Experiments in inorganic chemistry : including a brief introduction to analytical methods / arranged by Charles C. Blackshear.

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Publication/Creation

Baltimore, [Md.] : Friedenwald, 1893.

Persistent URL

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EXPERIMENTS

IN

INORGANIC CHEMISTRY

INCLUDING

A BRIEF INTRODUCTION TO ANALYTICAL METHODS

ARRANGED BY

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PREFACE.

This laboratory manual does not contain a complete series of exercises preparatory to analytical work, and is not intended for the use of those who expect to make such work a specialty. The object in its preparation has been to provide for students of Chemistry in the second year such exercises as will assist them in remembering many important relations in Inorganic Chemistry and give them some insight into the more important analytical methods. Many questions which would naturally accompany such a series of experiments have been purposely omitted in the text and reserved for the instructor in the class room or laboratory.

The exercises are presented in much the same manner as in Volhard's *Course of Experiments in General Chemistry (Translated by Renouf)*, though the arrangement is in many respects different.

THE WOMAN'S COLLEGE OF BALTIMORE, *July*, 1893.

NOTE FOR THE STUDENT.

In Part I attention is directed mainly to reactions peculiar to salts of the more important acids,—reactions by which the acidic constituents of compounds are distinguished from one another; in Part II to those peculiar to the compounds of the various metals,—the reactions by which the metals, or the basic constituents of compounds, are distinguished from one another. The sign (?), wherever it occurs, calls for the equation representing the reaction involved. The student is expected to deduce generalizations, and to point out features of similarity and of difference in the various elements.

CONTENTS.

PART I.

I.—CHLORIDES.

Use Potassium Chloride for the Reactions.

Pour some concentrated sulphuric acid on a small quantity of potassium chloride in a test tube (?). Allow the escaping gas to come in contact with a drop of silver nitrate on a stirring rod held over the mouth of the tube (?). The precipitate formed in this drop is easily soluble in ammonia; insoluble in nitric acid. The above is a common analytical test for chlorides.

To a solution of potassium chloride add a few drops of a solution of silver nitrate. The same precipitate is formed as above. It clots together when the tube is shaken, and assumes a violet color on exposure to the light. Dissolve in ammonia.

To a solution of potassium chloride add a few drops of a solution of mercurous nitrate (?); add a few drops of ammonia, and the precipitate becomes black.

To a solution of the salt add a few drops of a solution of lead acetate (?); add water and boil; the precipitate dissolves. On cooling it will crystallize from solution.

Silver chloride, mercurous chloride and lead chloride are the only common chlorides which are insoluble, or difficultly soluble.

Heat manganese dioxide with concentrated hydro-
chloric acid in a test tube (?). (A mixture of man-
ganese dioxide, potassium chloride and concentrated
sulphuric acid would answer the same purpose.) Test
the action of the escaping gas on moist litmus paper;
on paper moistened with a solution of potassium
iodide (?).

2.—BROMIDES.

Use Potassium Bromide.

Add concentrated sulphuric acid to a small quantity
of the dry salt in a test tube and heat (?). Explain
color of the escaping acid (?). Does hydrochloric
acid undergo a like decomposition under similar
circumstances?

To a solution of the salt add a few drops of a solution
of silver nitrate (?). The precipitate is yellowish white
and is soluble with difficulty in ammonia; otherwise it
resembles silver chloride.

To a very dilute solution of the salt add a little
chlorine water; if the solution is not extremely dilute a
yellow color is observed (?). Add a little chloroform
or carbon disulphide and shake; the bromine is
extracted from the solution, these reagents being
colored yellow to brown according to the proportion
of bromine. By the extraction of the bromine in this
way, by these reagents, it is possible to detect brom-
ides when present in so small a quantity that the addi-
tion of the chlorine water produces no apparent change
in the color of the solution. Bromine colors starch
paste yellow, hence starch paste might be used in such
experiments instead of chloroform or carbon disulphide.

By the action of sulphuric acid on a mixture of manganese dioxide and potassium bromide, bromine may be prepared (?). A solution of bromine in water is often used to effect oxidation. Is bromine as energetic an oxidizing agent as chlorine?

3.—IODIDES.

Use Potassium Iodide.

Add concentrated sulphuric acid to a small quantity of the dry salt in a test tube and heat. Hydriodic acid, formed in the first phase of the reaction (?), is oxidized with great readiness by the concentrated sulphuric acid. (Compare with hydrochloric and hydrobromic acids.) When sulphuric acid oxidizes hydriodic acid iodine is set free, the sulphuric acid being reduced, according to conditions, to hydrogen sulphide, sulphur or sulphur dioxide. Write the three equations representing these reactions. The following simple experiment illustrates the formation of each of the above decomposition products: To a piece of potassium iodide of the size of a pea add one drop of water and three or four drops of concentrated sulphuric acid, and heat gently; in connection with the vapor of iodine, hydrogen sulphide escapes, which can be recognized by its odor; at the same time a coating of sulphur forms on the inside of the tube above the acid. Add five or six more drops of the concentrated acid and continue to heat gently; the odor of hydrogen sulphide disappears and that of sulphur dioxide can then be distinctly recognized.

To a solution of potassium iodide add a few drops of a solution of silver nitrate (?). The precipitate has a yellowish color and is nearly insoluble in ammonia; otherwise it resembles silver chloride.

To a solution of the salt add a little chlorine water (?). On further addition of chlorine water the separation of iodine continues until all the potassium iodide has been decomposed. Add still more chlorine water; the iodine dissolves and finally a colorless solution is obtained (?). Bromine water will answer the same purpose as chlorine water in this experiment. If the quantity of iodide in solution is exceedingly small it can easily be detected by adding a little chlorine water, and then chloroform or carbon disulphide, and shaking; these reagents extract the free iodine, the chloroform assuming a red color, the carbon disulphide a violet color.

Dissolve a very small quantity of potassium bromide and potassium iodide in water, add a little carbon disulphide, and then add chlorine water cautiously; on shaking, the carbon disulphide is colored violet. Add more chlorine water; the violet color gradually disappears, owing to the oxidation of the iodine. On further addition of chlorine water the carbon disulphide assumes a yellow or brown color, the bromine being set free after all the iodine has been oxidized.

Iodine colors starch paste blue, hence starch paste may be used in such experiments as the above instead of chloroform or carbon disulphide. Add starch paste to a very dilute solution of potassium iodide, and then add a little chlorine water and note the blue color.

The color disappears on heating and appears again on cooling.

By the action of sulphuric acid on a mixture of manganese dioxide and potassium iodide, iodine may be prepared. Try the action of iodine on a solution of hydrogen sulphide (?). How does iodine compare with chlorine and bromine in oxidizing power?

4.—FLUORIDES.

Use Calcium Fluoride.

Place some pulverized calcium fluoride in a platinum crucible; add enough concentrated sulphuric acid to form a thin paste, and heat gently (taking care not to inhale the gas evolved) (?). The gas is colorless; concentrated sulphuric acid has not the power to decompose it, the affinity of fluorine for hydrogen being even greater than that of chlorine for hydrogen. The gas does not form a precipitate in a solution of silver nitrate, as silver fluoride is easily soluble (difference from silver chloride, bromide and iodide).

If the mixture in the platinum crucible be not heated and the crucible be covered with a piece of glass coated with paraffin, through which coating lines have been drawn, it will be found, after allowing it to stand for half an hour in a warm place, that the lines drawn through the paraffin are etched on the glass (?) (test for insoluble fluorides).

Heat some pulverized fluorspar in a test tube with concentrated sulphuric acid. The escaping gas acts on a drop of water on a stirring rod held over the

mouth of the tube, forming silicic acid as a precipitate and fluorsilicic acid in solution (?).

Calcium fluoride, being insoluble (compare with calcium chloride, bromide and iodide), is precipitated when calcium chloride is added to a solution of a fluoride or of hydrofluoric acid (test for soluble fluorides or hydrofluoric acid).

5.—CHLORATES.

Use Potassium Chlorate.

Heat potassium chlorate in a test tube (?). Dissolve the residue and add silver nitrate solution. Silver nitrate produces no precipitate in solutions of chlorates.

When potassium chlorate is heated on charcoal violent combustion ensues and the residue is potassium chloride (?).

Pulverize a piece of potassium chlorate not larger than a grain of rice, mix with a little sulphur, place in a mortar and rub with the pestle (?).

To a solution of the salt add dilute sulphuric acid. Chloric acid is set free in solution (?). Test the action of the mixture on heating with indigo solution (the blue color of the indigo gives place to the yellow color of the product of oxidation); with ferrous sulphate solution (write the equation for the action of oxygen on ferrous sulphate in presence of sulphuric acid).

Pour a drop or two of concentrated sulphuric acid on a piece of potassium chlorate not larger than a grain of rice; on gently warming, a dark yellow,

heavy gas (chlorine dioxide, formed by decomposition of the chloric acid first set free) is evolved (?), which, on heating higher, is decomposed with explosion.

6.—HYPOCHLORITES.

Use Sodium Hypochlorite.

Moisten blue litmus paper with a solution of sodium hypochlorite; on exposure to the air for a short time the paper becomes white. Here the carbon dioxide of the air sets hypochlorous acid free (?) (difference from chlorates), which acts as an oxidizing agent, bleaching the litmus.

On boiling a *dilute* solution of the salt decomposition takes place, the products being sodium chlorate and sodium chloride (?); on boiling a *concentrated* solution sodium chloride and oxygen are the products (?).

7.—CARBONATES.

Use Sodium Carbonate.

Test the reaction of a solution of sodium carbonate with litmus paper. The other soluble carbonates give the same reaction.

To a solution of the salt add any dilute acid (?). The gas evolved colors blue litmus paper faint red, and does not support combustion. Repeat the experiment, introducing the solution of sodium carbonate into a flask or large test tube provided with a stopper in which is fitted a thistle tube, which must pass below the surface of the solution and through which

the acid is to be poured, and a delivery tube, which is to be introduced into a solution of barium hydroxide. On adding the acid, the gas evolved passes into the solution of barium hydroxide, forming a precipitate (?). Add acid to the solution containing the precipitate; this dissolves the precipitate (?). The above is a common test for carbonates.

Add a solution of the salt to a solution of calcium chloride (?). The carbonates of the alkali metals only are soluble in water.

Some metals form, under most circumstances, basic carbonates. Add a solution of sodium carbonate to a solution of zinc chloride (?).

Some metals form no carbonates. Add a solution of sodium carbonate to a solution of aluminium sulphate (?).

Some carbonates insoluble in water (calcium carbonate, for example) are soluble in water into which carbon dioxide is introduced (?). What takes place when such a solution is boiled (?).

8.—NITRATES.

Use Potassium Nitrate.

Heat some potassium nitrate in a hard glass test tube with the blast lamp. What change takes place? How do most nitrates decompose under the influence of heat,—lead nitrate, for example (?).

Place a little of the salt on charcoal and touch it with an ignited match; a vigorous combustion ensues. Add, successively, small quantities of the salt to the

hot, sputtering mass in order to prolong the reaction until there is a sufficient quantity of the residue on the charcoal for careful examination. Remove this residue, dissolve it in water and, after filtering, test the solution with litmus paper, with hydrochloric acid (?), and with barium hydroxide (?) or barium chloride (?). Having ascertained the nature of this residue, write the equation for the reaction which took place on the charcoal.

To one drop of a solution of the salt in a test tube add two or three cc. concentrated sulphuric acid; add to this a cold solution of ferrous sulphate, pouring it very carefully down the side of the tube so that it may remain above the heavier sulphuric acid; a brown ring (or, if the solution of the nitrate is exceedingly dilute, an amethyst-colored ring) is seen at the point of contact of the two liquids. If the contents of the test tube are very warm the colored ring will not appear, owing to the instability of the colored compound $(NO.2FeSO_4)$ under the influence of heat. The above is the common test for nitrates, and is a very delicate one. Write equations for the reactions taking place. The ferrous sulphate acts as a reducing agent on the nitric acid first set free.

