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A TREATISE
ON
CHEMISTRY AND CHEMICAL
ANALYSIS

PREPARED FOR STUDENTS OF
THE INTERNATIONAL CORRESPONDENCE SCHOOLS
SCRANTON, PA.

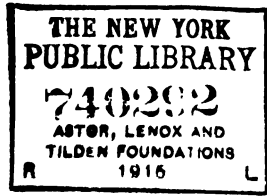
Volume III

QUALITATIVE ANALYSIS
WITH PRACTICAL QUESTIONS AND EXAMPLES

First Edition

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ROY W. B.
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QUALITATIVE ANALYSIS.

(PART 1.)

INTRODUCTORY.

DEFINITIONS AND DESCRIPTIONS.

1. Analysis.—Analysis in its most general sense is the process of resolving more or less complex substances into simpler ones. It is, therefore, the reverse of synthesis, which consists in building up complex compounds from simpler ones. Analysis consists in breaking these compounds up into their component parts.

It is divided into *qualitative* and *quantitative analysis*.

Qualitative analysis is that branch of chemical science which considers the methods of determining the elements that compose a compound or mixture of compounds, without reference to the quantities of these elements which the substance contains.

Quantitative analysis takes up the subject where qualitative analysis leaves it, and determines the exact amount of each element in a substance.

2. Methods of Qualitative Analysis.—There are two methods of qualitative analysis, known as the wet method and the dry method. The *wet method*, as its name implies, deals with solutions, while the *dry method* deals with solids. In most cases, separate quantities of these solids may be put into solution, by methods to be described later, and to these portions the wet method may also be applied.

§ 10

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Each method has its advantages. The dry method is short and simple in many instances, requires but little apparatus, and, in case of some of the simpler substances, quickly yields a result. Its use is almost indispensable in some cases, but in many instances it only gives indications, which must be confirmed by the wet method.

The wet method has the advantage that it is almost universally applicable, and its results are absolutely certain if the work of obtaining them is properly done.

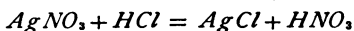
It is best to treat these two methods separately, so far as possible, in describing them and in the early part of the work, but after the student becomes familiar with them he will find it a great advantage to combine the two.

3. Abbreviations Used.—In analytical work, certain words occur so frequently that it is an advantage to use abbreviations for them. The following is a list of the most common ones used in this Course:

Ppt.—precipitate.	Conc.—concentrate.
Pptd.—precipitated.	Dil.—dilute.
Sol.—soluble.	O. F.—oxidizing flame.
Insol.—insoluble.	R. F.—reducing flame.
Sp. Gr.—specific gravity.	

4. Reaction and Reagent.—A *reaction* is a chemical change, and the substance that produces this change is called a *reagent*.

ILLUSTRATION.—If a small quantity of silver nitrate solution be placed in a test tube and a few drops of hydrochloric acid added, a white precipitate of silver chloride is formed according to the equation:



This change is called a reaction, and the hydrochloric acid, which produced the change, is a reagent.

The attention of the student is called to the fact that when a reagent is added to a metallic solution, the metallic compound formed is similar in composition to the reagent. Thus, if the reagent is a hydrate, a hydrate of the metal will be produced; a carbonate will form a carbonate of the metal; a sulphide produces a sulphide of the metal, etc. All

exceptions to this rule are given under "Department of the Metals with Reagents."

5. The Wet Method.—In wet analysis we determine the constituents of a solution of a substance by the reactions produced by certain common reagents. If there is but one metal in the solution, this becomes a very simple matter.

About half an inch of the solution to be tested is placed in a test tube and a small amount of the reagent is carefully added, drop by drop, while the place where the two liquids meet is closely watched. If no precipitate is formed, the test tube is emptied, washed well with common water, and rinsed out with distilled water. We are then ready to use a fresh portion of the solution and test in the same way with another reagent. *A dirty test tube must never be used. Neatness is essential in all successful analytical work.*

If we obtain a precipitate, the first thing to be noted is its color and general appearance. Its solubility may also help to establish its identity. If we wish to test its solubility in an excess of the reagent used to precipitate it, we pour out all but a small portion, and to this add more of the reagent. To test for its solubility in any other reagent, allow the precipitate to settle to the bottom of the tube as much as possible, pour off the supernatant liquid, retaining but a small quantity of the precipitate in the tube; to this add the desired reagent, shake it up, and observe the result.

By observing the reactions of a few common réagents and referring to the section on "Department of the Metals with Reagents," we can readily tell just what metal we have.

ILLUSTRATION.—If we add a few drops of hydrogen sulphide to a small quantity of a solution in a test tube and get a black precipitate, we know the metal is either silver, lead, mercurous, mercuric, or copper, for these are the only metals giving black precipitates with hydrogen sulphide. If to a fresh portion of the solution we add sodium hydrate and get a brown precipitate, we know the metal is silver, for that is the only one, of the five metals mentioned, that gives a brown precipitate with sodium hydrate.

When a result is obtained in this way it should always be confirmed by the other reactions given for the metal,

6. It will be noted that some of the metals form two series of compounds which differ widely from each other. Thus, mercury forms mercurous and mercuric compounds, which, in analytical chemistry, are treated as though they were salts of different metals.

APPARATUS NEEDED.

7. The only apparatus needed for the wet reactions, when there is but one metal in the solution, will be some test tubes, a set of reagents in properly labeled bottles, and a good burner. A Bunsen burner is preferable for this purpose, but where gas is not available, an alcohol lamp may be made to serve in its stead.

It is desirable that the student should become familiar with a few dry reactions in connection with the wet ones, and for this purpose he will need a blowpipe, a small piece of charcoal, a piece of platinum wire, a piece of platinum foil, a pair of forceps, a piece of blue glass, and, as the work proceeds, closed tubes, or matrasses, will be required.

8. **The Burner.**—A Bunsen burner, shown in Fig. 1, is made with a perforated metal cylinder *g* near the base, for regulating the air supply. In cases where the blowpipe is not used, a full supply of air is admitted, giving a non-luminous flame.

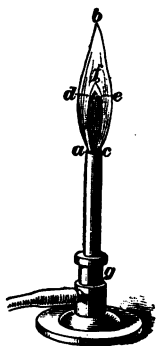


FIG. 1.

This consists of three parts: (1) An inner zone of unburned gas mixed with air, as seen at *afc*; (2) the outer mantle of burning gas mixed with an excess of air, shown at *abc*; and (3) the luminous cone *dfe*.

The different parts of this flame have two opposite effects. In the inner flame, the unburned gas, rich in carbon and hydrogen, tends to reduce the substance, while the outer flame, by heating the substance in the presence of the oxygen of the air, tends to oxidize it.

A substance to be reduced should be held in the luminous cone *dfe*, as reduction is most rapidly accomplished here.

A substance to be oxidized should be held just within the flame at *b*, as this is the point of most rapid oxidation. These points are meant when the reducing and oxidizing flames are mentioned.

If a substance is merely to be heated, it is held in the flame near the top, as this is the position of greatest heat. Some substances are volatilized and give a characteristic color to the flame, by which they may be recognized. For this purpose the substance is held in the lower part of the outer mantle *a b c*.

9. The Blowpipe.—By means of the blowpipe we obtain an intensely heated flame, which may be directed where we wish. There are several forms of blowpipe, the simplest being a small curved brass tube, terminating in an orifice about the size of a small needle. With this instrument, after blowing a while, the moisture which accumulates is blown into the flame. Several forms of blowpipe have been devised to avoid this. A good form is shown in Fig. 2. It consists of five parts. The mouthpiece *A* is usually made of hard rubber, and is pressed against the lips when in use. It fits into the tube *B*, which in turn is fitted into the moisture reservoir *C*. The tip holder *D* fits into the side of the moisture reservoir, and the tip *E* fits on to this.

In using the blowpipe it is often necessary to blow a steady stream of air through it for several minutes, and the student should practice until he can do this before attempting any of the following operations. To accomplish this, the mouthpiece is pressed against the lips, and the cheeks inflated. Then, by means of the muscles of the cheeks, a steady stream of air is forced through the blowpipe, while we breathe through the nostrils. The air

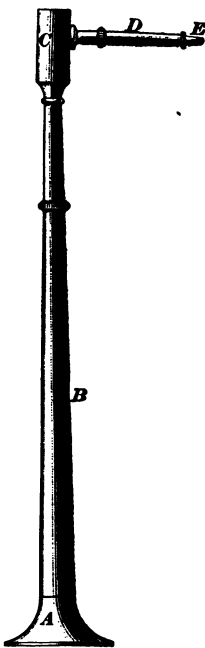


FIG. 2.

should never be forced from the lungs, as by this means we cannot keep up a steady stream. This operation may seem difficult at first, but by practice it will soon become easy.

In blowpipe work a rather small, luminous flame, obtained by turning the metal cylinder so as to reduce the supply of air, is used, and from this we can obtain either an oxidizing or reducing flame, according to the method of using the blowpipe. By placing the tip of the blowpipe just outside

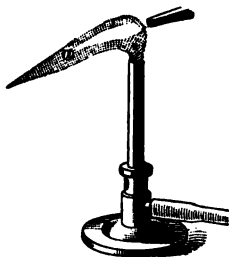


FIG. 3.

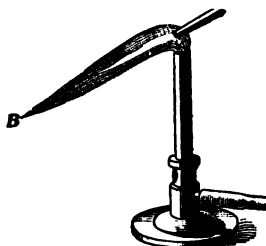


FIG. 4.

of the flame and blowing, we get a long, slightly luminous flame. A substance held at *a*, Fig. 3, is rapidly reduced by the unburned gas.

To get an oxidizing flame, the tip of the blowpipe should be placed just inside of the flame. Then, by blowing through it, a long, blue flame is obtained which will rapidly oxidize a substance held at the point *B*, Fig. 4, where it is intensely heated in the presence of an excess of air.

10. Charcoal.—In blowpiping, a small piece of fine-grained charcoal, made from soft wood, is largely used as a support. Common charcoal is very unsatisfactory, but the small blocks, for sale by all chemical dealers, are very good for this purpose. A small cavity is made in the charcoal, to hold the substance, and, after using, it must be well scraped out before the next operation.

11. Platinum Wire.—A short piece of fine platinum wire is essential in working by the dry method. It is well to heat one end of a small glass tube in the flame until it softens and begins to close; then, without

FIG. 5.

withdrawing it from the flame, insert one end of the wire and allow the glass to close over it, thus forming a handle which does not readily transmit heat. The result is shown in Fig. 5. The other end of the wire should be bent into a loop about $\frac{1}{2}$ inch in diameter.

This loop will serve to hold solid substances in the flame, to hold a drop of solution in the flame in order to observe if any color is thus imparted to it, and to hold the borax, or microcosmic bead, to be described later.

When not in use, it is a good plan to place the wire in dilute hydrochloric acid. Then, after burning it off, it is nearly always clean and ready for use. A good method of keeping the wire clean is to insert the glass handle in the perforation of a cork that is too large to go into a test tube, and by this means suspend the wire in a test tube containing hydrochloric acid, as shown in Fig. 6.



FIG. 6.

12. A small piece of platinum foil, which may be bent into the form of a spoon, and a pair of forceps with which to hold the foil, need no description. It is only necessary to say that platinum must never be heated in contact with the heavy metals, such as lead, mercury, etc., or their salts, for these will alloy with the platinum and ruin it.



FIG. 7.

13. Blue Glass.—A small piece of blue glass, which the operator may hold before his eye to look through at the colored flames produced by some of the metals, is indispensable when determining the alkalies.

14. Matrasses.—Closed tubes, or matrasses, are much used in analyzing solids, and may as well be described here. They are made in several forms. A good form may be made by cutting a piece of glass tubing, having an inside diameter of about $\frac{3}{16}$ of an inch,

into pieces about $3\frac{1}{2}$ inches long, and holding one end of each piece in the flame till it softens and closes. The result is shown in Fig. 7.

Solids may be dropped into this tube and heated at the closed end, by holding it in the flame. To protect the fingers from the heat, the tube may be held in the forceps, or a piece of paper may be folded and wrapped around it near the top, thus serving as a holder.

REAGENTS.

15. Preparation of Solutions.—In the outfit that we furnish to students, all reagents except nitric, hydrochloric, and sulphuric acids, and ammonium hydrate—or ammonia, as it is commonly called—are of the proper strength for use. Those mentioned are needed in two strengths, concentrate and dilute. The student is furnished with the concentrate solutions, and from these he can make the dilute solutions by adding a small portion of each to four times its volume of water, and mixing them well. The sulphuric acid must be added to the water slowly while the solution is constantly stirred, on account of the heat generated. In this, as in every case where water is mentioned, distilled water should be used. When a reagent is mentioned, the dilute solution is always meant unless the concentrate solution is specified.

For the benefit of students that do not obtain our outfit, the following directions are given for making up reagents:

Chemically pure substances should be used in every case.

