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QUALITATIVE ANALYSIS

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QUALITATIVE ANALYSIS

BY

WILLIAM BRIGGS, LL.D., M.A., B.Sc., F.C.S.

AND

R. W. STEWART, D.Sc.

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CONTENTS.

INTRODUCTION.

CHEMICAL ANALYSIS is divided into two branches, viz. QUALITATIVE Analysis, which has for its object the determination of the number and nature of the constituents of substances without reference to their proportions, and QUANTITATIVE Analysis, which seeks to ascertain the amount of the several constituents present in a substance. The present volume is restricted to the study of the former branch.

In its simpler form, qualitative analysis usually has reference to the examination of *salts, i.e.* combinations of metals and acid radicles, and in such cases the problem involved is the determination of the particular metals and acid radicles present in a substance.

In determining the metal or metals present in a given substance, we submit a portion of the substance to the action of various reagents. These reagents are applied in the dry way, *e. g.*, before the blowpipe, or in the wet way, *i. e.*, in the state of solution. The latter method is the more important. Usually, the phenomenon which we take advantage of in detecting any substance is the formation of a *precipitate,* when solutions of certain bodies are brought together. The formation of a precipitate, of course, is due to the interaction of the substances in solution giving rise to the production of a new compound which is insoluble, or only slightly soluble, in water.

Reagents are divided into *group reagents* and *special reagents.* The former are those which produce a similar general result with several metals—*e. g.*, Hydrochloric acid gives a precipitate with either silver, mercury, or lead, and is therefore the group reagent for those metals. Special reagents are those which we make use of for confirming the presence or absence of a certain metal.

In analysing a substance it is of the utmost importance that the reagents should be used in a systematic order; otherwise altogether erroneous results may be obtained.

The metals are usually divided into six* groups, according to their behaviour with the following reagents.

Group I. comprises those metals whose chlorides are insoluble in water, and which, therefore, are precipitated by hydrochloric acid (or, indeed, by any soluble chloride). They are Silver, Lead, and Mercury (ous).

Group II. comprises *those of the remaining metals* whose sulphides are insoluble in hydrochloric acid, and which, therefore, are precipitated by sulphuretted hydrogen in presence of that acid. They are Mercury (ic), Lead, Bismuth, Copper, Cadmium, Tin, Antimony, and Arsenic.

Group III. includes *those of the remaining metals* whose hydroxides are insoluble in water and in ammonium chloride solution, and which, therefore, are precipitated by ammonia in presence of ammonium chloride. They are Iron, Chromium, and Aluminium.

Group IV. consists of *those of the remaining metals* whose sulphides are insoluble in water, and which, therefore, are precipitated by ammonium sulphide in alkaline solutions. They are Nickel, Cobalt, Manganese, and Zinc.

Group V. includes *those of the remaining metals* whose carbonates are insoluble in water and ammonium salts, and which, therefore, are thrown down by ammonium carbonate in presence of ammonium chloride. They are Barium, Strontium, and Calcium.

Group VI. comprises *the remaining metals*, for which there is no general reagent. They are Magnesium, Potassium, Sodium, and Ammonium.

Special notice should be taken of the words "of the remaining metals," which appear so often in the above account. Group IV., for example, does not consist of all the metals which are precipitated by ammonium sulphide in alkaline solutions, but only of those not included in Groups I., II., and III., which are thus precipitated.

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* The student must be perfectly familiar with these divisions and the group reagents before commencing systematic analysis.

After each group reagent has been added, the precipitate must be filtered off and the next group reagent added to the filtrate, which is now free from the metal of the previous group. If there is no precipitate when a given group reagent is added, this indicates that no metal of this group is present. In this case it is of course unnecessary to filter before adding the next group reagent.

After separating the metals of a mixture into their respective groups, the next thing is to separate the members of each group from one another. The method adopted in each case depends upon the solubility of a certain compound (*e. g.*, the sulphide) of one or more metals in a given reagent, the corresponding compound of the other metal or metals of the group being insoluble. Tables for the separation of the metals of each group are given in Chapter IV. Finally, the presence of each metal is confirmed by the application of *special* or *confirmatory* tests, which depend upon reactions peculiar to the metal. These reactions are given in Chapter III.

In case the student is told that only one metal is to be looked for, the process of analysis is of course much simplified. All he has to do, after finding to which group the metal belongs, is to go through the Table for that group till he finds which metal is present, and then apply confirmatory tests. The student is strongly advised to practise analysing a large number of simple salts before attempting to analyse mixtures. It must be carefully borne in mind that analysis is founded upon a knowledge of the properties of the metals and acids, and is really an application of such chemical knowledge to the question in hand. The student should, therefore, in all cases endeavour to clearly understand the chemical changes which are produced in the various operations of chemical analysis. To this end he will derive great advantage by making it a rule to express by means of equations the various reactions which he performs. These equations should be written in a note-book at the time the experiments are being made in the laboratory.

A more complicated case of qualitative analysis presents itself when the substance to be examined contains not only salts but other bodies, such as free elements and oxides. An account of the processes to be adopted under these circumstances will be found in Chapter V.

Rules for Qualitative Analysis:—

(1) **Use small quantities** of the substance to be tested, even if you have a large stock of it at your disposal; otherwise reactions will often be masked, especially those performed in the dry way. If you have only a small allowance, treasure it, and always keep some in reserve to fall back upon.

(2) **Work systematically**, avoid making random shots, and **record your processes and results** in an orderly way.

(3) **Do not assume** what you think **ought** to have happened if it does not; the basis of your expectation may be erroneous, and in laboratory practice should be confirmed, though it is foolish to follow up an unsatisfactory result in an examination.

(4) **Make a note of seeming discrepancies** of results: you will probably find the explanation later yourself.

(5) **Keep your test-tubes and vessels scrupulously clean.** Wash them and your platinum wire at the end of your work each day; try the wire alone in the flame before using it.

(6) **Be exact in carrying out the directions given.**

This book has been printed on specially tough paper in order to adapt it for laboratory use.

LIST OF REAGENTS AND APPARATUS

REQUIRED FOR QUALITATIVE ANALYSIS.

Fluid Reagents.

In 6-oz. Stoppered Bottles.

Concentrated Sulphuric Acid.
Concentrated Nitric Acid.
Concentrated Hydrochloric Acid.

Dilute Sulphuric Acid.
Dilute Nitric Acid.
Dilute Hydrochloric Acid.

The dilute acids should be made by mixing one part of the pure acid with three parts of water.

Sulphuretted Hydrogen Water.
Ammonium Hydroxide.
Ammonium Chloride.
Ammonium Sulphide.

Ammonium Carbonate.
Sodium Hydroxide.
Sodium Carbonate.
Barium Chloride.

In 4-oz. Stoppered Bottles.

Sodium Phosphate.
Potassium Ferrocyanide.
Potassium Ferricyanide.
Potassium Chromate.
Ammonium Oxalate.

Calcium Sulphate.
Ferric Chloride.
Lead Acetate.
Mercuric Chloride.
Stannous Chloride.

Alcohol.

In 2-oz. Stoppered Bottles.

Platinic Chloride.
Silver Nitrate.
Cobalt Nitrate.

In 4-oz. Stoppered Bottles.

⁂ *These reagents are for occasional use as special tests.*

Hydrofluosilicic Acid.
Tartaric Acid.
Starch Paste.
Potassium Iodide.
Potassium Nitrate.
Potassium Cyanide.
Sodium Acetate.
Baryta Water.
Copper Sulphate.

Magnesium Sulphate.
Calcium Chloride.
Ammonium Molybdate.
Ammonium Sulphate.
Chlorine Water.
Carbon Disulphide.
Acetic Acid.
Chloroform.

Dry Reagents.

IN 2-OZ. WIDE-MOUTHED CORKED BOTTLES.

Fusion Mixture.
Sodium Carbonate.
Borax.
Potassium Nitrate.
Potassium Chlorate.
Starch.
Potassium Cyanide.
Ferrous Sulphate.
Calcium Hydroxide (slaked lime).
Manganese Dioxide.
Potassium Bichromate.
Sodium Sulphite.
Granulated Zinc.
Copper Turnings.

Apparatus.

Wash-bottle (p. 7). Sulphuretted Hydrogen apparatus (p. 14). (Ferrous Sulphide will be required for this apparatus.)
2 doz. test-tubes, 6 × ⅝ in. 2 boiling tubes, 8 × 1¼ in. Test-tube brush.
Test-tube stand to hold twelve at least. Piece of wire gauze.
Piece of platinum foil, 2 in. × 1 in. 3 inches platinum wire.
Black's blowpipe. 6 bulb-tubes. 3 watch-glasses.
2 porcelain evaporating basins, 2-oz. and 4-oz. 3 funnels, two 2-in. and one 3-in. Filter papers. Bunsen burner, or 1 spirit lamp, 4-oz.
Pair of brass or iron crucible tongs. Wedgwood ware mortar and pestle, 4-oz. at least. ½ lb. tubing and rod. Corks, assorted.
Pieces of charcoal for blowpipe work.
Litmus and Turmeric papers.

QUALITATIVE ANALYSIS.

CHAPTER I.

INTRODUCTORY EXPERIMENTS.

To bend a piece of glass tubing.—Take a piece of $\frac{3}{16}$-inch soft tubing, and hold it horizontally in the upper part of an ordinary luminous gas flame, with its length in the plane of the flame. Turn the tubing slowly round and round so as to heat it uniformly. When it begins to soften, remove it from the flame and bend it slowly and carefully to the required shape. Allow to cool, and *then* remove the coating of soot from the bend.

To cut narrow glass tubing with a file.—Take a piece of glass tubing and lay it on a table. Taking hold of it with the finger and thumb of the left hand near the point where it is to be cut, draw one edge of a sharp triangular file *once* across it, from heel to point. The tube can now be broken by forcibly attempting to bend it away from the file scratch, and at the same time trying to pull it apart. The cut ends must then have their sharp edges rounded by holding the tube vertically in the Bunsen flame, until the flame is coloured strongly yellow by the sodium of the glass.

To draw out a piece of glass tubing ; to make a jet.—Take a short piece of tubing and heat the middle portion in a small blow-pipe flame, supporting each end of the tube with the fingers, and continually turning it round so as to equally heat all sides ; when the tube is quite soft, remove it from the flame and slowly draw it out. The more slowly it is drawn out, the more gradually will the tube taper towards the centre. Then with a file cut the tube at a suitable point, round off the cut ends in the flame, and the jet is ready for use.

To make a Bulb-tube.—Take a piece of $\frac{3}{16}$-inch tubing about 6 inches long, and heat one end in the blowpipe flame until it is completely closed and rounded off. Before this rounded end becomes too thick, take it out of the flame, and holding the tube vertical blow into it steadily, but not too strongly, until a small bulb is blown at the heated end.

Use of Spatula.—It is often necessary to take a small quantity of some solid substance out of a bottle. For this purpose the spatula—an instrument very like a small table knife—is used. A small bone or ivory paper cutter answers the purpose very well. The blade of a penknife is sometimes used, but the use of iron or steel is objectionable. A platinum spatula is the best to use.

To fix a platinum wire in a glass holder.—Take 6 inches of narrow glass tubing and draw it out a little in the middle. Cut in two at the middle of the drawn-out part. Into the narrow cut end insert a piece of platinum wire about 2 inches long; then hold this end in the flame until the glass closes round the wire. A piece of glass rod makes a better holder. Draw the rod out and cut in two as described above. Then hold the narrow end of the rod in the flame until it is quite soft, and insert the piece of platinum wire into the soft end.

The platinum wire thus mounted will be in frequent use for flame tests, and should be kept dipping in hydrochloric acid in a test-tube. This can be done by fitting the holder with a cork which fits into the mouth of the test-tube. Kept in this way the wire is always clean.

Flame tests.—(1) Place a small quantity of solid sodium carbonate, Na_2CO_3, on a watch-glass. Lift a small portion of it with the loop of the platinum wire, and hold in the lower outer part of the Bunsen flame. The flame shows an intense yellow colour, characteristic of sodium compounds.

Clean the wire by holding it in the flame until all trace of the yellow coloration disappears. Then wash it in dilute HCl and again heat it.

(2) Take some baryta (or any barium salt) and heat it in the same way. The flame is of a yellowish-green colour, but possibly not very intense. Pour a few drops of HCl into a watch-glass, dip the loop of the wire in it, and take up with the moistened wire a few particles of the salt. On now placing the wire in the flame, the yellowish-green coloration will be much more intense. Now clean the wire by alternately dipping it in HCl and heating it in the flame. For a time the effect of this is merely to increase the intensity of the coloration, but after some time it becomes fainter, and by using fresh acid once or twice the wire can be thoroughly cleaned. Barium compounds are the most difficult to remove from the wire.

(3) Take some strontium nitrate and treat in the way described above. The flame is coloured an *intense* crimson; moistening with HCl makes the flame more intense. Clean the wire, wash it and put it away in a corked test tube or bottle.

Borax bead reactions.—Fused borax possesses the power of dissolving many metallic oxides and salts with formation of compounds which often possess distinctive colours, and so afford valuable tests.

(1) Take a piece of platinum wire fitted with a glass handle as already described, but without a loop at the end; heat in the Bunsen flame, and dip into powdered borax. Some of the salt will adhere to the wire. Again heat the wire, when the borax upon it will first "intumesce," *i.e.*, swell up from the escape of its water of crystallization, and then fuse quietly to a clear, colourless bead. Now take a small quantity of a manganese compound *e.g.*, $MnSO_4$ or MnO_2, and bring it into contact with the bead, and again heat in the *outer* part of the Bunsen flame; a characteristic *purple* or *amethyst* colour will be produced. If now the airholes at the base of the lamp be partially closed, so as to produce a slight luminous appearance in the upper

central portion of the flame, and the bead be heated in this flame ("reducing flame"), since there is an excess of coal-gas there, the oxide of manganese, existing as borate in the bead, will be reduced to a lower state of oxidation, and the bead will, when cooled (best in the coal-gas at the centre of the base of the Bunsen flame), be found to be colourless. Treated in a similar way, Chromium compounds give a *green* bead in either flame; Iron, a *reddish-yellow*, in the oxidizing, *greenish-yellow* in the reducing flame; Cobalt, a *bright blue* in either flame, etc., etc. In all cases only a very small quantity of the substance to be tested must be used, otherwise the colour produced is too dark to be recognizable.

The Blowpipe.—To acquire the proper use of the blowpipe will necessitate a good deal of practice. A *continuous* blast of air must be kept up; for this purpose it is necessary to blow without interfering with the breathing. The secret of doing so is to use the cheeks to blow with, and to breathe through the nose. If the cheeks be blown out, it will be found that the air can be forced out of the mouth by contraction of the cheeks at the same time as inspiration is effected through the nose. By long practice this may be done continuously. When blowing continuously, however, since the air is forced out of the mouth by the pressure of the cheeks—not by their contraction—they must be kept distended. It is not necessary to blow hard: a very gentle blast suffices.

To obtain the blowpipe flame, the air-holes at the bottom of a Bunsen burner are closed so as to give a smoky luminous flame, and the blast of air from the nozzle of the blowpipe is then directed across this flame so as to produce a long straight pointed flame. It is used for observing the effects of a very high temperature on different substances, and in some cases to effect their oxidation or reduction.

To oxidize a substance it is heated in the outer flame—that is, at the tip of the blowpipe flame. To effect reduction, the inner flame must be used—that is, the substance is heated in the centre of the blowpipe flame, which for this purpose must show a small luminous streak in the centre.

Experiments with the Blowpipe.—(1) Take a piece of hard charcoal and scrape a small groove near one end. In this groove place a small quantity of litharge (lead oxide) and direct on it a reducing flame. In a short time it will melt, and if the heating be continued long enough a globule of lead will remain on the charcoal. This is an example of reduction effected by the reducing-flame and the charcoal.

(2) Take some potassium nitrate, KNO_3, and, having placed it on charcoal as described in (1), bring the blowpipe flame to bear on it. It suddenly flares up, and burns a portion of the charcoal with it. This is *deflagration.*

(3) Take weights of powdered sodium carbonate, Na_2CO_3, and potassium carbonate, K_2CO_3, proportionate to their molecular weights, and mix them thoroughly. This mixture is known as *fusion mixture,* and should be kept ready for use. Take a small quantity of litharge (lead oxide), mix it with three or four times its weight of *fusion mixture,* and heat the mixture on charcoal before the blowpipe. The mass fuses, and in a short time small globules of lead appear and are readily fused into one large globule. The use of the fusion mixture is twofold—it prevents the fused litharge from being absorbed by the charcoal, and the fusion and reduction are more easily effected than in experiment (1). The fusion mixture here acts as a *flux.*

Note.—When a substance is to be *reduced,* it should be heated on *charcoal,* with some suitable flux, in the *reducing flame.* If *oxidation* is to be effected, it should be heated on the platinum wire, or on a piece of platinum foil in the oxidizing flame.

(4) Take some zinc oxide, ZnO, mix it carefully with fusion mixture, and heat on charcoal before the blowpipe. The oxide is reduced to the metallic state,* and zinc, being

---

* The student is not to suppose that the zinc can be *isolated* in this way.; it is far too easily oxidizable and the production of the metal is only a *transition stage.*

volatile, burns on passing through the outer flame with a bluish-green flame, forming the oxide which is deposited on the charcoal in the form of an *incrustation*, which is yellow when hot and white when cold. Now moisten the mass with a few drops of cobaltous nitrate, and again heat in the outer flame. The mass now assumes a fine green colour.

(5) Take a small quantity of tin oxide, and mix it with powdered potassium cyanide, KCN; place the mixture on charcoal, and cover it over with a little KCN, then heat before reducing blowpipe flame. The tin oxide is quickly reduced, and small globules of metallic tin are obtained. Substances that are not easily reduced by charcoal alone are readily reduced in the presence of KCN, owing to the tendency of that compound to take up oxygen or sulphur to form KCNO or KCNS.

(6) Powder some copper sulphate, and mix it with five or six times its weight of fusion mixture. Heat the mixture on charcoal before the inner blowpipe flame. The mass fuses, and the $CuSO_4$ is reduced to metallic copper, which is too infusible to be fused into a globule, and therefore remains on the charcoal as small reddish particles or scales which are not easily detected. Allow the mass to cool, remove it from the charcoal together with the crust of underlying charcoal, and place the whole in a small mortar. Powder it very finely, and transfer the powder to a small beaker. Pour on some water, and stir the whole for some time; on standing, the metallic particles sink quickly, so that if the water be poured off after a short time the copper will be found as a powder at the bottom of the beaker, and may be recognized by the effect of adding a few drops of nitric acid. Iron compounds may be similarly dealt with, and the iron particles are readily detected by means of a magnet.

Sublimation.—(1) Take some ammonium chloride, and place a small quantity in the bulb of a bulb-tube. Holding the stem of the tube with a pair of crucible tongs, heat this substance in the Bunsen flame. It gradually disappears from the bulb and condenses as a *white sublimate* in the upper part of the tube.

(2) Take some white arsenic, As_4O_6, and heat in a bulb-tube. A glittering white sublimate of As_4O_6 in octahedral crystals is obtained in the upper part of the tube. Mix some As_4O_6 with KCN and powdered charcoal, and heat the mixture in a bulb-tube. A brilliant black metallic mirror of arsenic is obtained in the upper part of the tube.

To make a Wash-Bottle.—Take a 16-oz. flask, either of the ordinary round form or, better, of the conical shape; fit it with a good cork or indiarubber stopper, in which bore two holes by means of a sharp cork-borer (moistened with glycerine in the case of the rubber cork). Then fit two pieces of tubing bent as shown in Figs. 1 and 2, taking care to round off the ends in the flame, and that the tube *n* ends very close to the bottom of the flask; to the end *n* of the longer tube fit a piece (about $1\frac{1}{2}$ inches) of narrow ($\frac{1}{8}$-inch diam.) indiarubber tubing, carrying at the other end a short piece (about 1 inch) of glass tubing drawn out to a jet. The wash-bottle is to be nearly filled

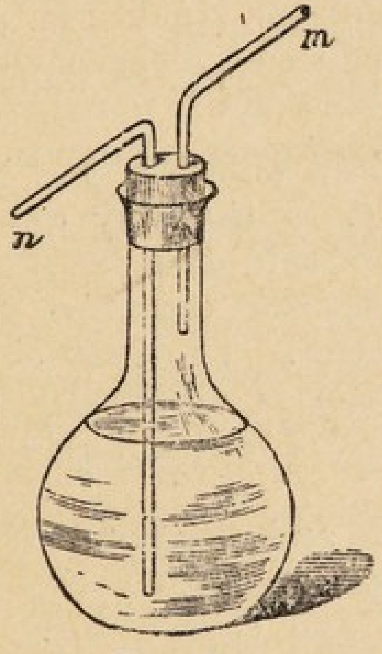

FIG. 1.

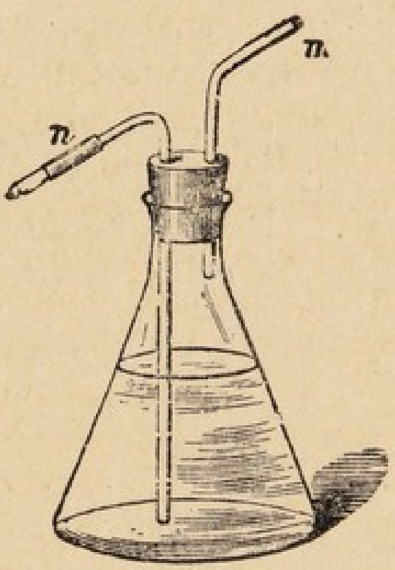

FIG. 2.

with distilled water, which can be expelled by blowing down the tube *m*, and the fine stream issuing from the jet can be directed in any desired direction by the flexibility of the rubber tubing. The wash-bottle is used chiefly for washing precipitates on filters and as a reservoir of pure water for general purposes.

To test the solubility of substances.—(1) Take some Epsom salts, $MgSO_4, 7H_2O$, and with a spatula place a very small quantity of it in a dry test-tube. Half fill the test-tube with water from the wash-bottle, using the jet of water to wash all traces of the salt down the sides of the tube. Close the tube with the thumb, and shake up the solution. It will then be found that all the substance has dissolved.

(2) Take a small quantity of lead chloride, $PbCl_2$, and attempt to make a solution of it in the way described above. It will be found that this salt does not dissolve readily in cold water. Now hold the test-tube in the Bunsen flame so as to boil the water. The lead chloride soon dissolves, and a clear solution is obtained. Allow this solution to stand and cool—the lead chloride again crystallizes out.

(3) Take some barium hydroxide and attempt to make a solution as above. It will be found that this substance is apparently insoluble in both hot and cold water. Take some red litmus paper and test the solution; it will be found to give a strong alkaline reaction, thus showing that a solution has been obtained, and that barium hydrate is slightly soluble in water. Also, place a few drops of the solution on a piece of clean platinum foil and heat over the Bunsen flame. A small white speck is left on the foil showing that the solution contained some solid substance.

(4) Take some pure barium carbonate and treat as above. It will be found insoluble in water (unless, as is frequently the case, it contains traces of the hydroxide). Take a fresh quantity of the substance in a test-tube and pour in some dilute hydrochloric acid, HCl. The carbonate rapidly

dissolves with *effervescence,* carbonic acid gas, CO_2, being evolved.

Precipitation is the basis of testing in the wet way. One of Berthollet's laws of double decomposition may be enunciated thus:—

"Two substances in solution will always decompose each other if it be possible, by double decomposition, to produce another substance less soluble than either of the original substances."

This law expresses the principle of testing by precipitation. For example, take a solution of barium chloride in a test-tube and add to it a small quantity of a solution of magnesium sulphate, $MgSO_4$. The following double decomposition is possible:—

$$\mathbf{BaCl_2 + MgSO_4 = BaSO_4} + \underset{\text{(soluble)}}{MgCl_2}.$$

Now barium sulphate, $BaSO_4$, is quite insoluble in water and acids, and therefore the reaction takes place and a white precipitate of $BaSO_4$ is produced.

This reaction now furnishes us with a test for the detection of barium compounds and also for sulphates; for the test is based on the insolubility of $BaSO_4$, and may therefore indicate Ba or H_2SO_4, but has nothing to do with Mg or HCl. A consideration of the reaction given below will further explain this:—

$$\mathbf{Ba}(NO_3)_2 + Na_2SO_4 = \mathbf{BaSO_4} + 2\ \underset{\text{(soluble)}}{NaNO_3}.$$

Substances employed in systematic analysis for the detection of other substances are called *reagents.*

Solutions of gases or of solids, with other liquids so employed, are called "*wet*" reagents; those used in the solid form, "*dry*" reagents. Solutions used as wet reagents should not be too concentrated.

Filtration.—*To fold a filter paper.*—If, as is usually the case, the precipitate is required as well as the clear liquid, an ordinary plain filter answers best. In cases where the amount of precipitate is only small, and the filtrate is the portion desired, a ribbed or folded filter should be used, as the liquid flows through such a paper much more quickly than through a plain filter.

To fold a plain filter.—Take a circular piece of filtering paper of the requisite size, and fold it in half. Then again fold it in half, so as to form a quadrant. Now open it in such a way that a cone of paper is formed having one thickness of paper on one side and three thicknesses on the other. Take a plain funnel (*i.e.*, not a fluted one) having an angle of 60° at the apex, and fit the filter paper carefully into it, and moisten the paper with water. The paper should be in contact with the glass in every part, and ought in all cases to be small enough to go entirely into the funnel, and leave a small portion of the glass uncovered all round its upper edge.

If, as sometimes happens, the angle of the funnel is not exactly 60°, it will be found that the paper will not fit accurately to the glass. In this case, fold the filter paper the second time not exactly in half, and open the smaller or larger side according to whether the angle of the funnel is less or greater than 60°.

A little care in folding and fitting the paper to the funnel is well repaid by the greater rapidity with which the liquid will flow through; and, since filtration is the most tedious operation in analytical work, any means by which it can be facilitated is well worth attention.

Certain precipitates—*e.g.*, silver chloride—filter easily and rapidly in the usual way, whilst others—*e.g.*, aluminium or ferric hydroxide—filter very slowly by the ordinary method. In order to increase the rapidity of filtration in such cases, the following arrangement may be used:—

The funnel and filtering paper are arranged as already described, but instead of allowing the filtrate to drop directly from the funnel into the test-tube or other vessel, fit to the lower end of the funnel, by means of a short length of indiarubber tubing, a piece of narrow glass tube bent round upon itself, near its upper extremity, as Fig. 3 :—The bend insures that the liquid shall entirely fill the tube, and there is therefore formed an unbroken column of liquid in the lower part of the tube, and this column by its weight, reduces the pressure on the lower side of the filter paper, and hence very greatly increases the rate of filtration. In using this arrangement it is important that the paper fits closely to the funnel, otherwise channels are formed for the admission of air, which, of course, altogether spoils the action of the long tube in reducing the pressure below the paper. The tube should be of as great a length as the filter-stand will allow, but a length of a few inches has a remarkable effect in accelerating filtration, especially of gelatinous precipitates like ferric hydroxide, a precipitate which is most tedious to filter by ordinary means. In making the bend in the tube, it will be found best to heat the tube at the proper place in a large flat flame, and, holding each end of the tube in the fingers, when the portion in the flame becomes quite soft, to bring the hands near together, at the same time giving one hand a slight twist. A loop will thus be formed, in a similar manner to the forming of a loop in a short piece of string, if it be held by one hand at each end, and the hands be then brought nearer together. A little practice will make this clearer than any amount of description.

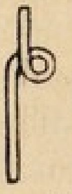
Fig. 3.

To fold a pleated filter paper.—Take a circular piece of filtering paper and fold it in half, then again, and again in half, then open so that its outline is a semicircle ; the creases produced by the other foldings are merely to serve as guides. Then, beginning at the straight side (*i.e.*, the diameter of the circle of which the paper now forms half), fold the paper from the centre to the circumference as far as the first crease : then turn the whole paper over, and fold the folded portion back an equal amount on the other side ; and so on, until the whole paper is folded into a sector-shaped piece. Press the paper well, so as to render the creases distinct, and then open it. A conical, pleated filter will thus be formed which, when supported by a funnel, will allow a liquid to flow through with great rapidity.

Filtration.—Take a solution of barium chloride, $BaCl_2$, and add a solution of sodium carbonate, Na_2CO_3, slowly, and finally drop by drop, until a precipitate is no longer formed. Fit a filter-paper into a funnel, and moisten it with a jet of water from the wash-bottle to make it fit closely to the glass. Then support the funnel on a suitable stand, and, having placed a test-tube or small beaker below to receive the *filtrate*, pour a portion of the contents of the test-tube gently on to the side of the filter-paper, taking care not to fill it too full. When this portion has filtered through, add another portion, and so on until the whole is filtered. To *wash* the precipitate on the filter-paper, direct a jet of water on to it so as to wash it down into the apex from the upper edge of the paper, fill up with water, and allow to stand until this water has all filtered through. Then fill up again several times until the washings show no alkaline reaction.

Testing the solubility of precipitates.—Take a small quantity of a solution of silver nitrate, $AgNO_3$, dilute it with water, and add dilute hydrochloric acid, HCl; a white curdy precipitate of silver chloride, $AgCl$, is obtained. Add a solution of ammonium hydroxide, NH_4OH, in excess, and shake up the mixture: the precipitate dissolves, showing that $AgCl$ is soluble in NH_4OH.

This is a convenient method of procedure applicable in most ordinary cases, but it is sometimes advisable to separate the precipitate from the accompanying liquid. This can be done thoroughly by filtration and washing, but more readily thus:—Allow the precipitate to subside, pour off the liquid and fill up with water. Again allow the precipitate to settle down and pour off the water. Repeat this once or twice. This method of washing by *decantation* is applicable only to heavy precipitates.

Marsh's Apparatus.—Take a wide-mouthed bottle of about 8 ounces capacity, fit it with a good cork or indiarubber stopper, in which bore two holes, one for an acid funnel, the other for a delivery tube; this should be bent back horizontally for 3 inches, and then back upon itself and cut off short; then fit it by means of a small cork to a small calcium chloride tube in order to dry the hydrogen. Connect the other end of this tube with a straight piece of hard glass tubing turned up at the end and drawn out to a jet. It is quite common, however, to use an ordinary form of a delivery tube drawn out to a jet. Place zinc (free from arsenic*) in the bottle and pour upon it pure sulphuric acid diluted with about five times its volume of water.

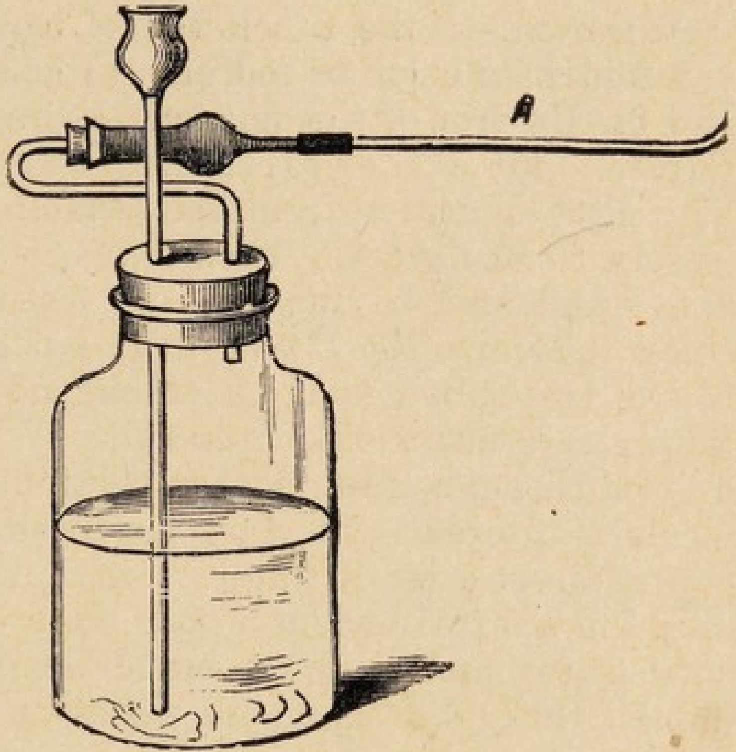

Fig. 4.

Allow the generation of hydrogen to proceed for a few minutes in order to expel all air from the apparatus, and then light the jet.

If the materials are pure, the flame will be almost colourless, and will yield no stain if a piece of porcelain be held in the flame (see p. 33). Great care must be taken that the jet is not lighted too soon; otherwise serious consequences may result, a mixture of hydrogen and air being highly explosive.

Sulphuretted Hydrogen.—This is best used in the form of gas, though a solution in water will suffice if the apparatus for the manufacture of the gas be not readily available.

One form of apparatus consists of two bottles with necks in the side connected together by a piece of india-

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* Commercial zinc contains arsenic; it would not therefore afford reliable evidence in testing matter for arsenic (*e.g.* the contents of a stomach where arsenical poisoning has been suspected).

rubber tubing. One bottle is partially, about half, filled with a mixture of fragments of iron sulphide and glass marbles, the latter being used to allow of the free passage of a liquid in the interstices between the pieces of iron sulphide; the other bottle contains dilute hydrochloric acid (1 of strong acid to about 2 or 3 of water). The upper neck of the bottle containing the iron sulphide is fitted with a cork carrying a tube which is bent at right angles and fitted either with a piece of indiarubber tubing and a pinch-cock, or, better, with a glass stop-cock.