Color a solution of potassium nitrate with indigo solution; add concentrated sulphuric acid and heat (?).

All nitrates are easily soluble in water.

By the action of concentrated sulphuric acid on potassium nitrate, nitric acid can readily be prepared (?). Treat copper filings with concentrated nitric acid. Treat tin with concentrated nitric acid. In both cases oxidation takes place; the copper is

transformed into nitrate corresponding to the oxide CuO (write equation), the tin into hydroxide corresponding to the oxide SnO_2 (the hydroxide appears to be a polymeric modification of $Sn\begin{smallmatrix}\diagup O \\ -OH \\ \diagdown OH\end{smallmatrix}$, and is known as metastannic acid). Write the equation for the formation of this substance by this reaction.

9.—NITRITES.

Use Potassium Nitrite.

Add concentrated sulphuric acid to a small quantity of potassium nitrite in a test tube; brownish red vapors of nitrogen trioxide are evolved (?).

To a solution of the salt add potassium iodide solution, starch paste and dilute sulphuric acid. Assuming that nitrous and hydriodic acids are first set free (?), show how the formation of the blue color can be explained by their action in presence of starch paste.

10.—SULPHIDES.

Use Sodium Sulphide.

Test the reaction of the solution of sodium sulphide with litmus paper. The other soluble sulphides give the same reaction.

Add dilute sulphuric acid to the solution of the salt and notice the odor of the escaping gas (?).

A drop of the solution placed on a silver coin stains the silver black (?).

To a solution of ferrous sulphate add sodium sulphide solution (?). The sulphides of the alkali metals

and of the alkaline earth metals only are soluble in water.

Some sulphides insoluble in water dissolve in solutions of soluble sulphides. Conduct hydrogen sulphide (prepared by the action of a dilute acid on ferrous sulphide (?)) into a solution of arsenic trioxide in dilute hydrochloric acid; arsenic trisulphide, As_2S_3, is precipitated; pour off the acid, wash the precipitate by decantation, and then treat it with sodium sulphide solution; it dissolves, forming a sulpho salt, Na_3AsS_3 (?).

The sulphides of the metals aluminium and chromium, if formed at all, break down at once in presence of water, the hydroxide of the metal and hydrogen sulphide being formed. To a solution of aluminium sulphate add ammonium sulphide; aluminium hydroxide is precipitated: $Al_2(SO_4)_3 + 3(NH_4)_2S + 6H_2O = 2Al(OH)_3 + 3(NH_4)_2SO_4 + 3H_2S$. If in this reaction aluminium sulphide, Al_2S_3, is first formed (?) it breaks down thus: $Al_2S_3 + 6H_2O = 2Al(OH)_3 + 3H_2S$.

11.—SULPHATES.

Use Potassium Sulphate.

Heat potassium sulphate in a test tube; it decrepitates (?). Place some of the decrepitated salt on charcoal and heat sharply for a little while in the reducing flame of the blowpipe (?). Test the residue with a silver coin (place a fragment on the coin and add a drop of water) (?); with litmus paper; with dilute sulphuric acid (?). The above is the common

test for sulphates in the dry way. If the sulphate is not a sulphate of an alkali metal or of an alkaline earth metal, it should be mixed with sodium carbonate before fusion on charcoal. This leads to the formation of soluble sulphide as before (?).

Add barium chloride solution to a solution of the salt (?); now add dilute nitric acid or dilute hydrochloric acid; the precipitate does not dissolve. (The common test for sulphates in the wet way.) The sulphates of barium, lead, strontium and calcium are the only common sulphates which are insoluble, or very difficultly soluble.

12.—SULPHITES.

Use Sodium Sulphite.

Heat some sodium sulphite in a test tube until it fuses and decomposes. Test the product with a silver coin (?); with litmus paper; with dilute sulphuric acid (?). In the decomposition which took place the only other substance formed, in addition to that indicated by these reactions, was sodium sulphate; all of the oxygen of the sulphite was used up in the formation of sulphate. Write the equation.

Add a few drops of concentrated sulphuric acid to a solution of the salt; effervescence ensues, the gas evolved (?) having a peculiar, penetrating odor. Add dilute sulphuric acid to the solution of the salt; the gas is not evolved until the solution is warmed (?).

Treat copper with concentrated sulphuric acid. The same gas is thus prepared as was evolved in the

above reactions (?). The heating of charcoal with concentrated sulphuric acid is another method by which this gas may be prepared (?).

Treat ferric chloride solution with sulphurous acid (?). Treat bromine water with sulphurous acid (?).

Conduct hydrogen sulphide into sulphurous acid (?). Add hydrochloric acid and zinc to sulphurous acid; hydrogen sulphide is evolved (?).

Sulphurous acid acts as a bleaching agent.

13.—THIOSULPHATES.

Use Sodium Thiosulphate.

Heat some sodium thiosulphate in a test tube until it decomposes. Test the product with a silver coin and with litmus paper; add dilute sulphuric acid to the solution of some of the product and note the precipitation of sulphur, as well as the odor of the escaping gas. In the decomposition which took place all of the oxygen of the thiosulphate was used up in the formation of sodium sulphate, just as in the decomposition of sodium sulphite, and the other substance formed was sodium pentasulphide. Write the equation for the decomposition. Write the equation for the action of the dilute sulphuric acid on the pentasulphide.

Add dilute sulphuric acid to a dilute solution of the salt; it soon becomes opalescent and has the odor of sulphurous acid (?).

In the reaction above mentioned, and in general, the thiosulphates behave like sulphites + sulphur.

Precipitate silver chloride by adding a few drops of

a solution of silver nitrate to a dilute solution of potassium chloride ; add sodium thiosulphate solution ; the precipitate dissolves (?).

14.—PHOSPHATES.

Use Di-sodium Phosphate.

Test the reaction of a solution of di-sodium phosphate with litmus paper.

To a solution of the salt add ammonium chloride solution, then ammonium hydroxide, and then magnesium sulphate solution ; a white crystalline substance is precipitated (?) (the addition of ammonium chloride prevents the formation and precipitation of magnesium hydroxide) ; add an excess of dilute acid ; the precipitate dissolves (?) ; now add an excess of ammonia ; the substance is reprecipitated. The above is a common test for orthophosphates, as is also that stated in the next paragraph.

To one drop of a solution of the salt add about 2 cc. of a solution of ammonium molybdate in nitric acid ; the liquid turns yellow ; heat it slightly ; a yellow crystalline substance (ammonium phospho-molybdate, $(NH_4)_3PO_4.(MoO_3)_{12}$) is precipitated. Ammonium phospho-molybdate is soluble in excess of phosphate, hence in applying the test only a very small quantity of the phosphate should be used.

The di-phosphates and tri-phosphates of the alkali metals only are soluble in water. All mono-phosphates are soluble in water.

Add calcium chloride solution to a solution of di-sodium phosphate ; the precipitate is, at first, quite

voluminous and consists of tri-calcium phosphate, mono-calcium phosphate being in solution ($4CaCl_2 + 4Na_2HPO_4 = Ca_3(PO_4)_2 + Ca(H_2PO_4)_2 + 8NaCl$); these phosphates afterwards act on each other, all the calcium being precipitated as crystalline di-calcium phosphate (?).

Add silver nitrate solution to the solution of the salt; yellow tri-silver phosphate is precipitated (?); filter, and test the reaction of the filtrate with litmus paper. Mono-, di- and tri-sodium phosphate yield the same precipitate when treated with silver nitrate.

By the following process the acidic constituent of phosphates can be separated from the basic in the form of insoluble tri-stannic phosphate, $Sn_3(PO_4)_4$, the base formerly present as phosphate remaining in solution as nitrate. Add to a few drops of di-sodium phosphate about two grams of granulated tin and about 20 cc. of concentrated nitric acid; heat gently, when the tin will gradually be changed to a white powder; evaporate to dryness on the water-bath, add hot water and filter; test the filtrate for phosphate. In the above reaction the nitric acid acts on the tin, forming meta-stannic acid (?), and this acts on di-sodium phosphate in presence of nitric acid, forming tri-stannic phosphate (?).

Heat di-sodium phosphate in a test tube; it melts in its water of crystallization; after this is driven off heat higher, when the dry salt will undergo change (?) and the residue will finally melt. Dissolve the residue in water and add silver nitrate solution; a white substance is precipitated (?) (difference from orthophosphates).

What is formed when a primary phosphate (mono-sodium phosphate, for example) is heated (?). Heat some microcosmic salt in a loop of platinum wire until it ceases to undergo change, and forms a transparent bead (?). If a solution of this residue is acidulated with acetic acid and added to a solution of albumen, the albumen is coagulated—that is, separated in insoluble form (difference from orthophosphates and pyro-phosphates).

15.—BORATES.

Use Sodium Tetraborate (Borax).

Heat sodium tetraborate in a loop of platinum wire; it loses its water of crystallization and fuses to a transparent bead, without undergoing further change.

Test the reaction of the solution of sodium tetraborate with litmus paper.

Place some of the salt in a loop of platinum wire, moisten with concentrated sulphuric acid and introduce into the flame of the Bunsen burner; the boric acid set free colors the flame green (test for borates). Instead of proceeding as above, the test may be made by placing some of the pulverized salt in a porcelain dish, adding a little concentrated sulphuric acid, and then alcohol, and igniting the alcohol; the flame has a green mantle.

By the action of sulphuric acid or other strong acids on a solution of sodium tetraborate, boric acid may be prepared (?). Introduce a piece of turmeric paper into a solution of boric acid; on drying, the paper assumes a reddish brown color, and this color is not

changed on subsequently introducing the paper into hydrochloric acid. (Alkalies impart to turmeric paper a similar color, but hydrochloric acid changes this to the original yellow.)

16.—SILICATES.

Use Sodium Silicate.

Test the reaction of a solution of sodium silicate with litmus paper.

Bring into the hot transparent bead formed by heating microcosmic salt in a loop of platinum wire, a fragment of sodium silicate, and heat again in the flame; the basic constituent of the silicate combines with the metaphosphate, forming orthophosphate (?), while the silicon dioxide separated can be observed as a white mass in the bead.

To the concentrated solution of sodium silicate add dilute acid (?). Many insoluble silicates cannot be decomposed in this manner. Such silicates may be fused with sodium hydroxide or carbonate, the silicate being thus transformed into sodium silicate, which can then be decomposed by acid; or, if this method does not effect decomposition, the silicate may be heated in a platinum crucible with calcium fluoride and concentrated sulphuric acid, the silicon being thus eliminated in the form of gaseous silicon tetrafluoride and the basic constituent of the silicate taking the form of sulphate. Precipitate a small quantity of silicic acid by adding hydrochloric acid to a concentrated solution of sodium silicate; wash, dry, and heat for a short time in a platinum crucible; then add a little hydro-

fluoric acid and warm (?); hold a drop of water on a stirring rod over the crucible (?).

Silicic acid does not form an ammonium salt. Treat the solution of sodium silicate with ammonium chloride solution (?).*

* On completion of this chapter the student should examine at least four mixtures, applying tests for salts of the common acids, hydrochloric, carbonic, nitric, sulphuric and phosphoric, any or all of which classes of salts may be contained in them.

PART II.*

I.—POTASSIUM.

Use Potassium Chloride.

Attach some potassium chloride to a platinum wire by placing the hot wire on some of the dry salt; hold in the flame of a Bunsen burner, and note the violet color imparted to the flame. The violet rays are transmitted through cobalt glass. While heating the salt in the flame look at the flame through a piece of cobalt glass; it appears reddish. Potassium salts in general impart a violet color to the flame.†

* Before beginning the work of this part the student is expected to perform the preliminary experiment, described in Appendix I, page 56, indicating methods adopted in the separation of the metals.