Ammonium Carbonate.—Dissolve 100 grams of the solid in 300 cubic centimeters of water and 100 cubic centimeters of concentrate ammonium hydrate, and dilute to 500 cubic centimeters with water.

Ammonium Chloride.—Dissolve 100 grams of the dry salt in a sufficient amount of water—say 400 cubic centimeters—and then add water to make 500 cubic centimeters of solution.

Ammonium Oxalate.—Add to 25 grams of the salt,

sufficient water to make 500 cubic centimeters of solution. Allow it to stand until it dissolves, shaking it occasionally.

Sodium Hydrate.—Dissolve 40 grams of the solid in water, and dilute this solution to 500 cubic centimeters with water.

Sodium Carbonate.—Dissolve 100 grams of the dry salt, or 270 grams of the crystals, in sufficient water to make 500 cubic centimeters of solution.

Sodium Phosphate.—Dissolve 50 grams of acid sodium phosphate $Na_2HPO_4 \cdot 12H_2O$ in sufficient water to make 500 cubic centimeters of solution.

Potassium Chromate.—Dissolve 50 grams in water and add water to this solution to make it up to 500 cubic centimeters.

Potassium Ferricyanide.—To 50 grams of the solid, add water enough to make 500 cubic centimeters of solution.

Potassium Ferrocyanide and Potassium Cyanide.—These are made of the same strength and in the same manner as potassium ferricyanide.

Potassium Iodide.—Dissolve 20 grams of the crystallized salt in 500 cubic centimeters of water.

Barium Chloride.—Dissolve 25 grams of the solid in 500 cubic centimeters of water.

Silver Nitrate.—Dissolve 20 grams of the crystals in 500 cubic centimeters of water.

Lead Acetate.—Dissolve 50 grams of the dry salt in water to which 1 cubic centimeter of acetic acid has been added, using water enough to make 500 cubic centimeters of the solution.

Mercuric Chloride.—Dissolve 25 grams of the crystals in 500 cubic centimeters of water.

Stannous Chloride.—Dissolve 25 grams of the solid stannous chloride in 75 cubic centimeters of concentrate hydrochloric acid, and enough water to make 500 cubic centimeters of solution. Some metallic tin should be kept in the solution, which should be kept in a tightly stoppered bottle.

Ferrous Sulphate.—To 75 grams of the crystals, add

water enough to make 500 cubic centimeters of solution. To this add about 1 cubic centimeter of concentrate sulphuric acid and a little metallic iron, and keep the solution from the air.

Cobalt Nitrate.—Dissolve 50 grams of the crystallized salt in water, and dilute the solution to 500 cubic centimeters with water.

Tartaric Acid.—Dissolve 100 grams of the solid tartaric acid in water sufficient to make 500 cubic centimeters of solution.

Acetic Acid.—Dilute the 33-per-cent. acid with twice its volume of water to make the dilute acid.

Hydrogen Sulphide.—Generate the gas as described in Experiment 50, Art. 105, *Inorganic Chemistry*, Part 1, and lead it into water until the water is saturated, when it is ready for use. The solution should be protected from the air.

Ammonium Sulphide.—Lead hydrogen-sulphide gas into a bottle two-thirds full of concentrate ammonium hydrate, until it is saturated, which is indicated by the bubbles coming through the liquid undiminished in size. Fill the bottle with concentrate ammonia and mix it well. Before using, dilute this with twice its volume of water.

Yellow Ammonium Sulphide.—This is made by adding a small quantity of flowers of sulphur to the common ammonium sulphide and shaking until dissolved. Enough sulphur should be added to give the solution an amber color.

Ammonium Sulphate.—Dissolve 50 grams of the solid ammonium sulphate in sufficient water to make 500 cubic centimeters of solution. Its principal use is in separating strontium and calcium.

Magnesium Sulphate.—Dissolve 50 grams of the crystallized salt in water enough to make 500 cubic centimeters of the solution.

Calcium Sulphate.—A saturated solution is always used. It is prepared by repeatedly shaking up some finely powdered calcium sulphate in a bottle of water, taking care to have more of the sulphate than the water will dissolve.

Allow it to stand for some time and decant the clear liquid for use.

Barium Hydrate.—To 25 grams of pure barium-hydrate crystals, add sufficient water to make 500 cubic centimeters of solution, and dissolve by the aid of heat. Filter into a bottle provided with a good stopper, and close the bottle at once to protect the solution from the air. The filtration is performed as directed in Art. 99, *Theoretical Chemistry*.

Acid Sodium Tartrate.—A saturated solution is used. It is prepared by placing in a bottle, about three-fourths filled with water, a little more of the solid salt than will be dissolved, and shaking repeatedly. Allow it to settle, and decant the clear solution as it is needed.

Ammonium Molybdate.—This may be made by dissolving 25 grams of powdered ammonium molybdate in 75 cubic centimeters of concentrate ammonia, by the aid of heat. Pour this solution slowly, and with constant stirring, into a mixture of 300 cubic centimeters of concentrate nitric acid and 200 cubic centimeters of water. This solution should be allowed to stand for at least 24 hours before using.

The directions in most cases are given for making 500 cubic centimeters, merely because that is a convenient quantity. More or less of any reagent may just as well be made, provided the proportions are not altered.

DEPARTMENT OF THE METALS WITH REAGENTS.

INTRODUCTORY.

16. We now come to the *deportment*, or *behavior*, of the metals with reagents. The student should not attempt to commit all these reactions to memory, but should make himself so familiar with them that he can readily distinguish any of the metals by their reactions. For this purpose only a

few reactions will generally be necessary, but the results thus obtained should always be confirmed by all the others given.

So far as possible, it is desirable to perform each of the following operations, using known solutions before attempting to analyze unknown ones.

The student will soon learn to form groups of the metals that are precipitated by the different reagents; as, for instance, he will learn that only three metals, silver, lead, and mercury, in the mercurous form, are precipitated by hydrochloric acid; five by sulphuric acid, etc. In this he will be assisted by the table at the end of this section.

Each student should keep, in a note book, a complete record of all work done. It is especially important that anything that is not understood at the time should be recorded in this book.

SILVER.

17. Silver is a white metal that fuses on the charcoal before the blowpipe, forming a bright, metallic globule. It does not volatilize, and no incrustation* is formed. To perform this and similar operations, a piece of the metal, about twice as large as the head of a pin, is placed in a small cavity in the charcoal, made to hold it, and the blowpipe flame is directed upon it. In all blowpipe work, only small quantities of the substance treated must be used. Silver is only very slowly acted upon by hydrochloric acid, forming insoluble silver chloride $AgCl$. It dissolves slowly in dilute sulphuric acid, forming silver sulphate, and dissolves very readily in nitric acid, forming silver nitrate $AgNO_3$.

This solution may be used for the silver reactions, but it is best to make a solution for this purpose from silver-nitrate crystals. In the case of each of the metals, directions are given for making a solution. Of course, any other solution would give the same reactions, but the solution given is most easily made, and is in the form in which we are most likely to find the metal in actual analysis.

* By an incrustation is meant a deposit on the charcoal surrounding, or near, the substance heated.

A silver solution may be made by dissolving about 2 grams of silver-nitrate crystals in 100 cubic centimeters of water and adding a drop or two of nitric acid. The acid is best added by means of a dropper, which may be made by drawing out a glass tube, and cutting it as shown in Fig. 35, *Theoretical Chemistry*. When the small end of this tube is dipped into the liquid, the liquid, of course, enters it, and may be retained in the tube by pressing the finger closely upon the upper end. If the finger is removed, the liquid will be released, and by this means we can get any amount of liquid we wish.

18. Reactions.—A silver solution gives the following reactions:

1. *Ammonium hydrate*, if added in very small amount to a rather strong neutral solution of silver that does not contain ammonium compounds, precipitates brown silver oxide Ag_2O , which is very soluble in an excess of the reagent. As silver oxide is very soluble in ammonia, and its formation is prevented by the presence of ammonium compounds, no precipitate is usually obtained. Most silver solutions contain free acid, hence, when ammonia is added, ammonium compounds are formed, which prevent the formation of a precipitate.

2. *Sodium hydrate* precipitates brown silver oxide Ag_2O , which is insoluble in an excess of the reagent, but very soluble in ammonia.

3. *Ammonium carbonate* precipitates white silver carbonate Ag_2CO_3 , which is easily soluble in excess.

4. *Sodium carbonate* gives a white precipitate of silver carbonate Ag_2CO_3 , which is insoluble in excess, but is readily soluble both in nitric acid and ammonia.

5. *Hydrogen sulphide* precipitates black silver sulphide Ag_2S , which is not easily dissolved in cold dilute acids, but soluble in boiling dilute nitric acid.

6. *Ammonium sulphide* gives the same precipitate as hydrogen sulphide. It may be well at this point to state that in every case where hydrogen sulphide gives a precipitate,

ammonium sulphide gives the same. The reverse, however, is not true, as we shall see later.*

7. *Hydrochloric acid* precipitates white silver chloride $AgCl$, which slowly changes to brown upon exposure to sunlight. It is insoluble in nitric acid, but is readily soluble in ammonium hydrate, from which solution it is reprecipitated by nitric acid.

8. *Copper* deposits metallic silver from its solutions. If a small piece of copper be dropped into a silver solution, it soon becomes gray, owing to the silver that is deposited on it. Upon rubbing, it becomes bright.

9. *Sodium phosphate* precipitates yellow silver phosphate Ag_3PO_4 , which is soluble in both nitric acid and ammonium hydrate.

10. *Potassium cyanide* precipitates white silver cyanide $AgCN$, which is soluble in excess of the reagent and in ammonium hydrate, but insoluble in nitric acid.

LEAD.

19. Lead is a soft, white metal when freshly cut, but soon tarnishes in the air. It fuses easily on the charcoal before the blowpipe, giving the flame a pale, bluish tinge, and depositing a yellow incrustation of the oxide PbO on the charcoal. This incrustation is volatile, and may be driven from place to place on the charcoal by directing the blowpipe flame upon it.

Lead is only slightly acted upon by hydrochloric or sulphuric acid. It is best dissolved by adding a little concentrate nitric acid and then an equal volume of water and heating if necessary.

A solution of the nitrate $Pb(NO_3)_2$ may be made by dissolving about 3 grams of the solid lead nitrate in 100 cubic

* The reason for this is that sulphides of some of the metals are not precipitated from acid solutions, but are precipitated from alkaline ones. Ammonium sulphide, being a strong alkali, renders the solution alkaline, and the precipitate is formed.

centimeters of water and adding a drop or two of nitric acid.

20. Reactions.—A lead solution gives the following reactions:

1. *Ammonium hydrate* precipitates white lead hydrate $Pb(OH)_2$, which is insoluble in excess of the reagent.

2. *Sodium hydrate* precipitates white lead hydrate $Pb(OH)_2$, which is easily soluble in excess of the reagent, forming a solution of $Pb(ONa)_2$.

3. *Ammonium carbonate* precipitates white basic lead carbonate of varying composition.

4. *Sodium carbonate* gives the same precipitate as ammonium carbonate.

5. *Hydrogen sulphide* precipitates black lead sulphide PbS , which is insoluble in dilute acids and alkalies when cold, but is dissolved in boiling dilute nitric acid. Hot concentrate nitric acid converts it into white insoluble lead sulphate. If we wish to obtain this white sulphate, there must be no liquid present to dilute the acid.

6. *Ammonium sulphide* gives the same reactions as hydrogen sulphide.

7. *Hydrochloric acid* precipitates white lead chloride $PbCl_2$, which is slightly soluble in cold, and readily soluble in hot, water. If this hot solution be allowed to cool, the lead chloride separates in long, white crystals.

8. *Sulphuric acid* precipitates white lead sulphate $PbSO_4$, which is nearly insoluble in dilute acids, but may be dissolved by adding tartaric acid and then a slight excess of concentrate ammonia, and heating.

9. *Potassium chromate* precipitates yellow lead chromate $PbCrO_4$, which is soluble in sodium hydrate, from which solution it is reprecipitated by nitric acid.

10. *Potassium iodide* precipitates yellow lead iodide PbI_2 , which is soluble in boiling water. Upon cooling, it separates from this solution in yellow crystals.

11. *Potassium cyanide* precipitates white lead cyanide $Pb(CN)_2$, which is insoluble in excess of the reagent, but is soluble in nitric acid.

MERCURY.

21. Mercury is a heavy, white liquid. It is but slightly acted upon by hydrochloric or sulphuric acid, but dissolves readily in nitric acid. It forms two series of compounds, known as *mercurous* and *mercuric*. When mercury is dissolved in the cold, in dilute nitric acid, if there is an excess of mercury present, mercurous nitrate $Hg_2(NO_3)_2$ is obtained. If it is dissolved in an excess* of hot concentrate nitric acid, mercuric nitrate $Hg(NO_3)_2$ is formed.

These solutions could be properly diluted and used for the reactions, but it is better to make up solutions as directed later.

