the bead obtained. The loss gives the amount of base metal originally present.

(*b*) Flatten; anneal; roll out thin; again anneal; roll into a cornet as in gold bullion assay; place in a parting flask, and boil for fifteen minutes with strong sulphuric acid, which dissolves out the whole of the silver. Wash, dry, and weigh the residue. The loss equals the silver originally present, plus the amount of pure silver added for cupellation.

(*c*) Add to the cornet twelve times its weight of silver and cupel with lead as before. Flatten bead; anneal; roll out again; anneal; coil into a cornet, and boil for a few minutes in dilute nitric acid, then with stronger acid as in gold parting. Wash thoroughly, dry, and weigh the residue. The loss gives the platinum, plus the silver added. The undissolved portion may be gold and osm-iridium.

Boil in aqua-regia, and weigh the residue if any, which is the osm-iridium. The loss in weight gives the gold.

(*d*) In platinum alloys containing much platinum not more than 2 grains should be taken for assay as the difficulty in cupelling is increased with the size of the button. Platinum will be dissolved in the sulphuric acid if too much silver is added, which would otherwise facilitate the cupellation.

PART III.

ASSAYING AND ANALYSIS BY WET METHODS.

Estimation of Bases and Acids with Methods of Separating Them from Each Other.

Group I.

Containing Silver, Mercurous Oxide, Lead.

Note.—In the following exercises, two portions of each substance should be worked as a check on each other.

§ 167. *Silver.*

Take 5 grains of pure silver; introduce into a conical flask; add sufficient dilute nitric acid to dissolve it; close the mouth with a small funnel, and heat gently till all is dissolved. Dilute with hot water and transfer to half pint beaker; add hot water till about half full; boil on sand bath; remove and add dilute hydrochloric acid with constant stirring as long as a precipitate is produced. A large excess of the precipitant must be avoided. Heat nearly to boiling with frequent stirring till the precipitate settles; pour off the supernatant liquid through a filter of known ash; wash the silver chloride twice in the beaker with hot water; then transfer to filter, and wash with water containing a little nitric acid, then with pure water. Dry thoroughly in water oven, and transfer precipitate to a dry watch glass. Incinerate the paper in a weighed porcelain crucible; add a few drops of nitric acid to dissolve any reduced silver; heat; then add a little hydrochloric acid; evaporate carefully to dryness; add the

precipitate from the watch glass, and heat the crucible till the edges of the chloride just begin to fuse ; allow to cool in a dessicator and weigh. Then—

143·5 : 108 : : Weight of precipitate : x.

EXAMPLE.

	Grains.
Suppose the crucible with ppt. weighs - -	107·112
,, crucible alone ,, - -	100·520
Weight of precipitate =	6·592

$$\frac{108 \times 6{\cdot}592}{143{\cdot}5} = 4{\cdot}961 \text{ grains of silver.}$$

$$\text{Then } \frac{4{\cdot}961 \times 100}{5} = 99{\cdot}22 \text{ per cent. of silver}$$

See note, § 222.

§ 168. *Lead.*

Dissolve 5 grains of lead in nitric acid ; remove excess of acid by evaporation ; dilute with water ; transfer to beaker, and add dilute sulphuric acid as long as a precipitate forms ; then add twice as much alcohol as there is sulphuric acid present ; allow to stand in a warm place till the lead sulphate completely subsides ; pour the clear liquid on to a filter ; wash the precipitate once or twice with dilute alcohol ; transfer to filter, and wash till all free sulphuric acid has been removed. Dry ; remove precipitate, and incinerate the paper in a weighed porcelain crucible ; cool ; moisten with nitric acid. Then add a few drops of sulphuric acid ; cautiously evaporate ; ignite moderately ; add the main bulk of precipitate ; again ignite ; cool, and weigh.

In cases where alcohol cannot be used, a greater excess of sulphuric acid is requisite.

If the liquid contain nitric acid it is advisable to evaporate after adding the sulphuric acid until the nitric acid is removed.

If hydrochloric acid be present, the precipitate and filter ash must be treated with strong sulphuric acid, evaporated, and ignited to convert any lead chloride into sulphate.

The amount of lead is calculated thus—

As 303 : 207 : : Weight of ppt. : x.

§ 169. *Mercurous Oxide.*

If nitric acid be present the solution should be evaporated to a small bulk, diluted considerably with cold water ; and then dilute hydrochloric acid mixed with twice its bulk of phosphorous acid added till all the chloride is precipitated ; allow to stand a few hours in a warm place ; filter off to weighed paper, which has been dried at 100° C. ; dry at same temperature ; cool in desiccator, and weigh. After deducting the weight of the paper—

235·5 : 200 : : Wt. of ppt. : x.

Mercurous oxide is generally converted into mercuric oxide for estimation, by heating with nitric acid, and adding hydrochloric acid by degrees till the mercury compound is dissolved.

§ 170. *Separation of Silver, Lead and Mercury in an amalgam.*

Take 25 grains and dissolve in nitric acid ; evaporate to small bulk ; dilute considerably with water ; boil ; add dilute hydrochloric acid in excess, with constant stirring till all is precipitated ; heat nearly to boiling for some time till the liquid is quite clear ; filter rapidly ; wash with boiling water several times ; dry ; ignite ; and weigh the silver chloride, with precautions as in § 167.