† Flame reactions are often made use of in analytical work. The examination of color imparted to the flame forms one of a series of preliminary tests to which it is customary to subject, at the start, a substance presented for analysis. The presence of the metals, potassium, sodium, strontium, and others is indicated in this way. Other preliminary tests consist in heating the substance in the microcosmic salt bead or borax bead, heating it with sodium carbonate on charcoal in the reducing flame of the blowpipe, and heating it on charcoal after moistening with cobalt nitrate solution. By such treatment the presence of other metals may be detected, as will be plain after further study of the metals.

To a concentrated solution of the salt add a few drops of perchloric acid (?). On heating, the crystalline precipitate dissolves; when the solution cools it separates again.

Add strong tartaric acid solution to the concentrated solution of the salt; on shaking, a crystalline substance is precipitated (?). Heat; the precipitate dissolves; on cooling, it separates again.

To a drop of the concentrated solution of the salt add a few drops of chlorplatinic acid solution (?). Add a small quantity of water and boil; the crystalline precipitate dissolves; on cooling, it separates again in small, well defined crystals. The precipitate formed in this reaction is insoluble in alcohol.

Nearly all potassium salts are easily soluble in cold water; the three precipitated in the above reactions are difficultly soluble in cold water.

2.—SODIUM.

Use Sodium Chloride.

Hold some of the salt in the flame. Look at the flame through cobalt glass; the yellow color disappears. Potassium in presence of sodium can easily be detected by observation of the flame color through cobalt glass.

To the concentrated solution of the salt add potassium metantimonate solution ($KSbO_3$); the corresponding sodium salt is precipitated (?).

Nearly all sodium salts are easily soluble in water; the salt precipitated above is difficultly soluble in water.

To one drop of a solution of sodium chloride on a watch-glass add three or four drops of chlorplatinic acid solution; evaporate nearly to dryness on the water-bath; on cooling, small, needle-shaped crystals of sodium chlorplatinate separate. This salt is easily soluble in cold water and in alcohol (difference from the corresponding potassium compound).

3.—AMMONIUM.

Use Ammonium Sulphate.

Heat ammonium sulphate in a test tube; the odor of ammonia is noticed. Ammonium salts in general decompose when heated (though the chloride sublimes there is really decomposition and recombination) and from most of them ammonia is evolved. How do ammonium nitrate and ammonium nitrite decompose when heated (?).

To a solution of the salt add sodium hydroxide solution (?); heat, and notice the odor; while heating hold over the solution a piece of filter paper moistened with copper sulphate solution (noticing color imparted to the paper), also a drop of hydrochloric acid or nitric acid on a stirring rod (?). Other metallic hydroxides act on the salt in the same way. In a small beaker mix a few drops of dilute ammonium sulphate solution with so much calcium hydroxide that the mass remains powdery; cover the beaker with a watch-glass on the under side of which is a piece of moist turmeric paper; the turmeric is colored brown; on treating the paper with acid the yellow reappears. If red litmus paper be

used instead of turmeric paper the paper is colored blue. The above is a very delicate test for ammonium compounds.

Treat ammonium sulphate solution with chlorplatinic acid, just as potassium chloride was treated with this reagent (?). The precipitate is very closely analogous in properties to the corresponding potassium salt. On ignition of the latter salt the residue consists of potassium chloride and platinum. What would remain after ignition of the ammonium salt?

Acid ammonium tartrate is likewise closely analogous in properties to the corresponding potassium salt.

Nearly all ammonium salts are easily soluble in cold water.

Add a little bromine water to ammonium hydroxide; a gas is evolved with effervescence (?).*

4.—BARIUM.

Use Barium Chloride.

Hold some of the salt in the flame; the flame color is yellowish green.

To a concentrated solution of the salt add potassium hydroxide solution or sodium hydroxide solution (?). On heating, the precipitate dissolves (with the exception of a little barium carbonate, the formation of which was due to alkali carbonate present in the hydroxide used); the solution has an alkaline reaction; filter hot; the substance is deposited again as the solution cools.

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*A mixture should be given at this point for examination for potassium, sodium and ammonium. The student may refer to directions in Appendix II, Division 1, page 60.

The carbonates of the alkali metals and ammonium carbonate precipitate barium carbonate from barium salt solutions. To the solution of barium chloride add ammonium carbonate and ammonium hydroxide, and boil (?). (The necessity of adding ammonium hydroxide and boiling in order to secure complete precipitation when ammonium carbonate is used is due to the presence of acid carbonate in the solution of ordinary ammonium carbonate, which would otherwise lead to the formation of soluble acid barium carbonate.)

To the solution of the salt add either dilute sulphuric acid or a solution of a sulphate (?). The precipitate does not dissolve in water or dilute acids. If barium sulphate is fused in a platinum crucible with about four times the quantity of sodium carbonate or potassium carbonate, it is completely changed to carbonate (?).

To the solution of the salt add potassium chromate solution (?). The precipitate is soluble in hydrochloric acid or nitric acid, but not in acetic acid.

Di-sodium phosphate precipitates the corresponding barium phosphate from barium salt solutions.

5.—STRONTIUM.

Use Strontium Chloride.

Hold some of the salt in the flame; it instantly imparts a dark red color to the flame.

Try the action of potassium or sodium hydroxide solution on the concentrated solution of the salt (?). Barium hydroxide likewise produces a precipitate in

the concentrated solution (?). (Try this.) The precipitate formed in these reactions resembles the corresponding barium compound.

To the solution of the salt add ammonium carbonate and ammonia, and boil (?).

Add dilute sulphuric acid or the solution of a sulphate to the solution of the salt; a voluminous precipitate is formed (?). This precipitate is nearly insoluble in water and in dilute acids.

Potassium chromate produces a precipitate in a *concentrated* solution of strontium chloride, but this precipitate is soluble in acetic acid.

Di-sodium phosphate reacts with strontium chloride just as it does with barium chloride.

Strontium nitrate is insoluble in a mixture of equal parts of alcohol and ether.

6.—CALCIUM.

Use Calcium Chloride.

Hold some of the salt in the flame; the flame color resembles that imparted by strontium compounds, but it is *yellowish* red and does not appear so quickly.

Try the action of potassium or sodium hydroxide on a strong solution of calcium chloride (?). The precipitate resembles the corresponding compound of barium and strontium; it is more difficultly soluble in water than the strontium compound, and still more so than the barium compound.

To the solution of the salt add ammonium carbonate and ammonia, and boil (?). Heat a small piece of marble on charcoal with the blowpipe for a few min-

utes (?); moisten the residue with water and test the reaction with litmus paper. (When highly heated, calcium carbonate loses its carbon dioxide more readily than does strontium carbonate, and still more readily than does barium carbonate.)

Add dilute sulphuric acid or a solution of a sulphate to a strong solution of calcium chloride ; a voluminous crystalline precipitate is formed ; in very dilute solutions of calcium salts the precipitate is not formed. (Compare the solubility of calcium sulphate with that of strontium sulphate and barium sulphate.)

Potassium chromate produces no precipitate in a solution of calcium chloride.

Di-sodium phosphate reacts with calcium chloride just as it does with strontium chloride and barium chloride.

Calcium nitrate is easily soluble in a mixture of equal parts of alcohol and ether (difference from strontium nitrate).

7.—MAGNESIUM.

Use Magnesium Sulphate.

Try the action of potassium or sodium hydroxide on magnesium sulphate solution (?). (The hydroxides of barium, strontium and calcium act in the same way.) The precipitate is almost insoluble in water, but enough so to cause an alkaline reaction. Ammonia likewise precipitates magnesium salts, but the precipitation is not complete, owing to the fact that magnesium salts combine with ammonium salts, forming soluble compounds which are not decomposed by ammonia. The following reactions will make this plain :

$$MgSO_4 + 2NH_4OH = Mg(OH)_2 + (NH_4)_2SO_4.$$
$$MgSO_4 + (NH_4)_2SO_4 = [MgSO_4(NH_4)_2SO_4].$$
$$2MgSO_4 + 2NH_4OH = Mg(OH)_2 + [MgSO_4(NH_4)_2SO_4].$$
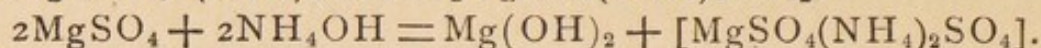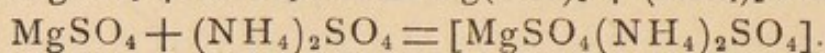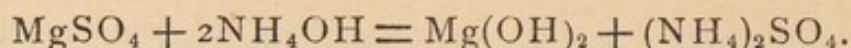
Add an ammonium salt solution to a solution of magnesium sulphate, and then add ammonia ; no precipitate is formed (explain). Add ammonia to an acidulated solution of magnesium sulphate; no precipitate is formed (explain). Magnesium hydroxide dissolves in solutions of ammonium salts (?).

Add sodium or potassium carbonate solution to a solution of the salt. The composition of the basic salt precipitated varies with the conditions of precipitation. Write the equation for the formation of the simplest one. The precipitate is soluble in ammonium salts. No precipitate is formed when ammonium carbonate is added to a solution of a magnesium salt containing ammonium salt.

Compare the solubility of magnesium sulphate with that of calcium sulphate, strontium sulphate and barium sulphate.

To the solution of the salt add ammonium chloride solution, ammonium hydroxide and di-sodium phosphate solution ; a crystalline precipitate is formed (?). This precipitate is soluble in dilute acid, and is reprecipitated from this solution by ammonia. Why is the addition of the ammonium salt necessary to its formation?*

* A mixture, soluble in water, and consisting of compounds of any or all of the metals potassium, barium, strontium, calcium and magnesium, should be given at this point for examination for those metals. Directions in Appendix II, Division 2, page 61.

8.—ALUMINIUM.

Use Aluminium Sulphate.

Heat aluminium sulphate in a test tube; it loses sulphur trioxide, but the decomposition is not complete. If heated on charcoal with the blowpipe only aluminium oxide remains. Place some aluminium sulphate on charcoal, moisten it with a few drops of cobalt nitrate solution and heat with the blowpipe; a blue substance (Thénard's Blue,—$\dfrac{AlO.O}{AlO.O}{>}Co$, a compound of the oxides of aluminium and cobalt) is formed (preliminary test for aluminium).

Test the reaction of the solution of aluminium sulphate with litmus paper.

To the solution of the salt add, gradually, sodium hydroxide solution (?); on continuing to add the sodium hydroxide, the precipitate formed dissolves (?). Divide this solution into three parts; to one part add, gradually, dilute hydrochloric acid; the precipitate reappears (?), but on continuing to add the acid it dissolves again (?); into another part introduce hydrogen sulphide; the substance is completely reprecipitated (?); to the third part add ammonium chloride solution and heat for a few minutes; the substance is completely reprecipitated (?).

To the solution of aluminium sulphate add ammonium hydroxide (?). In excess of ammonium hydroxide the precipitate is only slightly soluble, and if the solution is heated until the odor of ammonia disappears the precipitation is complete. Ammonium chloride facilitates the above precipitation, and in presence of

this reagent the heating to drive off all ammonia is unnecessary.

To the solution of the salt add sodium carbonate solution (?). The precipitate is only slightly soluble in excess of the sodium carbonate.

Add ammonium sulphide to the solution of aluminium sulphate (?).

To the solution of the salt add di-sodium phosphate solution; tri-aluminium phosphate, $AlPO_4$, is precipitated (?).

9.—CHROMIUM.

Use Chromic Sulphate and Potassium Dichromate.

Heat one of the salts in the bead formed by heating microcosmic salt or sodium tetraborate in a loop of platinum wire; in both the oxidizing flame and the reducing flame the bead is colored green * (preliminary test for chromium).