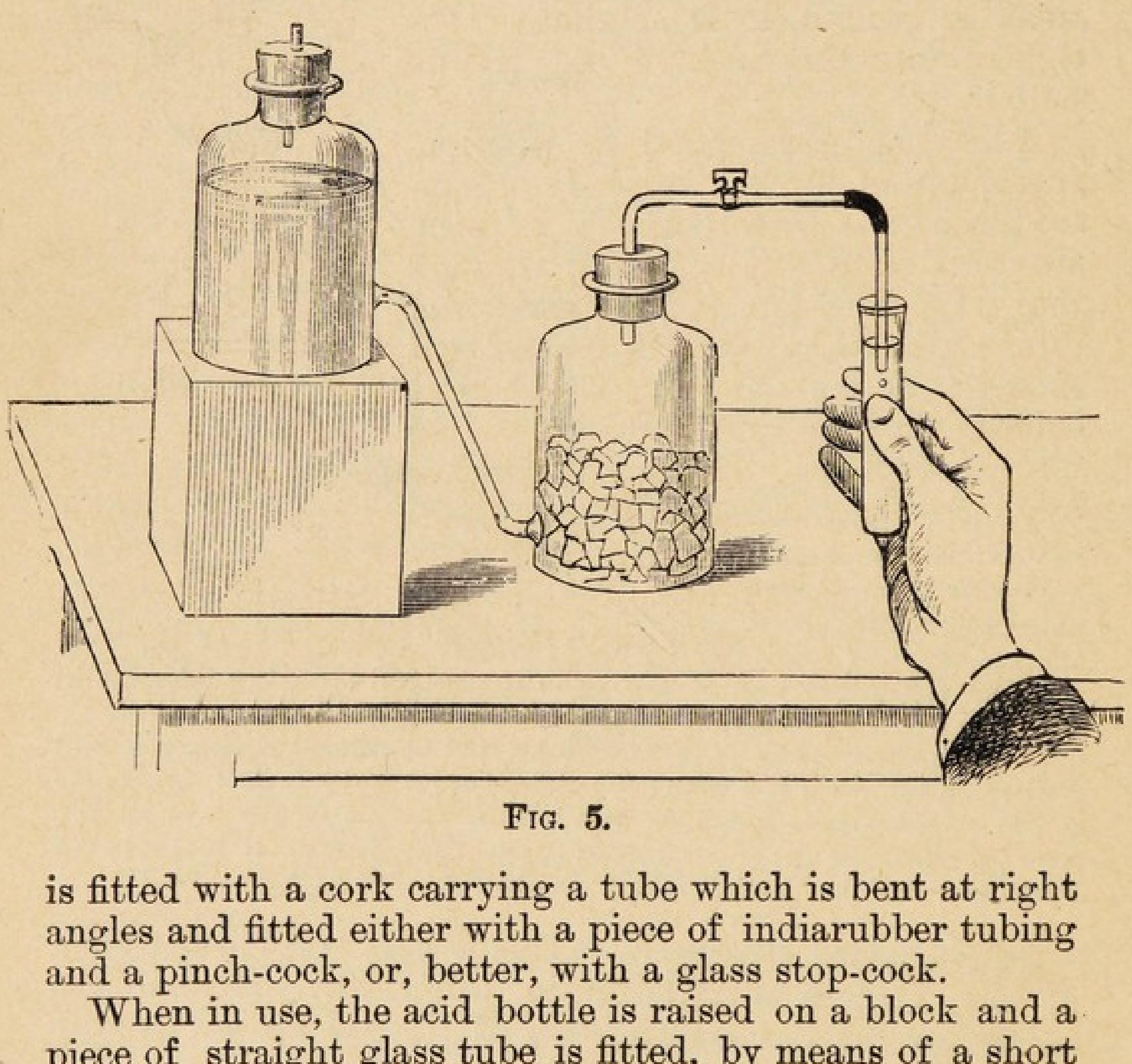

FIG. 5.

When in use, the acid bottle is raised on a block and a piece of straight glass tube is fitted, by means of a short length of indiarubber tubing, to the delivery tube of the other bottle, and the flow of the gas governed by the stop-cock or pinch-cock. When not in use, the position of the bottles is reversed, when the acid runs away from the iron sulphide, and all action ceases. This arrangement is shown in Fig. 5.

Kipp's Apparatus.—An alternative form of apparatus which is in very common use is shown in Fig. 6. It consists essentially of three bulbous portions, the lower two of which are in one piece and open into each other. The upper bulb terminates below in a tapering tube which reaches nearly to the bottom of the lower bulb; this tube is ground at D so that it fits tightly into the neck of the middle bulb.

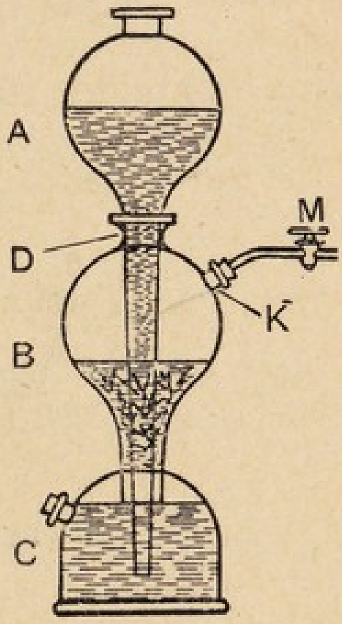

FIG. 6.

A having been placed in position, fragments of ferrous sulphide are introduced into B through K of such size that they will not drop through into C. The tap M is opened and dilute hydrochloric acid is poured into A till C is full and the liquid rises sufficiently high in B to cover the ferrous sulphide. The tap is now closed; the sulphuretted hydrogen produced soon pushes the acid out of B and up into A, thus stopping further action.

When the apparatus is to be brought into use the tap is opened; acid at once runs out of A and rises in B, thus coming in contact with the ferrous sulphide.

CHAPTER II.

REACTIONS OF THE METALS.

GROUP I.

METALS PRECIPITATED AS CHLORIDES.

Group-reagent—HCl.

SILVER, Ag . . .	**Pp.**	**Silver Chloride, AgCl**	(*white*).
LEAD, Pb	,,	**Lead Chloride, $PbCl_2$**	,,
MERCURY, Hg' . . (*Mercurous*)	,,	**Mercurous Chloride, Hg_2Cl_2**	,,

SILVER, Ag.

Solution—Silver Nitrate, $AgNO_3$.

1*. The group-reagent, **hydrochloric acid**, HCl, gives a *white curdy* precipitate of AgCl, which becomes violet on exposure to the light: *insoluble in hot water and nitric acid, soluble in ammonia, and in potassium cyanide* with formation of the compounds $AgNH_3Cl$ and $KAg(CN)_2$ respectively.

$$NH_3 + AgCl = AgNH_3Cl.$$
$$2\ KCN + AgCl = KAg(CN)_2 + KCl.$$

2. Potassium chromate, K_2CrO_4, gives, in *neutral* solutions, a *dark rea* precipitate of silver chromate, Ag_2CrO_4.

$$K_2CrO_4 + 2\ AgNO_3 = Ag_2CrO_4 + 2\ KNO_3.$$

The precipitate is readily soluble in mineral acids, except

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* The most important reactions are numbered in thick type.

hydrochloric acid, which converts it into insoluble silver chloride.

$$Ag_2CrO_4 + 2\ HCl = 2\ AgCl + H_2CrO_4.$$

3. **Potassium cyanide,** KCN, gives a *white curdy* precipitate of silver cyanide, AgCN, very soluble in excess of KCN with formation of $KAg(CN)_2$.

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

If the solution is rubbed upon a bright piece of copper, a white stain of silver is produced. This stain does not disappear on heating.

4. **Caustic potash,** KOH, or **caustic soda,** NaOH, gives a dark brown precipitate of silver oxide, Ag_2O.

$$2\ AgNO_3 + 2\ KOH = Ag_2O + H_2O + 2\ KNO_3.$$

The precipitate is soluble in ammonia with formation of $AgNH_3OH$.

$$Ag_2O + 2\ NH_3 + H_2O = 2\ AgNH_3OH.$$

Ammonia gives the same precipitate, soluble of course in excess.

5. **Sulphuretted hydrogen,** H_2S, gives a black precipitate of silver sulphide, Ag_2S, insoluble in dilute acids, except *hot* dilute nitric acid.

6. When a silver salt is mixed with sodium carbonate, Na_2CO_3, and heated on charcoal before the blowpipe, brilliant white malleable beads of silver are obtained. The silver salt is first converted into the carbonate, which is unstable, and readily breaks up into metallic silver, CO_2, and oxygen.

$$4\ AgCl + 2\ Na_2CO_3 = 4\ NaCl + 4\ Ag + 2\ CO_2 + O_2.$$

The beads of silver do not mark paper.

Silver nitrate is the only common soluble salt of silver.

LEAD, Pb.

Solution—Lead Nitrate, $Pb(NO_3)_2$.

1. The group reagent, **hydrochloric acid,** gives a *heavy white crystalline* precipitate of lead chloride, $PbCl_2$: *soluble in hot water*, but crystallizing out on cooling; *insoluble in ammonia.* No precipitate is formed in dilute solutions, because lead chloride is slightly soluble in cold water.

2. **Potassium chromate,** K_2CrO_4, gives a *bright yellow* precipitate of lead chromate, $PbCrO_4$: insoluble in dilute nitric acid and acetic acid. Caustic soda changes the colour of the precipitate from yellow to red, the normal chromate being converted into a basic chromate, $PbCrO_4, PbO$ (*chrome red*).

$$2\,PbCrO_4 + 2\,NaOH = PbCrO_4, PbO + Na_2CrO_4 + H_2O.$$

The red precipitate dissolves in excess of caustic soda, forming a red solution. [*Distinction from Bismuth.*]

3. **Potassium iodide,** KI, gives a *golden yellow* precipitate of lead iodide, PbI_2: soluble in boiling water, but crystallizing out in brilliant iridescent scales on cooling.

4. **Sulphuretted hydrogen** produces a *black* precipitate of lead sulphide, PbS. If the solution is strongly acid with HCl, a reddish-brown precipitate is first formed having the composition $PbS, PbCl_2$. Excess of H_2S or addition of water decomposes this compound thus—

$$PbS, PbCl_2 + H_2S = 3PbS + HCl.$$

Lead sulphide is insoluble in cold dilute acids, but dissolves readily in hot dilute nitric acid with formation of lead nitrate, free sulphur and oxides of nitrogen. We may suppose that the first change which takes place is

$$PbS + 2\,HNO_3 = Pb(NO_3)_2 + H_2S.$$

The sulphuretted hydrogen is then oxidized by the excess of nitric acid.

$$3\ H_2S + 2\ HNO_3 = 3\ S + 4\ H_2O + 2\ NO.$$

At the same time a portion of the lead sulphide is oxidized to lead sulphate. If strong nitric acid is used the whole of the sulphide is converted into sulphate.

$$PbS + 8\ HNO_3 = PbSO_4 + 4\ H_2O + 8\ NO_2.$$

Lead sulphide is insoluble in alkalies and alkaline sulphides.

5. **Dilute sulphuric acid, H_2SO_4,** gives at once in concentrated solutions a *white* precipitate of lead sulphate, $PbSO_4$: precipitation takes place in very dilute solutions only after a time; the addition of alcohol favours the precipitation.

The precipitate is soluble in caustic soda and caustic potash, and also in a solution of ammonium acetate + ammonia.

Lead sulphate also dissolves on long boiling with strong hydrochloric acid.

6. **Potassium hydroxide,** KOH, or **sodium hydroxide,** NaOH, gives a *white* precipitate which at first consists of a basic lead salt *i. e.*, a compound of the normal salt with the hydroxide, $Pb(OH)_2$. As more alkali is added the basic salt is completely converted into the hydroxide, the precipitate remaining white.

Excess of alkali redissolves the precipitate with formation of "potassium plumbite, K_2PbO_2," or "sodium plumbite, Na_2PbO_2."

$$2\ KOH + 2\ Pb(NO_3)_2 = Pb(NO_3)_2, Pb(OH)_2 + 2\ KNO_3.$$
$$2\ KOH + Pb(NO_3)_2, Pb(OH)_2 = 2\ Pb(OH)_2 + 2\ KNO_3.$$
$$2\ KOH + Pb(OH)_2 = K_2PbO_2 + 2\ H_2O.$$

Ammonium hydroxide, NH_4OH, behaves in a similar manner except that the precipitate is insoluble in excess.

7. Heat on charcoal with sodium carbonate, Na_2CO_3,

and potassium cyanide, KCN: beads of lead are formed, which are malleable, and mark paper.

Common soluble salts. Lead nitrate, $Pb(NO_3)_2$, and lead acetate, $Pb(C_2H_3O_2)_2$ (sugar of lead), are readily soluble in cold water. Lead chloride, $PbCl_2$, and lead iodide, PbI_2, are sparingly soluble in cold water, but readily soluble in hot water.

MERCURY (*mercurous*), Hg'.

Solution—Mercurous Nitrate, $Hg_2(NO_3)_2$.

1. The group reagent, **hydrochloric acid**, gives a *white* precipitate of mercurous chloride, Hg_2Cl_2 (*calomel*): *insoluble in hot water, blackened by ammonia.*

The blackening on the addition of ammonia is due to the separation of metallic mercury, dimercurammonium chloride, NHg_2Cl, being simultaneously formed.

$$Hg_2Cl_2 + 2NH_4OH = NH_2HgCl + Hg + 2H_2O + NH_4Cl.$$

When mercurous chloride is boiled with strong hydrochloric acid for a long time, it breaks up into mercury (which separates as a black precipitate) and mercuric chloride (which dissolves).

$$Hg_2Cl_2 = Hg + HgCl_2.$$

If nitric acid is substituted for hydrochloric acid complete solution takes place, a mixture of mercuric chloride and nitrate being formed. We may suppose that the mercurous chloride is first broken up into mercury and mercuric chloride, as represented in the above equation, and that the mercury then dissolves in the nitric acid with formation of mercuric nitrate.

$$3\,Hg + 8\,HNO_3 = 3\,Hg(NO_3)_2 + 4\,H_2O + 2\,NO.$$

Aqua regia brings about the solution more readily than nitric acid alone. The nascent chlorine produced by the action of the two acids on each other converts the Hg_2Cl_2 into $HgCl_2$.

2. **Potassium hydroxide**, KOH, or **sodium hydroxide**. $NaOH$, gives a *black* precipitate of mercurous oxide, Hg_2O.

$$2\,NaOH + Hg_2(NO_3)_2 = Hg_2O + 2\,NaNO_3 + H_2O.$$

[*Distinction from mercuric salts*, which give a *dark yellow* precipitate of mercuric oxide, HgO.]

3. **Stannous chloride**, $SnCl_2$, gives a *grey* precipitate of metallic mercury.

$$\begin{aligned} SnCl_2 + Hg_2(NO_3)_2 &= Hg_2Cl_2 + Sn(NO_3)_2. \\ SnCl_2 + Hg_2Cl_2 &= 2\,Hg + SnCl_4. \end{aligned}$$

[*Distinction from mercuric salts*, see p. 23.]

4. **Sulphuretted hydrogen** produces a *black* precipitate of mercuric sulphide + metallic mercury.

$$Hg_2(NO_3)_2 + H_2S = Hg + HgS + 2\,HNO_3.$$

Mercurous sulphide, Hg_2S, is unknown.

5. When any dry mercurous compound is heated in a tube with powdered charcoal and Na_2CO_3, the metal is reduced and volatilized, and deposited in the cooler parts of the tube in the form of a mirror made up of minute metallic globules.

6.* Acidulate a portion of a solution of any mercurous compound in a tube with nitric acid, and boil with a strip of pure electrolytic copper. A film of mercury is deposited on the copper. When dried between blotting-paper and heated in a tube, the mercury sublimes and the copper resumes its natural colour.

Mercurous nitrate, $Hg_2(NO_3)_2$, is the only common soluble mercurous salt.

[*] Compare Reinsch's test for arsenic (p. 34).

GROUP II.

METALS PRECIPITATED AS SULPHIDES.

Group-reagent—H_2S in presence of HCl.

DIVISION I.

Metals whose Sulphides are Insoluble in Alkaline Sulphides or Hydrates.

MERCURY, Hg'' (*mercuric*)	Pp.	**Mercuric Sulphide, HgS**	(*black*).
LEAD,* Pb	,,	**Lead Sulphide, PbS**	,,
BISMUTH, Bi	,,	**Bismuth Sulphide, Bi_2S_3**	,,
COPPER, Cu	,,	**Cupric Sulphide, CuS**	,,
CADMIUM, Cd	,,	**Cadmium Sulphide, CdS**	(*yellow*).

DIVISION II.

Metals whose Sulphides are Soluble in Alkaline Sulphides or Hydroxides.

TIN, Sn'' (*Stannous*)	Pp.	**Stannous Sulphide, SnS**	(*dk. brown*).
Sn^{iv} (*Stannic*)	,,	**Stannic Sulphide, SnS_2**	(*yellow*).
ANTIMONY, Sb	,,	**Antimony Sulphide, Sb_2S_3**	(*orange*).
ARSENIC, As	,,	**Arsenic Sulphide, As_2S_3**	(*yellow*).

DIVISION I.

MERCURY, Hg''

Solution—Mercuric Chloride,* $HgCl_2$.

1. The group-reagent,† **sulphuretted hydrogen, H_2S,** added slowly, gives first a *white* precipitate, which, as more of the reagent is added, first becomes *yellow*, then *brown*, and finally *black*. The *white* precipitate is a double compound of HgS and $HgCl_2$ ($HgCl_2$, 2 HgS); the *black* precipitate is HgS. There is some doubt about the composition of the yellow and brown compounds. HgS is insoluble in acids, but is partially converted into

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* Lead, as $PbCl_2$, is slightly soluble in cold water, and therefore occurs in Group II. as well as in Group I.

† Sulphuretted hydrogen may be used as a solution in water, or the gas itself may be passed into the solution from a suitable apparatus (see p. 14) until the precipitation is complete. The latter method, where practicable, is preferable.

$Hg(NO_3)_2$, 2 HgS (which is white) by boiling with strong HNO_3. HgS is also insoluble in ammonium sulphide and in caustic alkalies.

2. **Stannous chloride**, $SnCl_2$, gives, with mercuric salts, a *white* precipitate of mercurous chloride, Hg_2Cl_2, which, on boiling with excess of the reagent, gives grey metallic mercury. If the solution be poured off, and the precipitate boiled with hydrochloric acid, the mercury is obtained in small globules.

$$2\,HgCl_2 + SnCl_2 = Hg_2Cl_2 + SnCl_4.$$
$$Hg_2Cl_2 + SnCl_2 = 2\,Hg + SnCl_4.$$

3. **Potassium iodide**, KI, gives a precipitate which is *yellow* at first, but rapidly changes to *bright scarlet.* The precipitate consists of mercuric iodide, HgI_2.

$$2\,KI + HgCl_2 = HgI_2 + 2\,KCl.$$

The two different colours correspond to two different forms of mercuric iodide. The two forms crystallize in different shapes. At ordinary temperatures the scarlet form is more stable than the yellow, but above 126° C. the reverse is the case.

The precipitate of mercuric iodide is soluble in excess of either the mercuric salt or potassium iodide.

4. **Potassium hydroxide**, KOH, or **sodium hydroxide**, NaOH, gives in the cold a *yellow* precipitate of mercuric oxide, HgO, insoluble in excess.

$$2\,KOH + HgCl_2 = HgO + H_2O + 2\,KCl.$$

In the heat the precipitate obtained is *red*, but still consists of HgO. The difference in colour is due to difference in the size of the particles.

5. **Ammonium hydroxide**, NH_4OH, gives a *white* precipitate of *mercurammonium* chloride, NH_2HgCl (*infusible white precipitate*)—

$$2\,NH_4OH + HgCl_2 = NH_2HgCl + NH_4Cl + 2\,H_2O.$$

6. Repeat reactions 5 and 6 for Hg′. Similar results will be obtained.

Mercuric chloride, $HgCl_2$ (corrosive sublimate) is the most important soluble mercuric salt. Mercuric nitrate, $Hg(NO_3)_2$, is also soluble, but the salt is unstable, and when in solution tends to form insoluble basic salts.

LEAD, Pb.

Unless the solution be very dilute, lead is usually detected in Group I. If not so detected, a black precipitate of lead sulphide, PbS, will be obtained on addition of H_2S in Group II., if the solution be not too acid. For this reason, if there is a doubtful indication of a precipitate in Group I., and lead is suspected from preliminary examination (see Chap. iv.), H_2S should be passed through the original solution if that be acid, and not through the portion to which HCl has been added.

[This point is of importance in systematic analysis. On account of the slight solubility of $PbCl_2$ in cold water, Pb is not completely precipitated in Group I.; and if the solution be too acid, or too concentrated, it is not precipitated at all in Group II., and therefore appears in Group III., where it is often mistaken for some other metal.]

For other reactions of Lead, see Group I.

BISMUTH, Bi.

Solution—Bismuth Nitrate, $Bi(NO_3)_3$, dissolved in dilute nitric acid.

1. **Sulphuretted hydrogen** gives a *brownish-black* precipitate of bismuth sulphide, Bi_2S_3.

$$3\,H_2S + 2\,Bi(NO_3)_3 = Bi_2S_3 + 6\,HNO_3.$$

The precipitate is soluble in hot dilute nitric acid, but insoluble in ammonium sulphide and in caustic alkalies.

2. **Water** added in large quantity to a solution of bismuth, to which ammonium chloride, NH_4Cl, has first been added, **produces a white precipitate** of a basic chloride, BiOCl, which is insoluble in tartaric acid. [*Distinction from the basic chloride of antimony, SbOCl,* which is soluble in tartaric acid.]

$$BiCl_3 + H_2O = BiOCl + 2\,HCl.$$

3. **Potassium chromate,** K_2CrO_4, gives a *yellow* precipitate of the basic chromate, $Bi_2O(CrO_4)_2$—

$$2\ K_2CrO_4 + 2\ Bi(NO_3)_3 + H_2O = Bi_2O(CrO_4)_2 + 4\ KNO_3 + 2\ HNO_3.$$

The precipitate is soluble in dilute nitric acid, but insoluble in sodium hydroxide. [*Distinction from lead.*]

4. Dilute sulphuric acid, H_2SO_4, gives no precipitate. [*Distinction from lead.*]

5. **Caustic potash,** KOH, gives a white precipitate of bismuth hydroxide, $Bi(OH)_3$, insoluble in excess—

$$3\ KOH + Bi(NO_3)_3 = Bi(OH)_3 + 3\ KNO_3.$$

NaOH and NH_4OH behave in a similar manner.

6. Add caustic potash to stannous chloride, $SnCl_2$, till the precipitate of stannous hydroxide first formed redissolves, forming potassium stannite, K_2SnO_2. Now add a solution of a bismuth salt. A black precipitate of bismuth dioxide, Bi_2O_2, is formed.

$$2\ KOH + SnCl_2 = Sn(OH)_2 + 2\ KCl.$$
$$2\ KOH + Sn(OH)_2 = K_2SnO_2 + 2\ H_2O.$$
$$K_2SnO_2 + 6\ KOH + 2\ Bi(NO_3)_3 = Bi_2O_2 + K_2SnO_3 + 6\ KNO_3 + 3\ H_2O.$$

7. Mix with sodium carbonate, Na_2CO_3, and heat on charcoal before the blowpipe in the reducing flame: brittle metallic beads are obtained, and an *orange-yellow incrustation* is formed on the charcoal.

Most of the soluble bismuth salts are decomposed by water, insoluble basic salts being formed. Bismuth nitrate, $Bi(NO_3)_3$, the commonest salt, dissolves in a small quantity of water, especially if nitric acid is present. A large quantity of water decomposes the salt, and basic bismuth nitrate (bismuthyl nitrate or bismuth oxynitrate), $BiONO_3$, is formed.

COPPER, Cu.

Solution—Cupric Sulphate, $CuSO_4$.

1. **Sulphuretted hydrogen,** H_2S, gives a *black* precipitate of cupric sulphide, CuS—

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

The precipitate is soluble in hot dilute nitric acid, but insoluble in hot dilute sulphuric acid. It is *slightly soluble* in ammonium sulphide, but insoluble in caustic alkalies. The moist precipitate rapidly undergoes oxidation to cupric sulphate in the presence of air.

$$CuS + 2\ O_2 = CuSO_4.$$

If potassium cyanide is present sulphuretted hydrogen produces no precipitate with a copper salt. This is because a complex cyanide of potassium and copper, $KCu(CN)_2$, is formed which is not decomposed by H_2S. (See below under 4.)

2. **Ammonium hydroxide,** NH_4OH, when added in small quantities, produces a *greenish-blue* precipitate of a basic salt, $CuSO_4, Cu(OH)_2$, which is readily dissolved in excess of the reagent, forming a splendid *azure-blue liquid;* this coloration is easily perceptible, even if the solution contain only slight traces of copper. The blue solution contains ammonio-cupric sulphate, $CuSO_4, (NH_3)_4, H_2O$.

$$2\ CuSO_4 + 2\ NH_4OH = CuSO_4, Cu(OH)_2 + (NH_4)_2SO_4.$$
$$CuSO_4 + Cu(OH)_2 + 6\ NH_4OH + (NH_4)_2SO_4$$
$$= 2\ CuSO_4,(NH_3)_4, H_2O + 6\ H_2O.$$

3. **Potassium ferrocyanide,** $K_4Fe(CN)_6$ gives a *reddish-brown* precipitate of cupric ferrocyanide, $Cu_2Fe(CN)_6$, in neutral or slightly acid solutions, but not in alkaline solutions.

$$K_4Fe(CN)_6 + 2\ CuSO_4 = Cu_2Fe(CN)_6 + 2\ K_2SO_4.$$

A *brownish colour* is produced in very dilute solutions of copper salts; it is best seen when the reaction takes place in a watch-glass placed on a sheet of white paper. $K_4Fe(CN)_6$ affords one of the most delicate reactions for copper salts.

4. **Potassium cyanide,** KCN, gives a *greenish-yellow* precipitate of cupric cyanide, $Cu(CN)_2$.

$$2\ KCN + CuSO_4 = Cu(CN)_2 + K_2SO_4.$$

The precipitate rapidly loses cyanogen, forming cuprous cyanide, $Cu_2(CN)_2$.

$$2\ Cu(CN)_2 = Cu_2(CN)_2 + C_2N_2.$$

If excess of potassium cyanide is added the precipitate redissolves, forming a double cyanide of potassium and copper, $KCu(CN)_2$.

$$2\ KCN + Cu_2(CN)_2 = 2\ KCu(CN)_2.$$

As stated above, this compound is not decomposed by sulphuretted hydrogen. The explanation of this is that the ions of the double cyanide are K and $[Cu(CN)_2]$, not K, Cu and (CN), *i.e.*, there are *no free copper ions* (or more correctly only a *very few*). Now it is on the presence of free copper ions that the precipitation of copper by H_2S depends, the sulphur ions of H_2S combining with them to form insoluble CuS.

5. **Caustic potash,** KOH, **or caustic soda**, NaOH, gives a *bulky light blue* precipitate of cupric hydrate, $Cu(OH)_2$.

$$2\ KOH + CuSO_4 = Cu(OH)_2 + K_2SO_4.$$

The precipitate is insoluble in excess. If the mixture is boiled the precipitate becomes black, the cupric hydroxide losing part of its water.

$$3\ Cu(OH)_2 = Cu(OH)_2, 2\ CuO + 2\ H_2O.$$

6. If a piece of bright iron be dipped into a cupric solution acidulated with HCl, it becomes coated with copper; if clean iron filings be boiled in the solution, it

will lose its blue colour, the copper being wholly displaced by the iron.

$$CuSO_4 + Fe = FeSO_4 + Cu.$$

7. Mix with sodium carbonate, Na_2CO_3, and potassium cyanide, KCN, and heat before the inner blowpipe flame for some time : red metallic scales of copper are obtained.

Cupric sulphate, $CuSO_4$ (blue vitriol), is the commonest soluble salt of copper. Cupric nitrate, $Cu(NO_3)_2$, and cupric chloride, $CuCl_2$, are also readily soluble.

CADMIUM, Cd.

Solution.—Cadmium Chloride, $CdCl_2$.

1. **Sulphuretted hydrogen,** H_2S, gives a *fine yellow* precipitate of cadmium sulphide, CdS.

$$CdCl_2 + H_2S = CdS + 2\ HCl.$$

The precipitate is soluble in dilute sulphuric acid. [*Distinction from copper.*] The presence of much HCl prevents its formation. It is not soluble in ammonium sulphide or in caustic alkalies.

2. **Potassium hydroxide,** KOH, or **sodium hydroxide,** NaOH, gives a *white* precipitate of cadmium hydroxide, $Cd(OH)_2$.

$$2\ KOH + CdCl_2 = Cd(OH)_2 + 2\ KCl.$$

The precipitate is insoluble in excess.

3. **Ammonium hydroxide,** NH_4OH, gives the same precipitate, *soluble in excess.*

4. **Potassium cyanide,** KCN, gives a *white* precipitate of cadmium cyanide, $Cd(CN)_2$. The precipitate is soluble in excess forming $KCd(CN)_4$.

$$2\ KCN + CdCl_2 = 2\ KCl + Cd(CN)_2.$$
$$2\ KCN + Cd(CN)_2 = K_2Cd(CN)_4.$$

H_2S precipitates cadmium sulphide from this solution, whilst copper sulphide is not precipitated under similar conditions. The explanation is that $K_2Cd(CN)_4$ ionizes partly into K and $[Cd(CN)_4]$ and partly into K, Cd and (CN), *i.e.*, there are some free cadmium ions in solution, and these with the sulphur ions of the H_2S form cadmium sulphide.

5. Mix with sodium carbonate, Na_2CO_3, and heat on charcoal before the inner blowpipe flame: a *brown incrustation* of cadmium oxide, CdO, is obtained. (*This experiment must be carefully performed, for if heated too strongly the oxide is completely volatilized.*)

Cadmium chloride, $CdCl_2$, cadmium sulphate, $CdSO_4$, and cadmium nitrate, $Cd(NO_3)_2$, are common easily soluble salts of cadmium.

DIVISION II.

TIN (*Stannous*), Sn″.

Solution—Stannous Chloride, $SnCl_2$.

1. **Sulphuretted hydrogen**, H_2S, gives a *chocolate-coloured* precipitate of stannous sulphide, SnS.

$$SnCl_2 + H_2S = SnS + 2\ HCl.$$

This precipitate is insoluble in *colourless* ammonium sulphide but dissolves in *yellow* ammonium sulphide (which contains sulphur in solution) with formation of ammonium thiostannate, $(NH_4)_2\ SnS_3$.

$$SnS + \underbrace{(NH_4)_2S + S}_{\text{Yellow ammonium sulphide}} = (NH_4)_2\ SnS_3.$$

Addition of acid precipitates *stannic* sulphide, SnS_2, not stannous sulphide, from this solution.

$$(NH_4)_2SnS_3 + 2\ HCl = SnS_2 + 2\ NH_4Cl + H_2S.$$

Stannous sulphide is soluble in NaOH with a pinch of Na_2O_2 as oxidising agent, a mixture of sodium stannate and thiostannate being formed.

$$3\ SnS + 3\ Na_2O_2 = 2\ Na_2SnO_3 + Na_2SnS_3.$$

If an acid is added *stannic* sulphide is precipitated.

$$Na_2SnO_3 + 2\,Na_2SnS_3 + 6\,HCl = 6\,NaCl + 3\,SnS_2 + 3\,H_2O.$$

Stannous sulphide is insoluble in ammonium carbonate. It dissolves in hot strong hydrochloric acid, forming stannous chloride.

2. **Mercuric chloride,** $HgCl_2$, produces first a *white* precipitate of Hg_2Cl_2, which, when boiled with excess of the solution, becomes of a *greyish-black colour* owing to its reduction to metallic mercury. (For equations see p. 23.)

3. **Caustic potash,** KOH, and **caustic soda,** NaOH, give a *white* precipitate having the composition SnO, $Sn(OH)_2$. The precipitate is soluble in excess, forming potassium or sodium stannite.

$$2\,SnCl_2 + 4\,KOH = SnO, Sn(OH)_2 + 4\,KCl + H_2O.$$
$$SnO, Sn(OH)_2 + 4\,KOH = 2\,K_2SnO_2 + 3\,H_2O.$$

Ammonia produces a similar precipitate but it is insoluble in excess.

4. Add a strip of zinc to a solution acidulated with HCl: it becomes coated with a spongy mass of metallic tin. Platinum-foil, in contact with the strip of zinc, does not become blackened. [*Distinction from copper and antimony.*]

5. Mix with sodium carbonate, Na_2CO_3, and potassium cyanide, KCN, and heat on charcoal before the blowpipe: malleable beads of tin and a white incrustation on charcoal are obtained.

$SnCl_2$, 2 H_2O is the only common soluble stannous salt.

TIN (*Stannic*), Sn^{iv}.

Solution—Stannic Chloride, $SnCl_4$.

1. **Sulphuretted hydrogen,** H_2S, gives a *dull yellow* precipitate of stannic sulphide, SnS_2.

$$SnCl_4 + 2\ H_2S = SnS_2 + 4\ HCl.$$

The precipitate is soluble in *colourless* ammonium sulphide (and, of course, in yellow ammonium sulphide), forming ammonium sulphostannate, $(NH_4)_2SnS_3$.

$$SnS_2 + (NH_4)_2S = (NH_4)_2SnS_3.$$

The precipitate also dissolves in caustic alkalies, forming a stannate and a sulphostannate.

$$3\ SnS_2 + 6\ NaOH = 2\ Na_2SnO_3 + Na_2SnS_3 + 3\ H_2O.$$

SnS_2 is insoluble in ammonium carbonate. It dissolves in hot strong hydrochloric acid, forming stannic chloride, $SnCl_4$.

$$SnS_2 + 4\ HCl = SnCl_4 + 2\ H_2S.$$

2. **Caustic potash, KOH,** gives a white precipitate of stannic acid, H_2SnO_3.

$$4\ KOH + SnCl_4 = H_2SnO_3 + 4\ KCl + H_2O.$$

The precipitate is soluble in excess forming potassium stannate.

$$H_2SnO_3 + 2\ KOH = K_2SnO_3 + 2\ H_2O.$$

NaOH and NH_4OH behave in a similar manner.

Stannic acid is soluble in HCl and HNO_3.

3. Mercuric chloride, $HgCl_2$, gives no precipitate. [*Distinction from stannous salts.*]

4. Reaction 4 for stannous compounds applies also to stannic compounds.

$SnCl_4$ is the only common soluble stannic salt.
Sodium stannate, Na_2SnO_3, is also common.

