C	0·27279	3·66587
	$CaCO_3$	2·27481	0·43960
	CO_3	1·36361	0·73349
	$MgCO_3$	1·91583	0·52197
	Na_2CO_3	2·40898	0·41511
	Na_2O	1·40898	0·70974
	$Ca(HCO_3)_2$	1·84201	0·54288
	$Mg(HCO_3)_2$	1·66262	0·60146
	$NaHCO_3$	1·90921	0·52378
CHLORINE = 35·457, . .	..	..	..
AgCl, ...	Cl	0·24736	4·04269
	HCl	0·25440	3·93088
	ClO_3	0·58225	1·71748
	ClO_4	0·69387	1·44119
Cl.	Ag	3·04257	0·32867
	Ca	0·56533	1·76887
	Mg	0·34267	2·91827
	Na	0·64859	1·54181
CHROMIUM = 52·04, . .	..	..	..
$BaCrO_4$, ...	Cr	0·20537	4·86914
	Cr_2O_3	0·30079	3·33351
	CrO_3	0·39479	2·53299
Cr_2O_3, ...	Cr	0·68438	1·46118
	CrO_3	1·31562	0·76010
COBALT = 58·95, . . .	..	..	..
Co, ...	CoO	1·27142	0·78652
Co_3O_4, ...	Co	0·73427	1·36189
	CoO	0·93357	1·07116
$CoSO_4$, ...	Co	0·38030	2·62953
	CoO	0·48351	2·06820
Potassium Cobaltinitrite (anhy.), .	Co	0·13032	7·67286
	CoO	0·16570	6·03489

TABLE II.— *Continued.*

WEIGHED.	REQUIRED.	DIRECT FACTOR.	REVERSE FACTOR.
COPPER = 63·55,	..	..	..
Cu,	CuO	1·25177	0·79887
CuCNS,	Cu	0·52370	1·90948
	CuO	0·65556	1·52892
CuO,	Cu	0·79887	1·25177
Cu_2O,	Cu	0·88819	1·12589
Cu_2S,	Cu	0·79854	1·25228
	CuO	0·99959	1·00041
FLUORINE = 19·00,	..	..	..
CaF_2,	F	0·48662	2·05500
HYDROGEN = 1·0078,	..	..	..
H_2O,	H	0·11190	8·93630
IODINE = 126·932,	..	..	..
AgI,	I	0·54041	1·85046
	HI	0·54472	1·83582
PdI_2,	I	0·70406	1·42033
	HI	0·70968	1·40909
IRON = 55·84,	..	..	..
Fe_2O_3,	Fe	0·69940	1·42977
	FeO	0·8998c	1·11136
	Fe_3O_4	0·96657	1·03460
	$FeCl_3$	2·03170	0·49220
$FeSO_4$, $(NH_4)_2SO_4$, $6H_2O$,	Fe	0·14240	7·02258
	Fe_2O_3	0·20360	4·91168
$FePO_4$,	Fe	0·37024	2·70093
LEAD = 207·22,	..	..	..
$PbCl_2$,	Pb	0·74504	1·34222
$PbCrO_4$,	Pb	0·64103	1·55998
$PbSO_4$,	Pb	0·68327	1·46354
	PbO	0·73603	1·35864
	Pb_3O_4	0·75362	1·32694
PbS,	Pb	0·86600	1·15474
	$PbSO_4$	1·26742	0·78900
PbO_2,	Pb	0·86623	1·15443
$PbMoO_4$,	Pb	0·56429	1·77213
MAGNESIUM = 24·30,	..	..	..
CO_2,	$MgCO_3$	1·91583	0·52197
	MgO	0·91583	1·09191
MgO,	Mg	0·60298	1·65882
	$MgCO_3$,	2·09191	0·47803
	$Mg(HCO_3)_2$	3·63084	0·27542
	$MgSO_4$	2·98673	0·33481
	SO_3	1·98672	0·50334
$Mg_2P_2O_7$,	Mg	0·21836	4·57950
	MgO	0·36214	2·76134
	$MgCO_3$	0·75757	1·32001
	$Mg(HCO_3)_2$	1·31489	0·76052
	$MgSO_4$	1·08162	0·92454

TABLE II.—*Continued.*

WEIGHED.	REQUIRED.	DIRECT FACTOR.	REVERSE FACTOR.
MANGANESE = 54·95,	..	..	..
Mn,	MnO	1·29117	0·77449
	Mn_3O_4	1·38842	0·72034
Mn_3O_4,	Mn	0·72034	1·38842
	MnO	0·93009	1·07517
	MnO_2	1·13983	0·87732
$Mn_2P_2O_7$,	Mn	0·38716	2·58293
	MnO	0·49989	2·00045
MnS,	Mn	0·63150	1·58353
$MnSO_4$,	Mn	0·36471	2·74190
	MnO	0·47090	2·12357
MERCURY = 200·60,	..	..	..
Hg,	$HgCl_2$	1·35351	0·73882
	HgO	1·07976	0·92613
	HgS	1·15985	0·86218
HgS,	Hg	0·86218	1·15985
	HgO	0·93095	1·07417
MOLYBDENUM = 96·0,	..	..	..
MoO_3,	Mo	0·66667	1·50000
$PbMoO_4$,	Mo	0·26142	3·82521
	MoO_3	0·39213	2·55014
NICKEL = 58·69,	..	..	..
Ni,	NiO	1·27262	0·78578
Dimethylglyoxime compound,	Ni	0·20318	4·92162
	NiO	0·25858	3·86732
$NiSO_4$,	Ni	0·37925	2·63682
NITROGEN = 14·008,	..	..	..
N,	HNO_3	4·49857	0·22229
	NO_3	4·42661	0·22591
	N_2O_5	3·85551	0·25937
	NH_3	1·21588	0·82245
NH_3,	HNO_3	3·69986	0·27028
	NO_3	3·64068	0·27467
	N_2O_5	3·17097	0·31536
$(NH_4)_2PtC_6$,	N	0·06310	15·8481
	HNO_3	0·28384	3·52308
	NH_3	0·07671	13·0353
Pt,	N	0·14385	6·96745
	HNO_3	0·64565	1·54882
	NH_3	0·17450	5·73059
PHOSPHORUS = 30·982,	..	..	..
$Mg_2P_2O_7$,	P	0·27841	3·59182
	PO_4	0·85352	1·17161
	P_2O_5	0·63786	1·56775
Phospho-molybdate compound,	P	0·01650	60·588
	PO_4	0·05060	19·7632
	P_2O_5	0·03781	26·4454
P,	P_2O_5	2·29107	0·43648
$PbMoO_4$,	P	0·00703	42·234
PLATINUM = 195·2,	..	..	..
Pt,	K_2PtCl_6	2·49052	0·40152
	$(NH_4)_2PtCl_6$	2·27469	0·43962