To chromic sulphate solution add, gradually, sodium hydroxide solution (?); on continuing to add the sodium hydroxide the precipitate dissolves (?). Boil this solution; the substance is reprecipitated (?). (In

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* Colored compounds formed by heating salts of certain metals in the microcosmic salt bead are mixed salts of orthophosphoric acid, the metal oxide combining with the metaphosphate ; such compounds formed by heating the salts in the sodium tetraborate bead are mixed salts of orthoboric acid, the metal oxide combining with the sodium tetraborate. The following equations are simple examples illustrating such combination in each case :

$$CoO + NaPO_3 = CoNaPO_4.$$
$$5CoO + Na_2B_4O_7 = 2CoNaBO_3 + Co_3(BO_3)_2.$$
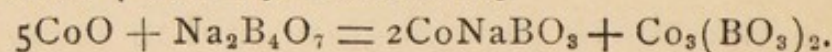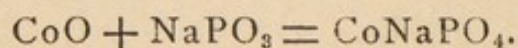
the solution of the corresponding aluminium compound no precipitate is formed on boiling.)

Ammonium hydroxide, sodium carbonate and ammonium sulphide react with chromic sulphate as with aluminium sulphate. Try these reactions.

To a very small quantity of the solution of chromic sulphate in a porcelain dish add concentrated nitric acid and a little potassium chlorate, and heat; the chromium compound is oxidized to dichromate, the characteristic color of the former changing to the yellowish red color of potassium dichromate.

To a solution of potassium dichromate add lead acetate solution; lead chromate, $PbCrO_4$, is precipitated (?).

To a solution of the dichromate add sodium hydroxide solution or sodium carbonate solution; the color changes to yellow (?); add dilute acid to this yellow solution; the color changes to yellowish red (?).

Heat some pulverized potassium dichromate with concentrated hydrochloric acid (?).

To the solution of the dichromate add dilute sulphuric acid or dilute hydrochloric acid, and then heat and conduct hydrogen sulphide into the solution; the solution becomes green and sulphur is precipitated (?).

Pour a cold saturated solution of potassium dichromate into one and a half times its volume of concentrated sulphuric acid; on cooling, red needles separate (?). Filter through glass wool with the aid of a filter pump; place some of the crystals on paper; explain the formation of the dark spots. Introduce blue litmus paper into a dilute solution of some of the

crystals ; the color of the litmus is changed to red, and when the paper dries it is bleached.

10.—MANGANESE.

Use Manganous Chloride and Potassium Permanganate.

Heat manganous chloride in the microcosmic salt bead in both the oxidizing flame and the reducing flame. Manganese compounds impart to the bead an amethyst color in the oxidizing flame; when placed in the reducing flame the bead becomes colorless.

To the solution of manganous chloride add sodium hydroxide solution (?). The precipitate, exposed to the air, soon becomes brown, owing to the formation of hydrate of the oxide Mn_3O_4.

Ammonium hydroxide partially precipitates manganous chloride solution. To a solution of the salt containing ammonium chloride add ammonium hydroxide; no precipitate is formed (explain). If this solution is allowed to stand, exposed to the air, all the manganese is gradually precipitated as hydrate of the oxide Mn_3O_4.

To the solution of the manganous salt add sodium carbonate solution ; normal carbonate is precipitated (?). The precipitate is soluble in ammonium salts.

Add ammonium sulphide to the solution of the manganous salt; a flesh-colored precipitate is formed (?). This precipitate is insoluble in ammonium salts. The presence of ammonium chloride facilitates complete precipitation, which is likewise true of the sulphides of

iron, zinc, cobalt and nickel. Hydrogen sulphide does not precipitate manganous salts, manganous sulphide being easily soluble in acids,—even in acetic acid.

To the solution of the manganous salt add bromine water and sodium hydroxide solution; the compound H_2MnO_3 is precipitated (?).

To the solution of the manganous salt add sodium acetate solution and bromine water, and warm:

$$MnCl_2 + 4NaC_2H_3O_2 + 2Br + 3H_2O =$$
$$H_2MnO_3 + 2NaCl + 2NaBr + 4C_2H_4O_2.$$
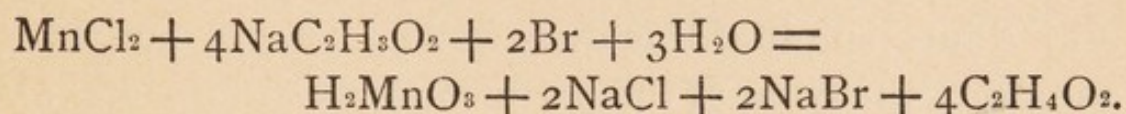
Heat slowly, in a crucible, 5 grams of potassium hydroxide with 3 grams of potassium chlorate; as soon as the mass fuses add 5 grams of pulverized manganese dioxide and heat for a little while just high enough to keep the mass in fusion; the manganese is oxidized and takes the form of potassium manganate (?). Add a small quantity of water and filter; add to this green solution more water; brown manganese perhydroxide is precipitated, while the color of the solution changes from the green of potassium manganate to the purple of the permanganate. In this reaction a portion of the manganate is oxidized to permanganate by virtue of the reduction of another portion to perhydroxide (hydrate of MnO_2).

To two or three drops of a dilute solution of manganous chloride add about 5 cc. of concentrated nitric acid, diluted with an equal volume of water; heat the solution and then drop into it some lead dioxide or minium; when this has settled notice the purple color of the solution. The color is due to the presence of permanganic acid:

$$2MnCl_2 + 5PbO_2 + 6HNO_3 =$$
$$2HMnO_4 + 2PbCl_2 + 3Pb(NO_3)_2 + 2H_2O.$$
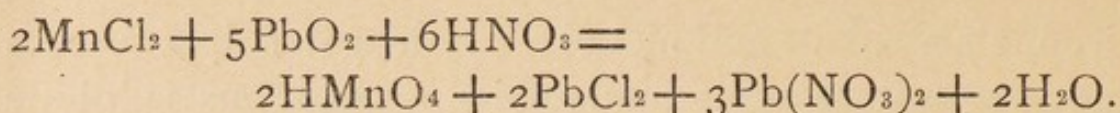
This is a very delicate test for manganese. As the stable form of manganese in the presence of acids is the manganous, it is necessary to use a large excess of the oxidizing agent in order to effect this oxidation to permanganic acid.

To a very dilute solution of potassium permanganate add dilute sulphuric acid, and then ferrous sulphate solution; the color of the permanganate disappears (?).

How does potassium permanganate break up when it acts as an oxidizing agent in alkaline solution?

11.—IRON.

Use Ferrous Sulphate and Ferric Chloride.

Heat one of the salts in the microcosmic salt bead in both the oxidizing flame and the reducing flame. In the oxidizing flame the bead is colored brownish red to yellowish red while hot, but when it becomes cold it is colorless; in the reducing flame it is colored bottle green.

Mix either of the salts with sodium carbonate and heat the mixture for a few minutes on charcoal in the reducing flame of the blowpipe; add water to the residue; a finely divided black substance (Fe_3O_4) which is attracted by the magnet remains undissolved. This and the preceding are preliminary tests for iron.

To a solution of ferrous sulphate add sodium hydroxide solution (?). The precipitate (which, if precipitated in such a way that the air could not have

access, would be white) is greenish, and on standing becomes reddish brown, ferric hydroxide being formed by oxidation (?).

Ammonium hydroxide partially precipitates a solution of a ferrous salt. The presence of ammonium chloride in the solution prevents the precipitation by ammonium hydroxide (explain) if air has not access, but on exposure of this ammoniacal solution to the air all the iron is gradually precipitated as ferric hydroxide.

To the solution of the ferrous salt add sodium carbonate solution (?). This precipitate, like ferrous hydroxide, is soon changed to ferric hydroxide (?).

Add ammonium sulphide to the solution of the ferrous salt (?). From a solution of a ferrous salt to which dilute hydrochloric acid has been added no iron is precipitated by hydrogen sulphide, as ferrous sulphide is soluble in dilute acid.

To the solution of the ferrous salt add potassium ferricyanide solution (?).

To the concentrated solution of the ferrous salt add oxalic acid solution; yellow ferrous oxalate is precipitated (?). Oxalic acid does not precipitate ferric salts.

To a solution of ferrous chloride add hydrochloric acid; while heating this solution add concentrated nitric acid drop by drop; it finally assumes the yellow color of the ferric salt (?); (a brown color noticed at first, which disappears on further heating, is due to solution of nitric oxide in the excess of ferrous salt).

Test the reaction of a solution of ferric chloride with litmus paper.

To a solution of ferric chloride add sodium hydroxide solution (?).

To a solution of the ferric salt add ammonium hydroxide (?). The precipitate is formed even in presence of ammonium chloride.

To a solution of the ferric salt add sodium carbonate solution (?).

Add ammonium sulphide to a solution of the ferric salt; a portion of the precipitate consists of sulphur (?). If hydrogen sulphide is added to the solution of the ferric salt sulphur only is precipitated (?).

To the solution of ferric chloride add potassium ferrocyanide solution (?). Potassium ferricyanide added to the solution of the ferric salt colors it brown, but no precipitate is formed.

To the solution of ferric chloride add potassium sulphocyanate solution; the solution is colored blood-red, owing to formation of ferric sulphocyanate (?). Potassium sulphocyanate added to a solution of a ferrous salt does not color it red, but on exposing the mixture to the air a red color appears, owing to oxidation.

Treat ferric chloride solution with zinc and hydrochloric acid ; reduction takes place (?).

12.—ZINC.

Use Zinc Sulphate.

Mix zinc sulphate with sodium carbonate and heat the mixture on charcoal in the reducing flame of the blowpipe; a coating of zinc oxide is formed on the

charcoal, which is yellow while hot but becomes white on cooling.

Place some zinc sulphate on charcoal, moisten with cobalt nitrate solution and heat with the blowpipe; a green substance (Rinmann's Green,—probably $Zn{<}^O_O{>}Co$) is formed.

To a solution of zinc sulphate add, gradually, sodium hydroxide solution (?); on continuing to add the sodium hydroxide the precipitate dissolves (?). Divide this solution into two parts; to one part add water (if not already quite dilute) and boil; most of the zinc is reprecipitated; into the other part introduce hydrogen sulphide; all the zinc is precipitated as sulphide (?).

To the solution of the salt add, gradually, ammonium hydroxide (?); on continuing to add the ammonium hydroxide the precipitate dissolves (?). Add ammonium hydroxide to the zinc sulphate solution to which ammonium chloride has previously been added; no precipitate is formed (explain).

Add sodium carbonate solution to the solution of zinc sulphate; basic carbonate is precipitated, the composition of which varies with the conditions of precipitation.

Add ammonium sulphide to the solution of the salt (?).

From a solution of a zinc salt to which dilute mineral acid has been added no zinc is precipitated by hydrogen sulphide, as zinc sulphide is soluble in such acid (in a neutral solution precipitation takes place, but it is incomplete). Zinc sulphide is insoluble in acetic acid.

Add sodium acetate solution to the solution of zinc sulphate and then introduce hydrogen sulphide; the zinc is completely precipitated (?).*

13.—COBALT.

Use Cobalt Nitrate.

Heat cobalt nitrate in the microcosmic salt bead in both the oxidizing flame and the reducing flame; in both it is colored blue.

To a small quantity of a solution of the salt add concentrated hydrochloric acid in excess; the color changes to blue; now add water in excess; it becomes red again (explain).

To the solution of cobalt nitrate add sodium hydroxide solution; blue, basic salt is first precipitated, but on further addition of the sodium hydroxide this changes to red cobaltous hydroxide, $Co(OH)_2$; this quickly changes in color and on boiling for some time becomes brown, owing to oxidation to cobaltic hydroxide (?).