MERCUROUS COMPOUNDS.

22. A solution for the mercurous reactions may be made by adding to 4 grams of solid mercurous nitrate 100 cubic centimeters of water, and about 1 cubic centimeter of dilute nitric acid; then add a few drops of metallic mercury, and heat gently, if necessary. A high temperature must be avoided, and some metallic mercury should remain in the solution, or it is likely to be partly changed to a mercuric compound.

23. Reactions.—A mercurous solution gives the following reactions:

1. *Ammonium hydrate* precipitates black amido-mercurous nitrate $Hg_2NH_4NO_3$ from this solution. The precipitate is insoluble in an excess of the reagent.

2. *Sodium hydrate* precipitates black mercurous oxide Hg_2O , which is insoluble in an excess of the reagent.

* By an excess of a reagent is meant more than is required to accomplish a certain object. When we speak of precipitating a metal with an excess of a certain reagent, we mean to use more of the reagent than would be required to unite with the metal to form a precipitate. To render an alkaline solution acid, with an excess of a certain acid, we would use more of that acid than would be required to neutralize the alkali. When we say that a precipitate is soluble in an excess of a reagent, we mean that when more of the reagent than is required to form the precipitate is added, it dissolves the precipitate at first formed.

3. *Ammonium carbonate* gives a white precipitate, which rapidly changes to gray, and finally to black, upon standing.

4. *Sodium carbonate* gives a white precipitate, more or less colored with yellow, owing to the fact that mercurous solutions nearly always contain small quantities of mercuric compounds. The carbonate precipitates are not important in determining mercurous compounds.

5. *Hydrogen sulphide* precipitates black mercuric sulphide HgS together with some free mercury. The precipitate is not dissolved by any dilute acid, but dissolves slowly in hot concentrate hydrochloric acid, and readily in aqua regia.

In this and similar operations, where aqua regia is used as a solvent, add to a small quantity of the substance a half-dozen drops of concentrate nitric acid, and then from two to three times as much concentrate hydrochloric acid, and heat if necessary. This mixture of concentrate acids is known as aqua regia. It acts as a powerful solvent, dissolving many substances that are not attacked by ordinary acids. It is the only solvent for gold and platinum.

Boiling concentrate nitric acid converts the black mercuric sulphide into a white, insoluble compound. The same precautions must be taken as described in Art. 20, 5.

6. *Hydrochloric acid* precipitates white mercurous chloride Hg_2Cl_2 , which is insoluble in cold dilute acids, is slightly acted upon by hot concentrate acids, and is readily dissolved by aqua regia. Ammonia converts this white chloride into black amido-mercurous chloride Hg_2NH_4Cl .

7. *Potassium chromate* precipitates brick-red basic mercurous chromate, which dissolves with difficulty in nitric acid.

8. *Potassium iodide* in very small quantities precipitates yellowish-green mercurous iodide Hg_2I_2 . If a little more of the reagent is added and it is allowed to stand, the precipitate changes into metallic mercury and bright-red potassium mercuric iodide $HgI_2(KI)_2$.

9. *Sulphuric acid* precipitates white mercurous sulphate Hg_2SO_4 , which is dissolved with some difficulty in nitric acid.

10. *Stannous chloride*, when added in a very small amount,

precipitates white mercurous chloride Hg_2Cl_2 . A little more of the reagent partly reduces this, giving a gray mixture of mercurous chloride and metallic mercury. An excess of stannous chloride reduces the whole to a dark-gray, almost black, precipitate of finely divided metallic mercury. The white precipitate is seldom seen, but the gray mixture usually is formed at once.

11. *Sulphurous acid* precipitates gray metallic mercury.

12. *Copper*, when placed in a mercurous solution, precipitates metallic mercury, which forms a gray coating on the copper. This may be rendered bright by rubbing with a dry cloth, and is driven off by heat.

MERCURIC COMPOUNDS.

24. The solution of mercuric nitrate, which is obtained when mercury is dissolved in an excess of hot concentrate nitric acid, may be used for the following reactions, after having the excess of acid evaporated off, and being properly diluted with water; or a solution for the purpose may be made by diluting some of the mercuric-chloride solution used as a reagent with a little more than its own volume of water and adding 2 or 3 drops of hydrochloric acid. But it is best to make up a solution for this purpose by dissolving about 2 grams of dry mercuric nitrate in 100 cubic centimeters of water to which 2 or 3 drops of concentrate nitric acid have been added.

25. Reactions.—A mercuric solution gives the following reactions:

1. *Ammonium hydrate* precipitates white amido-mercuric nitrate $HgNH_2NO_3$, which is somewhat soluble in an excess of the reagent, and is readily dissolved by acids.

2. *Sodium hydrate* precipitates a brown basic salt, if a very small quantity of the reagent is used. If more of the reagent is added, yellow mercuric oxide HgO is formed. This is easily dissolved by warm dilute acids.

3. *Ammonium carbonate* produces a white precipitate, which is soluble in ammonia and in acids.

4. *Sodium carbonate* precipitates a reddish-brown basic carbonate, probably $HgCO_3 \cdot 3HgO$.

5. *Hydrogen sulphide* gives a white precipitate when a very small amount of reagent is added. If we continue to add the reagent, the precipitate changes to yellow, reddish-brown, and finally to black HgS . The white precipitate at first formed is $2HgS, Hg(NO_3)_2$, and this mixed with the black HgS , in varying proportions, probably causes the intermediate colors. The black HgS is insoluble in alkalies, and in the acids used separately, but is dissolved by aqua regia.

6. *Ammonium sulphide* gives the same precipitate as hydrogen sulphide.

7. *Potassium iodide* precipitates red mercuric iodide HgI_2 , which is soluble in excess of the reagent.

8. *Stannous chloride* precipitates, at first, white mercurous chloride Hg_2Cl_2 . An excess of the reagent reduces this to gray metallic mercury.

9. *Copper* precipitates the mercury from mercuric solutions the same as from mercurous ones.

COPPER.

26. Copper is a rather hard metal, with a peculiar red color. It is malleable and ductile, and fuses with difficulty. It is scarcely attacked by hydrochloric or sulphuric acid, but is readily dissolved in nitric acid. A good solution for the following reactions is made by dissolving from $1\frac{1}{2}$ to 2 grams of copper-sulphate crystals $CuSO_4 \cdot 5H_2O$ in 100 cubic centimeters of water, and adding a drop or two of dilute sulphuric acid.

27. Reactions.—A copper solution gives the following reactions:

1. *Ammonium hydrate* precipitates a light-blue basic compound, which is very soluble in excess, giving the

solution a deep-blue color, owing to the formation of a soluble basic copper-ammonium sulphate.

2. *Sodium hydrate* precipitates light-blue copper hydrate $\text{Cu}(\text{OH})_2$, which is insoluble in an excess of the reagent, but soluble in ammonia and in acids. The precipitate is changed by boiling into black, hydrated copper oxide, probably $2\text{CuO}, \text{Cu}(\text{OH})_2$.

3. *Ammonium carbonate* gives the same reaction as ammonium hydrate.

4. *Sodium carbonate* precipitates blue basic copper carbonate $\text{CuCO}_3, \text{Cu}(\text{OH})_2$, which is converted into black, hydrated copper oxide by boiling.

5. *Hydrogen sulphide* precipitates black copper sulphide CuS , which is easily soluble in warm nitric acid or potassium cyanide.

6. *Ammonium sulphide* gives the same precipitate as hydrogen sulphide.

7. *Potassium cyanide* precipitates greenish-yellow copper cyanide $\text{Cu}(\text{CN})_2$, which is easily soluble in excess of the reagent, forming a colorless solution. The copper is not precipitated from this solution by hydrogen sulphide.

8. *Potassium ferrocyanide* precipitates reddish-brown copper ferrocyanide $\text{Cu}_2\text{Fe}(\text{CN})_6$, which is insoluble in dilute acids.

9. If a small piece of solid copper chloride, or a drop of the solution, supported on the loop of a platinum wire, be held in the flame of a Bunsen burner, it imparts a blue color to the flame, while the other volatile compounds of copper color the flame green.

10. *Iron*, when placed in a copper solution, slowly becomes coated with the copper. If the solution is strong and slightly acid, this action becomes quite rapid.

CADMIUM.

28. Cadmium is a white, rather soft metal, which easily fuses on the charcoal before the blowpipe, depositing a brown incrustation of the oxide CdO , which is volatile, and

may be driven from place to place on the charcoal by directing the blowpipe flame upon it. Cadmium is slowly dissolved in hydrochloric or sulphuric acid, but is much more readily dissolved by nitric acid, giving a solution of cadmium nitrate $Cd(NO_3)_2$. This solution may be used for the reactions, after boiling off the excess of acid and diluting with water, but it is better to make a solution for this purpose by dissolving about 2 grams of cadmium nitrate crystals in 100 cubic centimeters of water and adding a drop of nitric acid.

29. Reactions.—A cadmium solution gives the following reactions:

1. *Ammonium hydrate* does not usually give a precipitate in ordinary cadmium solutions, but if a single drop of dilute ammonia is added to a rather strong neutral solution, a white precipitate of cadmium hydrate $Cd(OH)_2$ is obtained. This precipitate is very soluble in ammonia, and its formation is prevented by the presence of ammonium salts.

2. *Sodium hydrate* precipitates white cadmium hydrate $Cd(OH)_2$, which is insoluble in excess of the reagent.

3. *Ammonium carbonate* precipitates white cadmium carbonate $CdCO_3$, which is quite readily dissolved in an excess of the ordinary reagent, owing to the ammonia which it contains. The precipitate would be but slightly attacked by the carbonate alone.

4. *Sodium carbonate* precipitates white cadmium carbonate $CdCO_3$, which is insoluble in excess of the reagent, but soluble in ammonia, potassium cyanide, and acids. Heating the solution aids in the formation of the precipitate.

5. *Hydrogen sulphide* precipitates yellow cadmium sulphide CdS , which is insoluble in cold dilute acids, ammonia, ammonium sulphide, and potassium cyanide, but is dissolved by boiling dilute acids.

6. *Ammonium sulphide* gives the same reaction as hydrogen sulphide.

7. *Potassium chromate* precipitates yellow basic cadmium chromate, which is insoluble in sodium hydrate, but is dissolved by nitric acid.

8. *Potassium cyanide* does not ordinarily produce a precipitate, but forms a soluble double cyanide of potassium and cadmium $Cd(CN)_2(KCN)_2$, from which yellow cadmium sulphide (CdS) may be precipitated by hydrogen sulphide.

BISMUTH.

30. Bismuth is a rather hard, brittle metal, having a white color with a slightly reddish tinge. It fuses easily on the charcoal before the blowpipe, forming a metallic globule, and depositing a yellow incrustation of bismuth oxide Bi_2O_3 . It is not attacked by dilute hydrochloric and sulphuric acids, but is readily dissolved in nitric acid, forming bismuth nitrate $Bi(NO_3)_3$. This solution may be used for the reactions, after diluting with water and keeping just enough nitric acid present to hold the salt in solution; or, we may make a solution for the purpose by dissolving about 2 grams of bismuth nitrate in about 1 cubic centimeter of dilute nitric acid, and 15 or 20 cubic centimeters of water. If this does not form a clear solution after heating, add nitric acid, a few drops at a time, until it clears up. Then dilute to 100 cubic centimeters with water. If a precipitate forms during dilution, add just nitric acid enough to dissolve it.

31. Reactions.—A bismuth solution gives the following reactions:

1. *Ammonium hydrate* precipitates white bismuth oxyhydrate $BiOOH$, which is insoluble in excess, but soluble in warm hydrochloric or nitric acid.

2. *Sodium hydrate* gives the same reaction as ammonium hydrate.

3. *Ammonium carbonate* precipitates white basic bismuth carbonate $Bi_2O_3CO_2$, which is insoluble in excess of the reagent.

4. *Sodium carbonate* gives the same reaction as ammonium carbonate.

5. *Hydrogen sulphide* precipitates dark-brown bismuth sulphide Bi_2S_3 , which is insoluble in cold dilute acids, and

in ammonium sulphide, but is dissolved by boiling nitric acid.

6. *Ammonium sulphide* gives the same reaction as hydrogen sulphide. In concentrate solutions these precipitates look almost black.

7. *Potassium chromate* precipitates yellow basic bismuth chromate $\text{Bi}_2\text{O}(\text{CrO}_4)_2$, which is insoluble in sodium hydrate, but readily soluble in nitric acid; hence, in solutions which contain much free acid, no precipitate is formed.

8. *Stannous chloride*, in an excess of sodium hydrate, precipitates black bismuth oxide Bi_2O_3 . To get this precipitate, add sodium hydrate to a little stannous chloride until the precipitate at first formed is dissolved in excess. Then, to this solution, add a little of the bismuth solution, a drop at a time.