The filtrate contains the mercury and lead. Evaporate to small bulk and add pure sulphuric acid in excess. Evaporate till the sulphuric acid begins to volatilise ; add

more sulphuric acid if necessary; then dilute with water; filter off the lead sulphate and treat it as in § 168.

Filtrate from lead sulphate must be evaporated to small bulk; diluted with water and a current of sulphuretted hydrogen passed into the liquid until all the mercury is precipitated as sulphide. The whole must be allowed to stand for some time in a warm place and filtered through a weighed paper (dried at 100°); washed with hot water; dried at same temperature as the filter paper and weighed.

If any nitric acid be present, the precipitate must be washed a few times with bisulphide of carbon or a hot solution of sodium sulphide to dissolve the free sulphur liberated by that acid.

As 232 : 200 : : Wt. of ppt. : x.

§ 171. *Another Method of Separation.*

Excess of nitric acid having been removed and solution diluted, sodium carbonate is added in slight excess, then potassium cyanide in excess; heat gently for some time and filter off the carbonate of lead. Wash the precipitate with water containing a little cyanide. Dry, ignite, and weigh as lead oxide.

As 223 : 207 : : Wt. of ppt. : x.

The filtrate containing silver and mercury is neutralised with nitric acid, and a little more added to insure complete precipitation of silver cyanide, which is filtered on to a weighed paper; washed; dried at 100° C., and weighed.

As 134 : 108 : : Wt. of ppt. : x.

The filtrate from the latter is evaporated to small bulk, neutralised with carbonate of soda, and sulphuretted hydrogen passed in till all the mercury is precipitated as HgS. This is allowed to settle; filtered; washed, and weighed as explained in § 170.

As free sulphur will be present, it should be treated with sodium sulphide, as described in § 170.

Group II.

Containing Mercury, Bismuth, Copper, Cadmium and Lead.

§ 172. *Mercuric Oxide.*

Twenty grains may be used to determine the mercury in the metallic state by distillation in a piece of glass combustion tubing about 12 inches long and ½-inch bore (Fig. 65). First put into the part $a\,b$ a mixture of dry bicarbonate of soda and chalk, then the mercury compound mixed with excess of quicklime in the part $b\,d$, then another layer of lime, and lastly a loose plug of asbestos. The end $e\,g$ is next drawn out with the blowpipe to a small jet which just dips beneath the surface of water in flask g during the operation. The tube and its contents are heated in an ordinary tube furnace till all the metal is volatilised. The part $a\,b$ is then strongly heated and the carbonic acid liberated expels the last traces of mercury. The contracted portion is cut off and any adhering mercury washed into the flask. When the metal has settled, the water is decanted off, the mercury transferred to a porcelain crucible, the water removed by blotting paper, and the last remnants by standing some time under a bell jar over strong sulphuric acid; then the metal is weighed.

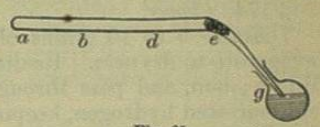

Fig. 65.

§ 173. *Bismuth Oxide.*

Dissolve 10 to 15 grains of the metal or compound in a little dilute nitric acid; dilute with water, disregarding any precipitate; boil; mix with carbonate of ammonia in slight excess and heat for some time nearly to boiling; filter; dry; and ignite, with the usual precautions, oxidising any reduced metal by nitric acid. Weigh the

Bi_2O_3. In the presence of sulphuric and hydrochloric acids, basic sulphide and chloride are precipitated, which are not decomposed by excess of ammonium carbonate, and thus give incorrect results. When this is the case, re-dissolve in nitric acid and re-precipitate.

As 464 : 416 :: Wt. of ppt. : x.

§ 174. *Copper.*

Dissolve 5 to 10 grains of copper in nitric acid and evaporate to dryness. Re-dissolve in hydrochloric acid; dilute; boil, and pass through the solution a current of sulphuretted hydrogen, keeping the liquid nearly to boiling in the meantime. When complete, allow to settle; test the supernatant liquid with sulphuretted hydrogen water; if it remains clear, filter quickly; wash continually with water containing sulphuretted hydrogen, and dry quickly on the filter. Burn the paper and transfer both ash and precipitate to a weighed porcelain crucible; add a little flowers of sulphur and ignite strongly in a stream of hydrogen, using gas blow-pipe; cool, and weigh as Cu_2S.

As 158 : 126 :: Wt. of ppt. : x.

The hydrogen may be introduced by having a hole in the cover of crucible, into which fits a fire-clay tube (Fig. 67) conveying the dry gas.

§ 175. *Cadmium.*

Five to ten grains of the metal may be dissolved in dilute acid; the solution diluted; boiled, and an excess of carbonate of soda added. The latter should be added cautiously till the solution is strongly alkaline; then boil; allow to settle; decant through filter, and wash the precipitate two or three times before transferring to the paper; wash well with hot water; dry; remove completely from paper; burn latter; allow to cool; oxidise with nitric acid; ignite; transfer precipitate and ash to crucible; ignite, and weigh the CdO.

128 : 112 :: Wt. of ppt. : x.

To avoid the loss of cadmium by volatilisation on ignition of the paper, the latter should be saturated with a solution of ammonium nitrate, dried, and then ignited.

§ 176. *Separation of Mercury, Bismuth, Copper and Cadmium in an alloy.*

Take 5 grains of each metal; dissolve in nitric acid; remove excess of acid by evaporation; dilute with water and add sodium carbonate in slight excess, then a solution of potassium cyanide; heat gently for some time; filter, and wash repeatedly. The precipitate is Bi_2O_3. Treat as in § 173.