Add ammonium sulphide to the solution of the salt (?). The precipitate is almost entirely insoluble in very dilute, cold hydrochloric acid; it is easily soluble in concentrated nitric acid and in aqua regia. Hydrogen sulphide does not precipitate cobalt salts if free mineral acid is present.

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* Two or three mixtures, soluble in water or dilute hydrochloric acid, and consisting of salts of any or all of the metals barium, aluminium, chromium, manganese, iron and zinc, should be given at this point for examination for those metals. In the first of these mixtures some phosphate should be present. Directions in Appendix II, Division 3, page 62.

To the solution of the salt add bromine water and then sodium hydroxide solution; a black precipitate is formed (?). Filter, and treat the precipitate with hydrochloric acid; chlorine is evolved (?).

To a concentrated solution of the salt add potassium nitrite solution and acetic acid; a yellow crystalline precipitate of cobaltic potassium nitrite is formed. Cobaltic potassium nitrite is a double compound of cobaltic nitrite and potassium nitrite ($Co(NO_2)_3 + 3KNO_2$). The oxidation of the cobalt is effected by the nitrous acid produced by the action of the acetic acid on a portion of the potassium nitrite. In dilute solutions of cobalt salts the precipitate is not formed at once, but if the solution is allowed to stand for some time all the cobalt is gradually precipitated in this form.

14.—NICKEL.

Use Nickel Sulphate.

Heat nickel sulphate in the microcosmic salt bead in both the oxidizing flame and the reducing flame; in both it is colored dingy purple-red.

To a solution of the salt add sodium hydroxide solution; an apple-green substance is precipitated (?). When heated, this does not undergo oxidation as did the corresponding cobalt compound.

Add ammonium sulphide to the solution of the salt (?). Like the corresponding cobalt compound the precipitate is almost entirely insoluble in very dilute, cold hydrochloric acid, and is easily soluble in concentrated nitric acid and in aqua regia. Hydrogen sulphide does not precipitate nickel salts if free mineral acid is present.

To the solution of the salt add bromine water and then sodium hydroxide solution (?). Treat the precipitate, after filtration, with hydrochloric acid (?).

When potassium nitrite and acetic acid are added to a dilute solution of a nickel salt no precipitate is formed. If the solution is very concentrated a brownish red substance is precipitated, which, however, does not correspond in composition to the cobalt compound precipitated under like conditions, and contains bivalent nickel. Its composition is $Ni(NO_2)_2.4KNO_2.$*

15.—BISMUTH.

Use Bismuth Nitrate.

Bismuth compounds mixed with sodium carbonate and heated on charcoal in the reducing flame of the blowpipe yield metallic bismuth and a dark yellow coating of bismuth trioxide.

Heat a small quantity of bismuth nitrate very carefully in a test tube; the residue is bismuth trioxide (?).

Add water to bismuth nitrate; the salt does not pass into solution, but is decomposed; heat and add dilute nitric acid, gradually, until solution is effected. The salt, though soluble in a very small quantity of water, is easily decomposed by more water; basic salt is precipitated and acid salt remains in solution. The composition of the basic salt precipitated is different under

* A mixture, soluble in water, and consisting of salts of any or all of the metals aluminium, chromium, manganese, iron, zinc, cobalt and nickel, should be given at this point for examination for those metals. Directions in Appendix II, Division 4, page 65.

different conditions. The following equation expresses a decomposition of this kind:

$$3Bi(NO_3)_3 + 3H_2O =$$

$$Bi{\overset{\diagup NO_3}{\underset{\diagdown OH}{\rule{0pt}{1em}-NO_3}}} + Bi{\overset{\diagup NO_3}{\underset{\diagdown OH}{\rule{0pt}{1em}-OH}}} + [Bi(NO_3)_3.3HNO_3].$$
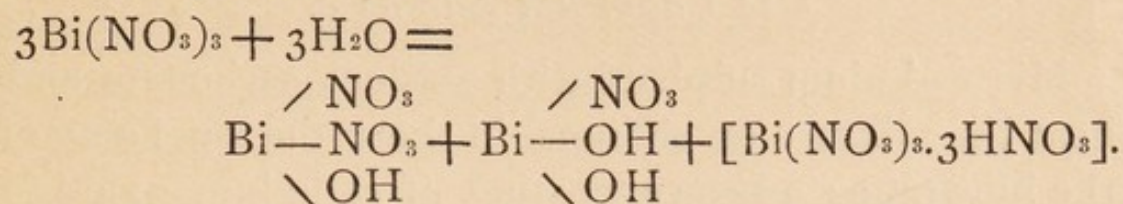
Use for the reactions below a solution prepared by dissolving the salt in water with the addition of a little dilute nitric acid.

To the solution of the salt add sodium hydroxide solution or ammonium hydroxide (?).

Introduce hydrogen sulphide into the solution of the salt (?). Filter, and then treat the precipitate with warm concentrated nitric acid; the bismuth passes into solution and sulphur is separated. The action of the nitric acid leads first to the formation of the nitrate of the metal, and to the separation of sulphur by oxidation, but some of the sulphur is then oxidized to sulphuric acid, and this changes some of the nitrate already formed to sulphate.

To a solution of stannous chloride add sodium hydroxide solution in quantity slightly more than sufficient to dissolve the substance which is at first precipitated; the solution contains the compound $Na_2Sn_2O_3$; now add a few drops of the solution of bismuth nitrate; a black precipitate of bismuth dioxide is formed. The tin compound is oxidized to Na_2SnO_3, while the bismuth compound is reduced:

$$4Bi(NO_3)_3 + Na_2Sn_2O_3 + 14NaOH =$$

$$4BiO + 2Na_2SnO_3 + 12NaNO_3 + 7H_2O.$$

This is a delicate test for bismuth.

16.—CADMIUM.

Use Cadmium Sulphate.

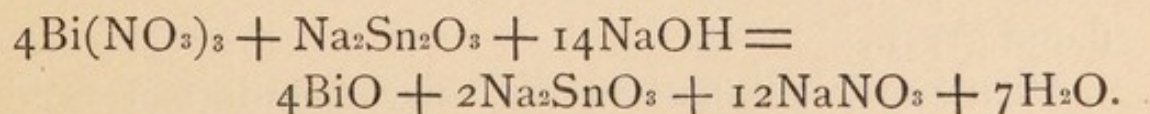Mix cadmium sulphate with sodium carbonate and heat the mixture on charcoal in the reducing flame of the blowpipe; a brown coating of cadmium oxide is formed.

To a solution of cadmium sulphate add sodium hydroxide solution (?).

To the solution of the salt add, gradually, ammonium hydroxide (?); on continuing to add the reagent the precipitate dissolves (?); on boiling this solution, if sufficiently dilute, the substance is reprecipitated (?).

Introduce hydrogen sulphide into the solution of the salt; yellow cadmium sulphide is precipitated (?). Filter, and then treat a portion of the precipitate with warm concentrated nitric acid; the acid acts on it as on the sulphide of bismuth; to the remainder of the precipitate add dilute sulphuric acid (1 part acid to 5 parts water) in considerable quantity, and boil; the sulphide passes into solution (?) (difference from copper); dilute this solution largely with water, and then introduce hydrogen sulphide; the sulphide is reprecipitated.

17.—COPPER.

Use Cupric Sulphate.

Hold some of the salt in the flame; it colors the flame green.

Heat cupric sulphate in the microcosmic salt bead in both the oxidizing flame and the reducing flame.

In the oxidizing flame the bead is colored green while hot, but on cooling it becomes blue; after heating in the reducing flame it appears, when cold, brownish-red and opaque.

Mix cupric sulphate with sodium carbonate and heat the mixture on charcoal in the reducing flame of the blowpipe; red metallic copper remains on the charcoal.

Add sodium hydroxide solution to a solution of the salt (?); add a sufficient quantity of the reagent for complete precipitation, and then boil; the precipitate becomes black (?). In presence of tartaric acid, sodium-potassium tartrate, glycerine and other organic compounds, alkaline hydroxides do not precipitate cupric salts. To a solution of cupric sulphate add sodium-potassium tartrate solution in considerable quantity, and then sodium hydroxide solution; the liquid assumes a deep blue color, but no precipitate is formed (owing to the formation of double tartrate of the alkali metals and copper, which is not decomposable by alkaline hydroxide). Reserve this solution for a future experiment.

Add ammonium hydroxide, gradually, to the solution of cupric sulphate; a bluish precipitate of basic salt is formed, which dissolves in excess of the ammonia, forming a dark blue liquid (delicate test for copper); from this solution crystals of the compound $CuSO_4.4NH_3.H_2O$ can be obtained under proper conditions.

Add sodium carbonate solution to a solution of the salt; basic carbonate is precipitated (?).

Introduce hydrogen sulphide into the solution of the salt (?). Warm concentrated nitric acid acts on the precipitate as on the sulphides of bismuth and cadmium.

To the solution of the salt add potassium ferro-cyanide solution; a precipitate of cupric ferrocyanide is formed (?) (the most delicate test for copper).

Introduce a piece of iron into a solution of the salt; the iron is coated with copper (?).

To the solution prepared by adding sodium-potassium tartrate and sodium hydroxide to cupric sulphate, add a few drops of a solution of grape-sugar, and heat; a yellow precipitate (cuprous hydroxide) is formed, which, on boiling, changes to red cuprous oxide, Cu_2O. Sodium hydroxide alone cannot precipitate the copper from the solution, but the grape-sugar which is added effects reduction, which leads to the precipitation in this form.*

18.—SILVER.

Use Silver Nitrate.

Silver compounds mixed with sodium carbonate and heated on charcoal in the reducing flame of the blow-pipe yield metallic silver.

To a solution of silver nitrate add sodium hydroxide solution; brown silver oxide is precipitated (?). When dry silver oxide is heated it easily decomposes into its constituents.

* A mixture, soluble in dilute hydrochloric acid, and consisting of salts of any or all of the metals cobalt, bismuth, cadmium and copper, should be given at this point for examination for those metals. Directions in Appendix II, Division 5, page 66.

To the solution of the salt add, gradually, ammonium hydroxide; the same precipitate is formed, but on continuing to add ammonium hydroxide it dissolves, the soluble compound $Ag_2O.2NH_3$ (fulminating silver) being formed.

To the solution of the salt add, gradually, potassium cyanide solution; a white, caseous precipitate is formed (?); on continuing to add potassium cyanide, this dissolves, forming the compound $KAg(CN)_2$.

Hydrochloric acid and soluble chlorides precipitate silver salts (?). To the solution of silver nitrate add sodium chloride solution; then add potassium cyanide solution; the precipitate dissolves (?). Silver chloride is soluble in sodium thiosulphate (?), and in ammonia. On exposure to the light, silver chloride first assumes a violet color, and finally becomes black.

Silver bromide and silver iodide, like silver chloride, are insoluble in water. How do these three compounds compare as regards solubility in ammonia?

Introduce hydrogen sulphide into the solution of silver nitrate (?). Warm concentrated nitric acid acts on silver sulphide as it does on the sulphides of bismuth, cadmium and copper.

Introduce a piece of zinc into the solution of silver nitrate; metallic silver separates (?).

19.—MERCURY.

Use Mercurous Nitrate and Mercuric Chloride.

Metallic mercury separates when most of the compounds of mercury are heated alone, and when any mercury compound is heated with sodium carbonate.

Mix mercuric chloride with sodium carbonate and heat the mixture in a hard glass test tube; mercury is deposited in the cooler part of the tube (?).

Add water to mercurous nitrate; complete solution is not effected, owing to the fact that water decomposes the salt, forming difficultly soluble basic salt. Filter, and use the filtrate for the following reactions, as a sufficient quantity will have passed into solution (complete solution could be effected by adding a few drops of dilute nitric acid and heating).

To the solution of mercurous nitrate add sodium hydroxide solution (?). On exposing the precipitate to the light, or on heating it suspended in water, it decomposes, mercury and mercuric oxide being formed (?).