9. *Water*, in a large quantity, precipitates white bismuth oxynitrate BiONO_3 , from solutions that are not too strongly acid. To perform this operation, a test tube is nearly filled with water, and 2 or 3 drops of the bismuth solution are added to it. If this solution is not too strongly acid, a precipitate will be formed almost immediately. If it does not appear in a few seconds, a little ammonium chloride should be added, when, if the solution does not contain a large amount of acid, a precipitate will form.

ANTIMONY.

32. Antimony is a hard, brittle, bluish-white metal, which easily fuses on the charcoal before the blowpipe, depositing a white volatile incrustation of antimony oxide Sb_2O_3 , while dense white fumes of this oxide are given off.

Antimony is oxidized but is not dissolved by nitric acid, and hydrochloric acid scarcely attacks it at all, but it is dissolved in aqua regia. A solution for the following reactions is best made by dissolving a trifle more than a gram of the dry antimony chloride SbCl_3 in hydrochloric acid and water and diluting to 100 cubic centimeters. Just enough

acid should be added to dissolve the salt, and hold it in solution.

33. Reactions.—An antimony solution gives the following reactions:

1. *Ammonium hydrate* precipitates white antimonious oxyhydrate $SbOOH$, which is insoluble in excess of the reagent.

2. *Sodium hydrate* precipitates white antimonious oxyhydrate $SbOOH$, which is easily dissolved by an excess of the reagent.

3. *Ammonium carbonate* precipitates white antimonious oxyhydrate $SbOOH$, which is but slightly soluble in excess of the reagent.

4. *Sodium carbonate* gives the same reaction as ammonia.

5. *Hydrogen sulphide* precipitates orange-red antimonious sulphide Sb_2S_3 , which is insoluble in cold dilute acids, but soluble in hot concentrate hydrochloric acid, sodium hydrate, or ammonium sulphide.

6. *Ammonium sulphide* precipitates orange-red antimonious sulphide Sb_2S_3 , which is soluble in excess of the reagent. From this solution the antimonious sulphide is reprecipitated by hydrochloric acid.

7. *Zinc*, when placed in a strongly acid solution of antimony, precipitates the antimony as a black powder. If a piece of platinum foil is placed in the solution in contact with the zinc, the antimony will be deposited upon it, making a black stain. This precipitate is insoluble in hydrochloric acid.

8. *Water*, in large excess, precipitates white antimonious oxychloride $SbOCl$. This precipitate is obtained in the same manner as the precipitate which water gives with bismuth (see Art. 31, 9).

ARSENIC.

34. Arsenic is a dark-gray, brittle solid, which easily volatilizes on the charcoal before the blowpipe, without fusing, yielding a white incrustation, and white fumes of

the oxide As_2O_3 , which have a characteristic garlic odor. Care must be taken not to inhale large quantities of these fumes, as they are poisonous.

Arsenic is not readily dissolved by any single acid, but aqua regia dissolves it easily, forming arsenic acid. It forms two oxides, As_2O_3 and As_2O_5 , which are *acid*, while oxides of the metals are *basic*. There are two series of compounds: arsenites, which are *arsenious* compounds; and arsenates, which are *arsenic* compounds.

ARSENIOUS COMPOUNDS.

35. A solution of sodium arsenite is the best for the general reactions. It is made by dissolving about 1 gram of sodium arsenite Na_2HAsO_3 in 100 cubic centimeters of water.

36. Reactions.—An arsenious solution gives the following reactions:

1. *Hydrogen sulphide* gives no precipitate if the solution is neutral, but generally gives the solution a yellow color. If a little hydrochloric acid is now added, a yellow precipitate of arsenious sulphide As_2S_3 is at once formed, which is soluble in ammonia, ammonium sulphide, or ammonium carbonate, but is insoluble in hydrochloric acid, even when concentrate.

2. *Ammonium sulphide* gives no precipitate in neutral or alkaline solutions, but if a little hydrochloric acid is added to the solution, yellow arsenious sulphide As_2S_3 is formed, which is readily soluble in excess of $(NH_4)_2S$, or in ammonia, but is insoluble in hydrochloric acid.

3. *Silver nitrate* gives a slight, almost white precipitate in neutral solutions, but, if a little ammonia is added, light-yellow silver arsenite Ag_3AsO_3 is formed. A little more ammonia dissolves the precipitate, as will also nitric acid.

4. *Copper sulphate* precipitates green copper arsenite $CuHAsO_3$, which is soluble in acids and in ammonia.

5. *Copper*, when placed in an arsenious solution to which considerable hydrochloric acid has been added, becomes coated with a gray film of copper arsenide Cu_3As_2 upon boiling.

ARSENIC SOLUTIONS.

37. A good solution for the arsenic reactions is made by dissolving about 1 gram of sodium arsenate Na_2HAsO_4 in 100 cubic centimeters of water.

38. **Reactions.**—An arsenic solution gives the following reactions:

1. *Hydrogen sulphide* gives no precipitate with neutral solutions, but if considerable hydrochloric acid is added, the hydrogen sulphide slowly reduces the arsenic solution to arsenious, and yellow arsenious sulphide As_2S_3 is formed. This reaction is greatly helped by heating the solution. If the hydrogen-sulphide solution is very weak, it reduces the solution slowly, so that the reaction only takes place after some time, or may even fail entirely; but when a current of hydrogen-sulphide gas is led through the solution, the reaction takes place immediately. The As_2S_3 is soluble in ammonia and ammonium sulphide; but a little free sulphur, thrown out* during the reduction, usually remains in the solution, giving it a milky appearance. From this solution As_2S_3 is reprecipitated by hydrochloric acid.

2. *Ammonium sulphide* gives no precipitate with neutral solutions, but if sufficient hydrochloric acid is added, a yellow precipitate of arsenic sulphide As_2S_3 is formed.

3. *Silver nitrate*, when added to neutral arsenate solutions, produces a characteristic reddish-brown precipitate of silver arsenate Ag_3AsO_4 , which is soluble in nitric acid and in ammonia.

4. *Magnesium sulphate*, under proper conditions, precipitates white crystalline, magnesium-ammonium arsenate $MgNH_4AsO_4 \cdot 6H_2O$, which is soluble in nitric acid. To get

* The term "thrown out" means that an element is liberated from its compounds, and remains undissolved in a solution.

this precipitate, a little magnesium-sulphate solution is placed in a test tube, and precipitated with an excess of ammonia. Just enough ammonium chloride is added to dissolve the precipitate thus formed, and a little of this solution is added to a little arsenate solution in another test tube. If the solutions are dilute, the precipitate forms slowly, but is hastened by vigorous shaking.

TIN.

39. Tin is a soft, white, malleable metal that fuses easily on the charcoal before the blowpipe, forming a metallic globule and a slight, white incrustation. It is not readily dissolved in the acids separately, but is dissolved in aqua regia, forming a mixture of stannous and stannic chlorides. Hot concentrate hydrochloric acid slowly dissolves it to a solution of stannous chloride SnCl_2 .

STANNOUS COMPOUNDS.

40. A solution for the stannous reactions is conveniently made by adding 5 cubic centimeters of concentrate hydrochloric acid and 15 cubic centimeters of water to $1\frac{1}{2}$ grams of stannous chloride and heating till it dissolves. If the solution appears milky after heating, add 5 cubic centimeters of hydrochloric acid and heat again, when it will clear up. Dilute this solution to 100 cubic centimeters with water.

41. Reactions.—A stannous solution will give the following reactions:

1. *Ammonium hydrate* precipitates white stannous hydrate $\text{Sn}(\text{OH})_2$, which is insoluble in excess of the reagent.
2. *Sodium hydrate* precipitates white stannous hydrate $\text{Sn}(\text{OH})_2$, which is soluble in excess of the reagent.
3. *Ammonium carbonate* precipitates white stannous hydrate $\text{Sn}(\text{OH})_2$, which is insoluble in excess of the reagent.
4. *Sodium carbonate* gives the same reaction as ammonium carbonate.

5. *Hydrogen sulphide*, when added to solutions containing much free acid, at first colors the liquid brown, but if more is added, a brown precipitate of stannous sulphide SnS is formed. If but little free acid is present, the brown precipitate is formed at once.

6. *Ammonium sulphide* precipitates brown stannous sulphide SnS . The brown stannous sulphide precipitated by hydrogen or ammonium sulphide is soluble in yellow ammonium sulphide. Hydrochloric acid precipitates yellow stannic sulphide SnS_2 from this solution. Yellow ammonium sulphide is made by adding sulphur, in the form of powder, to common ammonium sulphide and shaking till it is dissolved. It is a polysulphide of varying composition.

42. Stannous chloride acts as a reducing agent; that is, it tends to change reducible compounds to a lower state of oxidation, while it is changed to a stannic compound. Its reaction with mercuric compounds (Art. 25, 8) is a good example of this.

STANNIC COMPOUNDS.

43. A solution of stannic chloride $SnCl_4$ may be used for the stannic reactions. It is prepared by dissolving about $1\frac{1}{2}$ grams of stannous chloride in 5 cubic centimeters of concentrated hydrochloric acid and 15 cubic centimeters of water. Heat this to boiling and add potassium chlorate, a little at a time, until the solution becomes distinctly yellow. Then boil till the solution becomes clear, and the potassium chlorate will have oxidized the stannous to stannic chloride. After diluting to 100 cubic centimeters the solution is ready for use.

44. **Reactions.**—A stannic solution gives the following reactions:

1. *Ammonium hydrate* precipitates white stannic oxyhydrate, generally called metastannic acid $SnO(OH)_2$, which is insoluble in excess of the reagent.

2. *Sodium hydrate* precipitates white stannic oxyhydrate $\text{SnO}(\text{OH})_2$, which is soluble in excess of the reagent and in acids.

3. *Ammonium carbonate* precipitates white stannic oxyhydrate $\text{SnO}(\text{OH})_2$, which is insoluble in excess of the reagent, but soluble in acids.

4. *Sodium carbonate* gives the same reaction as ammonium carbonate.

5. *Hydrogen sulphide* precipitates light-yellow stannic sulphide SnS_2 , which is soluble in hot concentrate hydrochloric acid and in ammonium sulphide. From the solution in ammonium sulphide, it is reprecipitated by hydrochloric acid.

6. *Ammonium sulphide* precipitates yellow stannic sulphide SnS_2 , which is easily dissolved by an excess of the reagent. Hydrochloric acid reprecipitates it from this solution.

7. *Zinc* precipitates all the tin from both stannous and stannic solutions that contain an excess of hydrochloric acid, in the form of a dark-gray powder.

45. All compounds of tin, when mixed with sodium carbonate and placed on the charcoal before the blowpipe, are easily reduced to a bright metallic globule.

IRON.

46. Iron is a gray, hard, tenacious metal that is only fused at very high temperatures. It corrodes quite readily in the air, forming oxides. It forms two series of compounds, known as ferrous and ferric. It is easily dissolved by hydrochloric, sulphuric, or nitric acid.

FERROUS COMPOUNDS.

47. For the reactions, a solution of ferrous sulphate is the best. It is made by dissolving about 2 grams of the crystals in 100 cubic centimeters of water to which half a

cubic centimeter of concentrate sulphuric acid is added. This solution should be used when fresh, as all ferrous solutions are oxidized to ferric in the air.

48. Reactions.—A ferrous solution gives the following reactions:

1. *Ammonium hydrate* precipitates green ferrous hydrate $Fe(OH)_2$. Upon standing in the air for some time, this is partially oxidized and assumes a reddish-brown color.

2. *Sodium hydrate* precipitates light-green ferrous hydrate $Fe(OH)_2$, which is insoluble in excess. On standing in the air, its color changes to dark green and finally to reddish brown, owing to oxidation to ferric hydrate $Fe(OH)_3$, by the oxygen of the air.

3. *Ammonium carbonate* precipitates white ferrous carbonate $FeCO_3$, which almost immediately assumes a green color, and upon standing in the air becomes a reddish brown, owing to the formation of ferric hydrate.

4. *Sodium carbonate* gives the same reaction as ammonium carbonate.

5. *Hydrogen sulphide* does not precipitate iron or any of the following metals from acid solutions. Ferric solutions frequently, and some of the others more rarely, throw out free sulphur, giving the solution a milky appearance.

6. *Ammonium sulphide* precipitates black ferrous sulphide FeS , easily dissolved by hydrochloric or sulphuric acid.

7. *Potassium ferrocyanide* precipitates blue potassium ferrous ferrocyanide $K_4Fe_2(CN)_6$.

8. *Potassium ferricyanide* precipitates deep-blue ferrous ferricyanide $Fe_2Fe(CN)_{12}$, which is insoluble in dilute acids.

FERRIC SOLUTIONS.