TABLE II.—*Continued.*

WEIGHED.	REQUIRED.	DIRECT FACTOR.	REVERSE FACTOR.
POTASSIUM = 39·105, . .	..	..	..
$KClO_4$, ...	K	0·28222	3·54333
	K_2O	0·33996	2·94155
K_2PtCl_6, ...	K	0·16088	6·21760
	K_2O	0·19379	5·16028
K, ...	K_2O	1·20458	0·83017
SILICON = 28·08, . . .	..	..	..
SiO_2, ...	Si	0·46738	2·13960
SILVER = 107·880, . . .	..	..	..
Ag, ...	AgCl	1·32870	0·75261
	AgBr	1·74080	0·57445
	AgI	2·17721	0·45930
	Cl	0·32867	3·04257
	Br	0·74080	1·34990
	I	1·17658	0·84992
	AgCN	1·24108	0·80575
	$AgNO_3$	1·57482	0·63499
SODIUM = 23·000, . . .	..	..	..
Na, ...	Na_2O	1·34783	0·74193
	Na_2SO_4	3·08837	0·32379
	NaCl	2·54161	0·39345
Na_2O, ...	Na_2SO_4	2·29137	0·43642
	NaCl	1·88571	0·53030
	Na_2CO_3	1·70974	0·58489
STRONTIUM = 87·63, . .	..	..	..
$SrSO_4$, ...	Sr	0·47705	2·09624
	SrO	0·56417	1·77252
Sr, ...	SrO	1·18266	0·84558
SULPHUR = 32·065, . .	..	..	..
$BaSO_4$, ...	S	0·13737	7·27975
	SO_2	0·27446	3·64357
	SO_3	0·34300	2·91544
	SO_4	0·41154	2·42987
	H_2S	0·14600	6·84921
	H_2SO_3	0·35164	2·84385
	H_2SO_4	0·42018	2·37993
TIN = 118·70, ...	..	..	..
Sn, ...	SnO	1·13480	0·88122
	SnO_2	1·26959	0·78766
SnO_2, ...	SnO	0·89384	1·11877
TITANIUM = 47·90, . . .	..	..	..
TiO_2, ...	Ti	0·59950	1·66806
TUNGSTEN = 184·1, . .	..	..	..
WO_3, ...	W	0·79319	1·26073
ZINC = 65·38, ...	..	..	..
Zn, ...	ZnO	1·24470	0·80338
$Zn_2P_2O_7$, ...	Zn	0·42911	2·33041
	ZnO	0·53412	1·87223
ZnS, ...	Zn	0·67093	1·49048
	ZnO	0·83514	1·19741

TABLE III*a*.—Specific Gravities of Acids and Alkalies.

Sp. Gr. at 60°/60° F.	% H_2SO_4 (in gms./100 gms.).	Gms. H_2SO_4/1000 cc.	% HNO_3 (in gms./100 gms.).	Gms. HNO_3/1000 cc.	% HCl (in gms./100 gms).	Gms. HCl/1000 cc.	% NaOH (in gms./100 gms.).	Gms. NaOH/1000 cc.	Sp.Gr. at 60°/60° F.	Gms. NH_3/100 gms. of solution.
1·00	0·09	1	0·10	1	0·16	1.6	..	..	0·88	35·3
1·01	1·57	16	1·90	19	2·14	22	0·90	9	0·89	31·8
1·02	3·03	31	3·70	38	4·13	42	2·20	23	0·90	28·4
1·03	4·49	46	5·50	57	6·15	64	2·80	29	0·91	25·0
1·04	5·96	62	7·26	75	8·16	85	3·67	38	0·92	22·1
1·05	7·37	77	8·99	94	10·17	107	4·46	47	0·93	18·7
1·06	8·77	93	10·68	113	12·19	129	5·29	56	0·94	15·8
1·07	10·19	109	12·33	132	14·17	152	6·13	65	0·95	12·5
1·08	11·60	125	13·95	151	16·15	174	7·02	76	0·96	9·8
1·09	12·99	142	15·53	169	18·11	197	7·92	86	0·97	7·2
1·10	14·35	158	17·11	188	20·01	220	8·68	95	0·98	4·6
1·11	15·71	175	18·67	207	21·92	243	9·51	106	0·99	2·5
1·12	17·01	191	20·23	227	23·82	267	10·56	117	1·00	..
1·13	18·31	207	21·77	246	25·75	291	11·76	129		
1·14	19·61	223	23·31	266	27·66	315	12·44	141		
1·15	20·91	239	24·84	286	29·57	340	13·37	154		
1·16	22·19	257	26·36	306	31·52	366	14·21	165		
1·17	23·47	275	27·88	326	33·46	392	15·06	176		
1·18	24·76	292	29·38	347	35·39	418	15·91	188		
1·19	26·04	310	30·88	367	37·23	443	16·77	200		
1·20	27·32	328	32·36	388	39·11	469	17·67	212		
1·21	28·58	346	33·82	409			18·56	225		
1·22	29·84	364	35·28	430			19·58	239		
1·23	31·11	382	36·78	452			20·50	252		
1·24	32·28	400	38·29	475			21·32	265		
1·25	33·43	418	39·82	498			22·44	280		
1·26	34·57	435	41·34	521			23·39	295		
1·27	35·71	454	42·87	544			24·40	310		
1·28	36·87	472	44·41	568			25·25	325		
1·29	38·03	490	45·95	593			26·35	339		
1·30	39·19	510	47·49	617			27·04	352		
1·31	40·35	529	49·07	643			27·98	367		
1·32	41·50	548	50·71	669			28·83	381		
1·33	42·66	567	52·37	697			29·75	396		
1·34	43·74	586	54·07	725			30·72	412		
1·35	44·82	605	55·79	753			31·72	428		
1·36	45·88	624	57·57	783			32·75	446		
1·37	46·94	643	59·39	814			33·69	462		
1·38	48·00	662	61·27	846			34·67	478		
1·39	49·06	682	63·23	879			35·60	495		
1·40	50·11	702	65·30	914			36·53	511		
1·41	51·15	721	67·50	952			37·47	528		
1·42	52·15	740	69·80	991			38·42	546		
1·43	53·11	759	72·17	1032			39·31	562		
1·44	54·07	779	74·68	1075			40·16	578		

TABLE III*a*.—*Continued.*

Sp. Gr. at 60°/60° F.	% H_2SO_4 (in gms./100 gms.).	Gms. H_2SO_4/1000 cc.	% HNO_3 (in gms./100 gms.).	Gms. HNO_3/1000 cc.	% NaOH (gms./100 gms.).	Gms. NaOH/1000 cc.
1·45	55·03	798	77·26	1121	41·13	596
1·46	55·97	817	79·98	1168	42·1	614
1·47	56·90	837	82·90	1219	43·0	632
1·48	57·83	856	86·05	1274	44·1	651
1·49	58·74	876	89·60	1335	45·2	670
1·50	59·70	896	94·09	1411	46·2	690
1·51	60·65	916	98·10	1481	47·2	710
1·52	61·59	936	99·67	1515	48·2	730
1·53	62·43	956			40·0	750
1·54	63·43	977				
1·55	64·26	996				
1·56	65·08	1015				
1·57	65·90	1035				
1·58	66·71	1054				
1·59	67·59	1075				
1·60	68·51	1096				
1·61	69·43	1118				
1·62	70·32	1139				
1·63	71·16	1160				
1·64	71·99	1181				
1·65	72·82	1202				
1·66	73·64	1222				
1·67	74·51	1244				
1·68	75·42	1267				
1·69	76·30	1289				
1·70	77·17	1312				
1·71	78·04	1334				
1·72	78·92	1357				
1·73	79·80	1381				
1·74	80·68	1404				
1·75	81·56	1427				
1·76	82·44	1451				
1·77	83·32	1476				
1·78	84·50	1504				
1·79	85·70	1534				
1·80	86·90	1564				
1·81	88·30	1598				
1·82	90·05	1639				
1·83	92·10	1685				
1·84	95·60	1759				
1·84	99·20	1825				

TABLE III*b*.—Concentrated Solutions of Acids and Alkalies: Normality against Specific Gravity at $\frac{15^\circ\ C.}{4^\circ\ C.}$