The filtrate contains the mercury, copper and cadmium. Pass a current of sulphuretted hydrogen into the solution, or add sulphuretted hydrogen solution, as long as a precipitate forms. Allow to subside; wash repeatedly by decantation; treat precipitate once more with solution of potassium cyanide; heat gently; filter, and wash the sulphides of mercury and cadmium.

The filtrate contains the copper. Evaporate in fume chamber with the addition of nitric and sulphuric acids until all hydrocyanic acid is expelled; dilute with water; precipitate the copper as sulphide with sulphuretted hydrogen, and estimate as in § 174.

The precipitated sulphides of mercury and cadmium may be carefully washed off the filter into a porcelain basin and digested with dilute nitric acid until all the cadmium sulphide is dissolved. Filter the undissolved portion through a weighed paper, and well wash; dry at 100° C., and estimate mercury as in § 172.

Boil off excess of acid in filtrate; add excess of sodium carbonate, and determine the cadmium as described in § 175.

Group III.

Containing Tin, Antimony, Arsenic, Gold and Platinum.

§ 177. *Tin.*

Digest 10 grains of tin with dilute nitric acid at about 80° C. When all is converted to a white powder, dilute to four or five times the bulk with hot water and allow to stand in a warm place for several hours. Filter; wash with hot water; dry; remove to a watch glass; burn the paper; allow to cool; add 3 drops of nitric acid; dry; ignite; add the precipitate and strongly ignite, then weigh the SnO_2.

As 150 : 118 : : Wt. of ppt. : x.

§ 178. *Antimony.*

Digest 10 grains of antimony with dilute nitric acid, and proceed as with tin. But a little of the oxide of antimony is soluble in the nitric acid, so that the filtrate should be evaporated to dryness; the residue re-dissolved in hydrochloric acid; tartaric acid added; diluted with water, and a current of sulphuretted hydrogen passed through to precipitate the remaining antimony as sulphide. The latter is filtered, washed, and oxidised in a crucible with fuming nitric acid, and the main bulk added; dried; ignited, and weighed as Sb_2O_4.

As 304 : 240 : : Wt. of ppt. : x.

§ 179. *Arsenic.*

When ordinary nitric acid is used to dissolve arsenic or an arsenical compound the metal will be present chiefly in the form of arsenious acid. When fuming acid is employed, then the higher oxide is formed. Both oxides being present, adopt the following method. Evaporate the solution to remove nitric acid; reduce the arsenic acid by boiling with a solution of sodium sulphite; add

hydrochloric acid; largely dilute with water; heat to about 70° C., and pass sulphuretted hydrogen gas until the arsenic is precipitated as As_2S_3, together with free sulphur. Filter; wash; dissolve precipitate in ammonia; filter off sulphur, and well wash. The filtrate contains the arsenic. Add hydrochloric acid in the cold to re-precipitate the As_2S_3; allow to stand some time; filter on to weighed paper; wash; dry; dissolve any free sulphur with bisulphide of carbon; dry again at 100° C., and weigh.

As 246 : 150 : : Wt. of ppt. : x.

§ 180. *Gold.*

Take 5 grains of gold, dissolve in aqua regia at a moderate temperature; evaporate to dryness on water bath; re-dissolve in water and a little hydrochloric acid; add a solution of pure sulphate of iron in excess, and digest at a gentle heat in a porcelain dish for several hours; filter; wash; dry; ignite, and weigh the metallic gold.

Ammonium oxalate may be used instead of iron sulphate; or the gold may be precipitated with sulphuretted hydrogen as sulphide, which is readily decomposed by ignition.

§ 181. *Platinum.*

Dissolve 5 grains of platinum in aqua regia; evaporate cautiously to dryness; re-dissolve in the smallest quantity of water; add excess of ammonium chloride solution, then an equal bulk of alcohol. Allow to stand in a warm place for a few hours; filter; wash with alcohol; dry; ignite in a platinum crucible, and weigh the spongy platinum. Or collect precipitate on weighed paper; dry at 100°, and weigh.

Separation of the Constituents of Groups II. and III.

§ 182. *Principles on which the Separations are based :—* *Platinum and Gold* from all the rest by their insolu

bility in nitric acid, and the subsequent volatility of the chlorides of tin and antimony when subjected to a stream of chlorine gas.

Platinum from Gold by the insolubility of the double chloride of platinum and ammonium.

Antimony from Tin by the insolubility of sodium antimoniate in alcohol.

Silver from all the rest, except Mercurous Oxide, by the insolubility of its chloride in hot dilute nitric acid.

Lead from all the rest by the insolubility of its sulphate in alcohol.

Mercury from all the rest, except lead, by the insolubility of mercury sulphide in dilute nitric acid.

Bismuth and Lead from all the rest by the insolubility of their carbonates in potassium cyanide.

Cadmium from Copper by the solubility of copper sulphide in potassium cyanide.