49. Ferric solutions may be obtained by dissolving metallic iron in nitric acid, by oxidizing a ferrous salt by means of an oxidizing agent, such as nitric acid or potassium chlorate, or by dissolving a ferric salt, such as ferric chloride, in water, with the addition of a few drops of acid. A good

way to prepare a solution for the reactions is to dissolve about $1\frac{1}{2}$ grams of ferrous sulphate crystals in from 25 to 50 cubic centimeters of water, and heat to boiling. To this boiling solution add a few drops of concentrate nitric acid, and continue the boiling till the solution becomes a clear yellow, adding a few more drops of nitric acid, if necessary, to produce this change. The nitric acid completely oxidizes the iron in hot solutions.

50. Reactions.—A ferric solution gives the following reactions:

1. *Ammonium hydrate* precipitates reddish-brown ferric hydrate $Fe(OH)_3$, which is insoluble in excess of the reagent, but soluble in acids.

2. *Sodium hydrate* gives the same reaction as ammonium hydrate.

3. *Ammonium carbonate* precipitates reddish-brown ferric hydrate $Fe(OH)_3$, and CO_2 is set free. The precipitation is aided by boiling.

4. *Sodium carbonate* gives the same reaction as ammonium carbonate.

5. *Ammonium sulphide* reduces ferric compounds to ferrous, and precipitates black ferrous sulphide FeS . Hydrochloric acid dissolves this readily, leaving the free sulphur, thrown out during reduction, in the solution.

6. *Potassium ferrocyanide* precipitates dark-blue ferric ferrocyanide $Fe_4'''Fe_2''(CN)_{18}$, which is insoluble in dilute acids.

7. *Potassium sulphocyanide* imparts a deep-red color to ferric solutions, due to the formation of soluble ferric sulphocyanide $Fe(SCN)_3$. This reaction is very delicate, mere traces of a ferric compound giving a distinct color.

ALUMINUM.

51. Aluminum, or aluminium, is a white, very light, malleable metal, that is scarcely acted on by nitric or sulphuric acid, but is quite easily dissolved in hydrochloric acid.

It is only fused at very high temperatures, and is very hard to reduce from its compounds. Its valence is always III. A solution for its reactions may be made by dissolving about $2\frac{1}{2}$ or 3 grams of pure alum $AlK_2(SO_4)_3 \cdot 12H_2O$ in 100 cubic centimeters of water and a drop or two of concentrate sulphuric acid.

52. Reactions.—An aluminum solution gives the following reactions:

1. *Ammonium hydrate* precipitates white aluminum hydrate $Al(OH)_3$, which is insoluble in an excess of the reagent, but is easily dissolved by acids.

2. *Sodium hydrate* precipitates white aluminum hydrate $Al(OH)_3$, which is soluble in an excess of the reagent. From this solution aluminum hydrate is reprecipitated by ammonium chloride, especially when boiled, but hydrogen sulphide does not produce a precipitate in this solution.

3. *Ammonium carbonate* precipitates white aluminum hydrate $Al(OH)_3$, which is insoluble in an excess of the precipitant, but is readily dissolved by acids.

4. *Sodium carbonate* precipitates white aluminum hydrate $Al(OH)_3$, which is very slightly soluble in an excess of the reagent.

5. *Ammonium sulphide* precipitates white *aluminum hydrate*. To see this precipitate well, care must be taken. A small quantity of the solution is placed in a test tube, and a few drops of the reagent are added, allowing it to run down the side of the inclined tube so that it will not mix with the solution, but remain as a separate layer on the top. The precipitate appears where the two liquids meet.

6. *Sodium phosphate* precipitates white aluminum phosphate $AlPO_4$, which is insoluble in acetic acid.

CHROMIUM.

53. Chromium is a hard, heavy metal, with a strong affinity for oxygen. When acting as a base, it appears to be trivalent, but it takes more oxygen, forming an acid radical.

A solution for the reactions may be made by dissolving about 2 grams of chrome alum $CrK(SO_4)_2 \cdot 12H_2O$ in 100 cubic centimeters of water to which a drop or two of sulphuric acid is added.

54. Reactions.—A solution of chromium gives the following reactions:

1. *Ammonium hydrate* precipitates greenish-blue chromium hydrate $Cr(OH)_3$, which is slightly soluble in excess of the reagent. The part that dissolves gives the solution a reddish color. It may be reprecipitated by boiling off the excess of ammonia.

2. *Sodium hydrate* precipitates greenish-blue chromium hydrate $Cr(OH)_3$, which is soluble in excess of the reagent. It may be reprecipitated from this solution by ammonium chloride.

3. *Ammonium carbonate* precipitates greenish-blue basic chromium carbonate of varying composition.

4. *Sodium carbonate* gives the same reaction as ammonium carbonate.

5. *Ammonium sulphide* precipitates greenish-blue chromium hydrate $Cr(OH)_3$, which is very slightly soluble in an excess of the reagent.

55. Chromium compounds impart a yellowish-green color to the borax bead when hot, which changes to an emerald green upon cooling. To get this bead, heat the loop of the platinum wire and quickly dip it into borax, which will cling to the heated wire. This is then heated in the hottest part of the flame of a Bunsen burner, or in the blowpipe flame, until it is thoroughly fused and looks like a glass bead. It is now touched to a very small piece of a chromium compound, which will adhere to the soft, hot bead, and is again placed in the hottest part of the flame of the burner or the blowpipe until it is thoroughly fused. If the proper amount of the substance was taken, the bead will now assume the green color. The student must learn from experience the proper amount to take, but should guard against taking too large a quantity.

A little of one of the chromium precipitates may be tested

on the bead in this way, or enough of a rather strong chromium solution will adhere to the bead, especially if the bead is dipped into it several times, to give it a good color.

56. All chromium compounds, when fused on the platinum foil with sodium carbonate and potassium nitrate, are oxidized to chromates. To perform this operation, bend the platinum foil into the form of a spoon and place upon it about 1 cubic centimeter of dry sodium carbonate, and a little more than half as much potassium nitrate. To this add a piece of the wet chromium precipitate about half as large as a pea, or a much smaller piece of the dry compound. By means of the forceps, hold this in the hottest part of the Bunsen flame till it is thoroughly fused. When cool, place in a small beaker, or other convenient vessel, and dissolve off the fusion in equal parts of water and acetic acid, using only such a quantity as is necessary to dissolve it, and boil till all carbon dioxide is driven off. The chromium exists in the solution as an alkaline chromate, and gives the solution a slight yellow color. From this solution, lead acetate precipitates yellow lead chromate, which is easily soluble in sodium hydrate.

COBALT.

57. Cobalt is a steel-gray, rather hard, malleable metal, that is only fused at very high temperatures. It is slowly dissolved in hydrochloric or sulphuric acid, but dissolves readily in nitric acid. The solutions and crystalline salts are red, but the anhydrous salts are blue. A solution of the nitrate is best used for the reactions. It may be made by dissolving about 2 grams of the crystals, $Co(NO_3)_2 \cdot 6H_2O$, in 100 cubic centimeters of water and adding a drop or two of nitric acid.

58. Reactions.—A cobalt solution gives the following reactions:

1. *Ammonium hydrate* precipitates a blue basic cobalt compound, which easily dissolves in excess of reagent to a

brown solution. The presence of much free acid, or of ammonium salts, prevents the precipitation.

2. *Sodium hydrate* precipitates a blue basic compound which is insoluble in excess. If the precipitate in the excess of reagent be boiled, it changes to a pale-red precipitate of cobaltous hydrate $Co(OH)_2$. This soon changes to brown, owing to the formation of cobaltic oxide Co_2O_3 .

3. *Ammonium carbonate* precipitates a reddish basic cobalt carbonate, which is soluble in excess of the reagent, forming a red solution.

4. *Sodium carbonate* precipitates a reddish basic cobalt carbonate, which is insoluble in an excess of the reagent.

5. *Ammonium sulphide* precipitates black cobalt sulphide CoS , which is but very slightly soluble in hydrochloric acid, especially if it has been precipitated at a boiling temperature, but is dissolved by hot nitric acid.

6. *Potassium nitrite* gives a yellow precipitate, which is probably potassium cobaltic nitrite, from acetic-acid solutions. To get this precipitate, add ammonia to the solution till a slight precipitate is formed. Dissolve this in a slight but distinct excess of acetic acid, and to this solution add a stick of the dry potassium nitrite from 1 to 2 inches long, and stand aside for some time in a rather warm place. The cobalt is completely precipitated from a strong solution in a short time, and somewhat more slowly from a dilute one.

This is an important reaction, as it serves to separate cobalt and nickel, the cobalt being all precipitated, while the nickel remains in solution. Fresenius gives the probable composition of the precipitate as $2K_2Co(NO_2)_6, 3H_2O$.

59. Compounds of cobalt impart a deep-blue characteristic color to the borax bead, made as described under "Chromium," Art. 55.

NICKEL.

60. Nickel is a bright, hard, malleable metal with a yellowish-white color. It is very hard to fuse, and is not oxidized in the air at ordinary temperature, but slowly

oxidizes when ignited. It is slowly dissolved in hydrochloric or sulphuric acid, and very readily in nitric acid.

A solution of the nitrate may be used for the reactions. It is made by dissolving about 2 grams of the crystals $Ni(NO_3)_2 \cdot 6H_2O$ in 100 cubic centimeters of water, and adding a drop or two of nitric acid.

61. Reactions.—A nickel solution gives the following reactions:

1. *Ammonium hydrate* gives a slight greenish precipitate, which is very soluble in excess to a deep-blue solution. If ammonium salts are present, or if the solution contains much free acid, no precipitate is formed, but the blue solution appears at once.

2. *Sodium hydrate* precipitates green nickel hydrate $Ni(OH)_2$, which is insoluble in excess of the reagent, but is soluble in ammonium chloride.

3. *Ammonium carbonate* precipitates light-green basic nickel carbonate, which is soluble in excess of the reagent.

4. *Sodium carbonate* precipitates light-green basic nickel carbonate of variable composition, which is insoluble in excess of the reagent.

5. *Ammonium sulphide* precipitates black nickel sulphide NiS , which is but slightly soluble in cold dilute hydrochloric acid, but is readily dissolved by warm nitric acid.

ZINC.

62. Zinc is a bluish-white metal that tarnishes in the air, owing to the formation of a thin coat of basic zinc carbonate. It is rather brittle and is fusible. On the charcoal before the blowpipe, it fuses and deposits an incrustation of zinc oxide ZnO , which is yellow when hot and white when cold.

Chemically pure zinc is only slowly attacked by hydrochloric or sulphuric acid, but is dissolved in nitric acid. Common zinc, which contains small quantities of other

metals, dissolves readily in hydrochloric or sulphuric acid, and is largely used in the laboratory for the preparation of hydrogen, which is accomplished by dissolving zinc in one of these acids.

A solution for the zinc reactions is conveniently prepared by dissolving about 2 or $2\frac{1}{2}$ grams of zinc sulphate $ZnSO_4 \cdot 7H_2O$ in 100 cubic centimeters of water to which is added a drop of dilute sulphuric acid.

63. Reactions.—A zinc solution gives the following reactions:

1. *Ammonium hydrate* precipitates white zinc hydrate $Zn(OH)_2$, which is easily soluble in excess of the reagent. From solutions containing much free acid or ammonium salts the zinc is not precipitated by ammonia.

2. *Sodium hydrate* precipitates white zinc hydrate $Zn(OH)_2$, which is soluble in excess of the reagent. From this solution the zinc is not reprecipitated by ammonium chloride, but is reprecipitated by hydrogen sulphide.

3. *Ammonium carbonate* precipitates white basic zinc carbonate, which is soluble in excess of the reagent.

4. *Sodium carbonate* precipitates white basic zinc carbonate, which is only slightly soluble in excess.

5. *Ammonium sulphide* precipitates white zinc sulphide ZnS , which is insoluble in excess, but easily soluble in hydrochloric, sulphuric, and nitric acids. The precipitation is hastened by the presence of ammonium chloride, and also by warming.

6. *Potassium ferrocyanide* precipitates white zinc ferrocyanide $Zn_2Fe(CN)_6$, which is insoluble both in acids and in ammonia.

MANGANESE.

64. Manganese is a dull-gray, very hard, brittle metal. It only fuses at very high temperatures. It is rapidly oxidized in moist air or water, and is readily dissolved by acids.

A solution of manganese sulphate may be used for the

reactions. It is prepared by dissolving from 2 to 3 grams of the crystals, $MnSO_4 \cdot 7H_2O$, in 100 cubic centimeters of water, and adding a drop or two of dilute sulphuric acid.

65. Reactions.—A manganese solution gives the following reactions:

1. *Ammonium hydrate* precipitates white manganese hydrate $Mn(OH)_2$ from solutions that do not contain much free acid or ammonium salts. This rapidly changes to brown $MnOOH$. If much ammonium chloride is present, it prevents the immediate precipitation of the manganese, but after oxidizing it sometimes separates slowly from the solution.

2. *Sodium hydrate* precipitates white manganese hydrate $Mn(OH)_2$, which is insoluble in excess, but slightly soluble in ammonium chloride. Upon exposure to air the white precipitate changes to brown, owing to the oxidation of the manganese to $MnOOH$.