ARSENIC,* As.

Solution—Arsenious Oxide, As_4O_6, dissolved in dilute HCl (which contains Arsenious Acid, H_3AsO_2).

1. **Sulphuretted hydrogen,** H_2S, gives (*in acid solutions*) a *lemon yellow* precipitate of arsenious sulphide, As_2S_3.

$$3\ H_2S + 2\ H_3AsO_3 = As_2S_3 + 6\ H_2O.$$

The precipitate is soluble in ammonium sulphide, forming ammonium arsenite, $(NH_4)_3AsS_3$, and in caustic alkalies forming a mixture of arsenite and thioarsenite.

$$As_2S_3 + 3\ (NH_4)_2S = 2\ (NH_4)_3AsS_3.$$

$$As_2S_3 + 6\ KOH = \underset{\text{Potassium arsenite}}{K_3AsO_3} + \underset{\text{Potassium thioarsenite}}{K_3AsS_3} + 3\ H_2O.$$

It is also readily soluble in a concentrated solution of ammonium carbonate again forming a mixture of arsenite and thioarsenite.

$$As_2S_3 + 3\ (NH_4)_2CO_3 = \underset{\text{Ammonium arsenite}}{(NH_4)_3AsO_3} + \underset{\text{Ammonium thioarsenite}}{(NH_4)_3AsS_3} + 3\ CO_2.$$

2. Add **cupric sulphate,** $CuSO_4$, and then **sodium hydroxide,** NaOH, drop by drop, till in excess (to render the solution alkaline): a *fine green* precipitate of arsenite of copper ($CuHAsO_3$) is obtained.

$$H_3AsO_3 + CuSO_4 + 2\ NaOH = CuHAsO_3 + Na_2SO_4 + 2\ H_2O.$$

3. **Marsh's Test.**—Hydrogen is generated from zinc † and dilute sulphuric acid, both free from arsenic, in the apparatus described on p. 13, and the jet lit as soon as all the air in the apparatus is dis-

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* Arsenic, when present as an arsenate, that is, as As_v, is only precipitated as As_2S_3 *by passing the gas through the solution for some time.* In this form arsenic will be detected as an *acid* (see page 72).

† As already stated on p. 13 ordinary commercial zinc contains arsenic and is therefore useless for this test; special arsenic free from zinc must be employed.

placed by hydrogen. A small quantity of the solution is then poured down the acid funnel into the bottle. In a short time arseniuretted hydrogen, AsH_3, is produced and escapes, mixed with a large proportion of hydrogen. The escaping gas now burns with a bluish flame, and fumes of arsenious oxide, As_4O_6, are evolved. If a cold porcelain dish be held in the flame, a bright black stain of *metallic arsenic* is produced on the dish.

$$6\,AsH_3 + 3\,O_2 = 3\,As + 6\,H_2O.$$

This stain is readily dissolved by a drop of sodium hypochlorite, NaOCl. [*Distinction from antimony.*]

$$2\,As + 5\,NaOCl + 4\,NaOH = 2\,Na_2HAsO_4 + 5\,NaCl + H_2O.$$

Further, the stain is practically insoluble in hydrochloric acid, whereas that produced by antimony compounds under similar circumstances is soluble.

If, while the gas is still escaping, the delivery tube be heated by the flame of a Bunsen burner or spirit lamp, at a point a short distance from the jet, a black ring will be produced on the tube just beyond the flame. If the tube be now cut off at this point, and held in a slanting position over a flame so that the ring is gently heated, a sublimate of octahedral crystals will be formed at the jet end of the tube.

If the tube, with the sublimate, be dropped into a test-tube containing dilute hydrochloric acid, the arsenious oxide dissolves and a solution is obtained from which sulphuretted hydrogen will precipitate arsenious sulphide, as in Test 1.

4. **Hoffmann's Test.** *—By the aid of the apparatus employed for the previous test, generate arseniuretted hydrogen, AsH_3; but, instead of burning the gas, pass it by means of a piece of bent tubing into a test-tube containing a solution of silver nitrate. A black precipitate of metallic silver is produced, whilst nitric and arsenious acids remain in solution.

$$AsH_3 + 6\,AgNO_3 + 3\,H_2O = 6\,Ag + H_3AsO_3 + 6\,HNO_3.$$

When the gas has been passing for some minutes, filter the liquid in the tube, add some more silver nitrate and then a few drops of solution of ammonia for the purpose of neutralising the nitric acid. A *yellow* precipitate of Ag_3AsO_3 is obtained.

$$H_3AsO_3 + 6\,HNO_3 + 3\,AgNO_3 + 9\,NH_4OH = Ag_3AsO_3 + 9\,NH_4NO_3 + 9\,H_2O.$$

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* The same objection applies to this test as to Test 3, namely that ordinary zinc contains arsenic.

5. **Fleitmann's Test.**—Boil a piece of aluminium foil with a solution of caustic soda: hydrogen is given off. Add a few drops of a solution of As_4O_6; the escaping gas now contains AsH_3, which is recognised by its blackening a piece of filter-paper previously moistened with $AgNO_3$, and held over the mouth of the test-tube. [*Distinction from antimony*, the compounds of which are not reduced in alkaline solutions to SbH_3.]

6. **Reinsch's Test.**—The solution is mixed with HCl, and boiled with a clean piece of copper-foil. A grey film is deposited on the copper. The copper-foil, having been washed and dried, is then heated in a narrow open tube where the arsenic oxidizes, and arsenious anhydride, As_4O_6, is deposited in the cool part of the tube in octahedral crystals.

7. Mix with sodium carbonate, Na_2CO_3, and powdered charcoal, and heat in a small bulb-tube: a black *lustrous* metallic ring will be produced in the cool part of the tube. This ring, when treated as in Test 3, gives exactly the same results.

Arsenious oxide, As_4O_6, slightly soluble in water, but readily soluble in dilute HCl, is the only common arsenic compound.

ANTIMONY, Sb.

Solution—Antimonious Chloride, $SbCl_3$, dissolved in dilute HCl.

1. **Sulphuretted hydrogen**, H_2S, gives (*in acid solutions*) an *orange-red* precipitate of antimonious sulphide, Sb_2S_3.

$$3\ H_2S + 2\ SbCl_3 = Sb_2S_3 + 6\ HCl.$$

The precipitate is soluble in ammonium sulphide, forming ammonium thioantimonite, $(NH_4)_3SbS_3$.

$$3\ (NH_4)_2S + Sb_2S_3 = 2\ (NH_4)_3SbS_3.$$

It is also soluble in caustic alkalies, forming an antimonite and a thioantimonite—

$$6\ KOH + Sb_2S_3 = \underset{\text{Potassium antimonite}}{K_3SbO_3} + \underset{\text{Potassium thioantimonite}}{K_3SbS_3} + 3\ H_2O.$$

It is insoluble in ammonium carbonate, but dissolves in boiling strong HCl.

$$Sb_2S_3 + 6\ HCl = 2\ SbCl_3 + 3\ H_2S.$$

2. Water produces a white milkiness due to the precipitate of antimony oxychloride, SbOCl—

$$SbCl_3 + H_2O = SbOCl + 2\ HCl.$$

The precipitate is easily soluble in tartaric acid [*Distinction from bismuth*], forming antimonyl tartrate, $(SbO)_2C_4H_4O_6$.

$$SbOCl + C_4H_6O_6 = (SbO)_2C_4H_4O_6 + 2\ HCl.$$

3. If a piece of platinum-foil and then a strip of zinc be dropped into a solution of antimony acidulated with HCl, so that the metals touch one another, a *brown* or *black* film (metallic antimony) will coat the platinum: free nitric acid must, however, not be present.

4. **Marsh's Test.***—Apply this test as described for arsenic. On the introduction of the antimony solution to the apparatus, antimoniuretted hydrogen is produced, and the flame becomes bluish-green in colour. A black stain is produced by this flame on cold porcelain, just as in the case of arsenic; but the *stain is less lustrous, and is insoluble in sodium hypochlorite,* NaOCl.

$$4\ SbH_3 + 3\ O_2 = 4\ Sb + 6\ H_2O.$$

5. **Hoffmann's Test.***—Apply this test as for arsenic. A *black* precipitate is obtained in the solution of silver nitrate: this contains antimony as $SbAg_3$, whilst nitric acid remains in solution.

$$SbH_3 + 3\ AgNO_3 = SbAg_3 + 3\ HNO_3.$$

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* The objection to these tests referred to under Arsenic applies here as well of course.

Filter. Digest the precipitate with tartaric acid. The antimony dissolves with formation of antimonyl tartrate, leaving the silver. Filter and pass H_2S through the filtrate. An orange precipitate of Sb_2S_3 is formed.

6. Mix with sodium carbonate, Na_2CO_3, and potassium cyanide, KCN, and heat on charcoal before the inner blowpipe flame: brittle beads of antimony are produced which give off white fumes of antimonious oxide, Sb_4O_6.

Tartar emetic, potassium antimonyl tartrate, $K(SbO)C_4H_4O_6$, and antimonous chloride, $SbCl_3$ (*butter of antimony*), are the commonest antimony compounds. The former is readily soluble in water. The latter dissolves readily in a *small quantity* of water or in dilute HCl; a large quantity of water precipitates SbOCl.

GROUP III.

METALS PRECIPITATED AS HYDROXIDES BY NH_4OH IN THE PRESENCE OF EXCESS OF NH_4Cl.

Group-reagent—NH_4Cl and NH_4OH.*

IRON, Fe‴ (*Ferric*). Pp. Ferric Hydroxide, $Fe(OH)_3$ (*reddish-brown*).

[IRON, Fe″ (Ferrous). Ferrous salts are not completely precipitated by ammonia in the presence of NH_4Cl; hence, before testing for iron in this group, a few drops of nitric acid must be added and the solution boiled in order to convert any *ferrous* salt present into a ferric salt. If iron is found, the original solution must then be tested to discover whether it was initially present as a ferrous or ferric salt.]

CHROMIUM, Cr. Pp. Chromic Hydroxide, $Cr(OH)_3$ (*dark green*).
ALUMINIUM, Al. „ Aluminium Hydrate, $Al(OH)_3$ (*white*).

IRON (*Ferric*), Fe‴.

Solution—Ferric Chloride, $FeCl_3$.

1. Ammonium hydroxide, NH_4OH, gives a ***reddish-brown*** precipitate of ferric hydroxide, $Fe(HO)_3$.

$$3\ NH_4OH + FeCl_3 = Fe(OH)_3 + 3\ NH_4Cl.$$

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* When NH_4Cl and NH_4OH are both to be added to a solution, the NH_4Cl should be added first, because it is often added to prevent the precipitation of hydroxides by the NH_4OH.

The precipitate is insoluble in NH_4Cl. KOH and NaOH give a similar precipitate.

2. **Potassium ferrocyanide,** $K_4Fe(CN)_6$, gives a *dark blue* precipitate of *Prussian blue*, $Fe_4[Fe(CN)_6]_3$.

$$3\ K_4[Fe(CN)_6] + 4\ FeCl_3 = Fe_4{}''' [Fe''(CN)_6]_3 + 12\ KCl.$$

3. **Potassium ferricyanide,** $K_3Fe(CN)_6$, gives *no* precipitate, but a *deep green* (*very dilute solutions*) or *brown coloration.*

4. **Potassium thiocyanate,** KSCN, gives the solution a blood-red colour on account of the formation of $Fe(SCN)_3$.

$$3\ KSCN + FeCl_3 = Fe(SCN)_3 + 3\ KCl.$$

The colour of the solution is readily destroyed by a solution of mercuric chloride, $HgCl_2$.

5. **Ammonium sulphide,** $(NH_4)_2S$, gives a black precipitate of ferrous sulphide, FeS, mixed with sulphur.

$$3\ (NH_4)_2S + 2\ FeCl_3 = 2\ FeS + S + 6\ NH_4Cl.$$

Ferric chloride, $FeCl_3$, and iron alum, $K_2Fe_2(SO_4)_4$, $24H_2O$, are **the** commonest soluble salts of iron (Fe‴).

IRON (*Ferrous*), **Fe″.**

Solution—Ferrous Sulphate, $FeSO_4$.

1. **Ammonium hydroxide,** NH_4OH [also KOH and Na(OH)], gives a *light-coloured* precipitate of ferrous hydroxide, $Fe(OH)_2$, which rapidly turns *dirty green*, and more slowly *reddish-brown*, by reason of the absorption of oxygen, and formation of ferric hydroxide.

$$2\ NH_4OH + FeSO_4 = (NH_4)_2SO_4 + Fe(OH)_2.$$
$$4\ Fe(OH)_2 + O_2 + 2\ H_2O = 4\ Fe(OH)_3.$$

Complete precipitation of ferrous hydroxide by NH_4HO is prevented by the presence of ammonium salts.

2. **Potassium ferrocyanide,** $K_4Fe(CN)_6$, gives a *bluish-white* precipitate which speedily turns blue by absorption of oxygen.

If air is entirely excluded and the ferrous salt is quite free from ferric salt the precipitate is quite white and consists of $K_2Fe''[Fe''(CN)_6]$.

$$K_4[Fe''(CN)_6] + FeSO_4 = K_2Fe''[Fe''(CN)_6] + K_2SO_4.$$

Under ordinary conditions air is always present and so the precipitate is bluish.

3. **Potassium ferricyanide,** $K_3Fe(CN)_6$, gives a *dark blue* precipitate of $Fe_3''[Fe'''CN)_6]_2$ (*Turnbull's blue*). [*Distinction from ferric salts.*]

$$2\ K_3[Fe(CN)_6] + 3\ FeSO_4 = Fe_3''[Fe'''(CN)_6]_2 + 3\ K_2SO_4.$$

4. **Potassium thiocyanate,** KSCN, produces neither a precipitate nor change of colour when the solution is free from a ferric salt.

5. **Ammonium sulphide,** $(NH_4)_2S$, gives a black precipitate of ferrous sulphide, FeS.

$$(NH_4)_2S + FeSO_4 = FeS + (NH_4)_2SO_4.$$

Ferrous sulphate, $FeSO_4$ (green vitriol), is the common soluble salt of iron, Fe''. Ferrous ammonium sulphate, $Fe_2''(NH_4)_2(SO_4)_2$, is a common double salt soluble in water.

CHROMIUM, Cr.

Solution—Chromic Chloride, $CrCl_3$.

1. **Ammonium hydroxide,** NH_4OH, gives a *dull green* precipitate of chromic hydroxide, $Cr(OH)_3$, with most chromium salts.

$$CrCl_3 + 3\ NH_4OH = Cr(OH)_3 + 3\ NH_4Cl.$$

The precipitate is partially soluble in excess, forming a pinkish solution which contains ammonium chromite, $(NH_4)_2Cr_2O_4$.

$$6\ Cr(OH)_3 + 6\ NH_4OH = 3\ (NH_4)_2Cr_2O_4 + 12\ H_2O.$$

When the liquid is boiled the $Cr(OH)_3$ is completely precipitated, the chromite being decomposed thus—

$$(NH_4)_2Cr_2O_4 + 2\ H_2O = 2\ NH_3 + 2\ Cr(OH)_3.$$

2. **Potassium hydroxide,** KOH, and **sodium hydroxide,** NaOH, give the same precipitate soluble in excess of the alkali, and forming a *green* solution.

$$6\ KOH + 6\ Cr(OH)_3 = \underset{\text{Potassium chromite}}{3\ K_2Cr_2O_4} + 12\ H_2O.$$

If the solution is boiled with ammonium chloride the chromite is decomposed, and chromium hydroxide is reprecipitated

$$K_2Cr_2O_4 + 2\ NH_4Cl + 2\ H_2O = 2\ Cr(OH)_3 + 2\ NH_3 + 2\ KCl.$$

Cautious addition of hydrochloric acid also brings about the reprecipitation of the hydroxide; excess of acid redissolves it, forming the chloride.

$$K_2Cr_2O_4 + 2\ HCl + 2\ H_2O = 2\ Cr(OH)_3 + 2\ KCl.$$

3. Chromic compounds may be recognized by converting the chromic oxide into chromic acid. This can be done in several ways :—

(i) By gently warming chromium hydroxide suspended in water with **sodium peroxide,** Na_2O_2.

$$2\ Cr(OH)_3 + 3Na_2O_2 = \underset{\text{Sodium chromate}}{2\ Na_2CrO_4} + 2NaOH + 2\ H_2O.$$

(ii) By boiling a solution of $CrCl_3$ with NaOH, and **sodium hypochlorite,** NaOCl, or with **bromine water** and **caustic** soda (*i.e.*, NaOBr).

$$Cr(OH)_3 + 3\ NaOCl + 4\ NaOH = 2\ Na_2CrO_4 + 3\ NaCl + 5\ H_2O.$$

(iii) By fusion with alkaline carbonates and nitre. Chromium compounds, when mixed with fusion mixture and nitre, and fused on platinum-foil, give a yellow mass of potassium and sodium chromate.

In each case the chromate can be tested for by acidifying with acetic acid and then adding lead acetate when a yellow precipitate of lead chromate, $PbCrO_4$, is formed.

$$K_2CrO_4 + Pb(C_2H_3O_2)_2 = PbCrO_4 + 2\ KC_2H_3O_2.$$

4. Chromium compounds give an emerald green borax bead, both in the inner and outer flame.

Chromous chloride, $CrCl_2$, and chromic chloride, $CrCl_3$, are the most important compounds in which chromium occurs as a base. *Chrome alum*, $K_2Cr_2(SO_4)_4$, 24 H_2O, is a common soluble double salt. The *chromates* contain chromium as chromic acid.

ALUMINIUM, Al.

Solution—Alum, $K_2Al_2(SO_4)_4$, 24 H_2O.

1. Ammonium hydroxide, NH_4OH, gives a *white transparent gelatinous* precipitate of aluminium hydroxide, $Al(OH)_3$.

$$K_2Al_2(SO_4)_4 + 3\ NH_4OH = 2\ Al(OH)_3 + K_2SO_4 + 3\ (NH_4)_2SO_4.$$

If a large excess of cold ammonia is added the precipitate redissolves, but on boiling the solution, complete reprecipitation takes place. The presence of ammonium chloride, however, prevents the solution of the hydroxide in cold ammonia.

2. Potassium hydroxide, KOH, or **sodium hydroxide,** NaOH, also precipitates the hydroxide. The precipitate is readily soluble in excess, forming an aluminate.

$$NaOH + Al(OH)_3 = \underset{\text{Sodium aluminate}}{NaAlO_2} + 2\ H_2O.$$

Excess of ammonium chloride causes reprecipitation of the hydroxide.

$$NaAlO_2 + NH_4Cl + 2\ H_2O = Al(OH)_3 + NH_4OH + NaCl.$$

Boiling renders the reprecipitation complete.

The cautious addition of an acid also brings about this reprecipitation, but if excess of acid is added the hydroxide redissolves (unless the acid is a very weak one *e.g.*, carbonic acid). Thus in the case of hydrochloric acid we have

$$NaAlO_2 + HCl + H_2O = Al(OH)_3 + NaCl.$$
$$Al(OH)_3 + 3\,HCl = AlCl_3 + 3\,H_2O.$$

3. **Disodium hydrogen phosphate,** Na_2HPO_4, gives a *white bulky* precipitate of aluminium phosphate, $AlPO_4$, insoluble in NH_4OH and NH_4Cl.

$$2\,Na_2HPO_4 + K_2Al_2(SO_4)_4 = 2\,AlPO_4 + K_2SO_4 + 2\,NaHSO_4 + Na_2SO_4.$$

4. Heat on charcoal before the blowpipe: a white mass is obtained which is highly luminous while hot. Allow to cool, moisten with cobaltous nitrate, and heat again in the inner flame: a *fine blue mass* is obtained. [*Distinction from zinc.*]

The commonest substance containing aluminium is common (potash) alum, which is a soluble double sulphate of potassium and aluminium, $K_2Al_2(SO_4)_4, 24H_2O$. Ammonium-alum, $(NH_4)_2Al_2(SO_4)_4, 24H_2O$, is another common alum.

GROUP IV.

METALS PRECIPITATED AS SULPHIDES BY AMMONIUM SULPHIDE, $(NH_4)_2S$, IN PRESENCE OF NH_4OH AND NH_4Cl.

Group-reagent—NH_4Cl, NH_4OH, and $(NH_4)_2S$.

NICKEL, Ni . . .	**Pp. Nickel Sulphide, NiS** (*black*).
COBALT, Co . . .	**,, Cobalt Sulphide, CoS** (*black*).
MANGANESE, Mn .	**,, Manganese Sulphide, MnS** (*buff*).
ZINC, Zn	**,, Zinc Sulphide, ZnS** (*white*).

NICKEL, Ni.

Solution—Nickel Sulphate, $NiSO_4$.

[*Note that the colour of the solution is green. All aqueous solutions of nickel salts are of a greenish colour.*]

1. **Ammonium sulphide,** $(NH_4)_2S$, gives a *black* precipitate

of nickel sulphide, NiS: slightly soluble in excess if *yellow* ammonium sulphide is used, producing a dark brown liquid.

$$(NH_4)_2S + NiSO_4 = NiS + (NH_4)_2SO_4.$$

The precipitate is insoluble in acetic acid and practically so in dilute HCl. It dissolves slowly in hot concentrated HCl, rapidly in HCl + a crystal of $KClO_3$, and in aqua regia. If acetic acid is added to the black liquid referred to above the dissolved nickel sulphide is reprecipitated.

2. **Potassium hydroxide,** KOH, or **sodium hydroxide,** NaOH, gives an apple-green precipitate of $Ni(OH)_2$.

$$2\,KOH + NiSO_4 = Ni(OH)_2 + K_2SO_4.$$

The precipitate is insoluble in excess.

3. **Ammonium hydroxide,** NH_4OH, produces *in neutral solution* the same precipitate which. however, dissolves in excess of the reagent to a blue liquid, containing the compound $NiSO_4.4\,NH_3$. The precipitate is not formed in the presence of NH_4Cl or other ammonium salts. On this account there is no precipitate when ammonium hydroxide is added to an acid solution of a nickel salt; an ammonium salt is formed and prevents the precipitation.

4. **Potassium cyanide,** KCN, gives a *yellowish-green* precipitate of nickel cyanide, $Ni(CN)_2$: soluble in excess, giving a brownish-yellow solution. containing a double cyanide of nickel and potassium, $K_2Ni(CN)_4$.

$$2\,KCN + NiSO_4 = Ni(CN)_2 + K_2SO_4.$$
$$2\,KCN + Ni(CN)_2 = K_2Ni(CN)_4.$$

The solution undergoes no change when boiled in air. On adding caustic soda and bromine (*i.e.*, NaOBr)* or

---

* When bromine is added to caustic soda in the cold sodium hypobromite, NaOBr, is formed:

$$2\,NaOH + Br_2 = NaBr + NaOBr + H_2O.$$

sodium hypochlorite ($NaOCl$) and warming gently, a black precipitate of $Ni_2(OH)_6$ is obtained.

$$2\ K_2Ni(CN)_4 + NaOBr + NaOH + H_2O = Ni_2(OH)_6 + 4\ KCN + 4\ NaCN + NaBr.$$

5. **Potassium nitrite + acetic acid** gives no precipitate. [*Distinction from cobalt.*]

6. Heated on a borax bead, in the outer flame, compounds of nickel yield an intensely coloured bead, which appears *hyacinth-red* to *violet-brown* when *hot*, and *yellowish* to *sherry-red* when *cold*, according to the quantity of nickel present.

Nickel sulphate, $NiSO_4$, nickel chloride, $NiCl_2$, and nickel nitrate, $Ni(NO_3)_2$, are the commonest soluble nickel salts. They are all of a green colour and more or less deliquescent.

COBALT, Co.

Solution—Cobalt Nitrate, $Co(NO_3)_2$.

[*Note that the colour of the solution is a pale red. All aqueous solutions of cobalt salts are of a reddish colour.*]

1. **Ammonium sulphide**, $(NH_4)_2S$, gives a *black* precipitate of cobalt sulphide, CoS, insoluble in excess.

$$(NH_4)_2S + Co(NO_3)_2 = 2\ NH_4NO_3 + CoS.$$

The precipitate is insoluble in acetic acid and practically so in dilute hydrochloric acid, but dissolves slowly in the hot strong acid. It is readily soluble in HCl + a crystal of $KClO_3$, and in aqua regia.

2. **Potassium hydroxide**, KOH, **or sodium hydrate**, $NaOH$, gives a precipitate of a *blue* basic salt, which on exposure to the air becomes *olive-green*, owing to the absorption of oxygen. When heated, a rose-red cobaltous hydroxide, $Co(OH)_2$, is obtained, which contains usually a small quantity of dark brown cobaltic hydroxide, $Co_2(OH)_6$. The precipitate is dissolved by ammonium carbonate to an intensely violet-red fluid.

3. **Ammonium hydroxide**, NH_4OH, gives *in neutral solution* a *bluish-green* precipitate of a basic salt readily soluble in excess. The precipitate is not formed in the presence of ammonium salts (*e.g.*, ammonium chloride) and so when ammonium hydroxide is added to an *acid solution* of a cobalt salt, no precipitate is formed (*cf.* the similar behaviour of nickel, p. 42).

4. **Potassium cyanide**, KCN, produces a *reddish-brown* precipitate of cobaltous cyanide, $Co(CN)_2$, which is redissolved in excess of KCN, forming potassium cobaltous cyanide, $K_4Co(CN)_6$.

$$2\,KCN + Co(NO_3)_2 = Co(CN)_2 + 2\,KNO_3.$$
$$4\,KCN + Co(CN)_2 = K_4Co(CN)_6.$$

When this solution is boiled it absorbs oxygen from the air and is converted into potassium cobalticyanide, $K_3Co(CN)_6$.

$$4\,K_4Co(CN)_6 + O_2 + 2\,H_2O = 4\,K_3Co(CN)_6 + 4\,KOH.$$

The oxidation takes place more rapidly if a trace of free acid is present, so that a few drops of acetic acid should be added before boiling. If now this solution is allowed to cool and then gently warmed with caustic soda and bromine (NaOBr) or with sodium hypochlorite (NaOCl) *no* precipitate is formed, as these reagents do not decompose potassium cobalticyanide at a gentle heat. [*Distinction from nickel.*]

5. **Potassium nitrite** in the presence of *free* **acetic acid** gives a yellow precipitate of potassium cobaltinitrite, $K_3Co(NO_2)_6$. [*Distinction from nickel.*]

$$Co(NO_3)_2 + 7\,KNO_2 + 2\,C_2H_4O_2 = K_3Co(NO_2)_6 \\ + 2\,KNO_3 + 2\,KC_2H_3O_2 + H_2O + NO.$$

6. The borax bead is coloured *blue* in the outer and inner flame by cobalt compounds.

Cobaltous sulphate, $CoSO_4$, cobaltous nitrate, $Co(NO_3)_2$, and cobaltous chloride, $CoCl_2$, are the most important of the soluble cobalt salts.

MANGANESE, **Mn.**

Solution—Manganous Sulphate, $MnSO_4$.

1. **Ammonium sulphide,** $(NH_4)_2S$, gives a *flesh-coloured* precipitate of manganese sulphide, MnS. [*Distinction from* Ni, Co, *and* Zn.]

$$MnSO_4 + (NH_4)_2S = MnS + (NH_4)_2SO_4.$$

The precipitate is readily soluble in dilute mineral acids, and is even soluble in acetic acid. [*Distinction from* Ni, Co, *and* Zn.]

$$MnS + 2\ HC_2H_3O_2 = H_2S + Mn(C_2H_3O_2)_2.$$

2. **Sodium hydroxide,** NaOH, or **potassium hydroxide,** KOH, gives a *white* precipitate of manganous hydrate, $Mn(OH)_2$, insoluble in excess. The precipitate speedily absorbs oxygen from the air, and turns *dark brown* with the formation of the hydrated manganic oxide, Mn_2O_3, H_2O, which is insoluble in NH_4Cl.

$$2\ NaOH + MnSO_4 = Mn(OH)_2 + Na_2SO_4.$$
$$4\ Mn(OH)_2 + O_2 = 2\ Mn_2O_3, H_2O + 2\ H_2O.$$

3. **Ammonium hydroxide,** NH_4OH, produces the same precipitate, except when ammonium salts are present, when the precipitation is prevented.

[On adding NH_4Cl and NH_4OH to a solution of a manganese salt, a soluble double chloride of ammonium and manganese, $2\ NH_4Cl, MnCl_2$, is formed. On exposure to air, this solution is gradually oxidized, and the manganese precipitated as Mn_2O_3, H_2O. For this reason manganese may be precipitated in Group III., *but the precipitation does not take place until after exposure to the air for some time.* Ferric hydroxide is precipitated *immediately.*]

4. Fuse a *very small* quantity of a manganese salt with fusion mixture and a little potassium nitrate, KNO_3, on a piece of platinum-foil. A *deep green mass* remains. This

mass is a mixture of potassium and sodium manganates, K_2MnO_4 and Na_2MnO_4.

If the mixture is treated with a small quantity of water it forms a *deep green* solution of the manganates. Excess of water causes the colour of the solution to change to *pale pink*, the manganates being converted partly into permanganates ($KMnO_4$, $NaMnO_4$), and partly into hydrated manganic oxide, Mn_2O_3, H_2O.

$$8\,K_2MnO_4 + 6\,H_2O = 6\,KMnO_4 + Mn_2O_3, H_2O + 10\,KOH.$$

The permanganates cause the pink colour; the Mn_2O_3, H_2O falls as a brown precipitate. The conversion of manganates into permanganates is also readily brought about by the action of an acid (even carbonic acid).

$$8\,K_2MnO_4 + 5\,CO_2 + H_2O = 6\,KMnO_4 + Mn_2O_3, H_2O + 5\,K_2CO_3$$

$$8\,K_2MnO_4 + 5\,H_2SO_4 = 6\,KMnO_4 + Mn_2O_3, H_2O + 5\,K_2SO_4 + 4\,H_2O.$$

5. In the outer flame the borax bead is coloured *amethyst* when cold. In the inner flame the bead becomes nearly colourless.

The most important salts of manganese are manganous sulphate, $MnSO_4$, and manganous chloride, $MnCl_2$. Of these the sulphate is the more commonly met with. The manganic salts are very unstable.

ZINC, Zn.

Solution—Zinc Sulphate, $ZnSO_4$.

1. **Ammonium sulphide,** $(NH_4)_2S$, gives a *white* precipitate of zinc sulphide, ZnS.

$$ZnSO_4 + (NH_4)_2S = ZnS + (NH_4)_2SO_4.$$

The precipitate is soluble in dilute mineral acids but not in acetic acid. [*Distinction from Mn.*]

2. **Potassium hydroxide**, KOH, or **sodium hydroxide**, $NaOH$, gives a white *gelatinous* precipitate of zinc hydroxide, $Zn(OH)_2$, soluble in excess forming potassium zincate, K_2ZnO_2, or sodium zincate, Na_2ZnO_2.

$$2\,KOH + ZnSO_4 = Zn(OH)_2 + K_2SO_4.$$
$$Zn(OH)_2 + 2\,KOH = K_2ZnO_2 + 2\,H_2O.$$

The precipitation is incomplete in the presence of NH_4Cl, the zinc being converted into the double salt, $2\,NH_4Cl, ZnCl_2$, which is not completely decomposed by caustic alkalies.

$$ZnSO_4 + 4\,NH_4Cl = 2\,NH_4Cl, ZnCl_2 + (NH_4)_2SO_4.$$

This behaviour is quite different from that of aluminium, for it will be remembered that NH_4Cl reprecipitates aluminium hydroxide from a solution of sodium aluminate (see p. 40).

3. **Ammonium hydroxide**, NH_4OH, produces the same precipitate, soluble in excess forming ammonium zincate, $(NH_4)_2ZnO_2$. In the presence of NH_4Cl, however, no precipitate is formed, the double salt $NH_4Cl, ZnCl_2$ not being decomposed by ammonia.

4. **Potassium ferrocyanide**, $K_4Fe(CN)_6$, gives a *white* precipitate of $Zn_2Fe(CN)_6$.

$$K_3Fe(CN)_6 + 2\,ZnSO_4 = Zn_2Fe(CN)_6 + 2\,K_2SO_4.$$

The precipitate is insoluble in dilute acids.

5. Heat some of the dry salt on charcoal: a mass of zinc oxide, ZnO, remains, which is *yellow when hot*, and *white when cold*. Allow to cool, moisten with a drop of cobaltous nitrate, $Co(NO_3)_2$, and again heat. The mass now becomes *green*.

The more commonly occurring zinc salts are the sulphate (*white vitriol*), $ZnSO_4$, $7\,H_2O$, the chloride, $ZnCl_2$, and the acetate, $Zn(C_2H_3O_2)_2$.

GROUP V.

METALS PRECIPITATED AS CARBONATES BY AMMONIUM CARBONATE, $(NH_4)_2CO_3$, IN THE PRESENCE OF NH_4Cl AND NH_4OH.

Group-reagent—NH_4Cl, NH_4OH, $(NH_4)_2CO_3$.

BARIUM, Ba . . .	**Pp. Barium Carbonate, $BaCO_3$**	(*white*).
STRONTIUM, Sr. . .	**,, Strontium Carbonate, $SrCO_3$**	,,
CALCIUM, Ca . . .	**,, Calcium Carbonate, $CaCO_3$**	,,

BARIUM, **Ba.**

Solution—Barium Chloride, $BaCl_2$.

1. **Ammonium carbonate,** $(NH_4)_2CO_3$, gives a *white* precipitate of barium carbonate.

$$(NH_4)_2CO_3 + BaCl_2 = BaCO_3 + 2\ NH_4Cl.$$

2. **Dilute sulphuric acid,** H_2SO_4, and **all soluble sulphates**, give immediately a *heavy white granular* precipitate of barium sulphate, $BaSO_4$, even from very dilute solutions of barium salts.

$$H_2SO_4 + BaCl_2 = BaSO_4 + 2\ HCl.$$

The precipitate is insoluble in acids except hot strong sulphuric acid, which slowly converts it into the acid sulphate, $BaH_2(SO_4)_2$; it is also insoluble in alkalies and in ammonium sulphate.