Normality.	H_2SO_4.		HNO_3.		HCl.		NaOH.	
	Gms./ Litre.	Sp Gr.	Gms./ Litre.	Sp. Gr.	Gms./ Litre.	Sp. Gr.	Gms./ Litre.	Sp. Gr.
0·10 *N*	4·90	..	6·30	..	3·645	..	4·0	..
0·25 *N*	12·25	..	15·75	..	9·110	..	10·0	..
0·50 *N*	24·50	..	31·50	..	18·22	..	20·0	..
0·75 *N*	36·75	..	46·25	..	27·34	..	30·0	..
1·0 *N*	49·00	1·031	63·00	1·032	36·45	1·017	40·0	1·041
2·0 *N*	98·00	..	126·0	..	72·90	..	80·0	(10 % NaOH
3·0 *N*	147·0	..	189·0	..	119·35	..	120·0	= 1·115 sp.
4·0 *N*	196·0	..	252·0	..	145·80	..	160·0	gr.)
5·0 *N*	245·0	1·153	315·0	1·190	182·25	..	200·0	..
6·0 *N*	294·0	..	378·0	..	218·70	1·100*	240·0	..
6·2 *N*	..	..	388·0	1·200	..	..	..	..
7·0 *N*	343·0	..	441·0	..	255·15	..	280·0	..
8·0 *N*	392·0	..	504·0	..	291·60	..	320·0	..
9·0 *N*	441·0	..	567·0	..	328·05	..	360·0	..
10·0 *N*	490·0	1·290	630·0	1·305	364·50	1·160	400·0	1·330
11·0 *N*	539·0	..	693·0	..	400·95	..	440·0	..
12·0 *N*	588·0	..	756·0	..	437·40	1·190	..	..
12·8 *N*	..	..	..	..	469·00	1·200	..	..
15·0 *N*	735·0	..	945·0	..	..	..	..	..
15·6 *N*	..	..	985·0	1·412*	..	..	..	..
15·8 *N*	..	..	991·0	1·420	..	..	..	..
20·0 *N*	980·0	1·540	1260·0	..	..	..	..	..
22·4 *N*	..	..	1411·0	1·500	..	..	..	..
24·0 *N*	..	..	1515·0	1·520	..	..	..	..
25·0 *N*	1225	1·660	..	..	..	..	..	..
30·0 *N*	1470	1·768	..	..	..	..	..	..
35·0 *N*	1715	1·835	..	..	..	..	..	..
36·0 *N*	1764	1·840*	..	..	..	..	..	..

* "**Constant Boiling-Point Acids**" (at 760 mm.).

H_2SO_4 boils at 330° C. and contains 98·3 per cent. H_2SO_4
HNO_3 „ 120·5° C. „ 68 per cent. HNO_3
HCl „ 108·5° C. „ 20 per cent. HCl

TABLE III*c*.—Strengths of Acids and Alkalies.

(*Per cent. Ionisation at* 25° *C.*)

Normality.	HCl	HNO_3	H_2SO_4*	H_3PO_4*	Formic Acid.	Acetic Acid.	KOH	NaOH	NH_4OH	$Ba(OH)_2$
2 *N*	69·0	74·0	40·0	16·0	1·0	0·3	66·0	57·0	0·3	..
1 *N*	80·0	85·0	51·0	17·5	1·5	0·4	82·0	77·0	0·4	..
0·1 *N*	95·0	96·0	61·0	27·5	4·5	1·3	95·0	93·0	1·3	75 (abt.
0.01 *N*	99·8	99·3	80·0	59·0	13·4	4·2	99·9	99·5	4·1	88
0·001 *N*	100	100	99·7	89·0	35·8	12·8	100	100	12·5	96

* First H^+.

"Carbonic Acid," saturated solution at 25° C. and 760 mm. is 0·034 *N*, and is 0·33 per cent. ionised.

"Hydrosulphuric Acid," „ 25° C. and 760 mm. is 0·3 *N*, and is 0·00 per cent. ionised.

TABLE IV.—Physical Characteristics of the more Important Inorganic Compounds.

Name.	Formula.	Molec. Wt. or At. Wt.	Solubility. (In water, unless otherwise stated).	Effect of Heating.
Acetic acid,	CH_3COOH	60·04	Inf.	B. Pt. 118·1° C.
Aluminium,	Al	26·97	....	..
„ chloride,	$AlCl_3$	133·34	41/100 gms. W. at 15° Sol. ether.	B. Pt. 177·8° C
„ hydroxide,	$Al(OH)_3$	155·99	" Prac. insol." Sl. sol. NH_4OH ; but not in pres. of NH_4^+	..
„ oxide,	Al_2O_3	101·94	....	..
„ phosphate,	$AlPO_4$	121·96	"Insol." water ; sol. NH_4OH.	..
„ sulphate,	$Al_2(SO_4)_3$	342·13	26·7/100 gms. S. at 20°.	..
„ ammonium alum,	$Al_2(SO_4)_3$, $(NH_4)_2SO_4$. $24H_2O$	906·64	6·25/100 gms. W. at 15°, (anhy.). 12·66/100 gms. W. at 15°, ($24H_2O$).	..
„ potassium alum,	$Al_2(SO_4)_3$, K_2SO_4, $24H_4O$	948·75	5·0/100 gms. W. at 15°, (anhy.). 9·6/100 gms. W. at 15°, ($24H_2O$). 2227/100 gms. W. at 100°.	..
Ammonia,	NH_3	17·03	60/100 gms. W. at 15°. Sol. alcohol, ether.	..
Ammonium acetate,	CH_3COONH_4	77·07	Very soluble.	..
„ "carbonate,"	$(NH_4)_2CO_3$ + ammonium carbamate	..	25·4/100 gms. W. at 16·7°.	..
„ chloride,	NH_4Cl	53·50	35·2/100 gms. W. at 15°.	Subl.
„ molybdate,	$(NH_4)_2MoO_4$	196·08	Dec. by water into Acid Salt	..
„ nitrate,	NH_4NO_3	80·05	192/100 gms. W. at 15·2°.	Dec.
„ oxalate,	$(COONH_4)_2$, H_2O	142·10	3·5/100 gms. S. at 15°.	..
„ persulphate,	$(NH_4)_2S_2C_8$	228·21	58·2/100 gms. W. at 0°.	Dec. 80° C.
„ phosphate,	$(NH_4)_2HPO_4$	132·08	131/100 gms. W. at 15°.	..
„ platinichloride,	$(NH_4)_2PtCl_6$	444·02	0·67/100 gms. W. at 15°.	...