§ 183. *Separation of Gold, Platinum, Tin, Antimony, and Arsenic in an alloy.*

Take 20 grains of the alloy, roll out very thin, and cut into small pieces. Introduce into a porcelain boat placed in a glass tube (Fig. 66), and pass a current of dry chlorine gas while the outside of the bulb is being heated gently with a Bunsen's burner, and finally increased to redness. The chlorides of gold and platinum will be left, and the chlorides of the other metals volatilised. The gold and

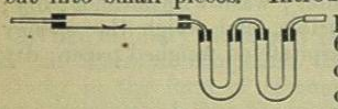

Fig. 66.

platinum chlorides are dissolved in water and a little hydrochloric acid, the platinum estimated as double chloride (§ 181), the gold in solution as metal (§ 180). The volatile chlorides are received in U-tubes containing water, and condensed. Transfer the solution to a beaker, and precipitate the three metals as sulphides with sulphuretted hydrogen; filter; transfer to beaker, and digest with a large excess of a saturated solution of oxalic acid; filter, and thoroughly wash. The filtrate contains the tin; add ammonia till alkaline; then add warm ammonium sulphide until the precipitate just redissolves; add excess of warm acetic acid, and allow the precipitated SnS_2 to settle in a warm place; then filter. As this precipitate has a great tendency to pass through the pores of the paper, the washing is effected by a solution of ammonium acetate containing a slight excess of acetic acid. Dry; ignite paper separately; then add the precipitate; cover the crucible with lid, and heat gently for some time; remove lid, and gradually increase the temperature, finishing with a strong heat; cool; then heat repeatedly with ammonium carbonate to a high degree to remove any sulphuric acid; cool again, and weigh the SnO_2.

As 150 : 118 : : Wt. of ppt. : x.

The precipitated sulphides of arsenic and antimony contain a little tin. They may be dissolved in ammonium sulphide, excess of oxalic acid added, and then boiled with sulphuretted hydrogen water. Filter and wash; extract tin from filtrate as before, and add the sulphide to the main bulk of precipitate. The separation of antimony and arsenic will be explained in the next paragraph.

§ 184. *Separation of Tin, Antimony, and Arsenic in an alloy.*

Oxidise the alloy with strong nitric acid in a porcelain crucible, adding the acid drop by drop till the oxidation is

complete. Dry on water bath; transfer to silver dish, rinsing out the crucible with a solution of sodium hydrate; dry again; add eight times the bulk of solid sodium hydrate, and fuse for some time. Cool and treat with hot water till the undissolved residue has the appearance of a fine powder; dilute with water; add one third the volume of alcohol; allow to stand several hours with frequent stirring; filter; wash with alcohol and water containing a few drops of carbonate of soda; continue the washing until the colour of a portion of the fluid running off remains unaltered on being acidified with hydrochloric acid and mixed with sulphuretted hydrogen water.

Rinse the antimoniate of soda from the filter; wash with hydrochloric and tartaric acids; heat gently till dissolved. Precipitate with sulphuretted hydrogen; filter through a weighed paper, wash rapidly with water containing a little sulphuretted hydrogen; dry at 100° C., and weigh. The precipitate retains a little water and free sulphur. A portion should be placed in a porcelain boat which is then inserted in a glass tube and cautiously heated while a current of carbonic acid is passed, until the orange ppt. becomes black; cool in carbonic acid and weigh. From the amount of anhydrous sulphide found, the amount in the whole precipitate may be calculated. Then:—

As 336 : 240 : : Wt. of ppt. : x.

The filtrate from the insoluble antimoniate contains the tin and arsenic. Add hydrochloric acid in excess; pass a current of sulphuretted hydrogen until all is precipitated, and allow to stand till the odour of sulphuretted hydrogen disappears. Treat the precipitate as in § 183 for estimation of tin. The arsenic sulphide is then filtered off; washed; dried at 100° C., and weighed. If any free sulphur is present it must be dissolved by washing with bisulphide of carbon, the precipitate again dried and weighed, and the drying repeated until the weight is constant.

Group IV.

Containing Iron, Aluminium, Chromium, Zinc, Manganese, Nickel and Cobalt.

§ 185. *Iron.*

Dissolve 10 grains of iron in nitric acid; remove excess of acid by evaporation; dilute with water; add ammonia in slight excess; heat nearly to boiling; decant on to filter; wash with hot water; wash precipitate on to filter with hot water; dry thoroughly; ignite in platinum crucible, and weigh.

As 160 : 112 : : Wt. of ppt. : x.

The precipitate may be examined for silica by dissolving in strong hydrochloric acid, evaporating to dryness and re-dissolving in hydrochloric acid, when any silica will be rendered insoluble and may be filtered off, washed, dried, ignited and weighed, and the weight deducted from the weight of the original iron precipitate.

§ 186. *Aluminium.*

Dissolve 25 grains of crystallised alum, which has been coarsely powdered and dried by pressure between filter paper. The solution is then mixed with a large excess of ammonium chloride, and a slight excess of ammonia added. Heat for some time; filter; wash with hot water till free from sulphuric acid; dry; ignite in a platinum crucible, and weigh the Al_2O_3.

As 102 : 54 : : Wt. of ppt. : x.

Note.—Fixed organic matter prevents the precipitation of alumina, which is also the case in some measure with the oxides of iron and chromium.

§ 187. *Chromium.*

25 grains of chrome alum may be employed. Dry as in § 186. Dissolve; make the solution moderately

dilute; heat nearly to boiling and add a slight excess of ammonia; heat again nearly to boiling until the supernatant liquid remains colourless; filter; wash; dry; ignite in a platinum crucible, and weigh the Cr_2O_3.

As 152·8 : 104·8 : : Wt. of ppt. : x.

Note.—Organic matter interferes with the precipitation.