3. *Ammonium carbonate* precipitates white manganese carbonate $MnCO_3$. In the air this precipitate slowly changes to brown.

4. *Sodium carbonate* precipitates white manganese carbonate $MnCO_3$, which is insoluble in excess of the reagent, but when freshly precipitated is soluble in ammonium chloride.

5. *Ammonium sulphide* precipitates flesh-colored manganese sulphide MnS , which is easily dissolved by acids.

6. If, to about half a cubic centimeter of lead dioxide in a test tube, we add a few drops of manganese solution, and then about 8 cubic centimeters of an acid made by mixing equal volumes of concentrate nitric acid and water, and boil the whole for about two minutes, permanganic acid $HMnO_4$ is formed, which gives the liquid a distinct red color. This may be seen as soon as the black insoluble matter has settled to the bottom.

66. Manganese compounds impart an amethyst-red color to the borax bead, when heated in the oxidizing flame. This

must be done as described under "Chromium," Art. 55. If this bead be reheated for some time in the reducing flame, it loses its color, on account of the reduction of the manganese to a colorless compound.

67. Compounds of manganese, when fused on platinum foil with sodium carbonate and potassium nitrate, are oxidized to manganates, and give a dark-green color to the fusion. This should be done as described under "Chromium," Art. 56.

BARIUM.

68. Barium compounds cannot be reduced on the charcoal before the blowpipe, but when heated very high these compounds become incandescent.

A good solution for the barium reactions is made by dissolving about 2 grams of barium chloride $BaCl_2$ in 100 cubic centimeters of water and adding a drop or two of dilute hydrochloric acid.

69. Reactions.—A barium solution gives the following reactions:

1. *Ammonium hydrate* does not give a precipitate with barium, strontium, or calcium solutions.

2. *Sodium hydrate* does not give a precipitate from ordinary barium solutions, but precipitates white barium hydrate $Ba(OH)_2$ from very strong solutions.

3. *Ammonium carbonate* precipitates white barium carbonate $BaCO_3$, which is insoluble in ammonium chloride, but soluble in hydrochloric acid. Heat aids the precipitation.

4. *Sodium carbonate* precipitates white barium carbonate $BaCO_3$, which dissolves in hydrochloric acid with effervescence.

5. *Ammonium sulphide* does not precipitate this or any of the following metals.

6. *Potassium chromate* precipitates yellow barium chromate, which is easily soluble in hydrochloric acid, but is insoluble in sodium hydrate or acetic acid. From the hydrochloric-acid solution it is reprecipitated by ammonia.

7. *Sulphuric acid* precipitates white barium sulphate $BaSO_4$. The precipitate is formed immediately, and is almost insoluble in all acids. A soluble sulphate may be used instead of sulphuric acid, and the same result obtained. Calcium sulphate precipitates barium sulphate from barium solutions immediately.

8. *Ammonium oxalate* gives no precipitate in dilute solutions, but in rather strong solutions it precipitates white barium oxalate BaC_2O_4 , which is easily soluble in nitric, hydrochloric, or acetic acid.

9. *Sodium phosphate* precipitates white hydrogen barium phosphate $HBaPO_4$ from neutral and alkaline solutions. The precipitate is very soluble in hydrochloric, nitric, or acetic acid, so that in a solution containing free acid, no precipitate is formed. Such a solution may have the acid neutralized by ammonia, after which it may be precipitated by the phosphate.

70. All volatile barium compounds, as, for example, the chloride, when brought into the flame, either in the solid or liquid state, on the loop of a platinum wire, impart a characteristic yellowish-green color to the flame.

STRONTIUM.

71. Strontium is a brass-yellow metal, but is seldom seen in the metallic form, owing to its great affinity for oxygen. Its compounds can only be reduced to the oxide before the blowpipe. At a high temperature this is luminous.

A solution for the wet reactions may be made by dissolving about 2 grams of strontium nitrate in 100 cubic centimeters of water to which a drop of nitric acid has been added.

72. **Reactions.**—A strontium solution gives the following reactions:

1. *Sodium hydrate* precipitates, from moderately strong solutions, white strontium hydrate $Sr(OH)_2$, which is dissolved by adding water and boiling. In very dilute solutions no precipitate is formed.

2. *Ammonium carbonate* precipitates white strontium carbonate $SrCO_3$, which is only very slightly soluble in ammonium chloride, but is soluble in hydrochloric, nitric, or acetic acid. Warming aids in the precipitation.

3. *Sodium carbonate* gives the same precipitate as ammonium carbonate.

4. *Potassium chromate* precipitates yellow strontium chromate $SrCrO_4$ from rather strong neutral solutions. This is easily dissolved by hydrochloric, nitric, or acetic acid, or by a large amount of water, so that in dilute solutions, or those containing much free acid, no precipitate is formed.

5. *Sulphuric acid* precipitates white strontium sulphate $SrSO_4$, which is very slightly soluble in water, so that in very dilute solutions the precipitate does not appear immediately. A saturated solution of calcium sulphate may be used instead of sulphuric acid, in which case the precipitate will appear after a few moments.

6. *Sodium phosphate* precipitates white hydrogen-strontium phosphate $HSrPO_4$ from neutral, and strontium phosphate $Sr_3(PO_4)_2$ from alkaline, strontium solutions. Both are soluble in acids, so that in strongly acid solutions no precipitate is formed.

7. *Ammonium oxalate* precipitates white strontium oxalate SrC_2O_4 , which is easily soluble in hydrochloric or nitric acid, but only slightly soluble in acetic acid.

73. Strontium compounds that are volatile give a crimson color to the flame, when held in it on the loop of a platinum wire. The chloride is the most volatile of the ordinary strontium compounds, so it is well to dip the substance into hydrochloric acid just before placing it in the flame.

CALCIUM.

74. Calcium is a yellow metal, but on account of its great affinity for oxygen it is rare in the metallic state. Its compounds can only be reduced to the oxide on the charcoal

before the blowpipe. This is infusible, and luminous at high temperatures, giving what is known as the calcium light.

A solution for the wet reactions may be prepared by dissolving about 2 grams of dry calcium chloride in 100 cubic centimeters of water and adding a drop or two of hydrochloric acid.

75. Reactions.—A calcium solution gives the following reactions:

1. *Sodium hydrate* precipitates white calcium hydrate $\text{Ca}(\text{OH})_2$, which is slightly soluble in water. Hence, in *very* dilute solutions no precipitate is formed.

2. *Ammonium carbonate* precipitates white calcium carbonate CaCO_3 . Heat aids the precipitation. The precipitate is soluble in acids with effervescence.

3. *Sodium carbonate* precipitates white calcium carbonate CaCO_3 , which is easily dissolved by dilute acids.

4. *Potassium chromate* gives no precipitate with calcium compounds.

5. *Sulphuric acid* precipitates white calcium sulphate CaSO_4 from concentrate solutions. As this is quite soluble in water, unless the solution is very strong, the precipitate forms slowly, and if the solution is dilute, no precipitate is formed. Of course, calcium sulphate would not precipitate calcium from its solutions.

6. *Ammonium oxalate* precipitates white calcium oxalate CaC_2O_4 , which is insoluble in acetic acid, but easily soluble in hydrochloric or nitric acid. The presence of free ammonia and heating both favor the formation of this precipitate.

7. *Sodium phosphate* gives a white precipitate. If the solution is slightly acid or neutral, this precipitate is HCaPO_4 , but if the solution is alkaline, the precipitate is $\text{Ca}_3(\text{PO}_4)_2$. It is easily dissolved by dilute acids, and is reprecipitated by ammonia.

76. All volatile calcium compounds, when held in the Bunsen flame on the platinum wire, impart a brick-red color to the flame. It is well to dip the substance in hydrochloric

acid just before placing it in the flame, in order to form volatile calcium chloride. If the calcium gives a very strong color to the flame it may be mistaken for strontium, but we may distinguish between them by looking at the flame through a blue glass, when the strontium flame appears purple, or rose color, while the calcium flame only shows a faint greenish-gray color.

MAGNESIUM.

77. Magnesium is a white metal that tarnishes very slowly in dry air, but much more rapidly if the air is moist. It burns in the air, with a dazzling white light, to magnesium oxide MgO .

A solution of magnesium sulphate may be used for the wet reactions. It is made by dissolving about 3 grams of the crystals $MgSO_4 \cdot 7H_2O$ in 100 cubic centimeters of water and adding a drop or two of sulphuric acid.

78. Reactions.—A magnesium solution gives the following reactions:

1. *Ammonium hydrate* precipitates white magnesium hydrate $Mg(OH)_2$, from neutral solutions that are free from ammonium salts. If the solution contains any considerable amount of free acid or ammonium salts, no precipitate is formed.

2. *Sodium hydrate* precipitates white magnesium hydrate $Mg(OH)_2$, from solutions that do not contain ammonium salts. The precipitate is soluble in acids and in ammonium chloride. From the solution in ammonium chloride the magnesium hydrate may be slowly reprecipitated by continued boiling.

3. *Ammonium carbonate* gives no precipitate under ordinary conditions.

4. *Sodium carbonate* precipitates white basic magnesium carbonate from solutions that do not contain ammonium salts. Heat aids the formation of the precipitate. It is

soluble in ammonium chloride, and is prevented from forming by the presence of ammonium salts.

5. *Sodium phosphate* gives no precipitate in acid solutions, but in alkaline solutions the magnesium is completely precipitated as white magnesium-ammonium phosphate $MgNH_4PO_4$, which is easily dissolved by acids, and is reprecipitated from this solution by ammonium hydrate.

79. Magnesium compounds, when highly heated on the charcoal before the blowpipe, are reduced to the white infusible oxide, which is luminous at high temperatures. If this is moistened with a drop of cobalt nitrate, and again ignited, it assumes a pale-rose color, which is permanent, and may be seen after cooling.

AMMONIUM.

80. The ammonium group NH_4 acts like a metal, forming the base of all ammonium compounds, and is, consequently, treated as a metal. When heated on the charcoal or platinum foil, all ammonium compounds are either decomposed or volatilized, those that are decomposed giving the peculiar odor of ammonia.

A solution for its reactions may be made by dissolving 2 or 3 grams of ammonium nitrate, or chloride, in 100 cubic centimeters of water.

81. Reactions.—Ammonium compounds give the following reactions:

1. *Acid sodium tartrate* precipitates white acid ammonium tartrate $H_2NH_4C_4H_4O_6$ from rather concentrate solutions. It is very soluble in acids, and quite soluble in water, so that in dilute solutions, or in those containing free acid, no precipitate is formed. The precipitate is not formed at once except in very strong solutions, but shaking favors its formation. It is sometimes obtained from the solution prepared as described above, but often fails.

2. *Platinum chloride* precipitates yellow ammonium-platinum chloride $(NH_4)_2PtCl_6$ from concentrate solutions.

This precipitate is insoluble in alcohol, but is dissolved by water; hence, in dilute solutions no precipitate is formed.

Probably no precipitate can be obtained from the solution described above, but the reaction is mentioned here as it is important in later work.

3. *Sodium hydrate*, when heated with any ammonium compound, decomposes it, setting free NH_3 . This is by far the best common test for ammonium, and, in fact, the only sure one. To apply this test, place a little of the solution to be tested in a test tube, add about an equal quantity of sodium hydrate, and heat. Ammonia gas is set free, which is recognized by its characteristic odor. If a piece of red litmus paper is moistened and held at the mouth of the tube, it is turned blue; or, if a drop of hydrochloric acid on a glass rod is held at the mouth of the tube where the gas comes in contact with it, white fumes of ammonium chloride NH_4Cl are formed.

POTASSIUM.

82. Potassium is a soft, silver-white metal when freshly cut, but tarnishes rapidly in air. It decomposes water, forming potassium hydrate KOH and setting free hydrogen, during which reaction heat enough is generated to ignite the hydrogen, which burns with a violet flame.

A solution for the reactions may be made by dissolving about 3 grams of potassium nitrate or chloride in 100 cubic centimeters of water.

83. Reactions.—A potassium solution gives the following reactions:

1. *Acid sodium tartrate* precipitates white acid potassium tartrate $KHC_4H_4O_6$ from neutral solutions that are not too dilute. It is easily soluble in acids and alkalies, and less so in water, so we cannot place a great deal of dependence upon it. Its formation is favored by shaking.

2. *Platinum chloride* precipitates yellow potassium-platinum chloride K_2PtCl_6 from concentrate solutions. It is insoluble in alcohol, but soluble in acids, alkalies, or water;

consequently, with the ordinary solution we may succeed or fail in getting it.

84. Potassium compounds, when brought into a colorless flame on a platinum wire, impart a bluish-violet color to the flame. This is by far the best method of recognizing potassium. Sodium and other impurities may partially obscure this color, but when viewed through the blue glass, their colors are absorbed and the potassium flame appears a reddish-violet color. After a little practice this flame may be identified with absolute certainty.