Ammonium phospho-molybdate, .	$(NH_4)_3PO_4$, $12MoO_3$, H_2O, $2HNO_3$ passing into $(NH_4)_3PO_4$, $12MoO_3$ at 160°-180° C.	1877·15	0·0238/100 gms. W. at 15°. 0·0137/100 gms. 5 per cent. NH_4NO_3 at 15°. 0·0203/100 gms. of 1 per cent. HNO_3 at 15°.	..
„ sulphate, . . .	$(NH_4)_2SO_4$	132·14	74·2/100 gms. W. at 15°.	..
„ sulphite, . . .	$(NH_4)_2SO_3$, H_2O	134·16	"Sol. in 1 pt. water at 12°."	..
„ sulphide, . . .	$(NH_4)_2S$	68·14	....	..
„ thiocyanate, . .	NH_4CNS	76·12	63/100 gms. S. at 20°.	..
Antimony, ...	Sb	121·76	....	..
Antimonous chloride, . . .	$SbCl_3$	228·13	815·8/100 gms. W. at 15°.	B. Pt. 220·2° C.
Antimonic chloride, . . .	$SbCl_5$	299·05	Deliquesces.	M. Pt. 2·8° C. B. Pt., Dec.
Antimonous oxide, . . .	Sb_2O_3	291·52	0·0018/100 gms. W. at 15°.	M. Pt. red heat.
Antimony tetroxide, . .	Sb_2O_4	307·52	"Insol."	M. Pt. 1060° C.
Antimonic oxide, . . .	Sb_2O_5	323·52	"Insol."	M. Pt. 450° C.
Antimonous oxychloride, . .	SbOCl	173·22	"Insol."	..
„ sulphide, . . .	Sb_2S_3	339·71	0·00017/100 gms. W. at 18°.	M. Pt. 546° C.
Antimonic sulphide, . . .	Sb_2S_5	403·84	"Insol."	Dec. <300° C.
Arsenic, ...	As	74·934	....	..
Arsenious chloride, . . .	$AsCl_3$	181·30	Dec. by water: sol. dil. HCl.	B. Pt. 121·9° C.
Arsenic chloride, ...	$AsCl_5$	252·22	....	..
Arsenious oxide, ...	As_2O_3	197·87	1·66/100 gms. W. at 15°.	Subl.
Arsenic oxide, ...	As_2O_5	229·87	39/100 gms. S. at 15°.	Subl. red heat.
Arsenious sulphide, . . .	As_2S_3	246·06	0·00005/100 gms. W. at 18°.	Subl. 700° C.
Arsenic sulphide, ...	As_2S_5	310·19	"Insol."	Subl.
Barium, ...	Ba	137·36	....	..
„ carbonate, . . .	$BaCO_3$	197·36	0·0022/100 gms. W. at 18°.	Dec. 1450° C.
„ chloride, ...	$BaCl_2$	208·27	35·7/100 gms. W. at 20°. "Insol." conc. HCl	..
	$BaCl_2$, $2H_2O$	244·30	....	...
„ chromate, . . .	$BaCrO_4$	253·40	0·00033/100 gms. W. at 15°.	..
„ hydroxide, . . .	$Ba(OH)_2$	171·38		
	$Ba(OH)_2$, $8H_2O$	315·50	3·23/100 gms. W. at 15°.	
„ oxide, ...	BaO	153·36	1·5/100 gms. W. at 0°.	BaO_2 at 450° C.
„ sulphate	$BaSO_4$	233·42	0·00024/100 gms. W. at 20°; sol. conc. H_2SO_4 More sol. in solns. of chlorides.	..

TABLE IV.—*Continued.*

NAME.	FORMULA.	MOLEC. WT. OR AT. WT.	SOLUBILITY. (In water, unless otherwise stated).	EFFECT OF HEATING.
Barium nitrate,	$Ba(NO_3)_2$	261·38	9·2/100 gms. W. at 20°.	..
„ thiosulphate,	BaS_2O_3, H_2O	267·51	0·267/100 gms. W. at 17°.	..
Bismuth,	Bi	209·00	....	..
„ *trichloride*,	$BiCl_3$	315·37	Decomp., BiOCl ppd. Sol. as $BiCl_3$ in HCl.	M. Pt. 227° C. B. Pt. 442° C.
„ hydroxide,	$Bi(OH)_3$	260·02	" Insol." water ; v. sl. sol. alk. hydroxides (0·0001/100 gms. *N* NaOH at 20°.)	..
„ nitrate, basic,	$BiONO_3$, H_2O	305·03	" Insol." ; sol. as $Bi(NO_3)_3$ in HNO_3.	..
„ trioxide,	Bi_2O_3	466·00	" Insol."	M. Pt. 850° C.
„ oxychloride,	BiOCl	260·46	" Insol." : sol. HCl as $BiCl_3$.	M. Pt. red heat.
„ sulphide,	Bi_2S_3	514·19	0·00002/100 gms. W. at 20°. 0·02/100 cc. *N* Na_2S at 25°. 0·08/100 cc. *N* Na_2S + NaOH at 25°.	..
Bromine,	Br	79·915	3·65/100 gms. W. at 15°. 216/1000 cc. *N* KBr soln. at 18·5°. 736/1000 cc. 3*N* KBr soln. at 0°.	B. Pt. 58·7° C. ..
Cadmium,	Cd	112·40	....	..
„ chloride,	$CdCl_2$	183·31	59·12/100 gms. S. at 15°.	..
	$CdCl_2$, $2H_2O$	219·34		
„ hydroxide,	$Cd(OH)_2$	146·42	0·00026/100 gms. W. at 25°. Very sol. in NH_4OH and NH_4 salts.	..
„ oxide,	CdO	128·40	" Insol."	..
„ sulphate,	$CdSO_4$	208·46	76·6/100 gms. W. at 20°.	M. Pt. 1000° C.
„ sulphide,	CdS	144·46	0·0000009/100 gms W. at 18°. Sl. sol. NH_4OH.	Subl. 970° C.

Calcium,	Ca	40·09	....	..
„ carbonate,	$CaCO_3$	100·10	0·0013/100 gms. W. at 16°. 0·0065/100 gms. W. at 20° (air). 0·1175/100 gms. W. at 15° (sat. with CO_2).	Dec. 825° C.
„ chloride,	$CaCl_2$	111·00	74·7/100 gms. W. at 20°.	M. Pt. 774° C.
„ fluoride,	CaF_2	78·09	0·0016/100 gms. W. at 18°.	M. Pt. 1300° C.
„ hydroxide,	$Ca(OH)_2$	74·10	0·165/100 gms. W. at 20°. 0·077/100 gms. W. at 100°.	..
„ oxalate,	$(COO)_2Ca$	122·09	0·00056/100 gms. W. at 18°.	Dec. at redness
„ oxide,	CaO	56·09	..	M. Pt. 2500° C.
„ sulphate,	$CaSO_4$	136·15	0·176/100 gms. W. at 0°. 0·210/100 gms. W. at 40°. 0·161/100 gms. W. at 100°. More soluble in NH_4 salts; soluble in dil. HCl (abt. 4 per cent. in 6 per cent. acid). " Insol." in alcohol.	M. Pt. 1360°.
Carbon,	C	12·0036	....	..
„ dioxide,	CO_2	44·00	171 cc./100 cc. W. at 0° and 760 mm.	..
„ monoxide,	CO	28·00	3·52 cc./100 cc. W. at 0° and 760 mm.	..
„ disulphide,	CS_2	76·13	0·187/100 cc. S. at 15°.	B. Pt. 46·2° C.
Chlorine,	Cl	35·457	2·6 cc./1 cc. W. at 15° and 760 mm.	..
Chromium,	Cr	52·04	....	..
„ trioxide,	CrO_3	100·04	62·45/100 gms. W. at 18°.	Dec.
Chromic oxide,	Cr_2O_3	152·08	....	M. Pt. 196° C. Dec.
Chromium hydroxide,	$Cr(OH)_3$	103·05	" Insol." water; sol. alkalies; sl. sol. NH_4OH; NH_4 salts do not affect solubility.	
„ chloride,	$CrCl_3$	158·41	Solubility depends upon proportions of the violet to green chloride. Actually, abt. 60/70 gms. salt dissolve in 100 gms. of solution at 25°.	B. Pt. 1200° C.
	$CrCl_3, 6H_2O$	266·50		
„ sulphate,	$Cr_2(SO_4)_3$	392·24	120/100 gms. W.; but similar remarks apply as above.	..
„ potassium alum,	$Cr_2(SO_4)_3, K_2SO_4, 24H_2O$.	998·91	12·51/100 gms. W. at 25° (anhydr.).	..