Add ammonium hydroxide to a solution of the salt; a black precipitate is formed as in the above reaction, but its composition ($NH_2Hg_2NO_3$) is different (?).

To the solution of the salt add hydrochloric acid or a solution of a chloride (?). The white, caseous precipitate is insoluble in water and in cold, dilute acids. Add ammonium hydroxide; the precipitate turns black, NH_2Hg_2Cl being formed (?).

To the solution of the salt add potassium bromide solution (?).

To the solution of the salt add, gradually, potassium iodide solution (?); on continuing to add potassium iodide the precipitate decomposes, mercury is deposited, and the compound K_2HgI_4 is present in solution. (The mercuric iodide formed by the decomposition of the precipitate combines with potassium iodide to form this compound) (?).

Introduce hydrogen sulphide into the solution of the salt; the precipitate is a mixture of mercuric sulphide and mercury (?). Filter, and heat the precipitate with aqua regia; the mercury passes into solution (mercuric chloride being formed) and sulphur separates.

Most of the mercur*ic* salts, like mercur*ous* salts, have a tendency to form basic salts; mercuric chloride and mercuric cyanide are the chief exceptions; both of them dissolve in water without undergoing change.

To the solution of mercuric chloride add sodium hydroxide solution; a yellow precipitate is formed (?). What change takes place when dry mercuric oxide is highly heated (?).

To the solution of mercuric chloride add ammonium hydroxide; a white precipitate (NH_2HgCl) is formed (?).

Add potassium iodide solution, gradually, to a solution of the salt; a vermilion-red precipitate is formed (?), which dissolves on continuing to add potassium iodide (?).

Introduce hydrogen sulphide into mercuric chloride solution; a white precipitate ($HgCl_2.2HgS$) is formed, which by more hydrogen sulphide is gradually changed to black HgS. Aqua regia acts on this black precipitate in the same way, of course, as on the mixture of mercuric sulphide and mercury.

To the solution of mercuric chloride add, gradually, dilute stannous chloride solution; a white precipitate is formed (?), which becomes gray on continuing to add stannous chloride (?).

Introduce a piece of zinc or copper into the solution of either the mercurous salt or the mercuric salt (?).

20.—LEAD.

Use Lead Nitrate.

Lead compounds mixed with sodium carbonate and heated on charcoal in the reducing flame of the blow-pipe yield metallic lead and a yellow coating of lead oxide.

To a dilute solution of lead nitrate add, gradually, sodium hydroxide solution (?); on continuing to add the reagent the precipitate dissolves (?).

Add ammonium hydroxide to the solution of the salt; a similar precipitate is formed, which is insoluble in excess of ammonium hydroxide.

To the solution of the salt add sodium carbonate solution (?).

To the solution of the salt add dilute hydrochloric acid or a solution of a chloride (?). The precipitate is difficultly soluble in cold water and in dilute acids. Add water and boil; it dissolves easily.

To the solution of the salt add potassium bromide solution (?).

To the solution of the salt add potassium iodide solution (?). Filter, and dissolve the precipitate in boiling acetic acid; on cooling it crystallizes in characteristic, lustrous yellow scales.

Add potassium chromate solution to the solution of lead nitrate; yellow lead chromate is precipitated (?).

Add dilute sulphuric acid or a solution of a sulphate to lead nitrate solution (?). Filter, and dissolve the precipitate by treating it with ammonium acetate, containing an excess of ammonium hydroxide (prepared by mixing about equal volumes of strong ammonium

hydroxide and strong acetic acid); now add potassium chromate solution; the lead is precipitated as chromate. Lead sulphate is also soluble in hot sodium hydroxide solution, sodium plumbite being formed (?).

Introduce hydrogen sulphide into the solution of lead nitrate (?). Filter, and treat the precipitate with warm concentrated nitric acid; the acid acts on it as on the sulphides of bismuth, cadmium, copper and silver, but in this case, inasmuch as the lead sulphate is difficultly soluble, sulphate separates together with the sulphur.

Introduce a piece of zinc into the solution of the salt (?).*

21.—TIN.

Use Stannous Chloride and Stannic Chloride.

All tin compounds when mixed with sodium carbonate and heated on charcoal in the reducing flame of the blowpipe yield metallic tin.

A dilute solution of stannous chloride soon undergoes change; oxidation takes place, and the insoluble substance called metastannic acid is precipitated.

To a solution of stannous chloride add, gradually, sodium hydroxide solution; the compound $\begin{matrix} Sn—OH \\ >O \\ Sn—OH \end{matrix}$ is precipitated (?); on continuing to add the reagent the precipitate dissolves (?). The above hydroxide loses

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*A mixture of any or all of the salts cupric nitrate, silver nitrate, mercurous nitrate and lead nitrate should be given at this point for examination for copper, silver, mercury and lead. Directions in Appendix II, Division 6, page 67.

water as easily as does cupric hydroxide, and passes over into black stannous oxide.

When sodium carbonate solution is added to a solution of stannous chloride the above hydroxide is likewise precipitated (?).

Introduce hydrogen sulphide into the solution of the stannous salt; a brown precipitate is formed. This precipitate does not dissolve in ammonium sulphide (monosulphide). Filter, and treat it with ammonium polysulphide; it dissolves, forming ammonium sulphostann*ate* (?); add dilute hydrochloric acid to this solution; a yellow substance is precipitated (?).

Add dilute stannous chloride solution, gradually, to a solution of mercuric chloride, and note the formation of a white precipitate (?), which becomes gray when more stannous chloride is added (?).

A dilute solution of stannic chloride undergoes change, metastannic acid being precipitated. The decomposition is facilitated by heating the solution.

To a solution of stannic chloride add sodium hydroxide solution; stannic acid, H_2SnO_3, is precipitated (?). Stannic acid is soluble in excess of sodium hydroxide (?). Metastannic acid, referred to above, appears to be a polymeric modification of stannic acid; it is this substance which is produced when tin is treated with concentrated nitric acid. How does metastannic acid differ from stannic acid in properties?

When sodium carbonate solution is added to a solution of stannic chloride, stannic acid is likewise precipitated (?).

Introduce hydrogen sulphide into the solution of

the stannic salt; a yellow precipitate is formed (?). Filter, and treat a portion of this precipitate with ammonium sulphide (?); add dilute hydrochloric acid to the solution thus obtained (?); heat the other portion of the precipitate with concentrated hydrochloric acid; it dissolves (?).

Introduce a strip of zinc into a solution of either the stannous or the stannic salt; a spongy mass of tin separates, attaching itself to the zinc (?).

22.—ANTIMONY.

Use Antimony Trichloride and Metantimonic Acid.

Any antimony compound when mixed with sodium carbonate and heated on charcoal in the reducing flame of the blowpipe yields metallic antimony, which, when heated in the oxidizing flame, is gradually converted into antimony trioxide; some of this passes off as a white cloud, some is deposited as a white coating on the charcoal. Try the experiment with metantimonic acid, $HSbO_3$.

Add water to antimony trichloride; it does not pass into solution, but is decomposed by the water, insoluble basic salt being formed; dissolve this by adding hydrochloric acid and heating. Use this solution for the experiments below.

To some of the antimony trichloride solution add water; formation of insoluble basic salt takes place as before. The presence of tartaric acid or of mono-potassium tartrate prevents the decomposition by water (in the latter case, soluble potassium antimonyl

tartrate, $K.SbO.C_4H_4O_6$, is formed). To some of the solution add a solution of either tartaric acid or mono-potassium tartrate, and then add water; no precipitation takes place.

To the solution of antimony trichloride add, gradually, sodium hydroxide solution (?); on continuing to add the reagent the precipitate dissolves, sodium metantimonite, $NaSbO_2$, being formed (?).

Sodium carbonate solution added to a solution of the salt precipitates the same compound as the above.

Introduce hydrogen sulphide into the solution of the salt (?). Filter, and treat a part of the precipitate with ammonium sulphide; it dissolves, forming ammonium sulphantimonite (?); add dilute hydrochloric acid to this solution; the sulphide is reprecipitated (?) (if the precipitate is dissolved in ammonium *poly*sulphide, ammonium sulphantimon*ate*, $(NH_4)_3SbS_4$, is formed, and when this is treated with the dilute acid the penta-sulphide, Sb_2S_5, is precipitated); heat the remainder of the precipitate with concentrated hydrochloric acid; it dissolves (?).

When water is added to antimony pentachloride, precipitation takes place; basic chloride is first formed, and this is afterwards converted into antimonic acid. Add water to a few drops of antimony pentachloride. The precipitate dissolves on adding concentrated hydrochloric acid and heating. The presence of tartaric acid prevents the precipitation by water.

When sodium hydroxide solution is added to antimony pentachloride, metantimonic acid is precipitated (?). This acid is soluble in excess of sodium

hydroxide, sodium metantimonate being formed (?). Sodium carbonate likewise precipitates metantimonic acid (?).

For the experiments below use a solution of metantimonic acid in hydrochloric acid.

Introduce hydrogen sulphide into the solution (?). The substance precipitated dissolves in ammonium sulphide, forming ammonium sulphantimonate (?); when this solution is treated with dilute hydrochloric acid the sulphide is reprecipitated (?). When the sulphide is heated with concentrated hydrochloric acid, antimony trichloride is formed and sulphur separates (?).

Add some of the solution to potassium iodide solution; the liquid is colored red from separation of iodine,—hydriodic acid is oxidized, while the antimony is reduced from the antimonic to the antimonious condition.

Introduce some of the solution, or some of the solution of the trichloride, into a vessel in which a piece of platinum foil has been placed, and then add a piece of zinc; black, metallic antimony separates, and the platinum foil is coated with it. If some tin compound were present, tin would also be separated, but in the form of a spongy mass, attaching itself to the zinc.

When an antimony compound is introduced into a vessel containing zinc and dilute sulphuric acid it is reduced, and the gas hydrogen antimonide is formed. What is formed when this gas is burned (?); what change does it undergo when a tube through which it is passing is heated?

23.—ARSENIC.

Use Sodium Metarsenite and Sodium Arsenate.

Mix either sodium metarsenite or sodium arsenate with sodium carbonate and heat the mixture on charcoal in the reducing flame of the blowpipe; reduction takes place, and a peculiar odor like that of garlic is noticed. The odor is probably due to the presence of a very low oxide of arsenic.

Arsenic trioxide is difficultly soluble in water; in hydrochloric acid it is more easily soluble; it dissolves easily in solutions of the hydroxides or carbonates of the alkali metals, forming metarsenites.

Acidulate a solution of sodium metarsenite with dilute hydrochloric acid and conduct hydrogen sulphide into the solution; arsenic trisulphide is precipitated (?). Filter, and treat a part of the precipitate with ammonium sulphide (?); add dilute hydrochloric acid to the solution thus obtained (?). (If the precipitate is dissolved in ammonium *poly*sulphide, ammonium sulpharsen*ate* is formed, and when this is treated with the dilute acid the pentasulphide is precipitated.) Arsenic trisulphide does not dissolve in concentrated hydrochloric acid, but if potassium chlorate is added to the concentrated hydrochloric acid it does dissolve, arsenate being formed. Dissolve the remainder of the precipitate by heating with concentrated hydrochloric acid and a little potassium chlorate. Arsenic trisulphide is also soluble in a concentrated solution of ammonium carbonate.

To the solution of the metarsenite add cupric sulphate

solution; the compound $CuHAsO_3$ (Scheele's Green) is precipitated; add sodium hydroxide solution; the precipitate dissolves, and the solution is colored blue; heat the blue solution; red cuprous oxide is precipitated. The copper is thus reduced, while the arsenic is oxidized from the arsenious to the arsenic condition.