Solutions of strontium or calcium sulphate—two sulphates which are but slightly soluble in water—constitute the most delicate test for barium.

3. **Potassium chromate,** K_2CrO_4, gives a *lemon-yellow* precipitate of barium chromate, $BaCrO_4$: soluble in nitric and hydrochloric acids, but insoluble in acetic acid. [*Distinction from strontium and calcium salts.* See pp. 49, 50.]

$$K_2CrO_4 + BaCl_2 = BaCrO_4 + 2\ KCl.$$

4. **Hydrofluosilicic acid,** H_2SiF_6, produces a *colourless*

crystalline precipitate of barium silicofluoride, $BaSiF_6$. [*Distinction of barium from strontium and calcium salts*, which give no precipitate.]

$$H_2SiF_6 + BaCl_2 = BaSiF_6 + 2\ HCl.$$

The precipitate subsides quickly, especially when an equal bulk of alcohol is added. This is because the precipitate is insoluble in alcohol whereas it is slightly soluble in water. It is also slightly soluble in dilute acids.

5. **Ammonium oxalate,** $(NH_4)_2C_2O_4$, gives a *white* precipitate of barium oxalate, BaC_2O_4, sparingly soluble in acetic acid, readily in HCl.

$$(NH_4)_2C_2O_4 + BaCl_2 = BaC_2O_4 + 2\ NH_4Cl.$$

6. Barium compounds, when heated in the lower part of a Bunsen flame, colour the upper part of the flame yellowish-green.

Barium chloride, $BaCl_2$, and barium nitrate, $Ba(NO_3)_2$, are the commonest soluble salts of barium.

STRONTIUM, Sr.

Solution—Strontium Chloride, $SrCl_2$.

1. **Ammonium Carbonate,** $(NH_4)CO_3$, gives a *white* precipitate of strontium carbonate, $SrCO_3$.

$$(NH_4)_2CO_3 + SrCl_2 = SrCO_3 + 2\ NH_4Cl.$$

2. **Dilute sulphuric acid,** H_2SO_4, **and all soluble sulphates,** produce a *white* precipitate of strontium sulphate, $SrSO_4$.

$$H_2SO_4 + SrCl_2 = SrSO_4 + 2\ HCl.$$

In dilute solutions the precipitate only appears after some time, more especially when calcium sulphate is used as the precipitant : heat favours the precipitation.

3. **Potassium chromate,** K_2CrO_4, gives no precipitate

unless the solution is *strong*, when a yellow precipitate of strontium chromate, $SrCrO_4$, is formed.

$$K_2CrO_4 + SrCl_2 = SrCrO_4 + 2\,KCl.$$

The precipitate is soluble in acetic acid. [*Cf.* barium, p. 48.]

4. **Hydrofluosilicic acid,** H_2SiF_6 gives no precipitate. [*Distinction from barium.*]

5. Strontium compounds colour the flame an *intense crimson.*

Strontium nitrate, $Sr(NO_3)_2$, and chloride, $SrCl_2$, are the commonest soluble compounds of strontium.

CALCIUM, Ca.

Solution—Calcium Chloride, $CaCl_2$.

1. **Ammonium carbonate,** $(NH_4)_2CO_3$, gives a *white* precipitate of calcium carbonate, $CaCO_3$.

$$(NH_4)_2CO_3 + CaCl_2 = CaCO_3 + 2\,NH_4Cl.$$

2. **Ammonium oxalate,** $(NH_4)_2C_2O_4$, gives a *white powdery* precipitate of calcium oxalate, CaC_2O_4, even in largely diluted solutions.

$$(NH_4)_2C_2O_4 + CaCl_2 = CaC_2O_4 + 2\,NH_4Cl.$$

The precipitate is insoluble in acetic and oxalic acids, but is readily soluble in nitric and hydrochloric acids.

3. **Dilute sulphuric acid** or **soluble sulphates** give, *from concentrated solutions,* a white precipitate of calcium sulphate, $CaSO_4$, which is slightly soluble in water.

$$H_2SO_4 + CaCl_2 = CaSO_4 + 2\,HCl.$$

4. **Potassium chromate,** K_2CrO_4, gives no precipitate. [*Distinction from barium.*]

5. **Hydrofluosilicic acid,** H_2SiF_6, gives no precipitate. [*Distinction from barium.*]

6. Calcium compounds colour the flame a yellowish-red.

The chloride and sulphate are the compounds of calcium most commonly met with.

GROUP VI.

No Group-reagent.

MAGNESIUM, Mg.	**SODIUM, Na.**
POTASSIUM, K.	**AMMONIUM, NH_4.**

MAGNESIUM, **Mg.**

Solution—Magnesium Sulphate, $MgSO_4$.

1. **Ammonia,** NH_4OH, gives a white precipitate of magnesium hydroxide, $Mg(OH)_2$.

$$2\,NH_4OH + MgSO_4 = Mg(OH)_2 + (NH_4)_2\,SO_4.$$

In the presence of NH_4Cl no precipitate is formed because of the formation of the soluble double chloride of ammonium and magnesium, $2\,NH_4Cl, MgCl_2$. This compound is not decomposed by ammonia.

If ammonia is added to magnesium *chloride* only *half* the magnesium is precipitated as the hydroxide; the other half is converted into the double chloride.

$$2\,NH_4OH + 2\,MgCl_2 = 2\,NH_4Cl, MgCl_2 + Mg(OH)_2.$$

[The double chloride formed in the presence of NH_4Cl is not precipitated by $(NH_4)_2CO_3$; hence magnesium is not precipitated in Group V., provided a sufficient quantity of NH_4Cl be present.]

2. **Caustic potash, KOH,** precipitates the hydroxide, $Mg(OH)_2$, unless ammonium chloride is present. NaOH, $Ba(OH)_2$ and $Ca(OH)_2$ give the same precipitate.

3. **Disodium hydrogen phosphate,** Na_2HPO_4, **in the** presence of NH_4OH and NH_4Cl, gives a *white crystalline* precipitate of ammonium magnesium phosphate, $MgNH_4PO_4$.

$$MgSO_4 + Na_2HPO_4 + 2\,NH_4Cl + NH_4OH$$
$$= MgNH_4PO_4 + (NH_4)_2SO_4 + 2\,NaCl + H_2O.$$

The separation from a dilute solution of a salt of magnesium is promoted by heating gently and stirring with a glass rod. Very dilute solutions give a precipitate only after standing some hours in a warm place.

4. Heat strongly before the blowpipe on charcoal: moisten the residue with cobaltous nitrate, and again heat: a *pale pink mass* will be obtained. [*Distinction from zinc and aluminium.*]

Magnesium sulphate, $MgSO_4$, and magnesium chloride, $MgCl_2$, are the commonest soluble magnesium compounds.

POTASSIUM, K.

Solution—Potassium Chloride, KCl.

1. Place a few drops of the solution on a watch-glass, and add to it two or three drops of chloroplatinic acid, H_2PtCl_6, and then a few drops of alcohol. If the solution is concentrated, a *dense yellow crystalline* precipitate of the chloroplatinate, K_2PtCl_6, is at once formed.

$$2\ KCl + H_2PtCl_6 = K_2PtCl_6 + 2\ HCl.$$

If the solution be dilute, the precipitate is obtained only after some time.

Its formation can be hastened by rubbing the bottom of the watch-glass with a glass rod. The precipitate forms along the lines where the rod comes in contact with the watch-glass. In very dilute solutions no precipitate is obtained.

Note.—Potassium iodide behaves abnormally. It gives a brown coloration owing to the liberation of iodine, but no precipitate, if only sufficient H_2PtCl_6 is present to oxidise the KI. (If more than this is present it will react with the KCl, produced as shown in the above equation, and a precipitate will be formed.)

$$2\ KI + H_2PtCl_6 = 2\ KCl + PtCl_2 + I_2 + 2\ HCl.$$

The solution should be boiled for a few minutes with the addition of nitric acid so as to expel the iodine. The addition of H_2PtCl_6 will then produce a precipitate of K_2PtCl_6.

2. Sodium hydrogen tartrate or tartaric acid gives in concentrated neutral or slightly acid solutions a *white crystalline* precipitate of acid potassium tartrate, $KHC_4H_4O_6$ (cream of tartar).

$$KCl + NaHC_4H_4O_6 = KHC_4H_4O_6 + NaCl.$$

Shaking or stirring favours the precipitation.

3. Place a few drops of the solution on a watch-glass and add some sodium cobaltinitrite, $Na_3Co(NO_2)_6$. Stir up with a glass rod. A *yellow* precipitate of potassium cobaltinitrite, $K_3Co(NO_2)_6$ forms along the lines where the rod touches the glass.

$$3\ KCl + Na_3Co(NO_2)_6 = K_3Co(NO_2)_6 + 3\ NaCl.$$

4. Potassium compounds colour the flame *violet*. Owing to the presence of traces of sodium in all potassium salts, this flame test is not always distinct. By looking at the flame through a piece of blue cobalt glass the potassium flame can be distinguished in the presence of sodium, but this method is not very reliable, and, unless the potassium flame is very distinct, its presence will need careful confirmation in the wet way.

The nitrate, chloride, bromide, iodide, carbonate, and sulphate are the most common potassium compounds.

SODIUM, **Na**.

Solution—Sodium Chloride, NaCl.

1. Chloroplatinic acid, H_2PtCl_6, sodium hydrogen tartrate, and tartaric acid give *no* precipitate.

2. Potassium pyroantimonate, $K_2H_2Sb_2O_7$, gives a *white crystalline* precipitate of sodium pyroantimonate, $Na_2H_2Sb_2O_7$, from *concentrated* neutral or alkaline solutions.

$$K_2H_2Sb_2O_7 + 2\ NaCl = Na_2H_2Sb_2O_7 + 2\ KCl.$$

3. Sodium compounds colour the flame an *intense golden-yellow.*

N.B.—This test is the most reliable for sodium, but it must be remembered that traces of sodium are always present, so that a faint yellow coloration of the flame may in general be neglected. When sodium is present in quantity, the colour is characteristic and *very* intense.

To make more certain, stand with your back to the light and look at the back of the hand illuminated by the sodium light. If sodium is present in quantity the hand will appear blackish grey.

All sodium compounds are soluble in water, the most common being the chloride, sulphate, nitrate, carbonate, and phosphate.

AMMONIUM, $\mathbf{NH_4}$.

Solution—Ammonium Chloride, NH_4Cl.

1. Chloroplatinic acid, H_2PtCl_6, produces in concentrated neutral or acid solutions a *dense yellow* precipitate of the chloroplatinate, $(NH_4)_2PtCl_6$.

$$2\,NH_4Cl + H_2PtCl_6 = (NH_4)_2\,PtCl_6 + 2\,HCl.$$

The experiment should be carried out as in the corresponding case of potassium (p. 52).

2. Ammonium salts behave like potassium salts with sodium hydrogen tartrate and sodium cobaltinitrite.

3. Add **caustic soda**, $NaOH$, or **caustic potash**, KOH, and heat gently. Ammonia, NH_3, is given off, and is readily recognised by smell, action on litmus paper, and by fuming when a glass rod dipped in HCl is brought near it.

$$NaOH + NH_4Cl = NaCl + NH_3 + H_2O.$$

4. Heat some dry ammonium chloride in a test-tube: a white sublimate is formed in the upper part of the tube. All ammonium salts are either volatilized or decomposed by heat.

5. *Nessler's solution* (potassic mercuric iodide, $HgI_2,2KI + NaOH$) gives a *brown* precipitate of NHg_2I, H_2O, or a *yellowish-brown coloration*, according to the amount of ammonia present.

$$2\,HgI_2, 2\,KI + 4\,NaOH + NH_4Cl = NHg_2I.H_2O + 3\,H_2O + 4\,KI + 3\,NaI + NaCl.$$

This reaction is too delicate for the analysis of ordinary salts, and should only be used for detecting traces of ammonia.

The most common salts of ammonium are the chloride, carbonate, sulphate, bromide, and nitrate.

CHAPTER III.

REACTIONS OF THE ACIDS.

SULPHURIC ACID, H_2SO_4.

Solution—Potassium Sulphate, K_2SO_4.

1. **Barium chloride,** $BaCl_2$, gives a *heavy white powdery* precipitate of barium sulphate, $BaSO_4$, insoluble in HCl. (See p. 48.)

2. Lead acetate, $Pb(C_2H_3O_2)_2$, gives a *heavy white* precipitate of lead sulphate, $PbSO_4$. (See p. 19.)

SULPHUROUS ACID, H_2SO_3.

Solution—Sodium Sulphite, Na_2SO_3.

1. Add HCl, and, if necessary, heat: the smell of burning sulphur is perceptible, SO_2 being evolved *without* the precipitation of sulphur. [*Distinction from thiosulphates.*]

$$Na_2SO_3 + 2\ HCl = 2\ NaCl + H_2O + SO_2.$$

2. To some pieces of granulated zinc in a test-tube add a little hydrochloric acid till a brisk effervescence takes place; then pour in some of the liquid to be tested, and hold a piece of filter-paper moistened with lead acetate in the escaping gas. Any sulphite present will be reduced by the hydrogen and converted into sulphuretted

hydrogen, H_2S, which will stain the paper black with lead sulphide.

$$H_2SO_3 + 6\ H = H_2S + 3\ H_2O.$$
$$H_2S + Pb(C_2H_3O_2)_2 = PbS + 2\ HC_2H_3O_2.$$

3. **Barium chloride**, $BaCl_2$, gives a *white* precipitate of $BaSO_3$, *soluble* in HCl.

$$BaCl_2 + Na_2SO_3 = BaSO_3 + 2\ NaCl.$$

Most sulphites contain small quantities of sulphate (from oxidation) and hence the precipitate with $BaCl_2$ is usually not completely soluble in HCl.

4. **Silver nitrate**, $AgNO_3$, gives a *white* precipitate of silver sulphite, Ag_2SO_3.

$$2\ AgNO_3 + Na_2SO_3 = Ag_2SO_3 + 2\ NaNO_3.$$

If the mixture is heated the precipitate becomes *black*, metallic silver being formed.

$$Ag_2SO_3 + H_2O = 2\ Ag + H_2SO_4.$$

5. **Lead acetate**, $Pb(C_2H_3O_2)_2$, gives a *white* precipitate of lead sulphite, $PbSO_3$, which remains unchanged on heating. [*Distinction from thiosulphates.*]

$$Pb(C_2H_3O_2)_2 + Na_2SO_3 = PbSO_3 + 2\ NaC_2H_3O_2.$$

THIOSULPHURIC ACID, $H_2S_2O_3$.

Solution—Sodium Thiosulphate, $Na_2S_2O_3$.

1. **Hydrochloric acid** or **dilute sulphuric acid gives**, on warming, a smell of SO_2, and a *whitish-yellow* precipitate of sulphur.

$$Na_2S_2O_3 + 2\ HCl = 2\ NaCl + H_2O + SO_2 + S.$$

2. **Silver nitrate**, $AgNO_3$, added gradually, in excess, gives, after some time, a *white* precipitate of silver thiosulphate, $Ag_2S_2O_3$.

$$2\ AgNO_3 + Na_2S_2O_3 = Ag_2S_2O_3 + 2\ NaNO_3.$$

The precipitate slowly decomposes, becoming *yellowish-brown* and then *black*, forming silver sulphide, Ag_2S, thus—

$$Ag_2S_2O_3 + H_2O = Ag_2S + H_2SO_4.$$

3. **Lead acetate**, $Pb(C_2H_3O_2)_2$, gives a *white* precipitate of lead thiosulphate, PbS_2O_3, which becomes *black* on boiling, the thiosulphate being converted into sulphide. [*Distinction from sulphites.*]

$$Pb(C_2H_3O_2)_2 + Na_2S_2O_3 = PbS_2O_3 + 2\ NaC_2H_3O_2.$$
$$PbS_2O_3 + H_2O = PbS + H_2SO_4.$$

HYDROSULPHURIC ACID, H_2S.

Solution—Ammonium Sulphide, $(NH_4)_2S$.

1. Heat with HCl : sulphuretted hydrogen gas is given off, which is known by its characteristic odour and the black stain it produces on paper moistened with lead acetate ; and most soluble sulphides, since they contain persulphides, give a white precipitate of sulphur.

2. Lead acetate gives a *black* precipitate of lead sulphide, PbS.

3. Soluble cadmium salts give a *fine yellow* precipitate of cadmium sulphide, CdS.

4. Heat a dry sulphide in a piece of glass tubing held obliquely over a flame : in general, sulphur dioxide gas, which may be recognized by its odour, is given off.

Tests 2 and 3 are applicable to the detection of H_2S as an aqueous solution or as a soluble sulphide.

Note.—All salts of sulphur acids may be detected thus :— Fuse with Na_2CO_3 on charcoal in the inner blowpipe flame. The sulphur is converted into sodium sulphide. Thus suppose calcium sulphite, $CaSO_3$, is the salt used. This is first reduced to calcium sulphide, CaS, by the charcoal, and then sodium sulphide is formed by double decomposition with the sodium carbonate.

$$CaSO_3 + 3\ C = CaS + 3\ CO.$$
$$CaS + Na_2CO_3 = CaCO_3 + Na_2S.$$

Place the mass on a bright silver coin, and moisten it. A *black stain* will be produced on the silver, due to the formation of silver sulphide, Ag_2S.

$$2\ Ag + Na_2S + H_2O = Ag_2S + 2\ NaOH.$$

If the mass be acidified, H_2S is given off.

$$Na_2S + 2\ HCl = H_2S + 2\ NaCl.$$

HYDROCHLORIC ACID, **HCl.**

Solution—Sodium Chloride, NaCl.

1. **Silver nitrate,** $AgNO_3$, gives a *white curdy* precipitate of silver chloride, $AgCl$: insoluble in strong boiling nitric acid (silver cyanide dissolves): soluble in dil. ammonia.

2. Mix with **manganese dioxide,** MnO_2, and conc. H_2SO_4, and heat: chlorine gas is given off, and may be recognized by its colour, odour, and bleaching action on moist litmus.

$$MnO_2 + 3\ H_2SO_4 + 2\ NaCl = MnSO_4 + 2\ NaHSO_4 + Cl_2 + 2\ H_2O.$$

Note.—Since common MnO_2 frequently contains chlorine (as chloride), a *blank test* should always be made, *i.e.*, some of the MnO_2 should be heated with H_2SO_4 to see whether any chlorine is evolved. If this is the case the sample must be rejected. The best manganese dioxide to use is "needle" or native "manganese."

3. Strong sulphuric acid, when added to a strong solution of a chloride or to the dry salt, produces acid fumes of HCl, seen more distinctly by blowing over the mouth of the tube.

$$H_2SO_4 + NaCl = NaHSO_4 + HCl.$$

CHLORIC ACID, $HClO_3$.

Solution—Potassium Chlorate, $KClO_3$.

1. Heat a small quantity of the dry salt in a test-tube: fusion first takes place, then oxygen is evolved and may be detected by means of a glowing splinter. When action ceases a residue of potassium chloride, KCl, remains. Dissolve this residue in water, and test for HCl by Tests 1, 2, and 3, above.

2. On adding strong H_2SO_4 to a few small crystals of $KClO_3$ in a test-tube, the mixture turns yellow, and a yellowish gas, chlorine peroxide, ClO_2, is evolved. On gently heating, a series of detonations occur.

$$3\,KClO_3 + 2\,H_2SO_4 = 2\,ClO_2 + KClO_4 + 2\,KHSO_4 + H_2O.$$

3. Strong HCl produces a yellow coloration, and a yellow gas is evolved consisting of a mixture of chlorine and chlorine peroxide (called *euchlorine*).

$$8\,KClO_3 + 24\,HCl = 4\,KCl + 6\,H_2O + \underbrace{6\,ClO_2 + 9\,Cl_2}_{\text{Euchlorine}}.$$

4. On charcoal potassium chlorate deflagrates like a nitrate, but more violently.

Note.—Most chlorates are soluble in water; hence the absence of wet tests, which are based on precipitations.

HYPOCHLOROUS ACID, HClO.

The hypochlorites are all soluble in water, and are found only in combination or mixture with the chlorides of the same metal. Bleaching powder, Ca(OCl)Cl, is the most familiar example of such a compound. When dissolved in water it breaks up into a mixture of calcium chloride and calcium hypochlorite.

$$2\,Ca(OCl)Cl = Ca(OCl)_2 + CaCl_2.$$

Hypochlorites are distinguished by their powerful bleaching action in the presence of acids.

1. **Shake** up some bleaching powder with water, and filter off; then add to the filtrate dilute sulphuric acid, H_2SO_4; chlorine is evolved, and may be recognized by colour, odour, and bleaching action.

$$CaCl_2 + Ca(OCl)_2 + 2\ H_2SO_4 = 2\ CaSO_4 + 2\ H_2O + 2\ Cl_2.$$

HYDROBROMIC ACID, HBr.

Solution—Potassium Bromide, KBr.

1. **Silver nitrate**, $AgNO_3$, gives a *yellowish-white* precipitate of silver bromide, AgBr.

$$AgNO_3 + KBr = AgBr + KNO_3.$$

The precipitate is insoluble in dilute nitric acid and almost insoluble in dilute ammonia, but dissolves in strong ammonia. [*Distinction from* HCl.]

2. Add **chlorine water** to the solution: the liquid becomes yellow from free bromine.

$$Cl_2 + 2\ KBr = 2\ KCl + Br_2.$$

Shake up with some carbon disulphide, CS_2, which does not mix with the solution, but dissolves out the bromine, and an *orange-coloured* solution of bromine in CS_2 sinks to the bottom.

3. Mix with MnO_2 and H_2SO_4, and heat: bromine vapour of a *reddish-brown* colour is evolved, which colours paper moistened with starch *yellow*. [*Distinction from iodine.*]

$$MnO_2 + 3\ H_2SO_4 + 2\ KBr = MnSO_4 + 2\ KHSO_4 + 2\ H_2O + Br_2.$$

HYDRIODIC ACID, **HI.**

Solution—Potassium Iodide, KI.

1. **Silver nitrate,** $AgNO_3$, gives a *yellow* precipitate of silver iodide, AgI.

$$AgNO_3 + KI = AgI + KNO_3.$$

The precipitate is insoluble in nitric acid and in dilute ammonia, and is only slightly soluble in strong ammonia, by which, however, it is turned white.

2. **Mercuric chloride,** $HgCl_2$, gives a yellow precipitate, changing to *scarlet*, of mercuric iodide, HgI_2: soluble in excess of $HgCl_2$ or of KI. (See p. 23.)

3. Add a *few drops* of **chlorine water;** the solution becomes *brown* from liberation of iodine.

$$2\ KI + Cl_2 = 2\ KCl + I_2.$$

Shake up with a little CS_2: a fine violet-coloured solution of iodine in CS_2 sinks to the bottom. [*If too much chlorine water is used, colourless* ICl_3 *is formed.*]

4. Mix with **manganese dioxide** and **sulphuric acid** and heat in a long test-tube: *violet*-coloured iodine vapour is given off, which condenses in the cool part of the tube in grey-coloured crystals, and turns paper moistened with starch paste *blue.*

$$MnO_2 + 3\ H_2SO_4 + 2\ KI = MnSO_4 + 2\ KHSO_4 + 2\ H_2O + I_2.$$

5. A mixture of **copper sulphate,** $CuSO_4$, and **ferrous sulphate,** $FeSO_4$, solutions gives a white precipitate of cuprous iodide, Cu_2I_2.

$$2\ KI + 2\ CuSO_4 + 2\ FeSO_4 = Cu_2I_2 + K_2SO_4 + Fe_2(SO_4)_3.$$

HYDROFLUORIC ACID, **HF.**

Most fluorides are insoluble in water. Those of the alkali metals and silver are, however, soluble. The only important fluorides are fluor spar, calcium fluoride, CaF_2, and cryolite, $3\ NaF, AlF_3$.

Solution—Potassium Fluoride, KF.

1. **Silver nitrate**, $AgNO_3$, gives no precipitate, since silver fluoride, AgF, is soluble in water. [*Distinction from the other halogens.*]

2. **Calcium chloride**, $CaCl_2$, gives a *white gelatinous* precipitate of calcium fluoride, CaF_2, difficultly soluble in HCl.

$$CaCl_2 + 2\ KF = CaF_2 + 2\ KCl.$$

3. **Barium chloride**, $BaCl_2$, gives a *white* precipitate of barium fluoride, BaF_2, difficultly soluble in HCl.

$$BaCl_2 + 2\ KF = BaF_2 + 2\ KCl.$$

4. Heat some powdered fluor spar with concentrated sulphuric acid in a test-tube. Acid fumes of hydrofluoric acid will be evolved, rendered more evident by blowing across the mouth of the tube. Note the oily appearance in the test-tube.

$$CaF_2 + H_2SO_4 = CaSO_4 + 2\ HF.$$

5. Mix some powdered fluor spar with some sand, introduce into a test-tube, add strong sulphuric acid, and warm gently. SiF_4 is evolved. Now introduce into the upper part of the tube a glass rod, on the end of which is a drop of water. The SiF_4 and the water react with precipitation of silicic acid, H_2SiO_3, which forms a white film on the rod.

$$3\ SiF_4 + 3\ H_2O = H_2SiO_3 + 2\ H_2SiF_6.$$

HYDROCYANIC ACID, **HCN**.

Solution—Potassium Cyanide, KCN.

1. **Silver nitrate**, $AgNO_3$, gives a *white* precipitate of

silver cyanide, $AgCN$, which is at first redissolved, but remains when an excess of $AgNO_3$ has been added.

$$AgNO_3 + KCN = AgCN + KNO_3.$$

$$AgCN + KCN = \underset{\text{Soluble}}{KAg(CN)_2}$$

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

Wash and dry the precipitate, and then heat to redness. Metallic silver remains. [Silver chloride, $AgCl$, melts when heated, but is not decomposed.]

$$2\ AgCN = 2\ Ag + C_2N_2.$$

2. **Dilute sulphuric acid,** H_2SO_4, when added to a very small quantity of KCN, gives the peculiar odour of hydrocyanic acid, HCN.

[N.B.—*This vapour is very poisonous.*]

$$H_2SO_4 + KCN = KHSO_4 + HCN.$$

3. When heated with **strong sulphuric acid,** carbon monoxide is evolved. (Test in the usual way.)

$$2\ KCN + 2\ H_2SO_4 + 2\ H_2O = K_2SO_4 + (NH_4)_2SO_4 + 2\ CO.$$

4. **Ferrous sulphate,** $FeSO_4$, and **ferric chloride,** $FeCl_3$, are added, then **sodium hydroxide,** and lastly excess of **hydrochloric acid**; a *deep blue* precipitate of *Prussian blue* is produced.

$$FeSO_4 + 2\ NaOH = Fe(OH)_2 + Na_2SO_4.$$

$$6\ NaCN + Fe(OH)_2 = K_4Fe(CN)_6 + 2\ NaOH.$$

$$3\ Na_4Fe(CN)_6 + 4\ FeCl_3 = Fe_4[Fe(CN)_6]_3 + 12\ NaCl.$$

5. Place a little of the solution in a small beaker, add a few drops of dilute sulphuric acid, cover the beaker with a watch-glass on the lower side of which a drop of yellow ammonium sulphide has been placed, and gently warm the beaker on a sand tray. After a few minutes, remove the watch-glass and evaporate the drop of ammonium sulphide upon its lower surface to dryness over the flame, taking

care not to overheat it; when cold, moisten the residue with a drop of ferric chloride solution: a blood-red coloration will be produced, due to the formation of ferric sulphocyanide, $Fe(CNS)_3$.

The explanation of the changes which take place is as follows :—HCN is evolved by the action of the H_2SO_4 on the cyanide. This with the yellow ammonium sulphide, $(NH_4)_2S + S$, forms ammonium thiocyanate, NH_4SCN.

$$\underbrace{(NH_4)_2S + S} + 2\ HCN = NH_4SCN + H_2S.$$

$Fe(SCN)_3$ is then formed by double decomposition between the NH_4SCN and the $FeCl_3$.

$$FeCl_3 + 3\ NH_4SCN = Fe(SCN)_3 + 3\ NH_4Cl.$$

Simply evaporating a portion of the original solution with a little yellow ammonium sulphide on the water-bath, and when dry adding $FeCl_3$, will, in many cases, be quite sufficient. This is one of the best tests for hydrocyanic acid.

HYDROFERROCYANIC ACID, $H_4Fe(CN)_6$.

Solution—Potassium Ferrocyanide, $K_4Fe(CN)_6$.

1. **Silver nitrate** gives a *white* precipitate of $Ag_4Fe(CN)_6$, insoluble in nitric acid, insoluble in ammonia.

$$K_4Fe(CN)_6 + 4\ AgNO_3 = Ag_4Fe(CN)_6 + 4\ KNO_3.$$

2. **Ferrous sulphate,** $FeSO_4$, free from ferric salt, gives a *white* precipitate, which speedily turns *blue* when exposed to the **air.** (See p. 38.)

3. **Ferric chloride,** $FeCl_3$, gives a precipitate of *Prussian blue.* (See p. 37.)

4. **Copper sulphate,** $CuSO_4$, gives a *reddish-brown* precipitate of cupric ferrocyanide, $Cu_2Fe(CN)_6$. (See p. 26.)

5. Warm with **dilute sulphuric acid.** Hydrocyanic acid

(recognized by its smell) is evolved from ferrocyanides of the alkali metals.

$$2\ K_4[Fe(CN)_6] + 3\ H_2SO_4 = K_2Fe[Fe(CN)_6] + K_2SO_4 + 6\ HCN.$$

6. All ferrocyanides are decomposed on heating with **strong sulphuric acid.** Carbon monoxide is evolved, and may be tested for in the usual way.

$$K_4Fe(CN)_6 + 6\ H_2O + 11\ H_2SO_4 = 2\ KHSO_4 + FeSO_4 + 6\ NH_4HSO_4 + 6\ CO.$$

7. Insoluble ferrocyanides are decomposed on boiling with caustic potash, potassium ferrocyanide being formed. In the case of Prussian blue, for example, the decomposition is represented by the equation,

$$Fe_4\ [Fe(CN)_6]_3 + 12\ KOH = 4\ Fe(OH)_3 + 3\ K_4Fe(CN)_6.$$

The ferric hydroxide precipitated may be filtered off, and Tests 2 and 3 applied to the filtrate, which contains the potassium ferrocyanide.

HYDROFERRICYANIC ACID, $H_3Fe(CN)_6$.

Solution—Potassium Ferricyanide, $K_3Fe(CN)_6$.

(This is the only common ferricyanide.)

1. **Silver nitrate** gives an *orange-red* precipitate of silver ferricyanide, $Ag_3Fe(CN)_6$, soluble in ammonia.

$$K_3Fe(CN)_6 + 3\ AgNO_3 = Ag_3Fe(CN)_6 + 3\ KNO_3.$$

2. **Ferrous sulphate,** $FeSO_4$, gives a *deep blue* precipitate of *Turnbull's blue.* (See p. 38.)

3. **Ferric chloride,** $FeCl_3$, gives *no* precipitate, but a *deep brown* or *greenish coloration.*

4. Ferricyanides of the alkali metals on warming with **dilute sulphuric acid** evolve hydrocyanic acid.

5. All ferricyanides, on boiling with **strong sulphuric acid**, are broken down and evolve carbon monoxide. The decomposition in the case of Turnbull's blue is represented by the equation,

$$Fe_3''[Fe'''(CN)_6]_2 + 12\ H_2SO_4 + 24\ H_2O = 3\ FeSO_4 + Fe_2(SO_4)_3 + 6\ (NH_4)_2SO_4 + 12\ CO.$$

6. Insoluble ferricyanides are decomposed on boiling with **caustic alkalies**, the ferricyanide of the alkali metal being formed. Thus with Turnbull's blue and caustic potash the decomposition is represented by the equation,

$$Fe_3''[Fe'''(CN)_6]_2 + 6\ KOH = 3\ Fe(OH)_2 + 2\ K_3Fe(CN)_6.$$

After filtering off the precipitate of ferric hydroxide Tests 2 and 3 may be applied to the filtrate containing the potassium ferricyanide.

NITRIC ACID, HNO_3.

Solution—Potassium Nitrate, KNO_3.

1. Take a weak solution of the nitrate, and dissolve in it a crystal of ferrous sulphate, $FeSO_4$. When quite cold, pour into the tube enough concentrated H_2SO_4 to form a distinct layer at the bottom. A deep *purple* or *brown-coloured* ring will appear where the liquids meet.

The nitrate in the presence of sulphuric acid is reduced to nitric oxide by the ferrous sulphate—

$$6\ FeSO_4 + 4\ H_2SO_4 + 2\ KNO_3 = 3\ Fe_2(SO_4)_3 + K_2SO_4 + 4\ H_2O + 2\ NO.$$

The nitric oxide dissolves in the excess of ferrous sulphate to form the brown compound $FeSO_4$, NO.

$$FeSO_4 + NO = FeSO_4, NO.$$

Note.—When the addition of $FeSO_4$ produces a precipitate (*e.g.*, with barium nitrate), a portion of the solution should be boiled with sodium carbonate, then filtered, concentrated, and the filtrate acidified with dilute H_2SO_4. The test may then be applied to this solution, whicl contains the acid as sodium nitrate, the base having been precipitated as a carbonate.

$$FeSO_4 + Na_2CO_3 = FeCO_3 + Na_2SO_4.$$

2. Heat with concentrated sulphuric acid and copper turnings: nitric oxide, NO, is given off, which is converted into brown fumes of nitrogen peroxide, NO_2, in the upper part of the tube, from absorption of oxygen.

$$3\ Cu + 8\ H_2SO_4 + 8\ KNO_3 = 3\ Cu(NO_3)_2 + 8\ KHSO_4 + 4\ H_2O + 2\ NO.$$

$$2\ NO + O_2 = 2\ NO_2.$$

3. A nitrate heated on charcoal deflagrates.

Note.—All nitrates are soluble in water; hence we have no precipitation reactions. Compare chloric acid.