TABLE IV.—*Continued.*

NAME.	FORMULA.	MOLEC. WT. OR AT. WT.	SOLUBILITY. (In water, unless otherwise stated).	EFFECT OF HEATING.
Citric acid,	$(CH_2)_2COH(COOH)_3$, H_2O	210·08	66/100 gms. S. at 0°.	..
Cobalt,	Co	58·95	....	..
Cobaltic hydroxide,	$Co(OH)_3$	109·97	"Insol."	..
Cobaltous hydroxide,	$Co(OH)_2$	92·97	0·0003/100 gms. W. at 15°; insol. KOH, sol. NH_4 salts.	..
Cobaltic oxide,	Co_2O_3	165·90	....	$Co_2O_3 \rightarrow Co_3O_4$ above 750° C.
Cobaltous oxide,	CoO	74·95	....	$Co_2O_3 \rightarrow CoO$ above 900° C
Cobalt oxide, -ous-ic,	Co_3O_4	240·85	....	Co_3O_4 stable up to 750° C. CoO stable above 900° C.
Cobaltic potassium nitrite,	$2Co(NO_2)_3$, $6KNO_2$, $3H_2O$	958·67	"Slightly soluble."	..
Cobaltous chloride,	$CoCl_2$	129·86	33·5/100 gms. W. at 20° (anhy.).	Subl.
	$CoCl_2$, $6H_2O$	237·96		
„ nitrate,	$Co(NO_3)_2$, $6H_2O$	291·07	49·73/100 gms. W. at 18°.	..
„ sulphide,	CoS	91·01	0·00038/100 gms. W. at 18°.	..
„ sulphate,	$CoSO_4$	155·01	33·05/100 gms. W. at 15°.	Dec. 880° C.
	$CoSO_4$, $7H_2O$	281·12	....	..
Copper,	Cu	63·55	....	..
„ ammonium chloride,	$CuCl_2$, $2NH_4Cl$, $2H_2O$	277·50	25·95/100 gms. S. at 20°.	..
Cupric chloride,	$CuCl_2$	134·46	207/100 gms. W. at 0°. Sol. alcohol.	Dec. 520° C.
Cuprous chloride,	CuCl	99·01	"Insol."	B. Pt. 950° C.
Cupric cyanide,	$Cu(CN)_2$	115·58	"Insol."; sol. KCN.	..

Cupric hydroxide,	$Cu(OH)_2$	97·57	"Insol." water; sol. NH_4OH, etc	..
„ oxide,	CuO	79·55	....	Loses O at 1040° C.
Cuprous oxide,	Cu_2O	143·10	"Insol."	..
Cupric sulphide,	CuS	95·61	0·000033/100 gms. W. at 18°. 0·0032/100 cc. sat. Na_2S soln.	Dec. (loses S) at 220° C.
Cuprous sulphide,	Cu_2S	159·16	0·0005/100 gms. W. at 15°.	..
Cupric sulphate,	$CuSO_4$	159·62	20·7/100 gms. W. at 20°.	..
	$CuSO_4$, $5H_2O$	249·69	....	..
Cuprous iodide,	CuI	190·48	0·0008/100 gms. W. at 18°.	..
„ thiocyanate,	CuCNS	121·63	0·023/100 gms. W. at 18°. Sol. NH_4OH.	M. Pt. 1084° C.
Iron,	Fe	55·84	....	..
Ferric chloride,	$FeCl_3$	162·21	74·4/100 gms. W. at 0°.	B. Pt. 315° C.
„ hydroxide,	$Fe(OH)_3$	106·86	0·000015/100 gms. W. ("cold").	..
„ oxide,	Fe_2O_3	159·68	....	Stable at redness; gives Fe_3O_4 at white heat.
„ phosphate,	$FePO_4$	150·82	"Insol.;" but $PO_4^{\equiv}$ is removed by water.	..
„ sulphate,	$Fe_2(SO_4)_3$	399·87	Sl. sol., anhy.; very sol., hydrated.	..
Ferrous ammonium sulphate,	$FeSO_4$, $(NH_4)_2SO_4$, $6H_2O$	392·14	18/100 gms. W. at 0°.	..
„ chloride,	$FeCl_2$	126·75	40/100 gms. S. at 15°.	..
„ hydroxide,	$Fe(OH)_2$	89·86	Sl. sol.; oxidises to -ic hydroxide in air.	..
„ oxide,	FeO	71·84	....	Fe_2O_3 at red heat.
„ sulphate,	$FeSO_4$, $7H_2O$	278·02	23·8/100 gms. W. at 15°.	..
„ sulphide,	FeS	87·90	0·00062/100 gms. W. at 18°.	..
„ ferric oxide,	Fe_3O_4	231·52	....	Most stable at high temps.
Fluorine,	F	19·00	....	..
Hydrobromic acid,	HBr	80·92	204/100 gms. W. at 15°; 67·1/100 gms. S. at 15°. 130/100 gms. W. at 100°.	..
Hydrochloric acid,	HCl	36·47	73·4/100 gms. W. at 18°; 42·3/100 gms. S. at 18°. 41/100 gms. alcohol at 20°; 25/100 gms. ether at 20°.	..
Hydrocyanic acid,	HCN	27·02	Inf.	..

TABLE IV.—*Continued.*

NAME.	FORMULA.	MOLEC. WT. OR AT. WT.	SOLUBILITY. (In water, unless otherwise stated).	EFFECT OF HEATING.
Hydrofluoric acid, . . .	HF	20·01	264/100 gms. W. ("cold").	..
Hydriodic acid, ...	HI	127·94	42,500 cc. HI/100 gms. W. at 10° and 760 mm.	..
Hydrogen, ...	H	1·008	2 cc./100 gms. W. at 0° and 760 mm.	..
„ peroxide, . . .	H_2O_2	34·02	Inf.	..
„ monoxide (water), .	H_2O	18·016	....	..
„ sulphide, . . .	H_2S	34·08	0·7/100 gms. W. at 0° and 760 mm.; 0·3/100 gms. W. at 30° and 760 mm. 4·37 cc./1 cc. W. at 0° and 760 mm.; 2·33/1 cc. W. at 30° and 760 mm. 17·9/1 (vol.) alcohol at 0° and 760 mm.; 6/1 at 24° and 760 mm.	
Iodine, ...	I	126·932	0·2765/1000 gms. W. at 18°; 0·92/1000 at 55°. 68/100 gms. S. at 25° 'S = 26 gms. per cent. KI, giving max. sol. of iodine). 24·5/100 gms. A at 25°: 20·6/100 cc. E at 16·6°. 17·8 gms./100 cc. CS_2 at 16·6°; 4·47 gms./100 cc. $CHCl_3$ at 25°.	
Iron (*see* Ferr—).				
Lead, ...	Pb	207·22	....	..
„ acetate, ...	$(CH_3COO)_2Pb, 3H_2O$	379·32	55·04/100 gms. W. at 25°.	..
„ carbonate, basic, . . .	$2PbCO_3, Pb(OH)_2$	775·63	0·00016/100 gms. W. ("cold").	..
„ chloride, ...	$PbCl_2$	278·13	0·909/100 gms. W. at 15°; 3·34/100 gms. W. at 100°. 0·36/100 cc. 1 % HCl (by wt.) 0·12/100 cc. 10 „ „ 0·52/100 cc. 20 „ „ } at 0° C. 1·75/100 cc. 30 „ „ 4·00/100 cc. 40 „ „ "Insol." in alcohol.	B. Pt. 954° C.