SODIUM.

85. Sodium is a soft, white metal that behaves much like potassium, except that it produces no precipitates with ordinary reagents. A solution may be made by dissolving 2 or 3 grams of sodium nitrate or chloride in 100 cubic centimeters of water.

86. As sodium gives no precipitates with ordinary reagents, we depend upon the flame to enable us to recognize it. This is easily done, as even small amounts of it impart an intense yellow color to the flame, which is not obscured by the presence of other elements. When viewed through a blue glass, the yellow color is absorbed and the flame appears almost colorless.

87. A crystal of potassium bichromate, when held close to the sodium flame, appears transparent and almost colorless in its light.

EXPLANATION OF TABLE 1.

88. If the student has performed and studied each of the reactions described under the different metals, he is now prepared to determine any single common metal in a solution, by means of these reactions. All the reactions necessary to determine any of these metals have been described, but the student will find that at first it is difficult to remember the reactions, and much time would be lost in looking

ANALYSIS OF MIXED SOLUTIONS.

90. We now have before us all the facts necessary to make out a scheme by which we can separate and determine several metals mixed together in a solution, but, as for this work, we need some apparatus in addition to that already in use, and as some of the operations differ from any thus far performed, we will describe these before proceeding to describe the process.

91. Apparatus Needed for Separations.—In addition to the apparatus already in use, we need a wash bottle, funnels, support for funnels, filter paper, beakers, a porcelain dish, a stirring rod, and a flask.

1. A wash bottle is made by fitting a flask with a stopper that has two perforations. Through one of these perforations a tube (*b*, Fig. 8) is passed so that the lower end just projects through the bottom of the stopper. The upper part of the tube is bent so that it forms an angle of about 60°. Through the other perforation a tube is passed, reaching nearly to the bottom of the flask. The top of this tube is bent so that it forms an angle of about 120°, and the end is drawn out, leaving a small opening. The tubes must fit tightly into the perforations in the stopper. By blowing in the tube *b*, the pressure of the air forces the water in the flask up through the tube *a* and out of the small opening in a fine jet that is very well adapted to the purpose of washing precipitates, and of washing out small particles of substance that adhere to a beaker. The tube *a* is often cut in two, about half way between the bend and the tip, and the two parts held together by placing over them a piece of rubber tubing that fits them closely. This makes it much handier to direct the jet of water. As hot water is often used in a wash bottle, the neck of the flask is frequently covered, to protect the hand from the

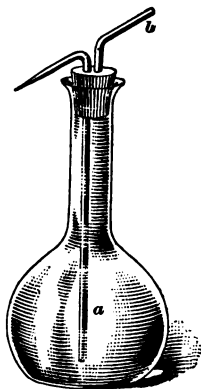


FIG. 8.

heat. This may be done by wrapping it with a cord, or by binding a ring of cork around it.

2. The funnels used in all ordinary analytical work must be of glass. The ring of a retort stand serves very well for a support in filtering.

3. Filter paper may be obtained from any chemical dealer, either in sheets, or cut in disks, ready for use. The papers 4 inches in diameter (10 centimeters) are the best size for qualitative work. The filter papers are folded as directed in Art. 99, *Theoretical Chemistry*.

4. A nest of beakers, a porcelain dish, a common glass stirring rod, and a flask require no description.

92. Washing Precipitates.—There are two methods of washing precipitates, known as *washing by decantation* and *washing on the filter*. In washing by decantation, the precipitate is allowed to settle to the bottom of the beaker and the clear liquid is poured off, or decanted; water is added, the precipitate is stirred up with it, and then is allowed to settle, and the water decanted. This may be repeated several times, the water carrying off a large part of the remaining impurity each time, until the precipitate is free from foreign matter.

In washing on the filter, the precipitate is separated from the liquid by means of filtration, as described in Art. 99, *Theoretical Chemistry*. After all the liquid has passed through, leaving the precipitate on the filter, a jet of water from the wash bottle is directed around the top of the filter paper, thus washing down any impurity that may be absorbed by this part of the paper, and washing the precipitate down nearer the cone of the paper. When a little more than enough water to cover the precipitate has been added in this way, allow it all to run through the filter before adding more. By repeating this operation a few times, the water carries all soluble matter through the filter, leaving the precipitate clean.

93. Concentrating Filtrates, or Solutions.—In separating the different metals, we precipitate some of them

from the solution, and then get others from the filtrate. The water used in washing the precipitates, of course, goes into the filtrates and in a short time our solution becomes too large. To avoid this we must concentrate the solution, and this is always done by evaporating off some of the water. This is rapidly accomplished by boiling the liquid. Liquids in a beaker must always be heated over a wire gauze. Stand the beaker on a gauze, resting on a tripod, and place the burner under it. The flame must never be turned high enough to reach around the side of the gauze and strike the beaker, or it will probably crack it. This applies to heating liquids in any glass vessel. The same care must be taken when heating water in a wash bottle.

GROUP SEPARATIONS.

94. As has already been indicated, when there are several metals in a solution, they are removed from the solution in groups by means of the so called *group reagents*, and the metals in each group are then separated from each other. There are six of these group reagents; and, by means of them, all the common metals may be divided into seven groups. The group reagents, in the order in which they are used, are: *hydrochloric acid*, *hydrogen sulphide*, *ammonium hydrate*, *ammonium sulphide*, *ammonium carbonate*, and *sodium phosphate*. There is no group reagent for the seventh group, as it consists of the metals that are not precipitated by any of the common reagents.

Group I consists of the metals that are precipitated as chlorides by hydrochloric acid. They are:

Silver..... white.
Lead (incompletely)... “
Mercurous..... “

Group II consists of the metals left in the filtrate that are precipitated as sulphides by hydrogen sulphide. On account of the solubility of lead chloride in water, some of the lead is precipitated in the second group. This group is divided

into two divisions, depending upon the solubility of the sulphides in ammonium sulphide and ammonium hydrate. The group is as follows:

DIVISION A.	DIVISION B.
<i>Insoluble in $(\text{NH}_4)_2\text{S}$ and NH_4OH.</i>	<i>Soluble in $(\text{NH}_4)_2\text{S}$ and NH_4OH.</i>
Lead black.	Antimony orange.
Mercuric. " "	Stannous. brown.
Copper " "	Stannic. yellow.
Cadmium yellow.	Arsenious. " "
Bismuth brown.	Arsenic. " "

Group III consists of the remaining metals that are precipitated as hydrates by ammonium hydrate in the presence of ammonium chloride. They are:

Iron reddish brown.
 Chromium greenish blue.
 Aluminum white.

Group IV consists of the remaining metals that are precipitated as sulphides by ammonium sulphide. They are:

Cobalt black.
 Nickel " "
 Zinc white.
 Manganese flesh color.

Group V consists of the metals not precipitated in any of the previous groups, but that are precipitated as carbonates by ammonium carbonate, in the presence of ammonium chloride. They are:

Barium white.
 Strontium " "
 Calcium " "

Group VI contains but one metal. It is not precipitated by any of the preceding group reagents, but is precipitated by sodium phosphate in the presence of ammonia and ammonium chloride. It is:

Magnesium white.

Group VII consists of the metals that are not precipitated by any of the common reagents, but must be recognized by special tests. They are:

Ammonium, Potassium, Sodium.

The rare metals are not treated here, as their treatment at this time would complicate the work too much. They are, therefore, taken up later and treated by themselves.

GROUP I.

95. About 20 cubic centimeters of the solution to be analyzed are placed in the smallest beaker and about 3 drops of concentrate hydrochloric acid added. If no precipitate is formed, this portion of the solution is ready for the next step, and should be treated for Group II. If the solution contains silver, lead, or mercurous compounds, they will be precipitated, except in the case of very small quantities of lead, which, on account of the solubility of its chloride in water, may not be precipitated in this group, but will come down in Group II. If a precipitate is formed, continue to add hydrochloric acid gradually, and with constant stirring, till all the metals of this group are precipitated, but taking care not to add a large excess of the reagent. We can tell when enough of the reagent has been added by allowing the precipitate to settle, and adding a drop or two of the reagent. The precipitation is complete when this no longer produces a precipitate in the clear liquid. Allow the precipitate to settle, and filter as directed in Art. **99**, *Theoretical Chemistry*, and wash two or three times on the filter with cold water. Receive the filtrate in the next to the smallest beaker and set it aside, to be treated for Group II. It is best before doing so, however, to add a drop or two of the reagent to the filtrate, in order to be sure that the precipitation was complete. If a precipitate is formed, it shows that the metals of this group have not been perfectly separated, and the reagent must be added till a precipitate is no longer formed. This must then be filtered and the precipitates united. This

applies to the succeeding groups as well as to this one, but in every case care must be taken not to add a large excess of the reagent.

Punch a hole in the apex of the filter with a stirring rod, and wash the precipitate through into the small beaker with hot water, using enough water to about half fill the beaker. Place this on the gauze and heat it to boiling while stirring it with a glass rod. If it all dissolves, there is only lead present, which should be confirmed by adding a few drops of sulphuric acid to a portion of it, and also by the other reactions for lead. If the precipitate does not all dissolve, it should be filtered while hot. The lead chloride will go through in the filtrate, and the silver and mercurous chlorides will remain on the filter. Test the filtrate for lead by adding sulphuric acid, and by means of potassium chromate, as described under "Lead," in the "Department of the Metals With Reagents." This may now be thrown away, the beaker washed, and placed under the funnel. Ammonium hydrate is now added to the precipitate on the filter. If silver chloride is present, it is dissolved and runs through the filter, forming a new filtrate, while the mercurous chloride is changed to a black, insoluble compound that remains on the filter. Nitric acid is added to the ammoniacal filtrate, or to a part of it, in sufficient quantity to render it slightly acid, when silver, if present, will be reprecipitated as chloride. The blackening of the precipitate on the filter, when ammonia is added, is proof of mercurous chloride; but this may be dissolved in a little aqua regia, and after evaporating the excess of acid and diluting, it may be confirmed by the use of stannous chloride, and by the other reactions for mercury.

GROUP II.

96. The first filtrate from Group I, or the slightly acid solution, if none of the members of Group I were present, is now ready to be treated for Group II. But before treating the whole of the solution with hydrogen sulphide, a small portion in a test tube should be tried to see if any of the

members of the second group are present. This may be done by adding a little of the hydrogen-sulphide solution, if proper precautions are taken to precipitate arsenic, if present. But it is best to run a little of the gas through this solution. If no precipitate is obtained in this *side test*, it is thrown out, and the main part of the filtrate is ready to treat for Group III. If a precipitate is obtained, it shows the presence of second-group metals, and the solution must be treated with hydrogen sulphide. The hydrogen-sulphide solution is too dilute for this purpose, so we must use the gas. It is prepared as described in Art. 105, Experiment 50, *Inorganic Chemistry*, Part 1, and is led into the solution until the precipitation of the metals of Group II is complete. This will generally take about 10 minutes. After a little practice the student can tell when the operation is complete by removing the beaker, blowing the gas away from the surface of the liquid, and observing if a strong odor of hydrogen sulphide is given off. If the odor is very strong, it indicates that the precipitation is complete.

Allow the precipitate to settle, and then, without disturbing the precipitate, lead a little more of the hydrogen sulphide through the clear liquid, to be sure that the metals of this group are completely precipitated. If a precipitate is formed, the treatment with hydrogen sulphide must be continued until precipitation is complete. Allow the precipitate to settle and pour as much as possible of the clear liquid through the filter without disturbing the precipitate. When the liquid has run through, wash the precipitate on to the filter with hot water and wash twice on the filter with hot water. Set the filtrate aside, to be treated for Group III. The precipitate may contain metals of either Division A or Division B, or may contain both. As the methods of separating the metals of the two divisions differ, we should always ascertain whether both divisions are present or not, and if metals belonging to but one division are present, we should learn to which division they belong before treating the whole precipitate. To do this, remove a portion of the damp precipitate about as large as a small pea to a small porcelain

dish, and add about one cubic centimeter of ammonia, and from half a dozen drops to half a cubic centimeter of yellow ammonium sulphide, depending upon the color of the precipitate. If the precipitate is light colored, only a few drops of the yellow sulphide is needed, or a little more of the common ammonium sulphide may be substituted; but if it is rather dark, indicating that tin may be present, more of the yellow sulphide must be used. In either case heat gently and stir with a glass rod for a few minutes. If all the precipitate dissolves, Division B alone is present. If it does not all dissolve, the insoluble part belongs to Division A.

This is filtered, washed once with hot water, and the filtrate rendered slightly acid with hydrochloric acid. Sulphur will be thrown out by the hydrochloric acid. If it merely makes the solution milky, it may be disregarded, but if the solution is colored yellow, it shows the presence of some of the members of Division B, and in this case the two divisions must be separated. If only metals belonging to one of the divisions are present, the precipitate is at once treated as described for the separation of the metals of that division.