NITROUS ACID, HNO_2.

Solution—Potassium Nitrite, KNO_2.

1. On addition of dilute sulphuric acid, H_2SO_4, a brown gas is given off, which consists of a mixture of NO_2 and NO.

$$2\ KNO_2 + H_2SO_4 = K_2SO_4 + NO + NO_2 + H_2O.$$

In the upper part of the tube the NO combines with the oxygen of the air and becomes converted into nitrogen peroxide, NO_2.

[No gas is evolved when nitrates are mixed with dilute sulphuric acid.]

2. A solution of ferrous sulphate gives a *dark brown coloration* on the addition of *dilute* sulphuric acid. [*Distinction from* HNO_3.]

The coloration is due to the formation of the compound $FeSO_4$, NO.

$$2\ FeSO_4 + 2\ KNO_2 + 3\ H_2SO_4 = Fe_2(SO_4)_3 + 2\ KHSO_4 + 2\ H_2O + 2\ NO.$$

$$FeSO_4 + NO = FeSO_4,\ NO.$$

In some cases (namely when the solution of the nitrate has an *acid reaction*) the coloration is produced *without* the addition of an acid.

3. A dilute solution of potassium iodide, KI, acidified with H_2SO_4, and to which some starch paste has been added, gives immediately the *blue* iodide of starch.

$$2\,KI + 2\,H_2SO_4 + 2\,KNO_2 = I_2 + 2\,NO + 2\,K_2SO_4 + 2\,H_2O.$$

CARBONIC ACID, H_2CO_3.

1. All carbonates are decomposed by dilute acids with evolution of CO_2. This may be detected by suspending a drop of lime-water on a glass tube over the gas, when the drop soon turns milky.

Distinction between normal and acid carbonates.

1. Acid carbonates or bi-carbonates evolve CO_2 on boiling, and are converted into normal carbonates, *e. g.*,

$$2\,KHCO_3 = K_2CO_3 + H_2O + CO_2.$$

2. Magnesium sulphate, $MgSO_4$, gives no precipitate in the cold with bicarbonates, because $MgH_2(CO_3)_2$ is soluble. On boiling the solution, however, the magnesium bicarbonate is decomposed and a white precipitate of normal carbonate is formed.

$$2\,NaHCO_3 + MgSO_4 = MgH_2(CO_3)_2 + Na_2SO_4.$$
$$MgH_2(CO_3)_2 = MgCO_3 + H_2O + CO_2.$$

Normal carbonates give a precipitate of $MgCO_3$ at once.

$$Na_2CO_3 + MgSO_4 = MgCO_3 + Na_2SO_4.$$

BORIC ACID, H_3BO_3.

Solution—Borax, $Na_2B_4O_7$.

1. Add HCl to a solution of borax; wet a piece of turmeric paper with the solution. The paper when dried

becomes reddish-brown, and, on treating with *dilute* caustic soda, changes to a purplish blue-black.

Dry the paper by coiling round the exterior of a test-tube, partially filled with water, and boiling the water in the tube over the Bunsen flame.

2. Place a small quantity of the dry salt in a test-tube; cover with alcohol, make into a paste with H_2SO_4, and ignite: the alcohol burns with a *green flame,* due to a compound of boric acid and alcohol.

$$Na_2B_4O_7 + H_2SO_4 + 5\ H_2O = 4\ H_3BO_3 + Na_2SO_4.$$

3. Place a small quantity of the dry salt on the loop of the platinum-wire, and heat in the Bunsen flame. The borate at once swells up, and then shrinks and fuses to a transparent glass, consisting of anhydrous borax. If the salt is moistened with HCl or H_2SO_4 before heating, and held just at the *edge* of the flame, the flame is tinged *green,* due to the free boric acid.

SILICIC ACID, H_2SiO_3.

Solution—Sodium Silicate, Na_2SiO_3.

1. Add HCl, and evaporate in an evaporating dish to dryness; when cold, moisten with HCl, heat, and add water: white flakes of silica, SiO_2, will remain undissolved.

$$2\ HCl + Na_2SiO_3 = H_2SiO_3 + 2\ NaCl.$$
$$H_2SiO_3 = H_2O + SiO_2.$$

The silicic acid first formed as in the first equation loses water when the evaporation is carried to dryness as represented in the second equation.

2. Fuse a colourless silicate in a bead of microcosmic salt: the silica floats about in the bead as a skeleton.

PHOSPHORIC ACID, H_3PO_4.

Solution—Sodium Phosphate, Na_2HPO_4.

1. **Silver nitrate,** $AgNO_3$, gives a *yellow* precipitate of silver phosphate, Ag_3PO_4, soluble in NH_4OH and in acids.

$$3\,AgNO_3 + Na_2HPO_4 = Ag_3PO_4 + 2\,NaNO_3 + HNO_3.$$

2. **Ammonium chloride,** NH_4Cl, **ammonium hydroxide,** NH_4OH, and **magnesium sulphate,** $MgSO_4$ ("*magnesia mixture*"), give a *white crystalline* precipitate of ammonium magnesium phosphate, NH_4MgPO_4.

$$2\,NH_4Cl + NH_4OH + MgSO_4 + Na_2HPO_4 = MgNH_4PO_4 \\ + (NH_4)_2SO_4 + 2\,NaCl + H_2O.$$

Precipitation is favoured in dilute solutions by agitation and allowing to stand for a time.

3. **Ammonium molybdate,** $(NH_4)_2MoO_4$, gives, on gently warming, a *finely divided yellow* precipitate in solutions containing excess of nitric acid. The precipitate probably has the composition $(NH_4)_3PO_4$, $12\,MoO_3$. In dilute solutions the liquid becomes yellow, but a precipitate is formed only after gentle warming and standing for some hours. The solution must not be too strong in phosphate.

4. **Barium chloride,** $BaCl_2$, gives a *white* precipitate of $Ba_3(PO_4)_2$, soluble in dilute acids. If the solution is neutralized by adding ammonia, $Ba_3(PO_4)_2$ is reprecipitated.

$$3\,BaCl_2 + 2\,Na_2HPO_4 = Ba_3(PO_4)_2 + 4\,NaCl + 2\,HCl.$$
$$Ba_3(PO_4)_2 + 6\,HCl + 3\,BaCl_2 + 2\,H_3PO_4.$$
$$3\,BaCl_2 + 2\,H_3PO_4 + 6\,NH_4OH = Ba_3(PO_4)_2 \\ + 6\,NH_4Cl + 6\,H_2O.$$

5. **Ferric chloride** gives a *yellowish-white* precipitate of ferric phosphate, $FePO_4$.

$$FeCl_3 + Na_2HPO_4 = FePO_4 + 2\,NaCl + HCl.$$

The precipitate is soluble in dilute mineral acids but *insoluble in acetic acid.*

ARSENIC ACID, H_3AsO_4.

Solution—Sodium Arsenate, Na_2HAsO_4.

1. **Silver nitrate**, $AgNO_3$, gives a *brick-red* precipitate of silver arsenate, Ag_3AsO_4. [*Distinction from phosphoric acid.*]

$$3\ AgNO_3 + Na_2HAsO_4 = Ag_3AsO_4 + 2\ NaNO_3 + HNO_3.$$

The precipitate is soluble in ammonia and in nitric acid.

2. **Ammonium chloride**, NH_4Cl, **ammonium hydroxide**, NH_4OH, and **magnesium sulphate**, $MgSO_4$, produce a *white crystalline* precipitate of NH_4MgAsO_4, similar in appearance and properties to NH_4MgPO_4.

$$Na_2HAsO_4 + 2\ NH_4Cl + NH_4OH + MgSO_4 = (NH_4)MgPO_4 \\ + 2\ NaCl + (NH_4)_2SO_4 + H_2O.$$

[The corresponding arsen*ious* compound, $(NH_4)MgAsO_3$, is soluble in water, so no precipitate is formed when an arsen*ite* is treated with $MgSO_4 + NH_4Cl + NH_4OH$.]

3. **Ammonium molybdate**, $(NH_4)_2MoO_4$, in excess gives, on boiling, a *yellow* precipitate, having the composition $(NH_4)_3AsO_4$, $12\ MoO_3$, in solutions made strongly acid with nitric acid.

4. Add concentrated hydrochloric acid; heat to boiling, and pass H_2S. A *yellow* precipitate of arsenious sulphide, As_2S_3, mixed with sulphur, is obtained. [*Difference from phosphate.*]

$$2\ Na_2HAsO_4 + 4\ HCl + 5\ H_2S = As_2S_3 + S_2 \\ + 4\ NaCl + 8\ H_2O.$$

The reduction proceeds much more quickly if sulphurous acid be added before passing H_2S.

5. **Ferric chloride,** $FeCl_3$, gives a white precipitate of ferric arsenate, $FeAsO_4$.

$$FeCl_3 + Na_2HAsO_4 = FeAsO_4 + 2\ NaCl + HCl.$$

The precipitate is soluble in dilute mineral acids, but *insoluble in acetic acid.*

6. **Copper sulphate,** $CuSO_4$, gives a *light blue* precipitate of cupric hydrogen arsenate, $CuHAsO_4$.

$$CuSO_4 + Na_2HAsO_4 = CuHAsO_4 + Na_2SO_4.$$

ARSENIOUS ACID, H_3AsO_3.

Solution—Arsenious Oxide, As_4O_6, dissolved in Hydrochloric Acid, HCl.

[*See Arsenic, page* 32.]

ALUMINATES.

Solution—Potassium Aluminate, $KAlO_2$, or Sodium Aluminate, $NaAlO_2$.

1. Test with litmus. The solution is alkaline.

2. Cautiously add dilute **hydrochloric acid.** A white precipitate of aluminium hydroxide forms soluble in excess of acid and in caustic potash or soda. For equations see pp. 40, 41. The precipitate may be filtered off and part of it just dissolved in HCl and Test 3 for aluminium (p. 41) applied; the other part is treated as in Test 4 (p. 41).

3. Add excess of **ammonium chloride** and boil. A white precipitate of aluminium hydroxide is again formed. See p. 40 for the equation.

STANNATES.

Solution—Potassium Stannate, K_2SnO_3, or Sodium Stannate, Na_2SnO_3.

1. Test with litmus. The solution is alkaline.

2. Cautiously add dilute **hydrochloric acid**. A white precipitate of stannic acid, H_2SnO_3, is formed, soluble in excess of acid and in caustic potash or soda.

$$K_2SnO_3 + 2\ HCl = 2\ KCl + H_2SnO_3.$$

3. Introduce a piece of bright metallic copper into the solution. A bright layer of metallic tin is formed on the copper. This may be dissolved in strong hydrochloric acid and Test 2 for tin (p. 30) applied.

CHROMIC ACID, H_2CrO_4.

Solution—Potassium Chromate, K_2CrO_4.

(All chromates are red or yellow.)

1. **Silver nitrate**, $AgNO_3$, gives a *dark red* precipitate of silver chromate, Ag_2CrO_4. (See p. 16.)

2. On adding **dilute sulphuric acid**, the colour of the solution darkens, owing to formation of dichromic acid, $H_2Cr_2O_7$. To this solution add sulphurous acid: the solution becomes *green* from reduction, thus:—

$$2\ H_2CrO_4 + 3\ H_2SO_3 = Cr_2(SO_4)_3 + 5\ H_2O.$$

3. **Lead acetate** gives a *yellow* precipitate of lead chromate, $PbCrO_4$. (See p. 18.)

4. On passing a current of H_2S gas through an acid solution of a chromate, reduction takes place; the solution becomes green owing to the formation of chromic chloride, $CrCl_3$ (if HCl is the acid used), and sulphur is precipitated. Thus—

$$2\ K_2CrO_4 + 3\ H_2S + 10\ HCl = 4\ KCl + CrCl_3 + 8\ H_2O + 3\ S.$$

Note.—This reaction should be carefully noted, as it is likely to cause some perplexity in testing for the metals of Group II.

PERMANGANIC ACID, $\mathbf{HMnO_4}$.

(Commonest permanganates, $KMnO_4$, $NaMnO_4$.)

Solution—Potassium Permanganate, $\mathbf{KMnO_4}$.

1. The purple colour of permanganate solutions is distinctive.

2. **Silver nitrate,** $AgNO_3$, gives a *dark red* precipitate of $AgMnO_4$.

$$KMnO_4 + AgNO_3 = AgMnO_4 + KNO_3.$$

3. Sulphurous acid, H_2SO_3, decolorizes the solution, the sulphurous acid being oxidized to sulphuric acid.

$$2\ KMnO_4 + 5\ H_2SO_3 = K_2SO_4 + 2\ MnSO_4 + 2\ H_2SO_4 + 3\ H_2O.$$

4. An acid solution is also decolorized by **ferrous sulphate** solution, the ferrous sulphate being converted into ferric sulphate, $Fe_2(SO_4)_3$

$$2\ KMnO_4 + 8\ H_2SO_4 + 10\ FeSO_4 = 5\ Fe_2(SO_4)_3 + K_2SO_4 + 2\ MnSO_4 + 8\ H_2O.$$

5. **Sulphuretted hydrogen,** H_2S, decolorizes an acid solution of a permanganate, sulphur being precipitated. For this reason a permanganate is decolorized in Group II.

$$2\ KMnO_4 + 5\ H_2S + 3\ H_2SO_4 = 2\ MnSO_4 + K_2SO_4 + 8\ H_2O + 5\ S.$$

FORMIC ACID, $\mathbf{H_2CO_2}$ or **H.COOH.**

Formic acid is a colourless, slightly fuming liquid, having a pungent and characteristic odour. When cooled down it solidifies, melting again at 9°, and boiling at 99°. It is miscible in all proportions with water, alcohol and ether. It has strong antiseptic properties, and is a powerful reducing agent. The formates as a rule are readily soluble in water, lead formate being the least so.

1. On heating a formate (or formic acid) with **strong sulphuric acid**, it is decomposed. **Carbon monoxide** is evolved, and may be burnt at the mouth of the tube, but no charring takes place.

$$2\ H.COONa + H_2SO_4 = 2\ H_2O + 2\ CO + Na_2SO_4.$$

But if a formate is heated with **dilute** sulphuric acid, *formic acid* itself is liberated, and can be recognized by its characteristic smell.

$$2\ H.COONa + H_2SO_4 = 2\ HCOOH + Na_2SO_4.$$

2. When dry formates are heated with **soda lime**, hydrogen is evolved.

$$H.COONa + NaOH = Na_2CO_3 + H_2.$$

3. On gently heating a *formate* with **strong sulphuric acid** and **ethyl alcohol**, the fragrant and characteristic odour of ethyl formate, somewhat resembling the smell of rum, is noticed.

$$H.COONa + H_2SO_4 + C_2H_5(OH) = \underset{\text{Ethyl formate}}{H.COO.C_2H_5} + NaHSO_4 + H_2O.$$

4. When **mercuric oxide** is added to cold dilute formic acid, it dissolves, forming *mercuric* formate.

$$HgO + 2\ HCOOH = H_2O + (H.COO)_2Hg.$$

On gently heating, this **mercuric formate** is converted into *mercurous* formate (a white substance), and carbon dioxide is evolved.

$$2\ (H.COO)_2Hg = (H.COO)_2Hg_2 + H.COOH + CO_2.$$

On further heating, the **mercurous formate** is reduced, and a grey precipitate of metallic *mercury* is produced.

$$(H.COO)_2Hg_2 = H.COOH + 2\ Hg + CO.$$

It will be seen on reference to the above equations, that *free formic acid* is produced at each of these stages. This is capable of dissolving more mercuric oxide and consequently a repetition of the above reactions takes place, until finally all the formic acid is oxidized. The final state of affairs may be represented by the following equation :—

$$H.COOH + HgO = CO_2 + H_2O + Hg.$$

This reaction may be made use of with **formates**, by adding mercuric oxide to the formate solution, warming, and then adding dilute sulphuric acid, drop by drop, to liberate the *formic acid*, which acts upon the *mercuric oxide.*

5. **Mercuric chloride** gives with formic acid or formates, on boiling, a **white** precipitate of *mercurous chloride*, or a **grey** precipitate of *metallic* mercury.

(1) $2\ HgCl_2 + H.COOH = Hg_2Cl_2 + 2\ HCl + CO_2.$
(2) $HgCl_2 + H.COOH = Hg + 2\ HCl + CO_2.$

6. In strong solutions of formates, or free formic acid, **silver nitrate** gives a *white* precipitate of *silver formate*, which on warming, or standing, is reduced to a **grey** precipitate of metallic silver, and carbon dioxide is evolved.

$$H.COOH + AgNO_3 = \underset{\text{Silver formate}}{H.COOAg} + HNO_3.$$
$$2\ H.COOAg = H.COOH + CO_2 + 2\ Ag.$$

It will be seen that here again formic acid is re-formed The final state of affairs may be represented as follows :—

$$H.COOH + 2\ AgNO_3 = 2\ Ag + CO_2 + 2\ HNO_3.$$

7. In neutral solutions of formates, **ferric chloride** gives a **red** coloration, but no precipitate in the cold. To a portion of this red solution, add a little hydrochloric acid, when the colour will be destroyed. If the rest of the solution is boiled, a reddish precipitate of a basic iron salt will be produced.

ACETIC ACID.

$H_4C_2O_2$ or $CH_3 . COOH$.

Acetic acid is a pungent-smelling, strongly-acid liquid. When anhydrous, it is known as "glacial acetic acid." It solidifies in the cold, forming large crystalline plates, which melt at 17°, and boil at 118°. It attacks the skin, and its vapour burns with a pale blue flame. With water, alcohol, and ether, it is miscible in all proportions, and it is largely used as a solvent in organic chemistry. All neutral acetates are soluble in water, and on ignition in the dry state yield inflammable vapours, consisting chiefly of acetone.

$$2\ CH_3 . COONa = \underset{\text{Acetone}}{CH_3 . CO . CH_3} + Na_2CO_3.$$

1. On heating an acetate with **strong sulphuric acid**, *acetic* acid is set free, and can be recognized by its smell (*cf.* formic acid).

$$2\ CH_3 . COONa + H_2SO_4 = 2\ CH_3 . COOH + Na_2SO_4.$$

2. When a mixture of equal parts of **arsenious oxide** and an *acetate* is heated, the intensely obnoxious and highly characteristic smell of **cacodyl oxide** is noticed.

$$As_4O_6 + 8\ CH_3 . COOK = 2\ \underset{\text{Cacodyl oxide}}{As_2(CH_3)_4O} + 4\ K_2CO_3 + 4\ CO_2.$$

This is one of the best tests for the presence of an acetate, but only small quantities of the substances should be used. As the liquid (cacodyl oxide) is exceedingly poisonous, the experiment should be performed in a fume cupboard, and care should be taken not to inhale the fumes.

3. In neutral acetate solutions, **ferric chloride** gives a **red** coloration. To a portion of this red liquid add a drop of hydrochloric acid; it will be turned **yellow**. If the rest of the solution is boiled, a brownish precipitate of basic ferric acetate will be thrown down, the solution become colourless, and at the same time the smell of acetic acid will be noticed.

$$(1)\ 3\,CH_3.COONa + FeCl_3 = 3\,NaCl + \underset{\text{Ferric acetate}}{(CH_3.COO)_3Fe}.$$

$$(2)\ (CH_3.COO)_3Fe + 2\,H_2O = \underset{\text{Basic ferric acetate}}{(CH_3.COO)(OH)_2Fe} + 2\,CH_3.COOH.$$

4. Silver nitrate gives in concentrated neutral solutions of acetates a *white crystalline* precipitate of silver acetate, but no precipitate is formed with free acetic acid. Silver acetate is not reduced to metallic silver, even after prolonged heating. [*Distinction from silver formate.*]

$$CH_3.COONa + AgNO_3 = NaNO_3 + \underset{\text{Silver acetate}}{CH_3.COOAg}.$$

5. When an acetate is gently warmed with **alcohol** and **strong sulphuric acid**, a pleasant smell of **ethyl acetate** (*acetic ether*,) somewhat resembling the smell of formic ether, is produced.

$$CH_3.COONa + C_2H_5.OH + H_2SO_4 = \underset{\text{Ethyl acetate}}{CH_3.COO.C_2H_5} + NaHSO_4 + H_2O.$$

6. On strongly heating a dry acetate with *soda lime*, marsh gas (methane) is evolved.

$$CH_3.COONa + NaHO = CH_4 + Na_2CO_3.$$

7. When **mercuric oxide** is dissolved in acetic acid, *mercuric acetate* is formed. On prolonged boiling, no reduction takes place, and when the solution is allowed to cool, white shining crystals of mercuric acetate separate out. [*Distinction from formic acid.*]

$$HgO + 2\,CH_3.COOH = H_2O + \underset{\text{Mercuric acetate}}{(CH_3.COO)_2Hg}.$$

OXALIC ACID, $H_2C_2O_4$ or

$$\begin{array}{c}COOH \\ | \\ COOH\end{array}$$

Oxalic acid crystallizes in colourless rhombic prisms containing two molecules of water ($H_2C_2O_4 . 2\ H_2O$). It is readily soluble in alcohol and in water, but ether only dissolves it sparingly. When the crystals are first heated, they melt at 100°, and the water of crystallization is driven off. At about 150°, the anhydrous acid sublimes, but it decomposes on rapid heating into *carbon dioxide* and *formic acid;* or into *carbon dioxide*, *carbon monoxide*, and *water*—

$$H_2C_2O_4 = CO_2 + H . COOH = CO_2 + CO + H_2O.$$

Oxalic acid is dibasic and forms two classes of salts—**acid** salts, in which only *one* hydrogen atom is replaced by a metal or radicle, *e. g.* acid sodium oxalate, $NaHC_2O_4$ and ethyl oxalic acid, $C_2H_5.HC_2O_4$, and **normal** salts, in which *both* hydrogen atoms are replaced by metals or radicles, or by one metal and one radicle, *e.g.*, neutral sodium oxalate, $Na_2C_2O_4$, ethyl oxalate $(C_2H_5)_2C_2O_4$, and potassium ethyl oxalate, $K(C_2H_5)C_2O_4$. We are also acquainted with salts termed **quadroxalates**, which we may look upon as compounds of equal molecules of the acid salt and of oxalic acid, thus—HKC_2O_4, $H_2C_2O_4$, $2\ H_2O$ (salts of lemon).

The oxalates, with the exception of those of the alkali metals, are mostly *insoluble* in water.

1. All oxalates are decomposed on heating, **without blackening.** Oxalates of metals whose *oxides* decompose on heating, leave the metal (*e.g.*, silver). Oxalates of the alkalies leave *carbonates.* Oxalates of the alkaline earths (*e.g.*, barium, calcium) leave the carbonates if not too strongly heated, but if great heat is applied, the oxides are left.

2. On heating an oxalate (or the acid) with **strong sulphuric acid**, it is decomposed, a mixture of **carbon dioxide** and **carbon monoxide** gases being evolved, but no blackening takes place. While the mixture is being heated, the test-tube should be held in as nearly a horizontal

position as possible, whilst a second test-tube containing lime water or baryta water is placed beneath, to catch the carbon dioxide as it pours out. The monoxide can be detected by applying a light to the mouth of the first tube.

$$Na_2C_2O_4 + H_2SO_4 = CO_2 + CO + Na_2SO_4 + H_2O$$

3. If a soluble oxalate is strongly acidified with sulphuric acid, gently warmed, and a solution of **potassium permanganate** added to it gradually, the latter will be **decolorized**, and at the same time carbonic acid gas is disengaged and may be detected in the usual way.

$$\begin{aligned} 5\ Na_2C_2O_4 + K_2Mn_2O_8 + 8\ H_2SO_4 &= 10\ CO_2 \\ &K_2SO_4 + 2\ MnSO_4 + 5\ Na_2SO_4 + 8\ H_2O. \end{aligned}$$

4. **Calcium chloride**, when added to a neutral or alkaline oxalate solution, produces a **white** *precipitate* of *calcium oxalate*, **insoluble** in *acetic acid* or ammonia, but **soluble** in dilute nitric or hydrochloric acids. If this precipitate is dried and heated in a crucible over a Bunsen flame, carbon monoxide is evolved and a residue of *calcium carbonate* left behind, which effervesces on the addition of acetic acid.

$$(1)\ Na_2C_2O_4 + CaCl_2 = \underset{\text{Calcium oxalate}}{CaC_2O_4} + 2\ NaCl.$$

$$(2)\ CaC_2O_4 = CaCO_3 + CO.$$

5. **Silver nitrate** gives, in neutral oxalate solutions, a **white** precipitate of silver oxalate, soluble in *nitric acid*, and in *ammonia*.

$$2\ AgNO_3 + Na_2C_2O_4 = \underset{\text{Silver oxalate}}{Ag_2C_2O_4} + 2\ NaNO_3.$$

The silver oxalate does not darken on being heated, but *carbon monoxide* is given off with a slight explosion, and silver carbonate is left behind. On further heating this is decomposed and metallic silver is produced.

$$\begin{aligned} Ag_2C_2O_4 &= Ag_2CO_3 + CO. \\ 2\ Ag_2CO_3 &= 4\ Ag + O_2 + 2\ CO_2. \end{aligned}$$

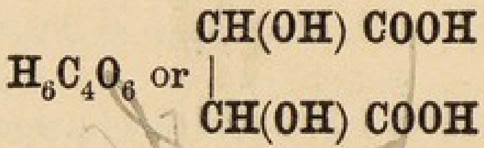
6. When a freshly prepared **ferrous sulphate** solution is added to a neutral *oxalate* solution, a yellowish colour is produced, and after standing for some time, a bright *yellow crystalline precipitate* of ferrous oxalate is thrown down.

$$K_2C_2O_4 + FeSO_4 = \underset{\text{Ferrous oxalate}}{FeC_2O_4} + K_2SO_4.$$

7. On strongly heating a dry neutral oxalate with **soda lime,** *hydrogen* is evolved and a carbonate is produced.

$$Na_2C_2O_4 + 2\ NaHO = 2\ Na_2CO_3 + H_2.$$

TARTARIC ACID.



$$H_6C_4O_6 \text{ or } \begin{array}{l} CH(OH)\ COOH \\ | \\ CH(OH)\ COOH \end{array}$$

Tartaric acid crystallizes in colourless transparent rhombic prisms, very *soluble* in *water* and *alcohol,* but *insoluble* in *ether.* It melts, with decomposition, at about 167°. Like oxalic acid, it forms both neutral and acid salts, a number of which are soluble in water, whilst *all* are soluble in dilute hydrochloric acid.

1. Heated in a dry tube, **tartrates** *swell up,* giving off an odour of **burnt sugar,** and leaving a black residue of carbon behind.

2. Heated in a test-tube with **strong sulphuric acid** tartrates **at once** blacken. Carbon monoxide is evolved and can be burnt at the mouth of the tube. Carbon dioxide and sulphur dioxide are also given off, the latter being recognized by its smell. In order that carbon dioxide may be identified in the presence of this gas, the apparatus shown in Fig. 7 is used.

In test-tube A is placed the tartrate and sulphuric acid; in B a saturated solution of potassium bichromate, which absorbs the sulphur dioxide; and in C some lime-water, which is rendered milky by the carbon dioxide.

3. If a little solid tartrate is gently heated to about 120°C., with conc. **sulphuric acid** containing one per cent. of **resorcin**, a beautiful **reddish-violet** colour is obtained. This test is conveniently performed on a small piece of porcelain.

4. To a tartrate solution, add a few drops of **ferrous sulphate** solution, one or two drops of **hydrogen peroxide**, and finally excess of **caustic potash**, when a deep **blue** or **violet** colour is obtained.

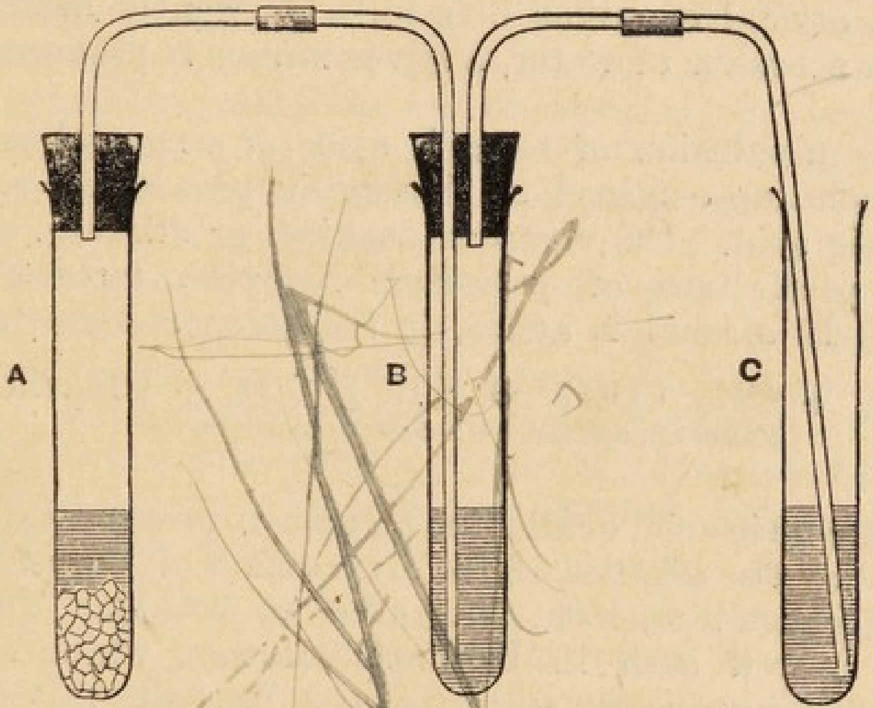


FIG. 7.

5. **Silver nitrate** solution gives, with **neutral** tartrates, a *white* precipitate of *silver tartrate*, soluble in ammonia and in nitric acid. If the precipitate is allowed to settle, the supernatant liquid poured off, just sufficient dilute ammonia to dissolve the residue added, and finally a gentle heat applied, the inside of the vessel will be coated with a *mirror* of *silver*. The experiment is best performed in a test-tube, which must be *perfectly clean*, and this should be heated in a beaker of water, to obtain a *bright mirror*.

$$2\ AgNO_3 + Na_2H_4C_4O_6 = 2\ NaNO_3 + \underbrace{Ag_2H_4C_4O_6}_{\text{Silver tartrate}}.$$

6. Calcium chloride produces, in **neutral** tartrate solutions, a white precipitate of *calcium tartrate*, soluble in *cold caustic potash* or *soda*. [*Distinction from calcium citrate.*]

$$CaCl_2 + Na_2H_4C_4O_6 = 2\ NaCl + \underset{\text{Calcium tartrate}}{CaH_4C_4O_6}.$$

Unless the tartrate solution is very concentrated, this precipitate only comes down after long standing or shaking. The precipitate is allowed to settle and the supernatant liquid poured off; a few drops of ammonia are added and then a crystal of silver nitrate. On gently heating the tube in a beaker of water, a silver *mirror* is produced.

7. To a solution of tartaric acid (or a neutral tartrate), add a solution obtained by dissolving potassium carbonate in acetic acid. On vigorous shaking or stirring, a heavy white precipitate of *potassium hydrogen tartrate* comes down. If alcohol is added, it furthers precipitation.

$$H_6C_4O_6 + \underset{\text{Potassium acetate}}{CH_3.COOK} = \underset{\text{Potassium hydrogen tartrate}}{KH.H_4C_4O_6} + CH_3.COOH.$$

8. Tartaric acid, or alkaline tartrates, prevent the precipitation by the alkalies of the hydroxides of copper, nickel, cobalt, chromium, iron, etc., even on boiling. This property is well seen in Fehling's solution, which is made by dissolving copper sulphate and Rochelle salt (sodium potassium tartrate) in water, and then adding caustic soda No precipitate is formed.

CITRIC ACID, $H_8C_6O_7$.

Citric acid crystallizes in transparent rhombic prisms containing one molecule of water of crystallization ($H_8C_6O_7 \cdot H_2O$). It is very soluble in water, fairly so in alcohol, but only sparingly so in ether. It melts at 100°, and soon after commences to lose water of crystallization, which, however, is not completely driven off till about 130°. On being heated in a test-tube, the acid melts and afterwards blackens, and irritating fumes of *aconitic acid* are given off.

Citric acid is a tribasic acid and forms three classes of salts as—$C_6O_7H_7K$, $C_6O_7H_6K_2$, and $C_6O_7H_5K_3$. A considerable number of citrates are freely soluble in water, especially those of the alkali metals.

1. Citric acid and its salts, when heated with **strong sulphuric** acid, are decomposed, the oxides of carbon being evolved. After **continued heating**, blackening takes place and sulphur dioxide is evolved (tartrates blacken *at once*).

2. **Calcium chloride** when added to a *neutral* solution of a citrate, gives **no** precipitate in the **cold**, even after much shaking and long standing, but on warming, the precipitate of calcium citrate comes down. If the solution is very dilute, it will need concentrating somewhat. The precipitate of calcium citrate is not formed in the presence of *free* citric acid even on boiling, but excess of an alkali favours its production. Calcium citrate is soluble in *ammonium chloride*, but *not* in *caustic soda* or *potash*. It is also distinguished from *calcium tartrate*, by being heated in a test-tube with a crystal of silver nitrate and a drop of ammonia. No mirror is formed, but after prolonged heating, reduction sets in.

$$2\,C_6O_7H_5K_3 + 3\,CaCl_2 = \underset{\text{Calcium citrate}}{Ca_3(C_6O_7H_5)_2} + 6\,KCl.$$

3. Lime water in excess gives no precipitate in the cold with citric acid or citrates, but on boiling, calcium citrate is thrown down. On cooling, the precipitate is re-dissolved.

4. In neutral solutions of citrates, **silver nitrate** gives a precipitate of *silver citrate*, soluble in ammonia. On heating, the silver is reduced, but without the formation of a mirror.

$$C_6O_7H_5Na_3 + 3\,AgNO_3 = \underset{\text{Silver citrate}}{C_6O_7H_5Ag_3} + 3\,NaNO_3.$$

5. Citrates, like tartrates, prevent the precipitation by the alkalies of the hydroxides of copper, nickel, cobalt, etc.

TABLE OF SOLUBILITIES.