Lead chromate, ...	$PbCrO_4$	323·26	0·00001/100 gms. W. at 18° C. ..
„ hydroxide, ...	$Pb(OH)_2$	241·24	0·016/100 gms. W. at 25°; sol. NaOH. ..
	$2PbO, H_2O$	464·46	
„ nitrate, ...	$Pb(NO_3)_2$	331·21	50/100 gms. W. at 17°. ..
„ iodide, ...	PbI_2	461·08	0·06/100 gms. W. at 15°. ..
„ monoxide (litharge), . .	PbO	223·22	.... M. Pt. 888° C.
„ , Red	Pb_3O_4	685·66	.... Dec. 500° C.
„ peroxide, ...	PbO_2	239·22	.... Dec. 290° C.
„ sulphate, ...	$PbSO_4$	303·28	0·0038/100 gms. W. at 15°; 0·0056/100 at 40°. M. Pt. 1170° C.
			11/100 gms. S. at 100° (S. = 45 gms. amm. acetate in 100 gms. S.)
			0·0033/100 cc. 0·0001 *N* H_2SO_4.
			0·0013/100 cc. of 0·001 *N* H_2SO_4.
			0·0005/100 cc. of 0·01 *N* H_2SO_4.
			"Nil" in 100 gms. of 10 *N* H_2SO_4 (?).
„ sulphide, ...	PbS	239·28	0·000086/100 gms. W. at 18°. M. Pt. 1015° C.
„ molybdate, ...	$PbMoO_4$	367·2	"Insol." ..
Magnesium, ...	Mg	24·30	.... ..
„ carbonate, . . .	$MgCO_3$	84·30	0·0018 gm. Mg/100 gms. W. at 20° (in air). Dec. 960° C.
			2·6 gms. $MgCO_3$/100 gms. W. at 20° (sat. CO_2 at 760 mm.).
			(*Note.*—Mg is dissolved as bicarbonate.)
„ ammonium phosphate,	$MgNH_4PO_4, 6H_2O$	245·49	0·052/100 gms. W. at 20°; 0·016/100 gms. 5 % NH_4Cl + 2 % NH_4OH at 20°. Dec.
„ ammonium arsenate, .	$MgNH_4AsO_4, 6H_2O$	289·40	0·038/100 gms. W. at 20°. Dec.
„ chloride, . . .	$MgCl_2$	95·21	55·2/100 gms. W. at 20°. M. Pt. 708° C.
	$MgCl_2, 6H_2O$	203·30	Loses HCl.
„ hydroxide, . . .	$Mg(OH)_2$	58·32	0·0008/100 gms. W. at 18°. ..
„ oxide, . . .	MgO	40·30	.... ..
„ hydrogen phosphate, .	$MgHPO_4, 7H_2O$	246·41	0·3/100 gms. W. ("cold"). "Insol." dil. NH_4OH. ..
„ pyroarsenate, . .	$Mg_2As_2O_7$	310·47	"Insol." ..
„ pyrophosphate, . .	$Mg_2P_2O_7$	222·56	"Insol." ..
„ sulphate, . . .	$MgSO_4$	120·36	26·2/100 gms. W. at 20°. ..
	$MgSO_4, 7H_2O$	246·47	

TABLE IV.—*Continued.*

NAME.	FORMULA.	MOLEC. WT. OR AT. WT.	SOLUBILITY. (In water, unless otherwise stated).	EFFECT OF HEATING.
Manganese,	Mn	54·95	....	..
„ chloride,	$MnCl_2$	125·86	73·9/100 gms. W. at 20°.	..
„ hydroxide,	$Mn(OH)_2$	88·97	0·00002/100 gms. W. at 18°, soln. oxidised in air: sol. amm. salts.	..
„ oxide (-ous),	MnO	70·95	....	..
„ dioxide,	MnO_2	86·95	....	Loses O at 535° C
„ oxide (-ous-ic),	Mn_3O_4	228·85	....	Stable form at redness.
„ ammonium phosphate,	$MnNH_4PO_4$, $7H_2O$	294·08	"Insol" water; 0·012/100 cc. of 2 % NH_4OH at 20°.	..
„ pyrophosphate,	$Mn_2P_2O_7$	283·86	....	..
„ sulphate,	$MnSO_4$	151·01	61/100 gms. W. at 15°: sol. alcohol.	Dec. 850° C.
„ sulphide,	MnS	87·01	0·00062/100 gms. W. at 18° (pink).	..
			0·00047/100 gms. W. at 18° (green).	..
Mercury,	Hg	200·60	....	..
Mercuric chloride,	$HgCl_2$	271·51	5·3/100 gms. W. at 15·5°.	B. Pt. 303° C.
Mercurous chloride,	HgCl	236·06	....	M. Pt. 302° C.
			0·0002/100 gms. W. at 18°.	B. Pt. 382° C. Subl.
„ nitrate,	$HgNO_3$, $2H_2O$	298·64	Very soluble.	Dec.
Mercuric iodide,	HgI_2	454·46	0·0004/1000 gms. W. at 18°: sol. alcohol.	B. Pt. 349° C.
„ oxide,	HgO	216·60	0·05 gm./1000 cc. W. at 25°.	Dec.
„ sulphide,	HgS	232·66	0·0000012/100 gms. W. at 18°.	Subl. 446° C.
Molybdenum,	Mo	96·0	....	..
Molybdic oxide,	MoO_3	144·0	1·06 gms./1000 cc. at 18°.	Subl. 450° C.
„ sulphide,	MoS_3	192·2	Sl. sol. (hydrolysed by hot water).	Loses S.
„ acid,	H_2MoO_4	162·0	Sl. sol.	..

Nickel,	Ni	58·69	..
„ ammonium sulphate,	$NiSO_4, (NH_4)_2SO_4, 6H_2O$	394·99	6·5/100 gms. W. at 20°. ..
„ chloride,	$NiCl_2$	129·60	39·1/100 gms. W. at 20°. Subl.
	$NiCl_2, 6H_2O$	237·70	
„ carbonyl,	$Ni(CO)_4$	170·70	Equiv. of 0·0064 gm. Ni/100 gms. W. at 10°. B. Pt. 43° C.
„ cyanide,	$Ni(CN)_2$	110·75	" Insol." ; sol. in excess of KCN. ..
„ dimethylglyoxime,	$\left(\begin{matrix}CH_3.CNOH\\ CH_3.CNO\end{matrix}\right)_2Ni$	288·85	" Insol." ; sol. conc. A. ; sol. ' strong ' acids ; insol. ' weak ' acids ; insol. NH_4OH. Subl. 250° C.
„ hydroxide (-ous),	$Ni(OH)_2$	92·71	0·0013/100 gms. W. (" cold "). Insol. alk., sol. NH_4OH. ..
„ hydroxide (-ic),	$Ni(OH)_3$	109·71	" Insol." Sol. NH_4OH. ..
„ oxide (-ous),	NiO	74·69	.... Takes up O at 400° C.
„ oxide (-ic),	Ni_2O_3	165·38	.... Loses O at 600° C.
„ oxide (-ous-ic),	Ni_3O_4	240·07	.... ..
„ nitrate,	$Ni(NO_3)_2, 6H_2O$	290·81	48·59/100 gms. S. at 18°. ..
„ sulphate,	$NiSO_4$	154·75	37·90/100 gms. W. at 22·6°. Dec. 840° C.
	$NiSO_4, 7H_2O$	280·86	V. sol. in alcohol.
„ sulphide,	NiS	90·75	0·0036/100 gms. W. at 18°. ..
Nitric acid,	HNO_3	63·02	Inf. ..
Nitrogen,	N	14·008	2·35 cc./100 cc. W. at 0° and 760 mm. ..
Oxalic acid,	$(COOH)_2$	90·04	8·69/100 gms. W. at 20°. M. Pt. 98° C.
	$(COOH)_2, 2H_2O$	126·06	
Oxygen,	O	16·000	4·9 cc./100 cc. W. at 0° and 760 mm. ..
Perchloric acid,	$HClO_4$	100·47	Soluble (gives various hydrates). B. Pt. 39° C. (explosive).
Phosphoric acid (Ortho),	H_3PO_4	98·01	81·7/100 gms. S. at 15°. ..
Phosphorus,	P	30·982	.... M. Pt. 44° C.
„ trioxide,	P_2O_3	109·96	Forms phosphorous acid, etc. ..
	(P_4O_6)	(219·92)	
„ pentoxide,	P_2O_5	141·96	Forms phosphoric acid. Subl. at red.
Platinum,	Pt	195·2	.... ..
„ chloride,	$PtCl_4$	337·1	Very soluble. Dec.