§ 188. *Zinc.*

10 grains of pure zinc may be dissolved in a little nitric acid, and the solution diluted to a moderate extent. Heat nearly to boiling in a porcelain vessel; add sodium carbonate cautiously till the solution is alkaline; boil; allow to stand some time; filter; wash with hot water; dry; ignite the paper; then add the precipitate; ignite strongly, and weigh the ZnO.

As 81 : 65 : : Wt. of ppt. : x.

§ 189. *Manganese.*

10 grains of pure black oxide of manganese may be employed for practice. Dissolve in hydrochloric acid; dilute, and proceed as in the case of zinc. Sometimes it happens that the filtrate is turbid, then evaporate to dryness; dissolve out the soluble matter with boiling water, and filter the residue on to a fresh paper. Dry and ignite both precipitates in a platinum crucible very strongly for fifteen minutes in an oxidising flame. Cool and weigh the Mn_3O_4.

As 229 : 165 : : Wt. of ppt. : x.

Note.—If iron is present, this must be precipitated first.

§ 190. *Nickel.*

Dissolve 10 grains of the metal in nitric acid; filter off any silica and carbon; remove excess of acid by evaporation; dilute with water; boil in porcelain dish, and add excess of sodium hydrate. Heat nearly to boiling for some time; allow precipitate to settle; filter; wash with boiling water; dry; and ignite the NiO in a weighed platinum crucible.

As 74·6 : 58·6 : : Wt. of ppt. : x.

§ 191. *Cobalt.*

10 grains of pure cobalt nitrate may be taken for practice. The solution is mixed with an excess of a strong solution of sodium hydrate and heated until the precipitate has a brownish colour; allow to settle; filter; wash with hot water; dry; ignite, and finally reduce to the metallic state by means of a current of dry hydrogen. This is effected in a porcelain crucible (Fig. 67) having a hole in the cover, into which fits a porcelain tube conveying the gas, the crucible being ignited in the meantime.

Fig 67.

§ 192. *Separation of the members of Group IV.*

Principles on which the separations are based.

Iron, Aluminium, and Chromium from the rest by the insolubility of their hydrates formed by ammonia or barium carbonate.

Aluminium and Chromium from the rest by the solubility of their oxides in tartaric acid and sodium sulphide.

Chromium from the rest by conversion to chromic acid on fusion with nitre and sodium carbonate.

Aluminium from Iron by the solubility of alumina in caustic potash.

Manganese from Zinc by the solubility of zinc carbonate in ammonium chloride.

Zinc from Nickel, Cobalt and Manganese by the insolubility of zinc sulphide in a solution made neutral with sodium carbonate and containing a little sodium acetate.

Nickel and Cobalt from Manganese and Iron by the insolubility of the sulphides of nickel and cobalt in very dilute hydrochloric acid.

Nickel from Cobalt by the formation of soluble cobalticyanide of potassium and of soluble double cyanide of nickel and potassium which is decomposed by bromine.

Ferric Oxide from Ferrous Oxide. First determining the total iron volumetrically by means of a solution of potassium bichromate, then dissolving another portion in sulphuric acid in an atmosphere of carbonic acid, and determining the FeO; the difference giving the amount of Fe_2O_3.

§ 193. *Separation of Iron, Aluminium and Chromium from Nickel, Cobalt, Zinc and Manganese.*

A chloride or nitrate solution may be employed, but not a sulphate.

Put the solution into a flask, which must contain a little free acid; add ammonium chloride; then add a moderate excess of freshly precipitated barium carbonate suspended in water. Cork the flask, and allow to stand some time in the cold, with occasional shaking. Iron and aluminium hydrates soon separate; chromium hydrate takes some time. Decant; wash two or three times by decantation with cold water; filter, and wash.

The precipitate and the filtrate contain baryta, which may be removed from each by adding dilute sulphuric acid after dissolving the precipitate.

§ 194. *Separation of Chromium from Iron and Aluminium.*

Fuse the oxides with two parts potassium nitrate and four parts sodium carbonate in a platinum crucible; boil the mass with water; rinse the contents into a beaker; add several crystals of potassium chlorate, then hydrochloric acid in excess; evaporate to the consistence of syrup, adding potassium chlorate occasionally to remove free hydrochloric acid; dilute with water; boil till all soluble matter is dissolved. Filter off the residue, and add ammonia to the solution to precipitate the alumina which has been dissolved; heat till the ammoniacal fluid has almost lost its alkaline character; allow to stand some time; filter, and wash with hot water. The filtrate contains the chromium.

Mix the filtrate with sodium acetate in excess; add acetic acid until the solution is strongly acid; then add a neutral solution of acetate of lead as long as a precipitate forms. Allow to stand in a warm place till all has subsided; filter on to weighed paper; wash; dry at 100° C., and weigh the $PbCrO_4$.

As 323·4 : 52·4 : : Wt. of ppt. : x.

§ 195. *Separation of Aluminium from Iron.*

Mix the hydrochloric acid solution with sodium hydrate till neutral, and pour the solution gradually into excess of nearly boiling soda in a platinum or silver dish, stirring all the time; filter; well wash; dry, and ignite. Weigh the Fe_2O_3. This precipitate contains some alkali, and should be dissolved in hydrochloric acid; boiled with nitric acid if necessary, and re-precipitated with ammonia, as in § 185.