TABLE SHOWING THE SOLUBILITY OF THE MORE COMMONLY OCCURRING SALTS.

NAME.	SOLUBLE IN WATER.	SOLUBLE IN, OR DECOMPOSED BY, ACIDS.	INSOLUBLE IN ACIDS.
Carbonates.	Acid carbonates of Ba, Sr, Pb, Mn, Mg, Fe″, and Ca, and alkaline carbonates.	All carbonates are decomposed with evolution of CO_2.	
Sulphates.	Most sulphates. (Ag_2SO_4 is difficultly soluble).	Some *basic* sulphates.	Sulphates of Pb, Ba, Sr and Ca.
Nitrates.	Most nitrates (a few *basic* nitrates excepted).	A few basic nitrates which are readily soluble in dilute HNO_3.	
Chlorides.	Most chlorides.	A few oxychlorides. (BiOCl and SbOCl).	Chlorides of Pb, Hg′, Ag, and Cu_2Cl_2.
Bromides.	Most bromides.	Cu_2Br_2 in HCl.	Bromides of Hg′, Ag, and Pb.
Iodides.	Most iodides.	HgI_2, Hg_2I_2 ($=HgI_2+Hg$), PbI_2, Cu_2I_2, decomposed by HNO_3 with evolution of I.	Iodides of Ag, Hg′, Hg″, Pb, and 'Cu′.
Chlorates.	All chlorates.		
Sulphides.	Sulphides of the alkali metals, and the metals of the alkaline earths. MgS and CaS *very slightly* soluble.	All other sulphides are decomposed by HCl (H_2S being evolved), or by HNO_3, or aqua regia, with separation of S.	
Phosphates.	Alkaline phosphates only.	Remainder are soluble.	
Chromates.	Alkaline chromates and chromates of Mg, Zn, Ca, Sr, Fe^{iv}, and Cu.	Chromates insoluble in water dissolve in acids (evolving chlorine in concentrated HCl).	

CHAPTER IV.

SYSTEMATIC ANALYSIS OF SALTS.

Preliminary Examination in the Dry Way.

If the substance is in solution, a portion should be evaporated to dryness on a water-bath while the examination in the wet way is being proceeded with. The residue after evaporation should then be examined as below, I.-IX.

I. **Note the general physical characteristics of the substance.**

On this point the previous experience of the student must be his guide. He should note the appearance, colour, lustre, crystalline form, etc., of all substances with clearly marked characteristics which come under his notice. It is useless to give any list of such substances, as they must be seen to be recognized.

II. **Heat a small portion of the powdered substance in a bulb-tube in the Bunsen flame.**

Observation.	Inference.
1. *The substance fuses and solidifies on cooling.*	Salts of the alkalies or alkaline earths.
2. *The substance changes colour—*	

Observation.	Inference.
(*a*) *Yellow* while *hot*, *white* on *cooling*.	ZnO, Sb_4O_6.
(*b*) From *white* to *yellowish-brown* when *hot*, *dirty light yellow* on *cooling*.	SnO_2.
(*c*) *Dark red* while *hot*, *yellowish-brown* on *cooling*.	Fe_2O_3.
(*d*) From *white* to *orange* and *reddish-brown*, *dull yellow* on cooling, fusible at an intense heat.	Bi_2O_3.
(*e*) From *yellow* to *reddish-brown* while *hot*, *yellow* when *cold*, fusible at a red heat.	PbO.
3. *The substance gives off water with or without fusion.*	Salts containing water of crystallization ; also *acid* salts (*e.g.* $NaHCO_3$)
4. *The substance first swells up and then shrinks.*	Alums, phosphates, borates.
5. *The substance volatilizes and condenses as a sublimate in the upper part of the tube*—	S, Hg, As, Sb, NH_4.
(*a*) *Reddish* drops, *yellow* when *cold*.	Sulphur or a sulphide.
(*b*) *Black* sublimate, which becomes *red* on rubbing.	HgS.
(*c*) *Yellow* sublimate.	As_2S_3, HgI_2.
(*d*) Sublimate of *small white octahedral crystals*.	As_4O_6.
6. *A gas is evolved*—	
(*a*) O (test with glowing splinter),	Chlorates, nitrates, peroxides.

OBSERVATION.	INFERENCE.
(*b*) Brown fumes of NO_2.	Nitrates of heavy metals, Pb, Bi, Hg, etc.
(*c*) NH_3 (smell and alkaline reaction).	Salts of NH_4, combined with a *non-volatile acid.*
(*d*) Violet vapours of iodine.	Iodides.
(*e*) CO_2 (lime-water test).	Carbonates (except those of the alkalies).
(*f*) Cl (bleaching action, smell and colour).	Hypochlorites and some chlorides and chlorates.
(*g*) Br (smell and colour).	Some bromides and bromates.
(*h*) SO_2(smell).	Sulphites, sulphur compounds.
(*i*) C_2N_2 (smell, rose-coloured flame.)	Cyanides of heavy metals.
(*k*) Burnt sugar smell and immediate blackening.	Tartrates.

III. **Heat a portion of the substance on charcoal in the outer blowpipe flame.**

1. *It decrepitates.*	NaCl, KI, etc.
2. *It fuses and sinks into the charcoal.*	Alkaline salts.
3. *It deflagrates.*	Chlorates, nitrates and certain oxides.
4. *A white mass remains, highly luminous while heated.*	Alkaline earths, Al_2O_3, SiO_2, ZnO, SnO_2.
5. *A coloured residue is left on the charcoal.*	Cu, Co, Ni, Mn, Fe, Cr.
6. *White fumes are given off.*	Hg, As, Sb, and NH_4 compounds.

OBSERVATION.	INFERENCE.
7. *An incrustation is formed on the charcoal—*	
(*a*) *White* incrustation.	NH_4, Hg, Sb, Zn.
(*b*) *White* (with garlic odour).	As.
(*c*) *Yellow* when *hot*, *white* when *cold.*	Zn.
(*d*) *Reddish-brown.*	Cd.
(*e*) *Straw colour.*	Sn.
(*f*) *Brown* when *hot*, *yellow* when *cold.*	Pb.
(*g*) *Brown* when *hot*, *orange* when *cold.*	Bi.

IV. Moisten the cold residue of III. (if white) **with cobalt nitrate,** $Co(NO_3)_2$ **and heat strongly.**

1. *The residue is coloured—*	
Blue.	Al_2O_3, phosphates, borates and silicates.
Pale pink (colour indistinct).	MgO.
Green.	ZnO.
Bluish-green (dirty).	Sn.

V. Mix a portion of the substance carefully with fusion mixture and a trace of KCN, and heat on charcoal in the inner blowpipe flame.

1. *A metallic bead is obtained.*	
(*a*) A white malleable bead which marks paper (*yellow incrustation* on charcoal).	Pb.
(*b*) Soft, white malleable bead (*slight yellowish incrustation*).	Sn.

OBSERVATION.	INFERENCE.
(*c*) Hard white malleable bead (*no incrustation*).	Ag.
(*d*) White brittle bead (*yellow incrustation*).	Bi.
(*e*) White brittle bead (*white fumes* and *incrustation*).	Sb.
2. *Red infusible scales.*	Cu.
3. *Magnetic metallic particles.*	Fe, Ni, Co.
4. *When the fused mass is placed on a bright silver coin and moistened with a drop of water, a black stain of* Ag_2S *is produced.*	Sulphur compounds.

VI. Hold a piece of the substance moistened with HCl on the loop of a CLEAN platinum wire in the Bunsen flame.

1. The flame is *yellow,*	Na.
2. ,, ,, *violet,*	K.
3. ,, ,, *intense crimson,*	Sr.
4. ,, ,, *yellowish-green,*	Ba.
5. ,, ,, *orange-red,*	Ca.
6. ,, ,, *green,*	H_3BO_3, or Cu.
7. ,, ,, *blue,*	Pb, Bi, $CuCl_2$, As_4O_6.

It is almost impossible to distinguish from one another by the eye, the colours given to the flame by Pb, Bi, As, Sb, and K. Arsenic compounds always evolve a visible white fume, and lead invariably corrodes the platinum.

VII. **If the substance is coloured, heat on borax bead.**

OBSERVATION.		INFERENCE.
Oxidizing Flame.	*Reducing Flame.*	
Green.	Green.	Cr.
Yellow (cold), brown (hot)	Dirty green, olive.	Fe.
Amethyst.	Colourless.	Mn.
Violet (hot) to yellow-brown (cold).	Grey and opaque.	Ni.
Blue.	Blue.	Co.
Green (hot), blue (cold).	Colourless or red.	Cu.
Black (too much of the substance has been used).		

VIII. **Heat a small quantity of the substance in a test-tube with a little dilute HCl.**

OBSERVATION.	INFERENCE.
1. *A gas is evolved—*	
(*a*) CO_2 (lime-water test).	Carbonates.
(*b*) H_2S (smell, and lead acetate paper test).	Sulphides, except those of the metals of Groups I. and II.
(*c*) SO_2 (smell of burning sulphur).	H_2SO_3.
(*d*) SO_2 and separation of yellow sulphur.	$H_2S_2O_3$.
(*e*) Cl (smell, and bleaching test).	Oxidizing agents, *e.g.*, chromates, chlorates, peroxides, HClO.
(*f*) HCN (smell of bitter almonds).	Cyanides.
(*g*) NO_2 (colour and smell).	Nitrite.
2. Smell like that of vinegar.	Acetate.

IX. **Heat in a test-tube with concentrated sulphuric acid:—**

OBSERVATION.	INFERENCE.
1. *A gas is evolved—*	
(*a*) HCl (smell and white fumes* with ammonia).	Chloride.
(*b*) HF (oily appearance in the tube).	Fluoride.
(*c*) I (violet vapours).	Iodide.
(*d*) Br (smell, colour and action on starch paper).	Bromide.
(*e*) NO_2 (smell and colour).	Nitrite or nitrate.
(*f*) ClO_2 (smell, colour and crackling).	Chlorate.
(*g*) CO (burns with blue flame).	Formate cyanide, or double cyanide.
(*h*) $CO + CO_2$.	Oxalate.
2. *Smell of vinegar.*	Acetate.
3. *Blackening* and evolution of CO, CO_2 and SO_2.	Tartrates (blacken immediately); citrates (blacken after a time).

EXAMINATION FOR BASES.

Preparation of Solution.

1. If the substance is solid, it should be finely powdered; then try if it is soluble in water, in the cold or on boiling. If insoluble in water, try first dilute HCl, then concentrated HCl. If insoluble in HCl, try aqua regia.

Note.—It will generally be found unnecessary to employ aqua regia, but, if used, the solution should be evaporated

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* A number of other acids also give white fumes with ammonia, *e.g.* HNO_3, HF, HBr.

to dryness with excess of HCl, and the residue dissolved in warm water before proceeding with the examination.

2. If the substance is insoluble in the above solvents, powder it very finely and mix thoroughly with five or six times its weight of pure fusion mixture. Heat the mixture on a boat made of a large piece of platinum-foil, first over the Bunsen flame, and then over the blowpipe. When cold, boil the foil and the fused mass with water until the whole mass is completely broken up and separated from the foil. The *solution* now contains the *acid* of the substance combined with K and Na, while the *residue* contains the *base* as an oxide or carbonate. Filter off and wash the residue with hot water until the washings give no alkaline reaction. Then—

(*a*) Test *filtrate* for *acids*, as directed in examination for acids.

(*b*) Test residue for bases by dissolving in dilute HCl and proceeding as detailed below.

Note.—The most commonly occurring insoluble substances are—native or ignited alumina and chromic oxide; silica and many silicates; barium, strontium and lead sulphates; silver chloride, cyanide, bromide, and iodide; many minerals, *e.g.* chrome iron ore, calcium fluoride; carbon.

3. If the substance is provided in solution, or is soluble in water, test with litmus paper. If the reaction is—

(*a*) *Acid.* Free acid, acid salt, or a normal salt having an acid reaction, may be present.

(*b*) *Alkaline.* Free alkali, peroxides of the alkali metals, or alkaline salts—carbonate, phosphate, borate, cyanide, silicate, and particularly stannate and aluminate.

(*c*) *Neutral.* Water, or one or more of a large number of salts, may be present.

When the solution is prepared, you must proceed to separate the metals present into groups, using Table A given below, and having done this you must find what metals of each group are present, using Tables I.-VIII.

TABLE A.

SEPARATION OF THE METALS INTO GROUPS.

<table>
<tr><td colspan="6">Prepare a solution as described on page 93.
Add dilute hydrochloric acid and, if a precipitate is formed, filter—wash the precipitate.</td></tr>
<tr><td rowspan="5">PRECIPITATE.
Metals of Group I.
Silver.
Lead.
Mercury (ous).</td><td colspan="5">FILTRATE.
Warm the filtrate, and pass H_2S gas through the liquid until it is saturated—filter.</td></tr>
<tr><td rowspan="4">PRECIPITATE.
Metals of Group II.
Digest with yellow ammonium sulphide, or with $NaOH$ + a little Na_2O_2, warm, and filter.
RESIDUE.
Mercury (ic)
Lead
Bismuth } II. <i>a.</i>
Copper
Cadmium
FILTRATE.
Arsenic
Antimony } II. <i>b.</i>
Tin</td><td colspan="4">FILTRATE.
Boil to expel all the H_2S, add a few drops of strong nitric acid to oxidize any ferrous to ferric salt. Test a small part for H_3PO_4 with ammonium molybdate. Boil the remainder up again; then add ammonium chloride and ammonia till alkaline; filter rapidly (to prevent oxidation of Mn).</td></tr>
<tr><td rowspan="3">PRECIPITATE.
Metals of Group III.
Iron.
Aluminium.
Chromium.
If phosphoric acid is present, the phosphates of Groups III., IV., and V., and Mg will be precipitated here.</td><td colspan="3">FILTRATE.
Add ammonium sulphide in slight excess (or add ammonia and pass in H_2S)—warm, and if necessary, filter.</td></tr>
<tr><td rowspan="2">PRECIPITATE.
Metals of Group IV.
Cobalt.
Nickel.
Zinc.
Manganese.</td><td colspan="2">FILTRATE.
Add ammonium carbonate and heat—filter.</td></tr>
<tr><td>PRECIPITATE.
Metals of Group V.
Barium.
Calcium.
Strontium.</td><td>SOLUTION.
Metals of Group VI.
Magnesium.
Ammonium.
Potassium.
Sodium.</td></tr>
</table>

NOTES ON THE SEPARATION OF THE METALS INTO GROUPS.

The separation of the metals into groups depends upon the following facts:—

Group I.—The insolubility of $AgCl$, $PbCl_2$, Hg_2Cl_2, all other chlorides being soluble.

Group II.—The insolubility of the following sulphides in dilute hydrochloric acid:—HgS, PbS, Bi_2S_3, CuS, CdS, As_2S_3, Sb_2S_3, Sb_2S_3, SnS_2, SnS.

Group II. (*b*).—The solubility of As_2S_3, Sb_2S_3, SnS_2, SnS, in yellow ammonium sulphide or in caustic alkalies + Na_2O_2.

Group III.—The precipitation of $Fe(OH)_3$, $Al(OH)_3$, $Cr(OH)_3$, on the addition of NH_4Cl and NH_4OH.

Group IV.—The insolubility of CoS, NiS, ZnS, MnS in *an alkaline* (*or neutral*) *solution.*

Group V.—The insolubility of $CaCO_3$, $SrCO_3$, $BaCO_3$, in *an alkaline* (*or neutral*) *solution.*

The following points should be carefully noted:—

Group I.—The hydrochloric acid must not be too strong, or *barium chloride* ($BaCl_2$), which is insoluble in strong HCl, may be precipitated. The precipitate in this case dissolves readily on adding water.

Group II.—It is well to dilute *considerably* before passing H_2S; mineral acids, especially nitric, unless greatly diluted, are likely to interfere. Cadmium, in particular, is difficult to precipitate in a strongly acid solution, and might pass forward to Group III., where it would be thrown down as a yellow sulphide on the addition of ammonium hydroxide. Antimony also is often kept in solution by hot moderately strong HCl; addition of water brings about precipitation.

On passing sulphuretted hydrogen through the solution a precipitate of sulphur is sometimes produced. This indicates the presence of an oxidizing agent:

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

The yellowish solution of $FeCl_3$ becomes colourless Similarly, chromates or dichromates change from yellow to green under the reducing action of H_2S; in all such cases turbidity due to sulphur occurs:

$$2\ K_2CrO_4 + 10\ HCl + 3\ H_2S = Cr_2Cl_6 + 4\ KCl + 8H_2O + 3\ S.$$

If arsenic acid (H_3AsO_4) is present, it is reduced by H_2S to the arsenious condition before it can be precipitated. This often takes a considerable time. It proceeds quicker on warming:

$$H_3AsO_4 + H_2S = H_3AsO_3 + H_2O + S,$$

and then $2\ H_3AsO_3 + 3\ H_2S = As_2S_3 + 6\ H_2O.$

Another method of procedure (not, however, altogether free from objection) is to boil with a solution of sulphur dioxide before passing H_2S, if arsenic has been detected in the preliminary examination. This will rapidly reduce arsenic acid, if present.

$$H_3AsO_4 + H_2SO_3 = H_3AsO_3 + H_2SO_4.$$

Be careful to boil the solution till the smell of SO_2 has completely disappeared before passing H_2S, or a precipitate of sulphur will be formed.

$$2\ H_2S + H_2SO_3 = 3\ H_2O + 3\ S.$$

In separating the two parts of Group II., *yellow* ammonium sulphide should be used. When freshly prepared, ammonium sulphide is colourless, and in this case should be digested with sulphur before use. Caustic potash or caustic soda may be used instead of ammonium sulphide if mercury is known to be absent (HgS being somewhat soluble in caustic alkalies). They are much cleaner to work with, but possess the disadvantage that stannous sulphide occasionally fails to dissolve. If, however, a little sodium peroxide is added, SnS dissolves readily, so that it is advisable to add some in any case. If copper is suspected, KOH or NaOH should be used, as CuS is slightly soluble in ammonium sulphide.*

GROUP III.—Before adding ammonia to precipitate the metals of this group it is necessary to boil off the H_2S, or the metals of Group IV. would be precipitated by the ammonium sulphide formed on neutralizing the free acid with ammonia. After this it is necessary to oxidize any ferrous to ferric salt by adding a few drops of HNO_3 and *boiling well*, the former salt being incompletely precipitated as $Fe(OH)_2$ by ammonia, in the presence of ammonium salts.

Ammonium chloride is added before ammonia to prevent magnesium and manganese from being partially precipitated as hydroxides; a double salt is formed in each case (*e.g.*, $NH_4Cl, MgCl_2$), which is not decomposed by ammonia. The ammonium chloride also prevents the partial precipitation of zinc, cobalt and nickel, double salts not decomposed by ammonia being also formed in these cases. Since, however, the hydroxides of Zn, Co and Ni are soluble in excess of ammonia, the presence of ammonium chloride is not essential so far as these metals are concerned.

The addition of NH_4Cl also renders the precipitation of $Al(OH)_3$ more complete.

Note.—It is very necessary to *boil* before filtering, because chromium is only completely precipitated by NH_4OH on boiling. (See p. 39.)

GROUP IV.—Nickel sulphide is somewhat soluble in ammonium sulphide, forming a brown solution; it is therefore necessary to avoid adding an excess of this reagent.

GROUP V.—It is usually necessary to concentrate the solution by boiling it in a porcelain basin before proceeding to Groups V. and VI.; otherwise it is difficult to precipitate Ca, Sr, Ba, and Mg at all completely.

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* When the solution is acidified the CuS comes back as a *yellow* precipitate *closely resembling* SnS_2.

TABLE I.

Separation of the Metals of Group I.

Pb, Ag, Hg(ous).

Pour *boiling* water on the filter, so as to cover the precipitate ; repeat the operation three or four times.		
Filtrate.	Residue.	
Allow to cool ; if lead is present in quantity, crystals of **Lead chloride** will be deposited. If the solution is very dilute, add a little H_2SO_4. Lead sulphate will at once be precipitated. —— Confirm by dissolving the lead chloride in hot water, and applying Test 2, page 18.	Transfer to a porcelain basin, and digest with a few drops of aqua regia ; dilute to about three times the volume. If a residue remains, filter.	
	Filtrate.	Residue.
	May contain **Mercury.** Confirm by Test 3, page 21.	**AgCl** or **SiO_2**. Digest at a gentle heat with a solution of ammonia. **Silver chloride** dissolves. **Silica** { is insoluble. Confirm by Test 2, p. 70 Filter if necessary. The silver chloride may be reprecipitated by adding HNO_3. It turns faintly violet on exposure to light.

NOTES ON THE SEPARATION OF THE METALS OF GROUP I.

The precipitate consists of $AgCl$, Hg_2Cl_2, or $PbCl_2$. Silicic acid may be precipitated here from an alkaline silicate:

$$Na_2SiO_3 + 2\ HCl = 2\ NaCl + H_2SiO_3.$$

It is of a flocculent nature and after being boiled is not dissolved by acids.

Antimony and bismuth may also be precipitated as oxychlorides by dilution of a strongly acid solution with water (or dilute acid).

$$BiCl_3 + H_2O = BiOCl + 2\ HCl.$$
$$SbCl_3 + H_2O = SbOCl + 2\ HCl.$$

The precipitate in this case is soluble in concentrated hydrochloric acid. Such a solution may be largely diluted with water and, disregarding the turbidity, may be added to the filtrate for Group II. and treated with H_2S, since this reagent converts the oxychlorides into sulphides.

If then a precipitate is produced in a strongly acid solution, always test its solubility in conc. HCl.

Note.—Since the only free acid likely to be present in quantity is HCl (for if aqua regia is used as solvent the HNO_3 is all expelled as directed on p. 91), there will be no Group I. metals present if the solution is strongly acid, for they are precipitated by HCl. Of course a strongly acid *solution* might be given for analysis, but in this case the free acid should be identified before testing for the metals, and if it is HNO_3 it should be expelled by evaporating to dryness with HCl; if it is H_2SO_4 the solution should be diluted with water before adding HCl.

The separation of $AgCl$, Hg_2Cl_2, and $PbCl_2$ is based on—

(*a*) The solubility of $PbCl_2$ in hot water, Hg_2Cl_2 and $AgCl$ being insoluble;

(*b*) The solubility of Hg_2Cl_2 by conversion into $HgCl_2$ with aqua regia (see p. 20), $AgCl$ being insoluble.

Lead chloride is slightly soluble, even in the cold, and hence, if lead is found in this group, there will be a little carried forward to Group II.

It should also be remembered that *mercurous* salts are precipitated in Group I., and *mercuric* salts in Group II.

TABLE II.

SEPARATION OF THE METALS OF GROUP II.*a*.

Pb, Hg, Bi, Cd, Cu.

<table>
<tr><td colspan="5">Digest the precipitated sulphides with boiling dilute nitric acid. If a residue remains, filter.</td></tr>
<tr><td rowspan="4">RESIDUE.
If black and dense, it is probably
Mercury sulphide.
If a light floating yellow mass, it is probably
Sulphur,
and may be neglected.
If white and heavy, it may be
$PbSO_4$ (see p. 19)
or
$Hg(NO_3)_2, 2 HgS$
(see p. 22).</td><td colspan="4">FILTRATE.
Cool, test a portion for lead by adding dilute sulphuric acid and an equal bulk of alcohol. If a white precipitate is formed, add dilute H_2SO_4 and alcohol to the remainder. Filter. If no precipitate is given, proceed to test for bismuth.</td></tr>
<tr><td rowspan="3">PRECIPITATE.
If white, it indicates
Lead.
Confirm by Test 7, page 19.</td><td colspan="3">FILTRATE.
Boil off the alcohol if present, add ammonia till it smells distinctly of the gas. If a white precipitate forms, filter.</td></tr>
<tr><td rowspan="2">PRECIPITATE.
Probably
Bismuth.
Confirm by dissolving in a few drops of concentrated HCl and adding water; Test 2, page 24.</td><td colspan="2">FILTRATE.
If it is colourless, test at once for cadmium by passing H_2S through it.
If it is blue, copper is present; add KCN drop by drop, until the blue colour disappears; then pass H_2S through the solution. If a precipitate is formed, filter.</td></tr>
<tr><td>PRECIPITATE.
If yellow, it indicates
Cadmium.</td><td>SOLUTION.
Copper.
Confirm by Test 6, page 27.</td></tr>
</table>

NOTES ON THE SEPARATION OF THE METALS OF GROUP II.*a*.

Note.—Assistance may often be gained and the labour of testing shortened by carefully observing the colour of the precipitate, *e.g.*, a clear yellow precipitate would exclude Hg, Bi, and Cu, the sulphides of which are brown or black. In a dark coloured precipitate, however, the yellow sulphides must of course be looked for.

The separation of Group II.*a* is based on—

(*a*) The insolubility of HgS in boiling dilute nitric acid, the other sulphides being converted into nitrates.

(*b*) The insolubility of $PbSO_4$.

(*c*) The insolubility of $Bi(OH)_3$ in ammonia, $Cu(OH)_2$ and $Cd(OH)_2$ being soluble.

(*d*) The fact that the double cyanide of potassium and copper, $KCu(CN)_2$, is not decomposed by H_2S, whilst the corresponding cadmium salt is decomposed and yields a precipitate of CdS.

TABLE III.

SEPARATION OF THE METALS OF GROUP II.*b*.

As, Sb, Sn.

<table>
<tr><td colspan="3">Wash the precipitated sulphides, obtained by acidifying the alkaline solution with HCl, till free from acid, and digest at a gentle heat with water (do not boil) to which some pieces of ammonium carbonate have been added. If a residue remains, filter.</td></tr>
<tr><td rowspan="2">FILTRATE.

This may contain arsenic. Acidulate with HCl, and, if necessary, pass H_2S through the liquid.

A yellow precipitate indicates the presence of

Arsenic.

Confirm by boiling with aqua regia, which converts the arsenic into H_3AsO_4, and applying Test 3, page 73.</td><td colspan="2">RESIDUE.
This may contain Sb_2S_3 and SnS_2.
Warm for some minutes (do not boil) with concentrated HCl in a small flask. Divide the solution into two parts.</td></tr>
<tr><td>Test for Antimony.
Heat go

By Test 3, page 35.</td><td>Test for Tin.
Boil in contact with metallic copper to reduce $SnCl_4$ to $SnCl_2$. Filter. Add $HgCl_2$ to the filtrate; a white precipitate becoming grey on boiling indicates
Tin.
Confirm by <i>ruby-red bead</i> obtained by making borax bead faintly blue with copper salt, then dipping it in the solution, and heating again in the inner flame of the Bunsen burner.</td></tr>
</table>

NOTES ON THE SEPARATION OF THE METALS OF GROUP II.*b*.

The soluble thio-salts, obtained by dissolving the sulphides in ammonium sulphide or in NaOH + Na_2O_2, are decomposed on adding hydrochloric acid. As_2S_3, Sb_2S_3, Sb_2S_5, and SnS_2 are reprecipitated.

The separation of these sulphides is based on—

(*a*) The solubility of As_2S_3 in a solution of ammonium carbonate;

(*b*) The solubility of Sb_2S_3, Sb_2S_5 and SnS_2 in hot concentrated hydrochloric acid, especially on addition of a crystal of $KClO_3$ from time to time,

and the subsequent precipitation of antimony on zinc-platinum in one portion of the solution, and of tin on metallic copper in another portion of the solution:

$$SnCl_4 + 2\ Cu = SnCl_2 + Cu_2Cl_2.$$

An alternative method of separation consists in warming the precipitated sulphides with conc. HCl. The sulphides of antimony and tin dissolves whilst As_2S_3 is insoluble.

TABLE IV.

Separation of the Metals of Group III.

Fe, Cr, Al.

PHOSPHATES ABSENT.

Suspend the precipitate in a little water, add a small quantity of sodium peroxide, and warm till effervescence ceases. Filter	
Filtrate.	Residue.
If *yellow*, *chromium* is present. Divide the filtrate into two parts : (1) Acidify with acetic acid and add lead acetate. Yellow precipitate indicates **chromium.** (2) Boil with solid NH_4Cl. White precipitate indicates **aluminium.**	This consists of $Fe(OH)_3$. Dissolve in HCl and confirm **Iron** by Tests 2 and 4, p. 37. Test the *original solution* by Test 3, p. 37, and Test 4, p. 38, to find out whether the iron was originally present in the **ferrous** or **ferric** state, or both.

NOTES ON THE SEPARATION OF THE METALS OF GROUP III.

See note at the head of Group II.*a*. A pure white precipitate would exclude Fe and Cr.

Phosphoric Acid.—If phosphates are present the precipitate may consist of phosphates of any or all of the metals of Groups III., IV., and V., or of Mg (as well as of the hydroxides of the metals of Group III.), for the phosphates of these metals† are insoluble in water, but soluble in dilute HCl. Now in Groups I. and II. the solution is kept acid, so the phosphates remain in solution. In Group III., however, it is rendered alkaline, so that if any of the metals referred to are present in solution, and also the (PO_4) group, a precipitate of a phosphate will be formed at once.

Suppose, for example, the original mixture consisted of calcium chloride, $CaCl_2$, and sodium phosphate, Na_2HPO_4. This would be found to be insoluble in water, because as soon as water was added the two salts would react with precipitation of calcium phosphate, $Ca_3(PO_4)_2$.

$$3\ CaCl_2 + 2\ Na_2HPO_4 = Ca_3(PO_4)_2 + 4\ NaCl + 2\ HCl.$$

The addition of HCl (the next solvent which would be tried) would, however, bring about complete solution.

$$Ca_3(PO_4)_2 + 6\ HCl = 3\ CaCl_2 + 2\ H_3PO_4.$$

When now ammonia is added in excess in Group III., the calcium phosphate is reprecipitated.

$$3\ CaCl_2 + 2\ H_3PO_4 + 6\ NH_4OH = Ca_3(PO_4)_2 + 6\ NH_4Cl + 6\ H_2O.$$

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† The phosphates of the metals of Groups I. and II. are also insoluble, but these metals have, of course, been removed while the solution was acid.

If then phosphates are present, it is necessary to remove the phosphoric acid before applying the group reagents. This is done as in Table V.

Boric and Hydrofluoric Acids.—What has been said with regard to phosphates applies also to borates and fluorides, the majority of which are insoluble in water; so that borates and fluorides of the metals of Groups III., IV., and V. or of Mg may be precipitated in Group III. The presence of boric acid or of hydrofluoric acid should have been detected in the preliminary examination. If either or both of these acids are present they must be removed by evaporating the filtrate from Group II. to dryness several times with excess of strong hydrochloric acid. The volatile acids, H_3BO_3 and HF, are gradually replaced by HCl. The evaporation should be performed in a fume cupboard. The residue is finally taken up with water and treated as usual.

Silicic Acid.—Silicates may be held in solution in Groups I. and II., *i.e.*, while the solution is acid, but in strong solution the addition of ammonia causes the precipitation of insoluble silicic acid. If the presence of silica is suspected, evaporate the filtrate from Group II. to dryness, and gently ignite. Add a few drops of strong HCl, then water, heat gently, and filter from the insoluble silica. Proceed as usual.

Organic Acids.—The salts of many of these (*e.g.*, oxalic acid) are insoluble in water, but soluble in dilute HCl (just like the phosphates), and so they are precipitated in Group III. If the presence of organic matter has been detected in the preliminary examination, the filtrate from Group II. should be evaporated to dryness, moistened with strong HNO_3, and gently ignited.* This **destroys the organic matter.** Treat the residue with a little hot con-

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* The ignition should not be too strong, or the aluminium and chromium hydroxides may become converted into the *insoluble* form of the oxides.

centrated HCl, add water, filter if any portion remains undissolved (it will be carbon), and proceed with the filtrate as usual. There is a second advantage in destroying the organic matter, namely, that the presence of many organic substances (*e.g.*, tartaric acid) prevents the precipitation of metals by alkalis (*e.g.*, NH_4OH in Group III).

The separation of Fe, Al and Cr is based on the conversion of $Al(OH)_3$ and $Cr(OH)_3$ into the soluble compounds $Na_2Al_2O_4$ and Na_2CrO_4, by Na_2O_2 + Water, $Fe(OH)_3$ remaining unattacked.

Manganese, if present, will most probably be partially precipitated in Group III. If so it will be found in the residue with the iron. It is therefore as well to always test this residue for manganese by boiling it with excess of a solution of bleaching powder for a considerable time. A *pink* solution (due to the formation of a *permanganate*) proves the presence of manganese.

Note.—Chromium present as chromate is not precipitated by ammonia. The presence of a chromate will be indicated in Group II, as already mentioned on p. 97. If sufficient H_2S has been added, all the chromate will have been reduced to chromic salt, which will give the normal reaction.

TABLE V.

TREATMENT OF GROUP III. IN THE PRESENCE OF PHOSPHORIC ACID.

<table>
<tr><td colspan="2">Dissolve the precipitate in the least quantity of dilute HCl.
1. To a small portion of the solution add potassium ferrocyanide ; dark blue precipitate indicates **iron.**
2. To the remaining portion of the solution add solid sodium carbonate until the acid is nearly neutralized. Then add sodium acetate and acetic acid. Now add ferric chloride, drop by drop, and allow the precipitate to settle, continuing the addition of $FeCl_3$ until the supernatant liquid is red. Boil. Filter.</td></tr>
<tr><th>PRECIPITATE.</th><th>FILTRATE.</th></tr>
<tr><td>Contains ferric phosphate and possibly aluminium and chromium. Examine for Al and Cr as described in Table IV.</td><td>May contain metals of Groups III. (except iron), IV., and V., and also magnesium, and should be added to the filtrate that is to be examined for the metals of these Groups.</td></tr>
</table>

NOTES ON THE TREATMENT OF GROUP III. IN THE PRESENCE OF PHOSPHORIC ACID.