Acidulate a solution of sodium arsenate with dilute hydrochloric acid; heat, and then introduce hydrogen sulphide, keeping the solution hot while it is being treated with the gas; arsenic pentasulphide is slowly precipitated (?). (If hydrogen sulphide is introduced into the cold solution, reduction takes place, sulphur is precipitated and then arsenic trisulphide (?), though some pentasulphide is also formed.) After filtration, treat some of the arsenic pentasulphide with ammonium sulphide (?); what takes place when the solution thus obtained is treated with dilute hydrochloric acid (?). Concentrated hydrochloric acid does not dissolve arsenic pentasulphide; a mixture of the concentrated acid and potassium chlorate acts on it as on the trisulphide. Arsenic pentasulphide is also soluble in a concentrated solution of ammonium carbonate.

To the solution of the arsenate add ammonium chloride solution, ammonium hydroxide and magnesium sulphate solution; a white crystalline precipitate is formed (?). This precipitate is soluble in dilute acid and insoluble in ammonia.

To a solution of ammonium molybdate in nitric acid add two or three drops of the solution of the arsenate and heat gently; a yellow crystalline precipitate of ammonium arseno-molybdate is formed.

Arsenic compounds mixed with sodium carbonate and potassium cyanide and heated in a tube yield metallic arsenic, which is deposited on the cold part of the tube, forming a bright mirror. Try this with sodium metarsenite, using an arsenic tube.

A mixture of dilute sulphuric acid, zinc and an arsenic compound gives rise to the formation of hydrogen arsenide, which is closely similar to hydrogen antimonide; it burns with a flame somewhat different in color from the antimonide flame, forming arsenic trioxide and water, and it is decomposed when a tube through which it is passing is heated (?). A delicate test for arsenic,—one commonly used in cases of poisoning and known as Marsh's test,—consists in treating the substance, as above indicated, so that hydrogen arsenide will be formed if arsenic is present, and then examining the hydrogen compound (if formed), and also the metal formed by its decomposition, in order that there may be no doubt that it is hydrogen arsenide and not hydrogen antimonide. A number of tests are applied; for example, the tube is heated where the metal is deposited in order to ascertain whether the metal is easily volatilized (antimony is volatilized with difficulty, and not until it is first fused), and the metal is touched with a drop of hot nitric acid, when it passes into solution, if arsenic, or is converted into a white substance (antimony trioxide and metantimonic acid), if antimony.

The following is an exceedingly delicate test for arsenic: Introduce a very small quantity of sodium metarsenite, or sodium arsenate, and a piece of zinc

into a test tube, and then add dilute sulphuric acid; push a stopper of cotton wool into the mouth of the tube, and then cover the tube with a piece of filter paper in the center of which one drop of a strong solution of silver nitrate (one part of silver nitrate to one part of water) has just been placed; the spot of silver nitrate turns lemon yellow, and on its border a brownish black circle is formed. The blackening would gradually spread until it reached the center, but, before it has time to do so, put a little water on the yellow spot, when it instantly turns black. The yellow compound has the composition $AsAg_3.3AgNO_3$. It is decomposed by water, with separation of metallic silver, thus:

$$2(AsAg_3.3AgNO_3) + 3H_2O =$$
$$12Ag + 6HNO_3 + As_2O_3.*$$
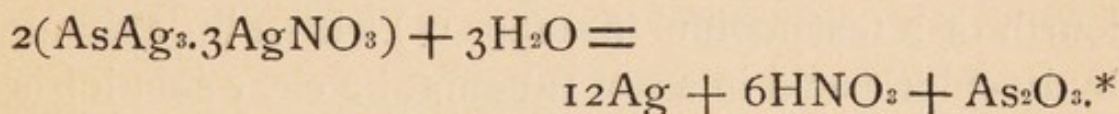
*A mixture of any or all of the compounds mercuric chloride, stannic chloride, metantimonic acid and arsenic trioxide should be given at this point for examination for mercury, tin, antimony and arsenic. Directions in Appendix II, Division 7, page 69.

Afterwards, a mixture, soluble in water or dilute hydrochloric acid, and containing compounds of any of the metals studied (no phosphate being present), should be given for examination for all the metals. Directions in Appendix II, Division 8, page 71.

APPENDIX I.

EXPERIMENT, INDICATING METHODS ADOPTED IN THE SEPARATION OF THE METALS.

Mix carefully very small quantities of each of the following compounds: Arsenic trioxide, bismuth nitrate, ferrous chloride, barium chloride, magnesium chloride, potassium nitrate (the ingredients should be finely pulverized). Heat some of this mixture (one-fourth of a teaspoonful is sufficient) with a little dilute hydrochloric acid in a test tube until a clear solution is obtained; dilute with water (if a precipitate appears on dilution dissolve it by adding a little dilute hydrochloric acid and heating); heat the solution, and conduct into it, while warm, a slow current of hydrogen sulphide, continuing until the liquid after being shaken and exposed to the air still retains the odor of hydrogen sulphide; the precipitate consists of the sulphides of arsenic and bismuth, these two elements being entirely removed from solution in this form. Filter, with the aid of a filter pump; remove the filtrate from the filter flask, retaining it for further examination, and then wash the residue on the filter paper at least three times with water (adding the water until it reaches the top of the filter paper each time, and waiting until it has entirely run through before adding the next

supply); * preserve the residue for subsequent separation of the arsenic and bismuth. Into the original filtrate from sulphides of arsenic and bismuth conduct hydrogen sulphide for a moment or two in order that there may be no uncertainty as to complete precipitation of the arsenic and bismuth; † if no precipitate is formed add to the solution ammonium chloride solution, an excess of ammonia, and then ammonium sulphide ; the precipitate is ferrous sulphide. Warm the contents of the vessel, and then filter and test the filtrate with a small quantity of ammonium sulphide ; if no precipitate is formed add to the liquid ammonia and ammonium carbonate solution, and heat until it boils ; the precipitate is barium carbonate. Filter, and test the filtrate with a small quantity of ammonium carbonate ; if no precipitate is formed add to the solution ammonia and di-sodium phosphate solution; the precipitate which forms, either at once or on shaking the tube, is ammonium-magnesium phosphate. Potassium is the only metal of the original mixture which still remains in solution. It is possible to separate this, also, in insoluble form, as will be pointed out in connection with one of the analyses which are to follow, though the method of procedure in such a case involves separation of the magnesium in a different form. It now remains to separate the arsenic and bismuth which were precipitated together as sulphides. This

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* All precipitates which are to be further examined should be thus carefully washed.

† It is advisable to always test filtrates in this way with the precipitating reagent.

may be done by the following process: Transfer the sulphides from the filter paper to a small flask, removing the last portions by means of a jet of water from a wash-bottle; allow the sulphides to settle, and then pour off as much of the water as possible; add ammonium polysulphide, digest thoroughly, and filter; brownish black bismuth sulphide remains on the filter paper; the arsenic is in solution in the filtrate; add to this filtrate dilute hydrochloric acid in excess; the arsenic is precipitated as sulphide.

The above experiment is a brief illustration of the process of precipitation of the metals by different reagents in the course of an analysis, and also (in the case of arsenic and bismuth) of the process of separation of elements precipitated together by the same reagent. There are a number of metals which, like arsenic and bismuth, are precipitated by hydrogen sulphide in acid solution, which, like iron, are precipitated by ammonia and ammonium sulphide, etc., and it is possible by the use of the proper reagents to thus divide all the metals which may be present in any solution into groups, the members of which may afterwards be separated from one another. The mixture just examined contained representative members of each of these groups. The following is a list of the members of the different groups (the rarer elements are omitted):

I. *Bismuth, Cadmium, Copper, Silver, Mercury, Lead, Tin, Antimony, Arsenic.*—Precipitated as sulphides by hydrogen sulphide in acid solution.

II. *Aluminium, Chromium, Manganese, Iron, Zinc, Cobalt, Nickel.*—Precipitated,—some as sulphides,

others as hydroxides, by ammonia and ammonium sulphide.

III. *Barium, Strontium, Calcium.*—Precipitated as carbonates by ammonium carbonate.

IV. *Magnesium only.*—Precipitated as hydroxide by barium hydroxide, as will be shown later.

V. *Potassium, Sodium.*—Precipitated separately by methods to be hereafter described.

It is, of course, important to use ammonium compounds as precipitating reagents instead of the corresponding compounds of sodium or potassium, in order to avoid the introduction of these metals into the solution. (The barium introduced as hydroxide for precipitation of magnesium would interfere with the remainder of the analysis, but it can be immediately removed by precipitation as carbonate by ammonium carbonate.) The presence of ammonium compounds in a mixture given for analysis can easily be detected by treatment of a separate portion of the substance in a manner to be described later.

Instead of studying the metals in the order above given it is more desirable to begin with the metals of the alkalies (group V) and to proceed in the order: groups III, IV, II, I. Such will be the order observed.

APPENDIX II.

DIVISION I.

Directions for Analysis indicated on Page 22.

Test for ammonium compounds by dissolving a small quantity of the substance, and treating a few drops of the solution with calcium hydroxide as directed in the chapter on ammonium sulphate.

If no ammonium compound is present dissolve some of the substance in water* and proceed as below; if such are present, first decompose the same by sharply heating a small quantity of the substance for a few minutes, in a porcelain crucible, with the Bunsen burner, then dissolve the residue in water and proceed. To five or six drops of the solution add several drops of chlorplatinic acid, and evaporate to a very small

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* If a specimen of a substance presented for analysis does not pass entirely into solution on boiling with water, it is best to try, next, dilute hydrochloric acid, then concentrated hydrochloric acid, then nitric acid (dilute and concentrated), then aqua regia,—always heating the solvent with the substance. (If preliminary examination has indicated the presence of silver, lead or mercury, nitric acid should be used at first, instead of hydrochloric.) Some substances are insoluble in any of the above solvents—for example, barium sulphate (which may be changed to carbonate by fusion with sodium carbonate, and the carbonate dissolved by treatment with hydrochloric acid), silver chloride, many silicates, etc., etc.

volume (a yellow precipitate which may appear on cooling shows the presence of potassium); add an equal volume of alcohol and let the solution stand for a few minutes in order that potassium remaining in solution may be precipitated. Filter (if a precipitate was formed), and evaporate the filtrate very nearly to dryness in a watch-glass on the water-bath; if sodium is present, small, yellow, needle-shaped crystals are deposited on cooling.

The presence of potassium and sodium may also conveniently be detected by adding to one portion of a concentrated solution of the substance (from which ammonium compounds have been removed) either tartaric acid or perchloric acid, and to another portion potassium metantimonate; a precipitate in the former case indicates potassium, in the latter sodium.

DIVISION 2.

Directions for Analysis indicated on Page 26.

To the solution of the substance add ammonium chloride, ammonium hydroxide and ammonium carbonate, and boil; a precipitate may contain barium, strontium and calcium. Filter, and reserve the filtrate; dissolve the precipitate in acetic acid, and add potassium chromate solution; if barium is present a yellow precipitate is formed. Filter, and add to the filtrate ammonium hydroxide and ammonium carbonate, and boil; a precipitate may contain strontium and calcium. Dissolve the precipitate, after filtration, in dilute nitric acid, and evaporate to dryness on the water-bath; add

to the residue a mixture of equal parts of alcohol and ether; if strontium is present the substance does not entirely dissolve. Filter, and evaporate the filtrate to dryness on the water-bath; a residue proves the presence of calcium.

Evaporate to dryness the filtrate from carbonates of barium, strontium and calcium, transfer the residue to a porcelain crucible and heat with the Bunsen burner to drive off ammonium salts; dissolve the residue in water, adding a few drops of dilute hydrochloric acid, if necessary, to facilitate solution; add an excess of barium hydroxide; if magnesium is present a precipitate is formed. Filter, and remove the barium present in solution by adding ammonia and ammonium carbonate, and boiling; filter, and evaporate the filtrate to dryness; transfer to a porcelain crucible and heat to drive off ammonium salts; dissolve the residue in water, and proceed to test for potassium by adding chlorplatinic acid as directed in Division 1.