The alkaline filtrate contains the aluminium. Add hydrochloric acid in excess; boil with the addition of potassium chlorate (to destroy any organic matter); concentrate by evaporation; dilute with water; boil; add ammonium chloride in quantity, then ammonia in slight excess; boil till free ammonia is expelled; allow the precipitate to settle; decant; wash with boiling water two or three times, decanting through the filter; transfer

precipitate to filter; wash; dry; ignite in a covered platinum crucible, as particles may be lost by the violent escape of the last traces of water. Weigh the Al_2O_3.

Note.—As sodium and potassium hydrates generally contain alumina, this must be tested for before using, and allowed for in the result.

§ 196. *Another Method of Separating Iron from Aluminium.*

Neutralise the excess of hydrochloric acid with sodium carbonate, and add sodium thiosulphate in sufficient quantity to reduce all the ferric to ferrous oxide; then add more of the thiosulphate, and boil until the odour of sulphurous acid has disappeared, when the alumina is precipitated as hydrate along with sulphur.

$$Al_2O_3.3SO_3 + 3S_2O_3Na_2 + 3H_2O = Al_2H_6O_6 + 3Na_2SO_4 + 3SO_2 + 3S.$$

Filter, wash, dry, ignite, and weigh the Al_2O_3.

The iron in solution may be estimated by adding hydrochloric acid; boiling to decompose excess of the thiosulphite; filtering off the free sulphur, then adding ammonium chloride, ammonia in excess, and ammonium sulphide until all the iron is precipitated. Filter, wash, dry, and ignite with a little sulphur in an atmosphere of hydrogen. Weigh the FeS.

As 88 : 56 : : Wt. of ppt. : x.

§ 197. *Separation of Manganese from Zinc and Nickel.*

Use a slightly acid solution. Add ammonium chloride, then ammonium carbonate in excess, and allow the white carbonate of manganese to settle in a warm place; filter through a double paper; wash with hot water; dry; ignite strongly, and weigh the Mn_3O_4.

§ 198. *Separation of Zinc from Nickel, Cobalt and Manganese.*

Use a hydrochloric acid solution. Add sodium carbonate until a permanent precipitate forms, then a few drops of hydrochloric acid to just re-dissolve it. Now pass a current of sulphuretted hydrogen till all the zinc sulphide is thrown down; add a few drops of very dilute sodium acetate; pass the gas again for some time; allow the whole to stand some time; filter; wash with water containing sulphuretted hydrogen; dry; transfer to weighed porcelain crucible; add a little sulphur, and ignite in current of hydrogen. Weigh the ZnS.

As 97 : 65 : : Wt. of ppt. : x.

Small quantities of zinc sulphide may be converted to oxide by strongly igniting in an open platinum crucible.

§ 199. *Separation of Manganese from Nickel and Cobalt.*

Use a hydrochloric acid solution. Add sodium carbonate in excess, then a moderate excess of acetic acid; then add to the clear liquid 3 to 4 cubic centimetres of sodium acetate solution (1 of salt to 10 of water) for each grain of nickel or cobalt present; heat, and pass sulphuretted hydrogen to saturation. When precipitation is complete, filter, and wash the sulphides of nickel and cobalt.

The filtrate contains the manganese, together with some nickel and cobalt. Concentrate the solution by evaporation; add ammonium sulphide, then an excess of acetic acid, when the remaining sulphides of nickel and cobalt will be thrown down; filter, and wash as before. Boil the filtrate with hydrochloric acid to remove the acetic acid; neutralise with ammonia; boil; add ammonium sulphide; boil for fifteen minutes; cool; add more ammonium sulphide, and filter through double filter; wash, dry, and ignite with sulphur in a current of hydrogen. Weigh the MnS.

As 87 : 55 : : Wt. of ppt. : x.

§ 200. *Separation of Nickel from Cobalt.*

Use a hydrochloric acid solution; evaporate to remove

excess of acid; dilute; add potassium cyanide until the precipitate at first formed re-dissolves; add a little more cyanide; boil for some time; cool; add bromine, and well shake. Allow to stand for some time, adding potash occasionally, so that the solution may remain alkaline to the end. In about an hour the whole of the nickel will be precipitated as a black powder, the cobalt being in solution. Add a little more bromine to bring down the last traces, filter and wash. As the precipitate contains alkali, dissolve in hydrochloric acid; dilute with water; add sodic hydrate in excess; heat for some time near to boiling; filter; wash; dry; ignite, and weigh the NiO.

As 74·6 : 58·6 : : Wt. of ppt. : x.

The filtrate containing the cobalt is acidified with hydrochloric acid, evaporated to dryness in a fume chamber, re-dissolved in water, and the solution mixed with excess of a strong solution of sodium hydrate. Heat until the precipitate has a brownish colour, allow to settle; filter; wash with hot water; dry; ignite, and finally reduce to the metallic state by means of a current of dry hydrogen. See § 191.

§ 201. *Estimation of Ferric and Ferrous Oxides.*

(*a*) Dissolve in hydrochloric acid or aqua regia if necessary; dilute, and add pure zinc; allow to stand until the solution is quite colourless, and estimate the total amount of iron present by means of a standard solution of potassic permanganate. (See Volumetric Analysis, § 366.)

(*b*) Weigh another portion, and dissolve by heating with sulphuric acid in a flask through which a stream of carbonic acid is constantly passing; dilute with water, and determine the amount of ferrous oxide as above. The difference gives the ferric oxide.