As ferric chloride has to be added to precipitate the phosphoric acid, it is necessary to test for iron before proceeding further.

The method of removing phosphoric acid which is adopted depends upon the fact that ferric phosphate is insoluble in acetic acid, the phosphates of the metals of Groups IV., V., and Mg being soluble ($AlPO_4$, like $FePO_4$, is insoluble, whilst $CrPO_4$ is soluble with difficulty).

The addition of sodium acetate causes the small quantity of free mineral acid still present to be replaced by free acetic acid.

$$NaC_2H_3O_2 + HCl = NaCl + HC_2H_3O_2.$$

The liquid is made more strongly acid by adding acetic acid. When ferric chloride is added, ferric phosphate is formed:

$$Ca_3(PO_4)_2 + 2\ FeCl_3 = 3\ CaCl_2 + 2\ FePO_4.$$

The calcium, barium, strontium, etc., are converted into chlorides, and remain in solution, whilst the $FePO_4$ is precipitated. Of course, if Al or Cr is present, and there is sufficient phosphoric acid present to combine with them, these metals will also be precipitated (wholly or partially), and so the precipitate may contain Cr and Al as well as Fe, and should be examined for them. There may not however be enough phosphoric acid present originally to combine with them at all, so that the filtrate, after the removal of phosphoric acid, must be examined for Al and Cr; or there may only be sufficient to combine with part of them, in which case Al and Cr will be found in both the precipitate and the filtrate.

When the supernatant liquid becomes *red*, it is a sign that all the phosphate has been precipitated and the iron is now being converted into ferric acetate, which is red. On boiling, this is converted into basic ferric acetate, which is precipitated. (See p. 79.)

Since however on cooling, even slightly, the basic salt redissolves in the acetic acid present with re-formation of the normal acetate, it is necessary to filter rapidly, and to boil up again each time after pouring some of the mixture on to the filter. The filtrate should be *colourless*, showing that all the iron has been removed.

Another way is to remove any iron present in filtrate by the addition of $NH_4Cl + NH_4OH$.

Note.—If a precipitate remains when acetic acid is added, this indicates that Fe, Al or Cr is present (or a mixture of them). If no precipitate remains, then these must be absent (except perhaps Cr), and one or more of the metals Ba, Sr, Ca or Mg must be present.

TABLE VI.

SEPARATION OF THE METALS OF GROUP IV.

Co, Ni, Zn, Mn.

<table>
<tr><td colspan="4">Digest the mixed sulphides <i>in the cold</i> (and excluding contact with air as far as practicable) with very dilute hydrochloric acid (dilute HCl to which an equal volume of water has been added). Filter if necessary.</td></tr>
<tr><td colspan="2">RESIDUE.
May contain CoS and NiS.
Warm the residue with strong hydrochloric acid, and add two or three small crystals of $KClO_3$.
Cobalt alone or in predominance gives a <i>pink</i> solution. Nickel alone or in predominance gives a <i>green</i> solution.
Boil the solution nearly to dryness to expel HCl, and add Na_2CO_3 till only faintly acid, and then KCN, drop by drop, till the precipitate which forms is just redissolved. Add a few drops of acetic acid, and boil. Cool, add excess of NaOH, and then bromine water, till the liquid becomes orange in colour. Heat gently (<i>do not boil</i>). Filter if necessary.</td><td colspan="2">FILTRATE.
May contain $MnCl_2$ and $ZnCl_2$.
Digest with two or three crystals of $KClO_3$, and boil down to small bulk; now add NaOH in excess. If a permanent precipitate is produced, filter.</td></tr>
<tr><td>PRECIPITATE.
If black,
Nickel.
Confirm by Test 6, page 43.</td><td>FILTRATE.
Evaporate to dryness and apply Test 6, page 44, for
Cobalt.</td><td>PRECIPITATE.
Test for
Manganese
by Test 5, page 46.</td><td>FILTRATE.
Pass H_2S gas through the solution; a white precipitate indicates
Zinc.
Confirm by Test 4, page 47.</td></tr>
</table>

NOTES ON THE SEPARATION OF THE METALS OF GROUP IV.

See note at the head of Group II.*a*. A pure white precipitate would point to zinc as the only metal present, whilst the only black sulphides in this group are those of Ni and Co.

If the liquid becomes *brown* it is a sure indication of the presence of nickel, nickel sulphide being slightly soluble in ammonium sulphide. Before proceeding to the next Group the brown filtrate from Group IV. must be acidified with acetic acid, warmed gently, and the precipitated NiS filtered off and tested for nickel by Test 6, p. 43.

The separation of Co and Ni from Zn and Mn depends upon the fact that CoS and NiS are insoluble in very dilute hydrochloric acid, ZnS and MnS being soluble.

The separation of cobalt from nickel depends upon the difference in properties between the double cyanides of nickel and cobalt, as explained on pp. 42–44.

An alternative method of separation is based upon the different behaviour of nickel and cobalt towards potassium nitrite + acetic acid. (See pp. 43, 44). The solution obtained by dissolving the sulphides of Co and Ni in HCl + $KClO_3$ is neutralized with caustic soda. Excess of acetic acid is then added, followed by excess of potassium nitrite (use one inch of the solid stick). Shake well. A yellow crystalline precipitate of $K_3Co(NO_2)_6$ is formed, becoming complete on standing for 15 minutes. The filtrate contains the nickel which may be precipitated as green $Ni(OH)_2$ by the addition of NaOH. Confirm nickel by submitting the precipitate to the borax bead test. (Test 6, p. 43.)

Perhaps the best method of dealing with nickel and cobalt is the following:—Divide the solution obtained by dissolving the sulphides of Ni and Co into two parts. Treat one part as in Table VI., proving the presence of nickel but neglecting the filtrate. Treat the other part by the $KNO_2 + C_2H_4O_2$ method described above, and prove the presence of cobalt, again neglecting the filtrate. There is then no need in either case to bring about *complete* precipitation before filtering, since the filtrate is not used.

The separation of zinc from manganese depends upon the fact that $Zn(OH)_2$ is soluble in NaOH, whereas $Mn(OH)_2$ is insoluble. (See pp. 45, 47.)

TABLE VII.

SEPARATION OF THE METALS OF GROUP V.

Ba, Sr, Ca.

<table>
<tr><td colspan="3">Dissolve the precipitated carbonates in dilute acetic acid, and add potassium chromate till the supernatant liquid is yellow. If necessary, filter.</td></tr>
<tr><td rowspan="2">PRECIPITATE
indicates the presence of
Barium.
Dissolve the barium chromate in HCl, and confirm by Test 6, page 49.</td><td colspan="2">FILTRATE.
To a small portion of the filtrate add dilute sulphuric acid, and, if a precipitate forms, add excess of dilute H_2SO_4 to the whole. Boil; filter.</td></tr>
<tr><td>PRECIPITATE
probably
Strontium.
Confirm by Test 5, page 50.</td><td>FILTRATE.
Add ammonia till the solution is alkaline, and then ammonium oxalate. White precipitate indicates
Calcium.
Confirm by Test 6, page 51.</td></tr>
</table>

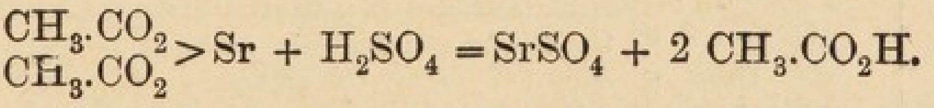
NOTES ON THE SEPARATION OF THE METALS OF GROUP V.

Some assistance may be gained in the determination of this group by noting the effect of adding a solution of $CaSO_4$ to a small portion of the acetic acid solution. An *immediate* white precipitate indicates *barium.* Strontium and calcium may of course be also present. A *white* precipitate produced *after* gently warming and shaking the solution for *some time* indicates *presence* of *strontium* and *absence* of barium. Calcium may of course be also present. *No* precipitate shows that *calcium alone* is present.

The separation of the metals of Group V. is based on—

(*a*) The insolubility of barium chromate in acetic acid.

(*b*) The precipitation of strontium sulphate by dilute sulphuric acid, calcium sulphate only being thrown down by sulphuric acid from concentrated solutions of calcium salts :



$$\begin{matrix}CH_3.CO_2\\CH_3.CO_2\end{matrix}>Sr + H_2SO_4 = SrSO_4 + 2\ CH_3.CO_2H.$$

The calcium is finally precipitated as calcium oxalate.

TABLE VIII.

SEPARATION OF THE METALS OF GROUP VI.

Mg, NH_4, K, Na.

1.	Test a portion of the original solution for **ammonium** salts by heating with caustic soda; if present, ammonia is given off and may be recognized by its smell and by its turning red litmus paper blue.
2.	Test a portion of the filtrate from Group V. (which should be concentrated on the water-bath) for the presence of magnesium by adding ammonia and then sodium phosphate. A white precipitate which becomes denser and crystalline on standing indicates the presence of **magnesium** salts.
3.	**Magnesium salts absent.**—Proceed at once to (4) with the rest of the filtrate from Group V. **Magnesium salts present.**—Evaporate the rest of the filtrate from Group V. to dryness, and ignite the residue in a porcelain crucible so long as white fumes (due to ammonium salts) are given off. To the residue add water and excess of baryta-water (till distinctly alkaline) and boil, thus precipitating $Mg(OH)_2$. Filter, and reject the residue. The filtrate contains $Ba(OH)_2$ (excess) and other barium salts, as well as, possibly, salts of potassium and sodium. To it add sufficient ammonium carbonate to precipitate the barium salts. Again filter, and reject the residue.
4.	The solution may contain salts of K, Na, and NH_4. Evaporate to dryness, and ignite to get rid of ammonium salts. If no residue is left, K and Na are absent. If a residue remains, dissolve in a little water. Add chloroplatinic acid until the supernatant liquid is yellowish, and then an equal volume of alcohol. A yellow precipitate of K_2PtCl_6 indicates the presence of **potassium.** Filter this off; the precipitate may be examined for confirmation according to Test 4, page 53.
5.	To ascertain whether there are any sodium salts in the filtrate from (4), it is necessary to get rid of the chloroplatinic acid (excess); to do this, add a small piece of starch, evaporate to dryness, and ignite. Boil up with water, and filter. The residue will be carbon and platinum; the filtrate will contain any sodium salts that were present. Evaporate to dryness, and, if a white residue is obtained, the presence of **sodium** salts may be inferred. Confirm by Test 4, page 54.

NOTES ON THE SEPARATION OF THE METALS OF GROUP VI.

The detection and separation of these metals is based on—

(*a*) The decomposition of ammonium salts and volatilization of ammonia by heating them in presence of caustic alkalies:

$$NH_4Cl + NaOH = NaCl + NH_3 + H_2O.$$

(*b*) The insolubility of magnesium ammonium phosphate ($MgNH_4PO_4$) in a neutral or alkaline solution:

$$MgCl_2 + NH_4OH + Na_2HPO_4 = MgNH_4PO_4 + 2NaCl + H_2O$$

As the precipitate is only formed *very slowly* in *dilute* solutions, the filtrate from Group V. should always be concentrated before adding NH_4OH and Na_2HPO_4. Even then the precipitate only forms slowly unless the solution is very strong, and its formation should be promoted by warming gently and stirring. Neglect of these precautions often results in magnesium being missed altogether.

Note.—Ca, Sr and Ba often escape precipitation by $(NH_4)_2CO_3$, and are precipitated by Na_2HPO_4, being mistaken for Mg. Whereas however, $MgNH_4PO_4$ always *settles completely* on standing, leaving the supernatant liquid *quite clear*, this is not the case when the precipitate is composed of phosphate of Ca, Sr or Ba.

Note.—There is no really satisfactory confirmatory test for magnesium.

(*c*) The separation of magnesium before testing for sodium and potassium. On adding baryta-water magnesium hydrate, $Mg(OH)_2$, is precipitated:

$$MgCl_2 + Ba(OH)_2 = Mg(OH)_2 + BaCl_2.$$

The barium chloride is next precipitated by ammonium carbonate:

$$BaCl_2 + (NH_4)_2CO_3 = BaCO_3 + 2\,NH_4Cl,$$

and the ammonium salt volatilized by heat.

(*d*) The insolubility of potassium chloroplatinate, the corresponding sodium salt being soluble:

$$2\,KCl + H_2PtCl_6 = K_2PtCl_6 + 2\,HCl.$$

Note.—If a *brown coloration* is produced when H_2PtCl_6 is added it proves the presence of an iodide in the solution

e.g. $2\,NaI + H_2PtCl_6 = 2\,NaCl + 2\,HCl + PtCl_2 + I_2$.

In this case the solution should be boiled with a little HNO_3 to expel iodine. Addition of a further quantity of H_2PtCl_6 will now precipitate potassium if present.

(*e*) In the decomposition of the excess of chloroplatinic acid, the starch* acts as a reducing agent and throws down metallic platinum, which is insoluble.

Alternative method of removing magnesium. The use of baryta water for the separation of magnesium is, of course, necessitated by the fact that sodium phosphate is inadmissible, since sodium is to be tested for in the filtrate. If, however, **ammonium** phosphate, $(NH_4)_2HPO_4$, is available, this may be used to precipitate the magnesium, thus avoiding the baryta-water method, which is rather elaborate. In this case the following is the course of procedure:—Concentrate the filtrate from Group V., add ammonia and ammonium phosphate in excess, and allow to stand in a warm place for some time. When a precipitate ceases to fall, filter and test the filtrate for Na and K.

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* Formaldehyde may preferably be used as reducing agent in place of starch. There is then no need to evaporate to dryness and ignite in order to bring about reduction, since chloroplatinic acid is reduced by formaldehyde on simply warming. The precipitate of platinum is filtered off and the filtrate tested for sodium as described.

EXAMINATION FOR ACIDS.

The tests for acids are each applied on separate portions of the same solutions; there is no separation of groups as in testing for bases.

In making the tests for acids, the student should be guided by—

(*a*) *The results of the preliminary examination.* In many cases the acid or acids will have been detected in this examination, and it is only necessary to confirm the results in the wet way.

(*b*) *The results of the examination for the bases.* The bases being now known, and the properties and solubility of the substance being determined, the field of search is often considerably narrowed. If no acid is found, the substance may consist of oxides or hydroxides, and here a knowledge of the nature of the bases helps to decide whether such compounds are likely to occur.

A knowledge of the commoner compounds of each metal is often helpful, but should not encourage random shots.

Preparation of Solution.

1. *The substance is in solution or soluble in water.*

If metals of Group I. or II. are present, remove them by boiling with a slight excess of pure sodium carbonate, filter, and use the filtrate for the examination for acids. If Groups I. and II. are absent, use the original solution.

2. *The substance is insoluble in water, but soluble in acids.*

Boil a portion of the solid with a strong solution of sodium carbonate, filter, and use the filtrate.

3. *The substance is insoluble in acids.*

Treat as described for the preparation of the solution for the examination for (see p. 92) bases, using the aqueous filtrate.

Divide the filtrate into six parts and treat these as follows :—

1. *Acidulate with* **HCl** *and add to different portions.*

(*a*) $BaCl_2$. White ppt. insoluble in boiling HNO_3.	H_2SO_4 or H_2SiF_6
(*b*) $FeCl_3$. Blue ppt. (turned brown by KOH, colour restored by HCl).	$H_4Fe(CN)_6$.
Blood-red coloration (bleached by $HgCl_2$).	HCNS.
(*c*) $FeSO_4$. Blue ppt. (turned brown by KOH, colour restored by HCl.	$H_3Fe(CN)_6$.

2. *Acidulate with* **HNO_3** *and add* $AgNO_3$. Only regard a precipitate which becomes curdy on boiling and shaking.

Precipitate is	
i. *Curdy white.* Soluble in strong boiling HNO_3 and in NH_4OH.	HCN.
ii. *Curdy white.* Insoluble in strong boiling HNO_3, soluble in NH_4OH.	HCl.
iii. *Curdy yellowish-white.* Soluble in strong NH_4OH.	HBr.
iv. *Curdy yellow.* Insoluble in NH_4OH, but turned white by it.	HI.

3. *Acidulate with* **acetic acid** and divide into three parts.

(*a*) Boil and add $CaCl_2$.* White ppt. sol. in HCl.	Oxalate.
(*b*) Boil and add $FeCl_3$. White ppt. sol. in HCl.	H_3AsO_4.
Yellowish - white ppt. soluble in HCl.	H_3PO_4.
(*c*) Add Pb $(C_2H_3O_2)_2$. Yellow precipitate.	H_2CrO_4.

4. *Acidify with* **HCl**, *boil to remove* CO_2, *just neutralize with* NaOH, *cool, and when quite cold add* **$CaCl_2$** *in excess.*

White ppt. soluble in cold KOH, repptd. on boiling; sol. in acetic acid.	Tartrate.
White gelatinous ppt. insoluble in cold KOH.	
(*a*) Insoluble in acetic acid, readily soluble in HCl.	Oxalate.
(*b*) Insoluble in acetic acid, difficultly sol. in HCl.	HF.
(*c*) Soluble in acetic acid.	H_3BO_3, H_3PO_4, H_3AsO_4.
No ppt. in the *cold*; *white* ppt. *on boiling*, insol. in KOH.	Citrate.

5. *Acidulate with* **HNO_3**, *boil, and just neutralize with dilute* NaOH. *Add* **$FeCl_3$**.

Red coloration, discharged by HCl.	Formate or acetate.

---

* If the presence of the H_2SO_4 has been proved by 1*a*, remove it by adding HCl and $BaCl_2$, and filtering off the precipitate of $BaSO_4$. Neutralize the filtrate with NaOH, acidulate with acetic acid, and then add $CaCl_2$.

6. *To a portion of solution add a solution of* **$FeSO_4$**, *and then pour down the side of the test-tube strong* **H_2SO_4**. See Note, p. 67.

A *brown ring** formed at the junction of the fluid indicates	HNO_3.

The acids found by the above examination should be confirmed, using the tests given in Chapter III. Some acids not included in the above scheme will have been detected by the preliminary examination.

Detection of certain acids in the presence of each other.

In some cases where two or more acids occur together in the same solution the reactions interfere with one another, and special methods of detection are needed. A few cases commonly met with are treated below.

Sulphite and Sulphate.

Add $BaCl_2$; the precipitate consists of barium sulphite and sulphate. Filter at once, wash the precipitate *well* with *hot* water (to remove $BaCl_2$ completely), and then pour dilute hydrochloric acid over it; the sulphite dissolves with evolution of SO_2, and the sulphate is unacted upon. If, therefore, barium salt (test with H_2SO_4) is found in the acid filtrate, *sulphite* must have been present; and, if an insoluble residue remained on the filter after treatment with HCl, *sulphate* is indicated.

Phosphate and Arsenate.

Acidulate with HCl, add a few crystals of sodium sulphite and warm gently for five minutes. The sulphur dioxide formed will reduce the *arsenate* to *arsenite*. Boil till all odour of SO_2 has disappeared, and then pass H_2S to throw down the whole of the arsenic as As_2S_3. Filter;

---

* *Note.—Iodides* and *bromides* also give a brown ring.

boil off H_2S from the filtrate, and test for *phosphate* according to Test 3, page 71.

Chlorate and Chloride.

Divide the solution into two parts; test one part for *chloride* with silver nitrate (Test 1, page 59). Evaporate the other part to dryness on a water-bath and warm the residue gently with concentrated hydrochloric acid; if euchlorine (a yellow gas with characteristic odour) is given off, *chlorate* is indicated.

Chloride, Bromide, and Iodide.

(*a*) *First remove the iodide.*—Add a solution of copper sulphate and ferrous sulphate, till the hydriodic acid is completely precipitated as white cuprous iodide, Cu_2I_2.

$$2\,CuSO_4 + 2\,FeSO_4 + 2\,KI = Cu_2I_2 + Fe_2(SO_4)_3 + K_2SO_4.$$

$$2\,CuSO_4 + SO_2 + 2\,H_2O + 2\,KI = Cu_2I_2 + 2\,KHSO_4 + H_2SO_4.$$

Filter; confirm iodine in the precipitate by heating with concentrated H_2SO_4. Violet vapours of iodine are evolved.

(*b*) Remove copper from the filtrate by adding excess of KOH, boiling and filtering; evaporate to dryness, mix the residue intimately with an equal amount of powdered potassium bichromate, and introduce into a small *dry* retort. Pour over it enough *concentrated* H_2SO_4 to just cover it, and heat gently. Brown fumes, consisting of a mixture of CrO_2Cl_2 and bromine, distil over, and condense to a brown liquid which may be collected in a tube slipped over the neck of the retort.

$$4\,KCl + K_2Cr_2O_7 + 3\,H_2SO_4 = 3\,K_2SO_4 + 3\,H_2O + 2\,CrO_2Cl_2.$$

$$6\,KBr + K_2Cr_2O_7 + 7\,H_2SO_4 = Cr_2(SO_4)_3 + 4\,K_2SO_4 + 7\,H_2O + 3\,Br_2$$

Add water to the distillate. The bromine dissolves as such, forming a reddish-brown solution; the CrO_2Cl_2 is converted into H_2CrO_4, which dissolves.

$$CrO_2Cl_2 + 2\ H_2O = H_2CrO_4 + 2\ HCl.$$

Divide the solution into two parts. Test one part for bromine by shaking up with CS_2 (see Test 2, p. 61). Test the other part for chromic acid by neutralizing and adding acetic acid and lead acetate. (See Test 3, p. 73). The presence of chromic acid shows that a chloride was originally present.

Nitrate and Nitrite.

To one portion add a solution of potassium iodide, a few drops of dilute H_2SO_4, and some starch paste. A blue coloration, due to iodide of starch, indicates nitrite. (See p. 69). If nitrite is present, it must be destroyed before testing for nitrates, by adding a little urea, $CO(NH_2)_2$, and dilute H_2SO_4 to the second portion of the solution, and warming till evolution of gas (nitrogen) ceases.

$$2\ KNO_2 + CO(NH_2)_2 + 2\ H_2SO_4 = CO_2 + 3\ H_2O + 2\ N_2 + 2\ KHSO_4.$$

The solution can then be tested for nitrates in the usual way.

Nitrate and Chlorate

Evaporate to dryness, and heat the residue to redness. The nitrate is converted into nitrite, and the chlorate into chloride. These can be tested for in the usual way.

Formate and Acetate.

Heat the substance supposed to contain formate and acetate with dilute sulphuric acid in a boiling tube fitted with a cork and delivery tube (a small retort is better). The formic and acetic acids will be liberated, and should be collected in a second tube kept immersed in cold water. Divide the distillate into two portions, **A** and **B**.

Portion A.	**Portion B.**
Add yellow *mercuric oxide* and shake till no more dissolves. Warm gently; *reduction* will take place. **Formic acid present.** Add more mercuric oxide and heat till all the formic acid is destroyed. Filter. *Neglect precipitate.*—**Filtrate = mercuric acetate.** Evaporate to dryness and grind in a mortar with strong sulphuric acid. **Smell of acetic acid.**	Neutralize with NaOH and evaporate to dryness. Divide into two portions, **C** and **D**. **C.** Heat with strong sulphuric acid; *carbon monoxide* evolved and burns at mouth of tube. **Presence** of **formic acid** confirmed. **D.** Heat with arsenious oxide in fume cupboard: indescribable odour of **cacodyl oxide. Presence of acetic acid confirmed.**

Oxalate and Tartrate.

To a neutral solution add *calcium chloride*; shake well and allow to stand for 20 minutes. Filter off the precipitate, which consists of calcium oxalate and tartrate.

Wash well on the filter-paper. Remove a small portion of the precipitate for confirmatory tests **C** and **D** below. Make a hole in the filter-paper and wash residue through into a boiling tube. Boil with a little *acetic acid*. Filter.

Residue = **Calcium oxalate.**	**Filtrate.**
Wash well and dry. Divide into two parts **A** and **B**.	Evaporate just to dryness and heat with a little strong sulphuric acid. Carbon monoxide and dioxide, and sulphur dioxide evolved, with immediate blackening. **Presence of Tartaric Acid.** Confirm as follows—
A. Place on a piece of platinum foil and heat over the Bunsen flame to convert into calcium carbonate. Allow to cool, and add *acetic acid*. Carbon dioxide evolved with effervescence. **Presence of Oxalic Acid** confirmed.	**C.** Heat one portion of residue (see above) on a piece of porcelain, with strong *sulphuric acid* containing *resorcin*. **Reddish-violet** *Coloration*.
B. Heat in a test-tube with strong *sulphuric* acid. *Carbon dioxide* and *monoxide* evolved, without blackening. **Presence of Oxalic Acid** confirmed.	**D.** Place second portion in a test-tube with a drop or two of ammonia, a crystal of silver nitrate, and a little water. Heat gently. **Mirror of metallic silver** produced.

Free Acids.

[Only the following common acids are considered here :—HCl, HNO_3, H_2SO_4, H_3PO_4, H_3BO_3, acetic acid, oxalic acid, tartaric acid, citric acid.]

If you find on going through the groups that no base is present, then—

(1) If the substance is *solid* it may be one of the

following acids, viz., H_3BO_3, oxalic acid, tartaric acid, citric acid, or a mixture of these.

Dissolve some of the substance in water and test with blue litmus. It will be turned red. Test for boric acid by means of turmeric. (See Test, p. 69.) Neutralize the solution with NaOH, and test for the other acids in the ordinary way.

(2) If the substance is a *liquid* it may be (*a*) H_2SO_4, HNO_3, or acetic acid, or (*b*) an aqueous solution of any of the acids mentioned in (1) or (2*a*), or of HCl or H_3PO_4.

(*a*) Of these acids, H_2SO_4 is an oily liquid, which when mixed with water gives rise to much heat. HNO_3 fumes strongly in the air and acts on copper with formation of brown fumes. Acetic acid is recognized by its odour.

(*b*) Proceed as follows :—

(1) Test with blue litmus, which will be turned red.

(2) Evaporate a portion of the solution to dryness. HCl, HNO_3, H_2SO_4, and acetic acid give off intensely acid fumes and leave no residue.

In the case of the other acids, the water is first driven off, leaving a residue of the acid. On further heating, H_3BO_3 and H_3PO_4 lose more water, leaving finally residues of B_2O_3 and HPO_3 respectively ; oxalic acid behaves as described on p. 80, tartaric acid as described on p. 82, and citric acid as described on p. 84.

(3) Neutralize the other portion of the solution with NaOH, and test for the acids in the ordinary way.

Hydroxides.

If you are given a solution which contains one or more metals, but no acid radicles, then the metals must be present as hydroxides. [Also since the only soluble hydroxides are those of K, Na, NH_4, Ba, Sr, Ca, Mg (slightly), only these metals can be present.] The solution will then answer to the following tests :—

1. Silver nitrate gives a brown precipitate of silver oxide, Ag_2O, soluble in ammonia. (See p. 17.)

2. Mercuric chloride gives a yellow precipitate of mercuric oxide, insoluble in excess. In the case of ammonia, the precipitate is white, consisting of mercurammonium chloride, $HgNH_2Cl$. (See p. 23.)

3. The solution is strongly alkaline.

CHAPTER V.

ANALYSIS OF MIXTURES WHICH MAY CONTAIN ELEMENTS AND COMPOUNDS.

In the previous pages the systematic analysis of salts has been dealt with; it is necessary, however, to be able to analyse mixtures which may contain bodies not belonging to this class of substances. Directions are given in this chapter for the analysis of a mixture which may contain elements or compounds. This examination should precede that for a mixture of salts, if elements are suspected to be present, but, as the processes are somewhat more complicated, the matter has been placed at this portion of the book.

Elements and compounds may, for the purposes of analytical investigation, be divided into three great classes:—

(1) The elements;
(2) The oxides and sulphides;*
(3) The salts.

We shall first endeavour to ascertain to which of these classes a substance under examination belongs, and with this object we make the following observations:—

(1) Examination of external characters, such as colour, lustre, hardness, malleability, etc.

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* Sulphides strictly belong, of course, to (3), but they are grouped along with the oxides for convenience.

(2) Changes which take place when the substance is heated (*a*) in a closed tube (where the action of air is limited); (*b*) in a tube open at both ends, so that the full effect of oxidation may be determined. These experiments will show whether the substance is fusible or readily volatile, and whether it forms an oxide, the nature of which may be also noted. (*c*) Changes which occur when the substance is heated in presence of reducing agents, such as hydrogen and carbon, and the products obtained under such treatment. (*d*) The action of water and mineral acids upon the body, and the nature of the products obtained.

Examination of liquid substances.—Excluding the gases, which are recognized by the properties described in the text-books, substances may be presented either in the liquid or solid form, or they may be dissolved in water. Some of the well-known gases may also be presented in solution in water, *e.g.*, HCl, HBr, HI, SO_2, NH_3, etc.; but they may still be recognized by their odour or reactions.

The commoner elements or compounds that exist in the liquid state are few, and we shall dispose of them first, and then proceed with the treatment of solids.

Of *elements* there are only two—*bromine* and *mercury:* the former a brown liquid, heavier than water, with a marked and characteristic odour; the latter a heavy liquid with a bright silvery lustre.

Of *compounds* there are water, HNO_3, H_2SO_4, acetic acid, carbon bisulphide, antimony pentachloride ($SbCl_5$), and tin tetrachloride ($SnCl_4$). With the exception of water, sulphuric acid, and carbon bisulphide, these liquids fume in moist air, and the fumes may be rendered more evident by holding a drop of ammonia solution near the liquid.

Carbon bisulphide may be distinguished from sulphuric acid or water by its odour, and by being a highly refracting liquid which readily ignites and yields SO_2 amongst the products of combustion:

$$CS_2 + 3\,O_2 = CO_2 + 2\,SO_2.$$

Water and sulphuric acid possess the following properties available for their distinction:—

(1) Water boils at 100° C., H_2SO_4 at 338° C. (with partial decomposition).
(2) Water is neutral to litmus, H_2SO_4 is strongly acid.
(3) H_2SO_4 is nearly twice (1·84 times) as heavy as water.

Of the remaining compounds it may be remarked that water mixes in all proportions with the free acids, but decomposes the chlorides of tin and antimony with the formation of white precipitates of oxychlorides. These compounds may be further recognized by their boiling point and acidity, and by the reactions described later.

Examination of a solid substance.—To determine if it is (*a*) an element, (*b*) an oxide or sulphide, (*c*) a salt.

From a solution, the solid may be obtained by evaporation on a water-bath; a substance in solution will usually be a salt, since the elements (except Br and I) and the oxides and sulphides (except those of the alkalis and alkaline earths) are practically insoluble in water.

THE DETECTION OF AN ELEMENT.

A. **By inspection.**—*Metals show a characteristic lustre.*

Note.—(*a*) The metals sodium and potassium show lustre only when freshly cut—they tarnish again instantly.
(*b*) Of the non-metals, only carbon (as graphite) and iodine show a lustre likely to be mistaken for "metallic lustre."
(*c*) Some mineral sulphides, and one or two oxides, in the crystallized condition present a lustrous appearance like that of the metals; these are:—

Sulphides of Fe, Co, Ni, Cu, Sb, and Pb *;
Oxides of Fe (hæmatite) and Pb (litharge).

The sulphides under (*c*) may be distinguished from the elements by roasting them in an open tube (see under H.) or by heating in presence of hydrogen.

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* Specimens of these minerals should be examined.

Colour of the elements :—

White or grey,	C, *Na*, *Mg*, *Al*, *K*, Cr, *Mn*, *Fe*, *Co*, *Ni*, Zn, As, *Ag*, Cd, *Sn*, Sb, *Pb*, Bi, (*Pt*).
Reddish,	*Cu*.
Yellow,	(*Au*).
Black,	I, amorphous carbon.

• *Note.*—Fe, Co, Ni, are distinguished from the rest as being the only elements attracted by a magnet.

Malleability.—Only the elements in italics in the above list are malleable at ordinary temperatures; the rest are brittle.

B. Heat the substance to dull redness in a dry test-tube.*

If the substance is an element other than Ag (Au, Pt), it will either melt, volatilize, or become dull, or even burn owing to oxidation.

Note.—(*a*) Sublime and condense on cool part of tube :—

S, sublimate yellow.
As, I, ,, black (Iodine *vapour* is violet).
Hg, ,, grey (globules).

(*b*) Melt easily:—Na, Mg, P, K, Zn, Cd, Sn, Sb, Pb, Bi. The first four of these take fire readily, and all oxidize to some extent.

(*c*) Some of the sulphides mentioned under A (*c*) on heating in a closed tube yield a sublimate of sulphur and a little sulphur dioxide. They will, however, be better dealt with under H.

C. Action of water and dilute acid.

Water at the ordinary temperature is without action on any of the elements except the alkali metals Na and K† (and the metals of the alkaline earths, Ba, Sr, Ca).

If there is no action, warm the substance in a small test-

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* Be careful to introduce the substance so as not to soil the sides of the tube; also do not employ large quantities of the material.

† These metals may be recognized by their softness and the readiness with which they tarnish; they should be introduced with *dry* fingers in very small portions into a large basin of water.

tube with dilute sulphuric acid. If an evolution of gas occurs and the gas is found to be *hydrogen*, it affords a proof that the substance under examination is a metal.

In order to settle this point, fill a rather larger test-tube with water and invert it in a basin of water; now fill the test-tube containing the substance completely with dilute acid, and bring it mouth upwards under the lip of the inverted test-tube. Collect a tube full of the gas and apply a light to the mouth. If it is found to burn without luminosity, the conclusion may be drawn that the gas is hydrogen.

Dilute sulphuric acid has, however, no action on the non-metals or on Cu, Ag, Hg, Pb, As, Sb, Bi; the action on Sn, Co, and Ni is slow. If, therefore, no hydrogen is evolved, the absence of an element must not be inferred.

Note.—CO_2 will be evolved from *carbonates*, SO_2 from *sulphites*, H_2S from *sulphides*, etc., in presence of dilute sulphuric acid, but these may be easily distinguished from hydrogen, and these salts are not likely to be mistaken for elements on account of the difference in their external appearance.