TABLE IV.—*Continued.*

NAME.	FORMULA.	MOLEC. WT. OR AT. WT.	SOLUBILITY. (In water, unless otherwise stated).	EFFECT OF HEATING.
Potassium,	K	39·105	.....	..
„ bromate,	$KBrO_3$	167·02	6·9/100 gms. W. at 20°.	Dec. at redness.
„ bromide,	KBr	119·02	62·5/100 gms. W. at 15°.	M. Pt. 730° C.
„ carbonate,	K_2CO_3	138·01	52·5/100 gms. S. at 20°.	M. Pt. 896° C.
„ chlorate,	$KClO_3$	122·56	6·1/100 gms. W. at 15°.	M. Pt. 357° C. and dec.
„ chromate,	K_2CrO_4	194·24	61·7/100 gms. W. at 20°.	M. Pt. 975° C.
„ chloride,	KCl	74·56	32·4/100 gms. W. at 15°.	M. Pt. 772° C.
„ cobalticyanide,	$K_3Co(CN)_6$	332·31	Very soluble ; insol. A.	..
„ cobaltinitrite,	$2Co(NO_2)_3$, $6KNO_2$, $3H_2O$	958·68	0·09/100 gms. W. at 0°.	Dec. 200° C.
„ cobaltocyanide,	$K_4Co(CN)_6$	371·46	Soluble ; insol. A.	..
„ cyanide,	KCN	65·12	Soluble ; 122/100 gms. W. at 103°.	M. Pt. 601° C.
„ dichromate,	$K_2Cr_2O_7$	294·29	12/100 gms. W. at 20°.	M. Pt. 397·5° C., Dec. 500° C.
„ ferrocyanide,	$K_4Fe(CN)_6$, $3H_2O$	422·42	About 30/100 gms. W. at 20°.	..
„ ferricyanide,	$K_3Fe(CN_6$	329·22	43/100 gms. W. at 20°.	..
„ hydroxide,	KOH	56·11	107/100 gms. W. at 15° ; 312/100 at 143°. Sol. alcohol.	M. Pt. 360° C.
„ iodide,	KI	166·04	144/100 gms. W. at 20°.	M. Pt. 680° C.
„ nitrate,	KNO_3	101·12	31·6/100 gms. W. at 20°.	M. Pt. 337° C., Dec. 400° C.
„ nitrite,	KNO_2	85·12	74·5/100 gms. S. at 17·5°.	M. Pt. 297·5° C.
„ perchlorate,	$KClO_4$	138·56	0·75/100 gms. W. at 0° ; 1·8/100 gms. at 20° 0·53/100 gms. of *N* $HClO_4$ at 25°; 0·05/100 gms. of 93 % A. ; 0·017/100 gms. 93 % A. + 2 % $HClO_4$. 0·010/100 gms. of 98 % A. ; 0·028/100 gms. of 98 % A. + 2 % $HClO_4$. (All at 25° unless otherwise stated.)	Dec. 411° C.

Potassium permanganate, . .	$KMnO_4$	158·06	6·34/100 gms. W. at 19·8°. Dec. 240° C.
„ persulphate, . .	$K_2S_2O_8$	270·34	3·15/100 cc. sat. sol. at 15°. Dec. 125° C.
„ platinichloride, . .	K_2PtCl_6	486·15	0·90/100 gms. W. at 10°. ..
			0·0025/100 gms. 90 °/₀ A. at 20°. ..
„ sulphate, . . .	K_2SO_4	174·28	11·11/100 gms. W. at 20°. M. Pt. 1069° C.
„ hydrogen sulphate, .	$KHSO_4$	136·18	51·4/100 gms. W. at 20°. M. Pt. 218·6° C.
„ thiocyanate, . .	KCNS	97·19	68·5/100 gms. S. at 20°. ..
Silicon, ...	Si	28·08	.... ..
„ fluoride, ...	SiF_4	104·08	Decomposes. ..
„ dioxide, ...	SiO_2	60·08	"Insol." W.; sol. hot alkalies if amorphous. M. Pt. 1600° C. + ?
Silver, ...	Ag	107·80	.... ..
„ bromide, ...	AgBr	187·80	0·000084/1000 cc. W. at 20°. M. Pt. 427° C.
			3·47/1000 cc. 10 °/₀ NH_4OH at 12°.
„ chloride, ...	AgCl	143·34	0·0015/1000 cc. W. at 18°. M. Pt. 451° C.
			Max. sol. in 30 °/₀ NH_4OH soln. (by wt.) = 7·2/100 gms.
„ cyanide, ...	AgCN	133·90	0·000043/1000 cc. at 17·5°. Dec.
			0·54/100 gms. 10 °/₀ NH_4OH at 18°.
„ fluoride, ...	AgF	126·88	165/100 gms. W. at 18·6°. ..
„ nitrate, ...	$AgNO_3$	169·89	222/100 gms. W. at 20°. M. Pt. 209° C.
„ iodide, ...	AgI	234·81	0·0000028/1000 cc. W. at 20°. M. Pt. 526° C.
			0·035/1000 gms. 10 °/₀ NH_4OH at 10°.
„ oxide, ...	Ag_2O	231·76	0·021/1000 gms. W. at 20°. Dec. 300° C.
„ sulphate, ...	Ag_2SO_4	311·82	0·79/100 gms. S. at 20°. M. Pt. 660° C.
„ sulphide, ...	Ag_2S	247·82	0·000136/1000 cc. W. at 18°. ..
Sodium, ...	Na	23·000	.... ..
„ acetate, ...	$CH_3COONa, 3H_2O$	136·08	46·5/100 gms. W. at 20°. ..
„ hydrogen arsenate, . .	Na_2HAsO_4	185·94	20·5/100 gms. W. at 17°. ..
„ bromate, ...	$NaBrO_3$	150·91	34·5/100 gms. W. at 20°. ..
„ carbonate, . . .	Na_2CO_3	106·00	16·4/100 gms. W. at 15°. M. Pt. 849° C.
	$Na_2CO_3, 10H_2O$	286·16	
„ hydrogen carbonate, .	$NaHCO_3$	84·01	9·6/100 gms. W. at 20°. ..
„ chloride, ...	NaCl	58·45	36/100 gms. W. at 20°; 40/100 at 100°. M. Pt. 801° C.
			0·11/100 gms. S. at 30°. S. conts. 35·6 gms. HCl per cent. (*i.e.* 10 *N* HCl).
			Less sol. in A. "Insol." A.-E. mixt.