For example—Suppose in the first case 40 per cent. of iron was found, and in the second case 30 per cent., then 30 per cent. is present in the form of FeO, and 10 per cent. in the form of Fe_2O_3.

Now 56 unites with 16 ∴ 30 unites with 8·6 = 38·6 per cent. of FeO. And 112 unites with 48 ∴ 10 unites with 4·3, which equals 14·3 per cent. of Fe_2O_3.

(*c*) Instead of passing a stream of CO_2, the oxides may be dissolved in a small flask as in Fig. 68, provided with a bent tube, and connected with another similar tube by a piece of india-rubber tubing, so that it may be closed when desired with a pinch tap. This tube dips beneath the surface of recently boiled water in the conical beaker (*b*). A lump of sodium bicarbonate is added to the flask (*a*) at the commencement of the experiment to expel residual air.

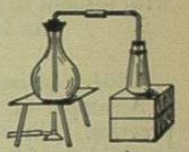

Fig. 68.

Group V.

Containing Barium, Strontium, Calcium and Magnesium.

§ 202. *Barium.*

Hydrochloric acid solution is employed. Heat nearly to boiling; add dilute sulphuric acid till complete precipitation is effected; allow to stand a few hours for the liquid to clear; decant the clear liquid; rinse on to the filter with a dilute solution of ammonium chloride to prevent any fine particles passing through the pores. The paper should never be more than half full as there is a tendency in the liquid to creep upwards. Wash till free from sulphuric acid; dry; ignite in platinum crucible, and weigh the $BaSO_4$.

As 233 : 137 : : Wt. of ppt. : x.

Where expedition is desired, the precipitation may be facilitated by continuous stirring for three or four minutes, and the solution at once filtered.

§ 203. *Strontium.*

Use a concentrated solution containing hydrochloric acid; boil; mix with sufficient dilute sulphuric acid to precipitate strontium sulphate; add an equal volume of alcohol; allow to stand several hours, and proceed as with barium. The precipitate should however be washed with alcohol to obtain a more correct result.

As 183·2 : 87·2 : : Wt. of ppt. : x.

§ 204. *Calcium.*

A sample of pure white marble may be analysed for practice. Dissolve in hydrochloric acid and filter off any insoluble residue. Evaporate to remove excess of acid; add ammonia until the solution is alkaline; then solution of ammonium oxalate in sufficient quantity to precipitate the calcium as oxalate; heat till the precipitate has subsided; pour the clear liquid through a filter; wash once or twice with hot water containing ammonia and ammonium oxalate; then wash the precipitate on to the filter; again wash with hot water; dry, and very gently ignite. Now add a little pure ammonium carbonate; moisten with water; dry and heat to very faint redness; cool, and weigh the $CaCO_3$.

Repeat this operation till the weight is constant.

As 100 : 40 : : Wt. of ppt. : x.

With the aid of a blow-pipe and platinum crucible the carbonate may be converted into oxide and weighed as CaO; but the temperature must be maintained at a white heat for some time.

§ 205. *Magnesium.*

Add ammonium chloride to the solution, then ammonia in slight excess. If any precipitate appears, add more ammonium chloride to re-dissolve it. Warm gently; add a solution of ammonium phosphate (microcosmic salt) in excess, and well stir with a glass rod, taking care not to touch the sides of the beaker; allow to stand

several hours in a warm place; filter; wash with water containing $\frac{1}{4}$th its volume of ammonia; dry; heat, gently at first, in a platinum crucible, then ignite strongly; cool and weigh the $Mg_2P_2O_7$.

As 222 : 48 : : Wt. of ppt. : x.

§ 206. *Separation of Barium, Strontium, Calcium and Magnesium.*

Principles on which the Separations are based:—

Barium, Strontium and Calcium from Magnesium by the solubility of magnesium carbonate in certain ammonium salts.

Barium from Strontium and Calcium by the insolubility of barium silico-fluoride.

Strontium from Calcium by the insolubility of strontium nitrate in alcohol and ether, or by the insolubility of strontium sulphate in ammonium sulphate.

§ 207. *Separation of Magnesium from Barium, Strontium and Calcium.*

Employ a nitric acid or an aqueous solution. Remove any excess of acid by evaporation; add ammonium acetate and ammonia in slight excess, then ammonium carbonate to precipitate the carbonates of barium, strontium and calcium (too much ammonium carbonate must be avoided); digest at a moderate temperature for a short time; cool, and filter.

To filtrate add hydrochloric acid; evaporate to dryness; re-dissolve in water, and estimate the Mg as pyrophosphate. (See § 205.)

The precipitated carbonates of barium, strontium, and calcium may be dissolved in hydrochloric acid, rendered nearly neutral, and hydrofluosilicic acid added in excess,

then $\frac{1}{3}$rd the volume of alcohol, and allowed to stand a few hours; precipitate collected on a weighed paper; washed with water and alcohol; dried at 100° C., and the BaF_2,SiF_4 weighed.

As 279·5 : 137 : : Wt. of ppt. : x.

The filtrate contains the strontium and calcium. Evaporate with nitric acid in a flask to dryness; cool; add equal volumes of alcohol and ether; close with a cork; allow to stand some time, with occasional shaking, and filter off the insoluble strontium nitrate; wash with alcohol and ether. Re-dissolve the insoluble nitrate in water and estimate the strontium as in § 203.

The filtrate containing the calcium is boiled with hydrochloric acid to remove alcohol, ether, and nitric acid; the solution diluted; neutralised with ammonia, and the calcium estimated as in § 204.