D. Warm gently in concentrated nitric acid.

In the case of the solid elements (both metals and non-metals) red fumes of the oxides of nitrogen are evolved. This may be generally relied on as indicating the presence of an element, but it must be remembered that it may also occur with *sulphides*, which may by appearance (see A, *c*) be mistaken for metals, or with a few other substances, such as oxalic acid, which have no resemblance to the metals.

E. Immerse the substance in a solution of copper sulphate to which one or two drops of dilute sulphuric acid have been added.

Many *metals* become coated with metallic copper, and the deposit may be readily recognized by its colour,* either by the naked eye or with a lens. The formation of such a coating of copper may be taken as positive evidence of the

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* *Note.*—This deposit of copper looks *black* viewed through a blue solution, so the solution should be poured off in order that the colour may be examined.

presence of a metal, though its absence cannot lead to an inference that no metal is present, since, with the noble metals, the metalloids (and non-metals), no deposit is formed.

The Detection of an Oxide or Sulphide.

F. **By inspection.**—*Oxides and sulphides are usually amorphous powders.*

It must be remembered, however, that many salts answer this description; further, crystalline salts that have been powdered may seem to be amorphous until they are examined with a lens. On the other hand, many oxides and sulphides are *crystalline*, especially as minerals, *e. g.*, SO_3, I_2O_5, corundum (Al_2O_3), silica (as quartz, etc.), CrO_3, hæmatite (Fe_2O_3), As_2O_3, SnO_2, Sb_2O_3, and a few hydroxides, *e. g.*, $Ba(OH)_2$, the sulphides mentioned in A (*c*), and also zinc blende (ZnS), realgar (As_2S_2), and orpiment (As_2S_3).

Colours of oxides :—

Yellowish,	Na_2O_2, Bi_2O_3, PbO.
Red,	CrO_3, Cu_2O, HgO. (Fe_2O_3,xH_2O, may be of various shades from yellow to brown).
Dark green,	Cr_2O_3.

The rest are either white or black (or dark brown).

Colours of sulphides :—

Yellow,	those of Na, K, Ca, Sr, Ba, As, Cd, Sn(ic), Sb.
Flesh-colour,	MnS.

The rest are either white or black (or dark brown).

G. **Heat the powder to dull redness in a closed tube.**

In the case of *oxides*, no acid vapours are given off (most salts on heating yield acid vapours), and no gas except *oxygen* is evolved, and after heating there is usually no visible change on cooling again. Solid oxides which decompose completely into their constituents on heating are those of Ag, I, Hg.

Oxides which change in character, forming lower oxides and giving off oxygen, are :—

SO_3 (white crystals) = SO_2 (gaseous) and oxygen.
CrO_3 (red crystals) = Cr_2O_3 (dark green powder), and oxygen.
PbO_2 (brown powder) = PbO (yellow powder) and oxygen.
Pb_3O_4 (red powder) = „ ,, ,, ,,

Some oxides volatilize and yield sublimates, *e.g.*, P_2O_5, As_2O_3, Sb_2O_3.

In the case of *sulphides*, sulphur and a little SO_2 may be given off, the former depositing as a sublimate on the upper part of the tube. For the recognition of sulphides heating in an open tube is advisable, as follows :—

H. **Heat the powder to a dull redness in a tube open at both ends.**

A tube, about 5 mm. bore, is taken and a little of the power introduced near one end of it, the tube being held in the flame slanting. If there be present sulphur or a sulphide, SO_2, and possibly sulphur, will be given off, and may be recognized in the fumes that pass up the tube, either by smell, acid reaction, or best by its action on potassium chromate.

Note.—(*a*) A sulphide may also be detected by heating with sodium carbonate, sodium sulphide being formed and recognized by producing a stain when brought on metallic silver and moistened with water.

(*b*) The behaviour of oxides (and salts) in the *open* tube does not differ materially from that observed in the closed tube.

K. **Action of water and dilute acid.**

The only solid *oxides* (or hydroxides) which dissolve freely in *water* are the oxides and hydroxides of Na and K, and barium hydroxide (with an alkaline reaction); the oxides of As and P, SO_3, CrO_3, I_2O_5, and the hydrated oxide of boron—boric acid—(with an acid reaction).

Of the *sulphides*, only those of the alkali metals (Na, K, and NH_4), the alkaline earth metals (Ba, Sr, Ca) and Mg are soluble in water; the latter, especially that of calcium, are not readily soluble. These aqueous solutions have an alkaline reaction.

Boil with dilute sulphuric acid.

With the *oxides* solution takes place without the evolution of gas, except that certain metallic oxides with a high percentage of oxygen such as MnO_2, CrO_3, etc. (and salts of these), may give off oxygen.

Some oxides *e. g.*, SiO_2, SnO_2, are insoluble, whilst others, such as Al_2O_3, Fe_2O_3, Mn_3O_4, when in the mineral condition, or if they have been ignited, dissolve slowly and with difficulty.

The *sulphides*, in presence of dilute sulphuric acid, dissolve *with the evolution of* H_2S. (Test as described at page 58.)

The following sulphides resist the action of the acid:—CuS, Bi_2S_3, HgS, Ag_2S; whilst PbS is converted into the white insoluble $PbSO_4$.

THE DETECTION OF A SALT.

The salts which are referred to in the following treatment are:—nitrates, nitrites, chlorates, carbonates, sulphates, sulphites, phosphates, arsenates, silicates, chromates, chlorides, bromides, iodides, and fluorides.

L. By inspection and in presence of water.

The salts are usually crystalline in character, and may be divided into two classes:—

(*a*) Those soluble in water.
(*b*) Those insoluble or almost insoluble in water.

Soluble in water:—Nitrates of all the metals; chlorates of all the elements; the chlorides, bromides, and iodides of all the elements, except Ag, Pb, and Hg (ous); all salts of the alkali metals; and the sulphates except those of Pb, Ba, Sr, Ca.

Insoluble in water:—The commonly occurring carbonates, phosphates, sulphites, arsenates, silicates, and chromates, except those of the alkali metals; the chlorides, bromides, iodides, and sulphates, mentioned above; the fluorides of the alkaline earth metals, and most other fluorides. (AgF is soluble.)

Note.—Of the salts insoluble in water, the following are usually soluble in dilute sulphuric acid:—carbonates (with decomposition), phosphates, arsenates, chromates, and (with decomposition) sulphites.

M. **Heat the substance to dull redness in a test-tube.** Salts, when heated, in some cases melt or volatilize, and frequently give off *acid* vapours, which may be detected by the white fumes formed when a glass rod, moistened with ammonia, is held within the tube. Any water which condenses on the upper part of the tube will in such cases also show a distinct *acid* reaction.

This occurs especially in the case of nitrates, sulphates, and many fluorides and chlorides.

Note.—(*a*) Salts which give off *carbon dioxide*:—Carbonates, except those of the alkali metals; all bicarbonates.

(*b*) Salts which give off SO_2:—Sulphites and some sulphates.

(*c*) Salts which give off *oxygen* only:—Chlorates, KNO_3, $NaNO_3$.

(*d*) Salts which give off brown vapours (N_2O_4, etc.):—Nitrates, (except KNO_3, $NaNO_3$.)

(*e*) Salts which readily melt:—Those of the alkali metals, and many salts with water of crystallization,

(*f*) Salts which give sublimates:—Salts of NH_4, As, Sb, Hg.

(*g*) Salts which undergo no apparent change:—Silicates, phosphates, arsenates, and chromates; sulphates of the alkali metals and alkaline earth metals and of lead.

N. **Warm gently with concentrated sulphuric acid.** From salts the volatile acids are expelled with, or without, decomposition; *e.g.*, nitric acid, carbon dioxide, sulphur dioxide (from sulphites), chloric acid (which breaks up into ClO_2, oxygen, and moisture), and the haloid acids HF, HCl, HBr, HI, the two latter undergoing partial decomposition, so that free Br or I may be found amongst the vapours.

Note.—SO_2 may be given off (arising from the decomposition of the sulphuric acid itself) in presence of certain *elements*, *e.g.*, C, S, Cu, Hg, etc. (*vide* preparation of SO_2); SiO_2 and SnO_2 may separate from silicates and stannates.

TABULAR STATEMENT OF PRELIMINARY EXAMINATION OF A SOLID SUBSTANCE.

Columns 1 and 2 give *general* observation and inference respectively.
,, 3 ,, 4 ,, *specific* ,, ,, ,, ,,

The more important properties are printed in italics.

I. External Characters.

Metallic lustre.	Metals and certain mineral sulphides.		
Malleable.	Certain metals.	Of a white or grey colour.	Na, K, Mg, Al, (Mn), Fe, Co, Ni, Ag, Sn, Pb, (Pt).
		Of a yellow colour.	(Au).
		Of a red colour.	Cu.
		Magnetic.	Fe, Co, Ni.
Brittle and lustrous.	Certain metals and mineral sulphides.	Of a white or grey colour.	Metals.
		Of a yellow colour, or black	Mineral sulphides.
Amorphous.	Usually oxides or sulphides and certain salts.	Colour.	(See p. 134.)

II. Heat to dull redness in a test-tube.

Melt readily.	Certain elements, salts of alkali metals, haloid salts of the alkaline earths, and salts with water of crystallization.	Elements which melt readily.	Na, P, S, K, Cd, Sn, I. Pb, Bi.

Easily ignite and burn.	Certain elements and some sulphides.	Elements which burn vigorously.	P, S, Na, K.
Change colour whilst hot.	Certain oxides. (See pp. 87, 88.)		
Swell up.	Certain salts. (See p. 88.)		
Volatilize and form sublimate.	Certain elements, oxides, and salts.	Vapour purple.	I, I_2O_5
		Vapour red-brown.	S
		Sublimate white.	P_2O_5, As_2O_3, Sb_2O_3, Hg_2Cl_2 NH_4Cl.
		Sublimate grey or black.	Hg, As, HgS.
		Sublimate yellow.	S, As_2S_3 and some other sulphides, HgI_2, HgO.
Give off gases.	Peroxides and certain salts. (See p. 86.)		

III. Heat to redness in tube open at both ends.

No change.	Certain metals, many oxides, and salts.	Metals which do not change.	Ag, (Au, Pt).
Change from lustrous to dull.	Metals and mineral sulphides.		
Become dull and give off SO_2.	Mineral sulphides.		
Other changes as in II., *e.g.*, as to gases given off—sublimates, etc.			

IV. Bring a little of the substance in contact with water.

Water decomposed and H evolved.	Metals of alkalies (and alkaline earths).		
Liquid is alkaline.	Oxides, sulphides, and certain other compounds of alkalies and alkaline earths.		
Liquid is acid.	Oxides of non-metals. Salts of weak bases.	Salts with acid reaction.	Those of Fe, Al, and those salts of strong acids in which only part of the hydrogen is replaced by a metal, *e.g.*, $NaHSO_4$.
Insoluble.	Elements, oxides, and sulphides (except the above), and many salts.		

V. Warm with dilute sulphuric acid in a test-tube.

Inflammable gas evolved.	Certain metals and sulphides.	The gas is H.	Metals (except those named below).
		The gas is H_2S, as shown by smell.	Sulphides.
		No gas evolved from the metals.	Ag, Hg, Pb, (Au, Pt), Cu, As, Sb, Bi.
Other gases evolved.	Salts.	CO_2.	Carbonates and bicarbonates.
		SO_2.	Sulphites.
		Cl_2.	Hypochlorites.
		NO_2 (red brown).	Nitrites.

Dissolve and evolve no gas.	Most oxides and salts.	Insoluble residue.	C, S, I, and above metals. SnO_2, Sb_2O_3, and Al_2O_3, Fe_2O_3. Cr_2O_3 if ignited, or mineral chlorides, bromides, and iodides of Ag, Hg(ous), Pb. Compounds of Bi, Pb, Ba, Sr, Ca.

VI. Special tests.

If there is evidence of the presence of a **metal,**

(1) **Warm gently with concentrated nitric acid.**

Red peroxide of nitrogen evolved.	Metals and sulphides; with sulphides there is usually also a separation of sulphur, which floats on the surface.	Non-metals also give rise to red fumes.	C, S, P, I.

(2) **Immerse in a solution of copper sulphate.**

Red coating of metallic copper.	Many metals.		

If there is evidence of a **sulphide,** apply the following test :—

(3) **Mix intimately with Na_2CO_3 and heat. Place on a silver coin and moisten with a little water.**

Brown stain forms.	Sulphides.		

If there is evidence of a salt, apply the following test :—

(4) **Warm with concentrated sulphuric acid.**

Gases or acid vapours evolved.		SO_2.	(Elements), sulphites.
		CO_2.	Carbonates and bicarbonates.
		O_2.	Peroxides, or salts of these.
		Cl_2.	Hypochlorites.
		Chlorine peroxide	Chlorates (crackling).
		HCl.	Chlorides.
		HBr (and Br).	Bromides.
		HI (and I).	Iodides.
		HNO_3 (and NO_2).	Nitrates.
From a solution an insoluble white residue separates.	Silicates ; salts of Bi, Pb, Ba, Sr, Ca ; stannates and antimonates of alkalies.		

Now proceed with the following special tests, which are calculated to give more specific information as to the constituents of the substances under examination, without regard to the form of combination in which they exist :—

(1) Reduction on charcoal. followed by an examination of the residue. (See page 89.) If a metallic residue is obtained, this may be dissolved by warming with dilute nitric (or hydrochloric) acid, and applying the individual tests as described. (Pages 16 et seq.)

(2) Borax bead tests. (See page 92.)

(3) Flame coloration. (See page 91.)

(4) Treatment of insoluble substances. (See page 94.)

A SELECTION OF MODEL ANALYSES.

1. Simple salt. White, crystalline; soluble in water; neutral.

Experiment.	*Observation.*	*Inference.*
	PRELIMINARY EXAMINATION.	
Heated in a dry bulb-tube.	Brown nitrogen peroxide evolved.	Nitrate of heavy metals.
,, with HCl.	[White insoluble substance formed on addition of acid; dissolves on heating.]	[Grp. I. (Pb)]
,, ,, H_2SO_4.	Oxides of N.	HNO_3.
,, ,, Na_2CO_3.	Deflagrates: metallic malleable bead which marks paper; blue flame.	Pb.
,, on platinum wire.	Blue flame.	Pb, As, Sb.
	WET EXAMINATION FOR BASE.	
Added HCl.	White pp.: dissolves on boiling: H_2S added to solution thus obtained: *reddish-brown* and finally black pp. is obtained.	**Pb.**
,, KI.	Yellow pp.	,,
,, K_2CrO_4.	,,	,,
	EXAMINATION FOR ACID.	
Boiled with Na_2CO_3 to remove Pb, neutralized with HNO_3, and added $BaCl_2$.	No pp.	—
Added $AgNO_3$.	,,	—
Pptd Pb from sol. with Na_2CO_3, filtered, acidified with H_2SO_4, and added $FeSO_4$, and H_2SO_4.	Brown ring formed.	HNO_3.
$FeSO_4$ pptates. Pb as $PbSO_4$. See p. 67, Note.		
Base, PbO.	**[Lead Nitrate, $Pb(NO_3)_2$.]**	**Acid, HNO_3.**

2. Soluble salt. White, crystalline; soluble in a very small amount of water, and giving milky-white precipitate with excess of water.

PRELIMINARY EXAMINATION.

Experiment.	*Observation.*	*Inference.*
Heated in dry bulb-tube.	Brown nitrogen peroxide evolved.	Nitrate of heavy metal.
,, with HCl.	—	—
,, ,, H_2SO_4.	Nitrogen peroxide evolved.	HNO_3.
,, on charcoal with Na_2CO_3.	Brittle metallic beads, with orange-yellow incrustation.	Bi.
,, with platinum wire.	Blue flame.	Pb, As, Sb, Bi.

WET EXAMINATION FOR BASE.

Added HCl.	Milky-white pp. dissolving in excess of HCl.	Absence of Grp. I. Probably Sb or Bi present.
,, H_2S.	Brownish-black pp.	Hg, Pb, Bi, Cu, Sn.
Treated pp. with Am_2S.	Insoluble.	Hg, Pb, Bi, Cu.
Boiled pp. with strong HNO_3 and a few drops of dilute H_2SO_4. Add nitric acid. Boil. Pp. dissolves. Add H_2SO_4. No pp. shows Pb is absent.	Soluble.	**Bi.**

EXAMINATION FOR ACID.

Preliminary examination conclusively shows presence of nitric acid.

Base, Bi_2O_3. **Acid, HNO_3.**

[Bismuth Nitrate, $Bi(NO_3)_3$.]

3. Simple salt. Orange-red,* amorphous powder, insoluble in water, soluble in strong HCl, with decomposition.

PRELIMINARY EXAMINATION.

Experiment.	*Observation.*	*Inference.*
Heated in dry tube.		
,, with HCl.	Smell of H_2S } Confirmed by blackening of lead acetate paper.	A sulphide.
,, H_2SO_4.	,, ,,	,,
,, on charcoal with Na_2CO_3.	Residue gives black stain on silver coin.	Sulphur compound.
,, on platinum wire.	Violet flame with white fumes.	K, Pb, As, Sb, Bi.

WET EXAMINATION FOR BASES.

Added HCl (to dissolve).	Soluble in the concentrated acid with evolution of H_2S.	Absence of Grp. I.
,, H_2S to diluted solution.	Orange-red pp.	Sb.
Treated pp. with $(NH_4)_2S$.	Soluble.	,,
,, ,, ,, $(NH_4)_2CO_3$.	Insoluble.	,,
In Marsh's apparatus.	Black stain, insoluble in NaClO.	,,

EXAMINATION FOR ACID.

The preliminary experiments conclusively show presence of sulphide, which was confirmed by the evolution of H_2S on boiling with HCl.

Base, Sb_2O_3. **Acid, H_2S.**

[Antimony Sulphide, Sb_2S_3.]

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* The colour of the native sulphide which is not soluble in cold HCl is dark grey.

4. Simple substance. White amorphous powder; insoluble in water, soluble in HCl.		
PRELIMINARY EXAMINATION.		
Experiment.	*Observation.*	*Inference.*
Heated in dry bulb-tube.	Becomes yellow-white when cool.	Zn.
,, with HCl.	Dissolves with slight effervescence.	CO_2 (*traces*).
,, ,, conc. H_2SO_4.	—	—
,, on charcoal with Na_2CO_3.	Yellow when hot, white when cold.	Zn.
,, ,, ,, ,, $Co(NO_3)_2$.	Heated mass becomes green.	Zn.
,, ,, platinum wire.	Reddish flame.	Trace Ca (?).
WET EXAMINATION FOR BASE.		
Added HCl (as solvent).	—	Absence of Grp. I.
,, H_2S.	—	,, ,, II.
,, NH_4Cl, NH_4OH.	—	,, ,, III.
,, ,, ,, $(NH_4)_2S$.	White pp., insoluble in acetic acid.	**Zn.**
,, NaOH.	White gelatinous pp., soluble in excess.	,,
EXAMINATION FOR ACID.		
Boiled portion of solid substance with Na_2CO_3, filtered, neutralized filtrate with HNO_3, and added		
$BaCl_2$.	—	—
$AgNO_3$.	—	—
Fe_2Cl_6.	—	—
Substance is *insoluble* in water		Absence of HNO_3 and $HClO_3$.
[No acid present.]		
Base, ZnO.	**[Zinc Oxide.]**	

5. Simple Salt. White, crystalline; soluble in water.

Experiment.	*Observation.*	*Inference.*
PRELIMINARY EXAMINATION.		
Heated in a dry tube.	Substance sublimes and gives off NH_3.	NH_4 salt.
,, with HCl.	—	—
,, ,, H_2SO_4.	—	—
WET EXAMINATION FOR BASE.		
Added HCl.	No pp.	Absence of Grp. I.
,, H_2S.	,, ,,	,, ,, II.
,, NH_4Cl, NH_4OH.	,, ,,	,, ,, III.
,, ,, ,, and $(NH_4)_2S$.	,, ,,	,, ,, IV.
,, ,, ,, ,, $(NH_4)_2CO_3$.	,, ,,	,, ,, V.
,, KOH to the original solution and heated.	Odour of ammonia.	NH_4.
EXAMINATION FOR ACID.		
Added $BaCl_2$.	A white pp., soluble in HCl.	—
,, $AgNO_3$ to another portion.	A yellow pp., soluble in HNO_3.	H_3PO_4. [Arsenic has been proved absent.]
To another portion added NH_4Cl, NH_4HO, and $MgSO_4$.	A white crystalline pp.	H_3PO_4.

Base, NH_4OH. **Acid, H_3PO_4.**

[Ammonium Hydrogen Phosphate, $(NH_4)_2HPO_4$.]

6. Simple salt. White, crystalline; soluble in water; neutral.

Experiment.	*Observation.*	*Inference.*
PRELIMINARY EXAMINATION.		
Heated in dry bulb-tube.	Fuses.	Alkaline salt.
,, with HCl.	SO_2 evolved, and solution yellow with separated sulphur.	$H_2S_2O_3$.
,, ,, H_2SO_4.	H_2S, and finally SO_2 evolved, sulphur [yellow] separated.	,, [H_2S.]
,, on charcoal with Na_2CO_3.	Residue gives black stain on silver coin.	Compounds of S.
,, ,, platinum wire.	Yellow flame.	Na.
WET EXAMINATION FOR BASE.		
Added HCl.	SO_2 evolved on heating, and S precipitated	[$H_2S_2O_3$.] Absence of Grp. I.
,, H_2S.*	No pp.	Absence of Grp. II.
,, NH_4Cl, NH_4OH.	,, ,,	,, ,, ,, III.
,, ,, ,, and $(NH_4)_2S$.	,, ,,	,, ,, ,, IV.
,, ,, ,, ,, $(NH_4)_2CO_3$.	,, ,,	,, ,, ,, V.
,, ,, ,, ,, $NaHPO_4$.	,, ,,	,, ,, Mg.
Boiled solution with NaOH.	NH_3 *not* given off.	,, ,, NH_4.
Added $PtCl_4$ and alcohol.	No pp.	,, ,, K.
Metal present must be **Sodium**, confirmed by preliminary examination.		
EXAMINATION FOR ACID.		
Added $BaCl_2$.	White pp. soluble in HCl; solution slowly precipitates sulphur.	$H_2S_2O_3$.
,, $AgNO_3$.	White pp. soluble in excess of solution; on adding excess of $AgNO_3$ and gently heating, pp. becomes black with Ag_2S.	**$H_2S_2O_3$.**
	Confirmed by preliminary examination.	
Base, NaOH.	**[Sodium Thiosulphate, $Na_2S_2O_3$.]**	**Acid, $H_2S_2O_3$.**

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* If a white pp. is obtained, it is S, due to action of SO_2, liberated by HCl on SH_2.

7. Simple Salt. Yellow, crystalline; soluble in water.

PRELIMINARY EXAMINATION.		
Experiment.	*Observation.*	*Inference.*
Heated in a dry tube.	—	—
,, with HCl.	Solution darkens.	Chromate.
Heated on charcoal before blowpipe flame.	Residue coloured.	—
Fused a portion of residue in borax bead.	A green bead in both flames.	Cr.
Heated another portion in flame on platinum wire.	Violet-coloured flame.	K.
WET EXAMINATION FOR BASE.		
Added HCl.	Solution darkens. No pp.	A chromate. Absence of Grp. I.
To the above added H_2SO_3.	Solution turns green.	A chromate.
Boiled off excess of H_2SO_3, and to a portion of solution added H_2S.	No pp.	Absence of Grp. II.
To remainder of solution added NH_4Cl and NH_4OH.	A dull green pp.	Cr.
Filtered, and to small portions of filtrate added (i.) $(NH_4)_2S$, (ii.) $(NH_4)_2CO_3$, and (iii.) Na_2HPO_4.	No pp.	Absence of Grps. IV. and V., and of Mg.
Evaporated to dryness main portion of filtrate, and ignited until fumes ceased to come off.		
Took up residue with HCl, and added $PtCl_4$.	A yellow crystalline pp.	**K.**
EXAMINATION FOR ACID.		
Added $BaCl_2$.	A yellow pp.	H_2CrO_4.

Base, K_2O. **Acid, H_2CrO_4.**

[Potassium Chromate, K_2CrO_4.]

8. Required to find the notable impurity in Chrome Alum,($K_2Cr_2(SO_4)_4 \cdot 24\,H_2O$) a violet crystalline substance soluble in water.

Examination for Base.

Experiment.	*Observation.*	*Inference.*
Added HCl to aqueous solution.	No pp.	Gp. I. abs.
,, H_2S ,, ,,	,,	Gp. II. abs.
Boiled original solution with a few drops of HNO_3. Added NH_4Cl and NH_4OH and boiled.	Reddish-brown pp.	Fe
Filtered. Dissolved pp. in dil. HCl. Added $K_4Fe(CN)_6$.	Blue pp.	Fe
Added KCNS to original solution.	Blood red coloration destroyed by $HgCl_2$	*Ferric* iron
Added $K_3Fe(CN)_6$ to original solution.	Brown coloration.	*Ferric* iron

Examination for Acid.

Sulphate is known to be present and carbonate, etc., which are precipitated by $BaCl_2$ in neutral solution, are absent, because the salt is completely soluble in water.

Heated dry sub. with conc. H_2SO_4.	No acid fumes.	HCl & HNO_3 absent.
Added $HNO_3 + AgNO_3$ to solution.	No. pp.	HCl, etc., absent.
Added $FeSO_4$ solution and poured conc. H_2SO_4 down the side of the tube.	No brown ring.	HNO_3 abs.

The impurity, therefore, is **Ferric Iron** present, most probably as **Iron Alum—$K_2Fe_2(SO_4)_4 \cdot 24\,H_2O$.**

9. Required to find the notable impurity in Strontium Nitrate ($Sr(NO_3)_2$, a colourless crystalline substance soluble in Water.

Examination for Base.

Experiment.	*Observation.*	*Inference.*
Added HCl to aqueous solution.	No pp.	Gp. I. absent.
,, H_2S ,, ,,	,,	Gp. II. absent.
Boiled original solution with a few drops of HNO_3. Added AmCl + AmOH.	,,	Gp. III. absent.
Added Am_2S to part of alkaline liquid.	,,	Gp. IV. absent.
Added Am_2CO_3 to remainder.	White pp.	Ba, Sr, Ca.
Filtered. Added Na_2HPO_4 to filtrate.	No pp.	Mg absent.
Dissolved Gp. V. pp. in acetic acid. Added K_2CrO_4 to part of solution.	,,	Ba absent.
Added excess of H_2SO_4 to remainder and boiled. Filtered off $SrSO_4$. Added ammonia to filtrate till alkaline and then ammonium oxalate.	White pp.	Ca.
Tried flame test with some of calcium oxalate pp. (+HCl).	Yellowish-red coloration.	Ca.

Examination for Acid.

Added $BaCl_2$ to aqueous solution.	No pp.	H_2SO_4, etc., absent.
Added $HNO_3 + AgNO_3$ to aqueous solution.	,,	HCl, etc., absent.

The impurity is **Calcium Nitrate—$Ca(NO_3)_2$.**

10. Mixture containing two bases and two acids. Pink crystalline deliquescent substance, soluble in water.

PRELIMINARY EXAMINATION.

Experiment.	*Observation.*	*Inference.*
Heated in bulb-tube.	Water of crystallization evolved. Then HCl.	Chloride—probably $MnCl_2$ from colour of salt.
,, with HCl.	—	—
,, conc. H_2SO_4.	HCl evolved.	Chloride.
,, on charcoal with Na_2CO_3 and a little KNO_3.	Green mass.	Mn.
,, on platinum wire.	—	—

WET EXAMINATION FOR BASES.

Added HCl to aqueous solution.	No pp.	Gp. I. absent.
,, H_2S. ,, ,,	,,	Gp. II. absent.
Boiled original solution with a little HNO_3. Added AmCl+AmOH.	,,	Gp. III. absent.
Added Am_2S to part of alkaline solution.	Black pp.	Ni or Co and possibly Mn or Zn.
Added remainder of alkaline solution and more Am_2S. Filtered. Added Am_2CO_3.	No pp.	Gp. V. absent.
Added Na_2HPO_4.	,,	Mg absent.
Digested Gp. IV. pp. with very dilute HCl in the cold. Filtered. Digested filtrate with $KClO_3$ and evaporated to small bulk. Added excess of NaOH.	Dirty-coloured pp.	Mn.
Tried borax bead test with Mn pp.	Amethyst coloration when cold.	Mn.
Warmed part of Gp. IV. pp. insol. in dil. HCl with conc. HCl+$KClO_3$.	Green solution.	Ni.
Boiled solution nearly to dryness to expel HCl. Nearly neutralized with Na_2CO_3 and added KCN till the pp. first formed just redissolved. Boiled. Allowed to cool. Added NaOH+Br and warmed gently.	Black pp.	Ni.
Tried borax bead test with small portion of black pp.	In the outer flame violet-brown when hot; yellow when cold.	Ni.

EXAMINATION FOR ACIDS.

Added $BaCl_2$ to aqueous solution.	White pp. insol. in HCl.	Sulphate.
Added HNO_3+$AgNO_3$.	White pp. sol. in ammonia.	Chloride.
Heated solid substance with MnO_2+ conc. H_2SO_4.	Yellowish-green gas evolved smelling like chlorine and bleaching moist litmus paper.	Chloride.

Metals found—Ni, Mn. Acid radicles—SO_4, Cl.

11. Solution containing two bases and two acids. Colourless. Alkaline.

Examination for Bases.

Experiment.	*Observation.*	*Inference.*
Added HCl.	No pp.	Gp. I. absent.
Gently warmed.	Gas evolved with effervescence. Smell of SO_2. $K_2Cr_2O_7$ paper turned green and KIO_3 + Starch paper turned blue.	Sulphite—probably of Na, K or NH_4.
Boiled till smell of SO_2 was gone. Passed H_2S.	No pp.	Gp. II. absent.
Boiled to remove H_2S. Added a few drops of HNO_3 and boiled again. Added AmCl+AmOH.	"	Gp. III. absent.
Added Am_2S to part of alkaline solution.	"	Gp. IV. absent.
Added Am_2CO_3 to remainder.	"	Gp. V. absent.
Added Na_2HPO_4.	"	Mg absent.
Boiled original solution with NaOH.	Gas evolved smelling of NH_3 and turning red litmus blue.	NH_4.
Boiled till smell of NH_3 disappeared. Neutralized solution with HCl. Put a little on a watch-glass. Added $PtCl_4$ and rubbed with glass rod.	Yellow pp.	K.
Evaporated a further quantity of solution to dryness and tried flame test.	Violet.	K.

Examination for Acids.

Boiled with dil. HCl to expel SO_2. Just neutralized with NaOH and added $BaCl_2$.	White pp.	Phosphate, etc.
Added ammonium molybdate+HNO_3.	Yellow coloration in cold. Yellow pp. on boiling.*	Phosphate.

* This pp. could not be due to arsenate, for if the latter had been present it would have been reduced to H_3AsO_3 on boiling with HCl+sulphite (present in the original solution) as above. On passing H_2S a yellow pp. of As_2S_3 would have been obtained.

Metals found K, NH_4. Acid radicles SO_3, PO_4.

12. Simple salt. White amorphous powder, insoluble in water.

Heated sub. in a hard test-tube. Swelled up; odour of burnt sugar. Black residue which effervesced with dil. HCl. On treating another portion of residue with water and filtering, the filtrate was alkaline, but did not effervesce with dil. HCl. Probably Ca, Ba or Sr Tartrate.

Treated remainder of residue with HCl.—Filtered. Examined the filtrate for the metal.

Passed H_2S through a part. No pp. Gp. II. absent.

Added NH_4Cl and NH_4OH to remainder. No pp. Gp. III. absent.

Added $(NH_4)_2S$ to part of alkaline solution.—No pp. Gp. IV. absent.

Added $(NH_4)_2CO_3$ to remainder.—White pp. Ca, Ba or Sr present. Filtered. Dissolved pp. in dil. acetic acid.

Added K_2CrO_4 to part of solution.—No pp. Ba absent.

Added $CaSO_4$ to another part.—No pp. on shaking and standing. Sr absent.

The metal present is, therefore, **Calcium.** Confirmed by (1) $(NH_4)_2C_2O_4$—white pp. insol. in acetic acid. (2) Flame test—dull red flame.

Examination for the acid. *Heated original sub. with dil. H_2SO_4*—no smell. H.COOH and CH_3.COOH absent.

Heated with conc. H_2SO_4.—Immediate blackening with evolution of CO, CO_2, and SO_2. Tartaric acid present.

Preparation of neutral solution of acid.—Boiled original sub. with Na_2CO_3. Filtered. Neutralized filtrate with dil. HCl and warmed to remove CO_2. Added NaOH till *just* neutral to litmus.

Applied the following confirmatory tests for tartaric acid.

(1) $CaCl_2$—White pp. soluble in cold NaOH.

(2) $AgNO_3$.—White pp. Pp. was allowed to settle, the supernatant liquid poured off. Just sufficient ammonia was added to dissolve the pp. On heating a silver mirror was produced.

The salt is **Calcium Tartrate—$CaC_4H_4O_6$.**

13. Simple salt. Colourless, crystalline; soluble in water; neutral.

Heated sub. in a hard test-tube.—White residue, soluble in water; effervesced with dil. HCl. Acid present in form of K or Na salt [only K and Na carbonates—of those which might be formed—are sol. in water].

Heated portion of residue on Pt. wire after moistening with HCl.—Violet coloration. K present.

Confirmed K by adding $PtCl_4$ to HCl solution of residue. Yellow crystalline pp.

Heated original sub. with dil. H_2SO_4.—No smell. $H.COOH$ and $CH_3.COOH$ absent.

Heated original sub. with conc. H_2SO_4.—CO and CO_2 evolved (the CO burnt with a blue flame and the CO_2 turned lime-water milky). Oxalic acid present.

Confirmed oxalic acid by adding $CaCl_2$ to a solution of the salt in water. White pp. insol. in acetic acid, soluble in dil. HCl.

The salt is **Potassium Oxalate.**—$K_2C_2O_4$.

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