TABLE IV.—*Continued.*

NAME.	FORMULA.	MOLEC. WT. OR AT. WT.	SOLUBILITY. (In water, unless otherwise stated).	EFFECT OF HEATING.
Sodium fluoride,	NaF	42·00	4·3/100 gms. S. at 18°.	M. Pt. 980° C.
„ hydroxide,	$NaOH$	40·01	109/100 gms. W. at 20°; 521/100 gms. W. at 192°; 52·2/100 gms. S. at 20°· 83·9/100 gms. S. at 192°.	M. Pt. 318° C.
„ hypochlorite,	$NaClO$	74·45	Soluble.	Dec.
„ nitrate,	$NaNO_3$	85·01	88/100 gms. W. at 20°.	M. Pt. 310° C. Dec. 380° C.
„ nitrite,	$NaNO_2$	69·01	45·8/100 gms. S. at 20°.	M. Pt. 271° C. and dec. 320° C.
„ oxalate,	$(COONa)_2$	134·00	3·22/100 gms. W. at 15·5°.	..
„ oxide,	Na_2O	62·00	....	..
„ peroxide,	Na_2O_2	78·00	....	Loses O at red.
„ phosphate,	Na_2HPO_4	141·99	7·66/100 gms. W. at 20°.	..
	Na_2HPO_4, 12 H_2O	358·18		
„ silicate,	Na_2SiO_3	122·08	Soluble (considerable hydrolysis). "Insol." A.	..
„ sulphate,	Na_2SO_4	142·07	19·4/100 gms. W. at 20°. "Insol." A.	M. Pt. 884° C.
	Na_2SO_4, 10H_2O	322·23	Less sol. in A.	
„ monosulphide,	Na_2S	78·09	15·30/100 gms. S. at 18°.	"Infusible."
	Na_2S, 9H_2O	240·21		
„ sulphite,	Na_2SO_3	126·03	25·31/100 gms. W. at 18·2°.	Dec.
	Na_2SO_3, 7H_2O	252·18		
„ hydrogen sulphite,	$NaHSO_3$	104·07	Soluble.	..
„ tartrate,	$Na_2C_4H_4O_6$, 2H_2O	230·06	29/100 gms. W. at 6°.	..
„ thiosulphate,	$Na_2S_2O_3$	158·13	40-50/100 gms. S. at 20°. (Depends on hydration.)	..
	$Na_2S_2O_3$, 5H_2O	248·21		
Tin,	Sn	118·70	....	..
Stannic oxide,	SnO_2	150·7	....	Refractory.
„ chloride,	$SnCl_4$	260·53	Soluble. Hydrolyses.	B. Pt. 114° C.
„ sulphide,	SnS_2	182·87	0·00002/100 gms. W. ("cold").	Dec. redness.

Stannous chloride,	$SnCl_2$	189·61	138·6/100 cc. S. at 18°.	B. Pt. 603° C.
„ hydroxide,	$Sn(OH)_2$	152·72	0·000013/1000 cc. W. at 25°.	..
„ sulphide,	SnS	150·76	0·000002/1000 cc. W. (" cold ").	..
Strontium,	Sr	87·63	....	..
„ carbonate,	$SrCO_3$	147·64	0·00109/100 cc. W. at 24° : 1·19/1000 cc. W. sat. with CO_2 at 760 mm. (24°).	Dec. 1075° C.
„ oxide,	SrO	103·63	Becomes $Sr(OH)_2$, which is sl. sol.	..
„ sulphate.	$SrSO_4$	183·69	0·1143/1000 cc. W. at 17·4° : " insol." in A.	..
Sulphur,	S	32·065	....	B. Pt. 444·6° C.
„ dioxide,	SO_2	64·06	47·28 cc./1 cc. W. at 15° and 760 mm.	B. Pt. —10° C.
„ trioxide,	SO_3	80·06	Decomp.	..
Sulphuric acid,	H_2SO_4	98·080	Inf.	..
Sulphurous acid,	H_2SO_3	82·080	See SO_2 .	..
Tartaric acid,	$H_2C_4H_4O_6$ / $C_2H_2(OH)_2(COOH)_2$	150·06	139·44/100 gms. W. at 20° (active) ; racemic is less soluble (20·6/100 gms. W. at 20°).	..
Titanium,	Ti	47·90	....	..
„ dioxide,	TiO_2	79·90	....	..
Tungsten,	W	184·1	....	..
„ trioxide,	WO_3	232·0	" Insol."	Subl. bright redness.
Uranium,	U	238·15	....	..
Uranyl acetate,	$UO_2(C_2H_3O_2)_2$, $2H_2O$	424·24	Soluble.	..
„ nitrate,	$UO_2(NO_3)_2$, $6H_2O$	502·27	56/100 gms. S. at 21°.	..
Vanadium,	V	50·95	....	..
„ pentoxide,	V_2O_5	181·90	0·8/100 gms. W. at 20° : sol. conc. acids, sol. alkalies.	M. Pt. 658° C.
Zinc,	Zn	65·38	....	..
„ carbonate,	$ZnCO_3$	125·38	0·021/100 gms. W. at 25°.	Loses CO_2 at 300° C.
„ chloride,	$ZnCl_2$	136·29	368/100 gms. W. at 20° ; sol. A.	M. Pt. 365° C. / B. Pt. 732° C.
„ hydroxide,	$Zn(OH)_2$	99·40	0·0042/1000 cc. W. at 18° (as ZnO).	..
„ oxide,	ZnO	81·38	„ „ „	..
„ pyrophosphate,	$Zn_2P_2O_7$	304·72	....	..
„ sulphate,	$ZnSO_4$	161·44	50·88/100 gms. W. at 15°.	Dec. 600° C.
	$ZnSO_4$, $7H_2O$	287·55	143/100 gms. W. at 0°.	
„ sulphide,	ZnS	97·44	0·0069/1000 cc. W. at 18°.	..

TABLE V.—Temperature Corrections for Volumetric Reagents.

Assumed: 1. Measured in glass the coefficient of expansion of which is 0·000025.
2. Apparatus standardised at 15° C. (or 60° F.).
3. Solution made up at 15° C. (60° F.).

Corrections per Litre.

Temperature.	Water or 0·1 *N* Solutions (or Weaker).	*N* HCl.	*N* HNO_3, H_2SO_4, KOH, NaOH, Na_2CO_3.
15° C.	..	..	..
20° C.	— 0·75 cc.	— 1·00 cc.	— 1·30 cc.
25° C.	— 1·80 cc.	— 2·15 cc.	— 2·8 cc.
30° C.	— 3·10 cc.	— 3·50 cc.	—4·4 cc.

NOTES.—Use of the table.

1. Suppose a solution is made up at 20° C. instead of 15° C. At 15° C it will be 0·75 cc. per litre too strong (0·1 *N* solution).

2. Suppose the solution is made up at 20° C. and is to be titrated against a solution made up at 15° C.: then, for 0·1 *N* solutions, an allowance of 0·75 cc. per litre will have to be made, plus in the case of the one and minus in the case of the other, whichever is taken as the standard solution.

3. Solutions made up at the same temperatures, whatever they are, can be titrated against one another without correction only if they come under the same headings above. Thus: *N* H_2SO_4 can be titrated against *N* NaOH, but if *N* NaOH is used with *N* HCl, even if they were made up at the same temperature, an allowance must be made (0·9 cc. per litre at 30° C.) if the titre is appreciable.

4. In most cases, there is no need to make any allowance provided that the burette readings come below 100 cc., but for larger volumes, allowance must be made.

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