Group VI.

Containing Potassium, Sodium and Ammonium.

§ 208. *Potassium.*

The solution should be concentrated and made slightly acid with hydrochloric acid. If other acids are present the solution must be evaporated to dryness, re-dissolved in water and a little hydrochloric acid. Then add a concentrated solution of platinum chloride in slight excess; evaporate to a small bulk on a water bath; add an equal bulk of alcohol; filter through a tared paper; dry at 100° C., and weigh the $PtCl_4,2KCl$.

487·3 : 78 : : Wt. of ppt. : x.

§ 209. *Sodium.*

Ten grains of pure sodium chloride may be employed for practice. First clean, ignite, and weigh a platinum

crucible and lid; add the 10 grains of salt; place the crucible on a triangular support in an inclined position; partly cover the mouth with the lid; add sufficient sulphuric acid, drop by drop, very cautiously, to convert the salt into sulphate; very gently warm the crucible with a Bunsen flame, beginning at the top; as the fumes diminish, gradually increase the temperature to redness, and maintain at this point for about a quarter of an hour; allow to cool, and weigh the Na_2SO_4. Heat again, cool, and re-weigh. Repeat, if necessary, until the weight is constant.

142 : 46 : : Wt. of ppt. : x.

§ 210. *Ammonium* (NH_4).

The operation is conducted the same as for potassium, $PtCl_4,2AmCl$ being precipitated; but all the constituents except platinum are volatile on ignition, so that the amount of ammonium may be calculated from the weight of spongy platinum obtained. 194·3 parts by weight of platinum are associated with 36 parts of ammonium.

§ 211. *Separation of Sodium, Potassium and Ammonium.*

Principles on which the Separations are based :—

Potassium and Ammonium from Sodium by the insolubility of the double chlorides of platinum with potassium and ammonium.

Potassium from Ammonium by the volatility of ammonia and ammonium salts.

§ 212. *Separation of Potassium, Sodium and Ammonium.*

Convert the salts into chlorides, if not already present as such. In case of nitrates, the evaporation must be repeated several times. In presence of phosphates, borates, and sulphates, special methods must be adopted (see Fresenius' *Quantitative Analysis*). The hydrochloric

acid solution must be evaporated and ignited to remove ammonium compounds; re-dissolved in water, and platinum chloride added to precipitate the potassium as ($PtCl_4$, 2KCl); filter, etc., as in § 208; dry at 100° C., and weigh.

§ 213. *Separation of Ammonium from Potassium and Sodium.*

Weigh the total quantity of the mixed salts in a tared platinum crucible; heat gently with the lid on, gradually increasing the temperature to a low, red heat, and maintaining it at that point till the ammonium salt has volatilised. The decrease in weight shows the amount originally present.

Ammonium may be estimated by boiling the substance containing it with sodium hydrate, conducting the evolved ammonia into hydrochloric acid, and estimating as in § 210.

ESTIMATION OF ACIDS.

Group I.

Containing Sulphuric, Phosphoric, Boracic and Silicic Acids.

§ 214. *Sulphuric Acid.*

Acidify the solution, if necessary, with hydrochloric acid; heat nearly to boiling, and add barium chloride in sufficient excess; heat for some time, with frequent stirring, until the liquid becomes clear, and proceed as in § 202.

As 233 : 96 : : Wt. of ppt. : the SO_4 present.

§ 215. *Phosphoric Acid.*

Take 5 grains of pure crystallised phosphate of soda for practice ($POHONa_2O_2 + 24OH_2$), and estimate the

P_2O_5 as phospho-molybdate of ammonia. Concentrate the solution by evaporation, if necessary, to a small bulk; make it slightly acid with nitric acid, and add 40 c.c. of the molybdate solution described in § 104*c*. (54 c.c. of this solution are required for 1 grain of P_2O_5.) Shake vigorously till the precipitate is well formed; heat to boiling, and allow to settle in a warm place for a few hours. Test a portion of the supernatant liquid, to ascertain if the precipitation is complete; filter and wash very thoroughly with a solution of ammonium nitrate (containing 14 grammes or 232 grains of salt in 100 c.c. of solution, slightly acidulated with nitric acid, and also containing a little molybdate solution). Now dissolve the phospho-molybdate precipitate in the smallest quantity of ammonia, and wash the filter with dilute ammonia. Add to the solution hydrochloric acid, until the precipitate formed just re-dissolves with difficulty, then add 2 c.c. of the magnesia mixture given in § 104*d*. Shake as before, and allow to stand some time; then add one-third the bulk of ammonia. Allow to stand a few hours; filter; wash with ammonia diluted with three times its bulk of water; dry; raise very cautiously to a strong red heat: cool, and weigh the $Mg_2P_2O_7$.

As 222 : 142 : : Wt. of ppt. : the P_2O_5 present.

Instead of the above double precipitation, the phospho-molybdate precipitate may be washed with dilute nitric acid; filtered; dried at 100° C., and weighed. It contains 1·63 per cent. of P_2O_5. Or the sodium salt could be at once precipitated with magnesia mixture.

§ 216. *Boracic Acid.*

There is no borate sufficiently insoluble to allow the acid to be precipitated in that form, so that this acid is usually estimated by loss.

When no other acid is present, the solution is mixed with a known weight, say 53 grains of pure anhydrous carbonate of soda, which must be sufficient to render it