DIVISION 3.

Directions for Analyses indicated on Page 36.

In the first of these substances phosphate is present, and before proceeding with the analysis the acidic constituent of the phosphate must be separated and removed. This is rendered necessary by the fact that when ammonium chloride, ammonium hydroxide and ammonium sulphide are added to a solution containing phosphate and the metals studied, there can be precipitated, in addition to hydroxides or sulphides of

some of these metals, the compounds aluminium phosphate, ammonium-magnesium phosphate and phosphates of barium, strontium and calcium. Having been convinced of the presence of phosphate by testing a small portion of the substance, proceed as follows: Place some of the substance in a porcelain dish; add about 30 to 35 cc. of concentrated nitric acid and a few pieces of granulated tin; after evaporation to dryness on the water-bath add hot water and filter; test a small portion of the filtrate to ascertain whether phosphate is now present. Complete separation having been effected, proceed, as follows, with the remainder of the filtrate.

Add ammonium chloride, ammonium hydroxide and ammonium sulphide; a precipitate may contain aluminium and chromium hydroxides, the sulphides of manganese, iron and zinc, and sulphur. Warm and filter; set the filtrate aside, and proceed to treat the precipitate as follows: Treat with cold, very dilute hydrochloric acid; this dissolves everything with the exception of sulphur; boil the solution with nitric acid to oxidize ferrous to ferric salt (having previously filtered, if necessary); the oxidation being complete (test by adding potassium ferricyanide to a sample of the solution) add ammonium chloride and then ammonium hydroxide; a precipitate may contain aluminium hydroxide, chromic hydroxide and ferric hydroxide. Filter; set the filtrate aside, and treat the precipitate as follows: Place it in a porcelain dish and dissolve in a little concentrated nitric acid; add a little potassium chlorate and boil for a few minutes; the oxidation of

the chromium causes the solution to assume the color of the chromate; add a little water and an excess of sodium hydroxide, and heat; iron remains precipitated. Filter; acidulate the filtrate with nitric acid, and then add an excess of ammonium hydroxide; aluminium is precipitated. Filter; acidulate the filtrate with acetic acid and add lead acetate solution; chromium is precipitated.

Acidulate the filtrate from the mixed hydroxides of aluminium, chromium and iron (which filtrate may contain zinc and manganese) with dilute hydrochloric acid; add sodium acetate, heat the solution to boiling and conduct hydrogen sulphide into it; zinc is precipitated. Filter; add sodium hydroxide until nearly all of the free acetic acid is neutralized; heat gently and add bromine water; on allowing the solution to stand manganese is gradually precipitated.

With the filtrate from the precipitate formed on adding ammonium chloride, ammonium hydroxide and ammonium sulphide proceed to the separation of barium according to the directions in Division 2.

The remainder of the substances given for analysis at this point do not contain phosphate. To solutions of these substances in water or dilute hydrochloric acid add, directly, ammonium chloride, an excess of ammonium hydroxide, and ammonium sulphide, and proceed as above.

DIVISION 4.

Directions for Analysis indicated on Page 38.

To a solution of the substance add ammonium chloride, ammonium hydroxide and ammonium sulphide; the precipitate may contain aluminium and chromium hydroxides, the sulphides of manganese, iron, zinc, cobalt and nickel, and sulphur. Warm and filter (the filtrate may be rejected since calcium, strontium, barium, magnesium, potassium and sodium are not present, otherwise it would be necessary to treat it, later, in accordance with the directions in Divisions 2 and 1); treat the precipitate with cold, very dilute hydrochloric acid; the aluminium, chromium, manganese, iron and zinc pass into solution.* Filter, and reserve the filtrate; dissolve the precipitate in concentrated nitric acid, and evaporate the solution to a small volume; neutralize with sodium carbonate solution, add potassium nitrite solution in considerable quantity, and several drops of acetic acid; allow the solution to stand for 24 hours; cobalt is precipitated. Filter, and

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* Since the sulphides of cobalt and nickel are not entirely insoluble in the dilute acid, traces of these metals may pass into solution; such traces are precipitated in the course of an analysis at the point at which zinc sulphide is usually precipitated alone, imparting a gray or black appearance to a precipitate which would otherwise be white. The zinc may be separated from these traces of cobalt and nickel by dissolving the sulphides in nitric acid and adding an excess of sodium hydroxide and filtering; the zinc, which is present in the filtrate as sodium zincate, may be reprecipitated as sulphide by hydrogen sulphide.

add an excess of sodium hydroxide to the filtrate; nickel is precipitated as green nickelous hydroxide.

The filtrate above, which may contain aluminium, chromium, manganese, iron and zinc, is now to be boiled with nitric acid to oxidize ferrous to ferric salt, and further treated as directed in Division 3.

DIVISION 5.

Directions for Analysis indicated on Page 42.

Dissolve the substance by heating with a little dilute hydrochloric acid, and then dilute with water (basic bismuth chloride may be precipitated on dilution with water, but this makes no difference, as the subsequent treatment with hydrogen sulphide converts this into bismuth sulphide); heat; introduce hydrogen sulphide; a precipitate may contain bismuth, cadmium and copper. Filter, and reserve the filtrate; treat the precipitate with warm concentrated nitric acid; the metals pass into solution, and sulphur separates, which may be blackened by minute particles of sulphides. Dilute with water and filter; add an excess of ammonium hydroxide; bismuth is precipitated (if, at the same time, the solution turns blue, copper is present in solution). Filter, add an excess of dilute hydrochloric acid, and then heat the solution and introduce hydrogen sulphide; a precipitate may contain cadmium and copper. Filter; add to the precipitate dilute sulphuric acid in considerable quantity, and boil for a short time; black cupric sulphide remains undissolved. Filter, dilute the filtrate largely with water, and then

introduce hydrogen sulphide; a yellow precipitate is cadmium sulphide.

With the filtrate from the precipitate formed when hydrogen sulphide was introduced into the solution of the original substance proceed to the separation of cobalt by adding ammonium chloride, ammonium hydroxide and ammonium sulphide, as directed in Division 4.

DIVISION 6.

Directions for Analysis indicated on Page 47.

If the substance does not dissolve in water, dissolve it by adding about two or three drops of dilute nitric acid and heating (this small quantity of nitric acid will not interfere with the analysis); add to the solution about three or four drops of dilute hydrochloric acid; if either a mercurous compound, a silver compound or a lead compound is present, a precipitate is formed on adding the hydrochloric acid,* but the subsequent treatment with hydrogen sulphide will convert any chloride thus precipitated into sulphide; now heat the solution somewhat, if not already warm, and introduce hydrogen sulphide; the precipitate may

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* The addition of sufficient hydrochloric acid to the cold solution would precipitate all of the silver and mercur*ous* mercury and a part of the lead (lead chloride is somewhat soluble in cold water and in dilute acids), and in this precipitate separation could be effected by first boiling with water, which dissolves the lead chloride, and then treating the residue with warm aqua regia, which dissolves the mercurous chloride. The removal of the precipitate formed by hydrochloric acid and its treatment in this way is, however, entirely unnecessary.

contain copper, silver, mercury and lead. Filter (the
filtrate may be rejected since no metals were present in
the original solution other than those precipitated thus
by hydrogen sulphide, otherwise it would be necessary
to treat it, later, in accordance with the directions in
Division 4 and those preceding); treat the precipitate
with warm concentrated nitric acid; copper, silver and
lead pass into solution, while an undissolved residue
may contain mercury and some of the lead (in the form
of lead sulphate). Add a little water, filter, and
reserve the filtrate; treat the residue with ammonium
acetate containing an excess of ammonium hydroxide.
Filter, and add potassium chromate to the filtrate; if
lead is present in this filtrate a yellow precipitate is
formed; heat the residue insoluble in the ammonium
acetate with aqua regia, and evaporate to dryness on
the water-bath; heat the residue with water, filter, and
add stannous chloride, gradually, to the filtrate; the
formation of a white precipitate, which turns gray on
adding more of the reagent, proves the presence of
mercury. Instead of stannous chloride, potassium
iodide may be added to the filtrate, which produces a
red precipitate if mercury is present.

To the filtrate above, which may contain copper,
silver and lead, add dilute sulphuric acid, and evapo-
rate until heavy white fumes of sulphuric acid are given
off; now dilute with water; an undissolved residue, or
a precipitate formed on adding the water, is lead sul-
phate. Filter, and add hydrochloric acid to the filtrate;
if silver is present a precipitate is formed. Filter, and
proceed to examine the filtrate for copper by adding

an excess of ammonium hydroxide as directed in Division 5. (Inasmuch as the substance did not contain bismuth there is no precipitation, in this case, when ammonia is added, but if copper is present the solution of course turns blue.)

DIVISION 7.

Directions for the first Analysis indicated on Page 55.

Dissolve the substance by heating with a little dilute hydrochloric acid; dilute largely with water, and introduce hydrogen sulphide into the warm solution; the precipitate may contain mercury, tin, antimony and arsenic. Filter (the filtrate may be rejected since no metals were present in the original solution other than those precipitated thus by hydrogen sulphide, otherwise it would be necessary to treat it, later, in accordance with the directions in Division 4 and those preceding); add ammonium polysulphide to the precipitate and digest thoroughly; this reagent dissolves, of course, only the sulphides of tin, antimony and arsenic. Filter (if there is an undissolved residue), keep the residue for subsequent examination, and proceed to treat the filtrate as follows: Add an excess of dilute hydrochloric acid; a colored precipitate may contain tin, antimony and arsenic. (If only a white, milky precipitate is formed it consists of sulphur, and neither of these metals is present.) Filter, and then heat the precipitate for a short time with a little concentrated hydrochloric acid; a yellow undissolved residue contains arsenic. Dilute with water; filter; reserve the

filtrate (which may contain tin and antimony), and prove that the yellow compound contains arsenic, in the following manner: Heat it for a short time with concentrated hydrochloric acid and a little potassium chlorate; the arsenic passes into solution; add to this solution ammonium chloride, an excess of ammonium hydroxide, and magnesium sulphate; a white crystalline precipitate is formed. Place the above filtrate, which may contain tin and antimony, in a porcelain dish containing a piece of platinum foil and a piece of zinc; tin and antimony, if present, are gradually separated, the platinum being covered with a black coating of antimony. When the reduction is completed pour off the clear liquid carefully from the metals, and then add to the latter a little concentrated hydrochloric acid, and heat; tin passes into solution as stannous chloride, and the balance of the zinc dissolves, but antimony remains undissolved. Test for tin by diluting with water, filtering, and adding the filtrate to a small quantity of mercuric chloride solution; if tin is present a white precipitate is formed, and if the quantity of tin is sufficient this white precipitate changes, of course, to gray when more of the filtrate is added.

If the substance given for examination had to be tested for the metals bismuth, cadmium, copper, silver and lead, in addition to mercury, tin, antimony and arsenic, the next step would be to treat that portion of the hydrogen sulphide precipitate which did not dissolve in ammonium polysulphide with warm concentrated nitric acid, proceeding, then, as further directed in Divisions 6 and 5, but inasmuch as the

residue in this case can contain no other metal besides mercury, it is only necessary to prove the presence of mercury by heating with aqua regia, evaporating to dryness on the water-bath, and treating the residue with stannous chloride as directed in Division 6.

DIVISION 8.

Directions for the second Analysis indicated on Page 55.

If the substance is soluble in water, add to the solution a small quantity of dilute hydrochloric acid, heat, and then introduce hydrogen sulphide and proceed as further directed in Division 7 and those preceding.

If the substance is insoluble in water, dissolve by heating with a small quantity of dilute hydrochloric acid, then dilute with water, introduce hydrogen sulphide into the warm solution and proceed as above.