97. Separation of the Two Divisions of Group II.—The precipitate is removed, as completely as possible, from the filter to a porcelain dish. If the precipitate is dark colored, it may contain tin, and in that case from 2 to 3 cubic centimeters of yellow ammonium sulphide are added, then about an equal amount of common ammonium sulphide, and finally a little more than enough ammonium hydrate to cover the precipitate is added. In case the precipitate is light colored, stannous sulphide must be absent, and in that case only a few drops of the yellow sulphide should be added, and the quantity of common ammonium sulphide should be increased about the same amount that the yellow sulphide is decreased. In either case, gradually heat the mixture, while it is being stirred, until it begins to boil. By this time the metals of Division B will all be in solution. Add to this about twice its volume of hot water, and after allowing it to stand for a few moments to settle, filter it, and wash several

times with hot water. The precipitate will now contain the members of Division A, and the filtrate contains the metals of Division B.

98. Separation of the Metals of Division A.—This precipitate—or the original precipitate, if it were found to contain only the metals of Division A—is removed as completely as possible to a small porcelain dish, and covered with a mixture of equal parts of concentrate and dilute nitric acid. It should be heated slowly and with constant stirring until it boils. The sulphides of lead, copper, cadmium, and bismuth will be dissolved, while the sulphide of mercury remains as a black, insoluble precipitate. Sulphur will also be thrown out during the solution of the sulphides, but this may easily be recognized, and is disregarded. It generally collects in a pasty mass, which may be somewhat colored by small quantities of undissolved sulphides. The excess of acid is evaporated off, and about 25 cubic centimeters of hot water is added. Filter, and wash two or three times with hot water. A black precipitate indicates mercury, but it should be confirmed by dissolving a little of the precipitate in aqua regia, evaporating the excess of acid, diluting slightly, and testing with stannous chloride. Other tests for mercury may also be applied. The filtrate, containing the metals whose sulphides are soluble in nitric acid, is treated with a few drops of sulphuric acid, to test for lead. If a precipitate is formed, continue the addition of the sulphuric acid, drop by drop, till all the lead is precipitated as sulphate. Filter, wash once, and confirm the presence of lead by the solubility of the sulphate in tartaric acid and ammonia, as directed in Art. 20, 8.

A slight excess of ammonia is now added to the filtrate. Bismuth, if present, will be precipitated as white bismuth hydrate, while copper and cadmium, if present, form precipitates that are at once dissolved in excess. If the solution assumes a deep-blue color, it is conclusive evidence of the presence of copper. The precipitate, if one is formed, is probably bismuth, but if the lead was not all removed, it will be precipitated at this point, and if the third-group metals

were not thoroughly washed out of the original precipitate, they may come down here, so we must confirm the presence of bismuth. To do this, dissolve a little of the precipitate in a few drops of hot concentrate hydrochloric acid in a test tube, and drive off most of the acid by heating. Pour a few drops of this solution, a drop at a time, into a test tube nearly filled with cold water. If a white precipitate is formed, it is conclusive evidence of the presence of bismuth; but if too much acid were left in the bismuth solution, no precipitate will be formed. In that case a little hydrogen sulphide is added to the acid solution in the test tube of water that failed to give a precipitate. A brown precipitate confirms bismuth, while the absence of a brown precipitate proves that it is not present.

The ammoniacal filtrate is next examined for copper and cadmium. If it is colored blue, copper is present, but if colorless, it shows the absence of copper. In that case, to a small quantity of it in a test tube, add hydrogen sulphide, which will precipitate cadmium, if present, as yellow cadmium sulphide. If the solution is blue, a little of it is taken in a test tube, and just enough potassium-cyanide solution added to entirely destroy the color. To this colorless solution add hydrogen sulphide, which will precipitate cadmium, as yellow cadmium sulphide, but will not precipitate copper from the cyanide solution.

In separating the cadmium and copper by this method, traces of other metals are sometimes present, and give the cadmium sulphide a dark color. For this reason some chemists prefer the following method of separating them.

Render the filtrate from the bismuth slightly acid with hydrochloric acid, and pass a current of hydrogen-sulphide gas through it till the copper and cadmium are both completely precipitated. Filter and wash the precipitate two or three times with hot water and a few drops of hydrogen-sulphide solution. Remove the precipitate to a porcelain dish as quickly as possible, in order to avoid the oxidizing action of the air, treat it with warm dilute sulphuric acid, and bring to boiling in order to expel the hydrogen sulphide

generated by the action of the sulphuric acid upon the sulphides. Cadmium sulphide will be dissolved, while copper sulphide remains as a black insoluble compound. It should be filtered at once, and the precipitate examined for copper, by dissolving it in nitric acid and applying the reactions given for copper. To test the filtrate for cadmium, add ammonia in sufficient quantity to render the solution alkaline, and then add just enough hydrochloric acid to render it distinctly acid, and again pass a current of hydrogen sulphide through it, when cadmium, if present, will be precipitated as yellow cadmium sulphide. This method is more difficult to perform properly than the first method given.

99. Separation of the Metals of Division B.—1. The metals of Division B are in solution in the filtrate from the metals of Division A. This filtrate is rendered acid with hydrochloric acid, when more or less sulphur is thrown out, depending on the amount of yellow ammonium sulphide used, and the metals are precipitated as yellow or orange-colored sulphides. The hydrochloric acid must be added as long as a precipitate is formed. When precipitation is complete, filter and wash the precipitate two or three times with hot water. When the water has run through, remove the precipitate to a porcelain dish, and add enough concentrated hydrochloric acid to cover the precipitate. Heat until it has boiled for two or three minutes, when the sulphides of tin and antimony will be dissolved and all the hydrogen sulphide expelled. The arsenic will remain as a yellow sulphide and some free sulphur will be thrown out.

In case the original precipitate contained only metals of Division B, it should not be treated with sulphides, but should be transferred to a porcelain dish at once, and treated with hydrochloric acid, as just described.

The hydrochloric-acid solution is diluted with about twice its volume of water, filtered, and the precipitate washed twice on the filter with hot water. The arsenic, if present, will be in the precipitate, and antimony and tin in the filtrate. Remove the precipitate to a small porcelain dish

and add a small amount of concentrate nitric acid. If the precipitate is so small that it cannot be removed from the filter, the part of the paper containing the precipitate may be placed in the dish and the acid added. In either case, heat until the precipitate is dissolved and most of the acid is driven off; then add a little water and filter to remove free sulphur and filter paper, receiving the filtrate in a test tube. Then place a little magnesium sulphate in another test tube, precipitate it with ammonia, using considerable excess, and dissolve the precipitate thus formed by adding ammonium chloride. To this solution add some of the filtrate from the other tube, taking care that the solution remains alkaline, and shake violently. A white, crystalline precipitate proves the presence of arsenic.

Another method often used to confirm arsenic, is to remove a little of the precipitate, supposed to be As_2S_3 , to the charcoal and heat it before the blowpipe. Dense white fumes, with a garlic odor, prove the presence of arsenic.

To examine the acid filtrate for tin and antimony, place in it several pieces of zinc, and when the acid begins to act on them, place a piece of platinum foil in contact with one of the pieces of zinc and leave it thus for a few seconds. If antimony is present, some of it will be deposited on the platinum, forming a black stain. Remove the platinum and allow the acid to act on the zinc, until all chemical action ceases, and some zinc remains undissolved. During this action some of the antimony escapes as SbH_3 , and the rest is deposited on the zinc as metallic antimony, in the form of a black powder. The tin is all deposited either as a gray powder or as a gray, spongy mass of metallic tin. The pieces of zinc are now removed and the adhering metals are washed back into the dish and allowed to settle. Decant the clear liquid, and wash two or three times by decantation, finally decanting as much of the water as possible. Add a little concentrate hydrochloric acid and heat to boiling. The tin will dissolve to stannous chloride, while the antimony remains unchanged. Add a little water and filter, receiving the filtrate in a test tube. This is tested for stannous chloride by means of

mercuric chloride, and by other reactions for stannous compounds.

The antimony is further confirmed by dissolving a little of the black powder in aqua regia, driving off the excess of acid, diluting with water, and precipitating with hydrogen sulphide. If a white precipitate is formed when water is added to dilute the solution, this in itself is proof of antimony.

2. The metals of this division are sometimes separated by another method. In this case the precipitated sulphides of Division B, after washing on the filter, are transferred to a porcelain dish, a saturated solution of acid ammonium carbonate is added in sufficient quantity to cover the precipitate, and this is heated for a few minutes, with constant stirring. The arsenic is changed into the two soluble compounds, ammonium sulphoarsenite and ammonium arsenite, while the antimony and tin remain unchanged. Filter, and wash two or three times with hot water. The precipitate will contain the antimony and tin, and the arsenic will be in the filtrate. The precipitate is removed to a porcelain dish, dissolved in concentrate hydrochloric acid, and the tin and antimony separated as described in the first method.

The alkaline filtrate is treated with an excess of hydrochloric acid, when arsenic, if present, will be precipitated as yellow arsenious sulphide. This is sufficient evidence of arsenic, but it may be confirmed by either of the methods previously given.

GROUP III.

100. The filtrate from Group II, or, in case the *side test* showed that the solution did not contain any of the metals of Group II, the filtrate from Group I is next treated for Group III. If the second group has been precipitated from this solution, it will contain hydrogen sulphide, which must be expelled by boiling, before adding ammonia, or ammonium sulphide will be formed, and the fourth group be precipitated with the third. If the solution is growing too large, it is best to boil it in a beaker, thus concentrating the solution at the same time that the hydrogen sulphide is driven off. But if

the solution is not too large, it is best to boil it in a flask. The student must be sure that all the hydrogen sulphide is expelled before proceeding. The odor of the vapor is a good indication, or a piece of filter paper saturated with a solution of lead or silver, held in the vapor driven off by the heat, will be colored as long as hydrogen sulphide is present. If sulphur is thrown out in the solution during this operation, it should be filtered off before proceeding.

There are several things that may complicate the separation of the metals of this group. Manganese may be partially precipitated with this group, and if phosphoric or oxalic acid is present, the phosphates or oxalates of the alkaline earths are either partly or wholly precipitated when ammonia is added. In the presence of phosphoric acid, part of the iron and aluminum are precipitated as phosphates, and barium, strontium, calcium, and magnesium phosphates may also be precipitated. When oxalic acid is present, the oxalates of barium, strontium, and calcium are precipitated with this group. Fortunately, these acids do not ordinarily occur in solutions that are treated for the group separations, and the student may never have to separate the metals in a solution containing them, but in case he should meet them in a solution, methods for the treatment of this group, when they are present, are given, after describing the ordinary method for the separation of the metals of this group.

In any case the solution is heated to boiling and a few drops of concentrate nitric acid are added, to oxidize ferrous compounds to ferric. If a brown color is formed, continue to add the acid, drop by drop, and boil till the solution becomes clear. Now add about 10 cubic centimeters of ammonium chloride, and then slowly add ammonium hydrate in slight but distinct excess, while the solution is constantly stirred. Continue the boiling for about one minute, and be sure that the solution still smells distinctly of ammonia. Filter as soon as the precipitate has partly settled, while the solution is still hot, and wash two or three times with hot water. The filtrate is now ready to be treated for Group IV, and the precipitate should be tested for phosphoric and

oxalic acids. If they are found to be present, the precipitate is treated as described later. If they are absent, the metals are separated by the usual method.

101. Ordinary Method of Separating the Metals of Group III.—If iron is present in the solution, some of the manganese will generally be precipitated with the iron. To test for manganese, remove a small portion of the precipitate to the platinum foil, and fuse with sodium carbonate and potassium nitrate, as directed in Art. 67. A dark-green color proves the presence of manganese, which is sufficient if we merely want to know whether it is present in the solution or not. But if we wish to separate it from the metals of this group, the whole precipitate is removed to a beaker and dissolved in about 25 cubic centimeters of hydrochloric acid by the aid of heat. Bring this solution to boiling, precipitate with a slight excess of ammonia, and filter at once. Wash the precipitate on the filter once with hot water, and add this filtrate to the one previously obtained, to be treated for Group IV. The precipitate will contain the metals of Group III.

A small portion of the precipitate is dissolved in hydrochloric acid, the solution diluted a little, and potassium ferrocyanide added, when iron, if present, will give a characteristic blue precipitate, which is conclusive proof of the presence of iron.

The remainder of the precipitate is now removed to a beaker and dissolved in dilute hydrochloric acid, by the aid of heat, using as little acid as possible. When all is dissolved, add considerable excess of sodium hydrate, and bring to boiling. This will dissolve the aluminum hydrate at first formed, while the iron and chromium remain as a precipitate. Filter and wash two or three times with hot water on the filter. Test the precipitate for chromium by fusing a little of it on the platinum foil, as directed in Art. 56. The bead test may also be used for both chromium and manganese. There are two good methods of testing the filtrate, and, as a rule, both should be used. They are:

1. Place a little of the alkaline filtrate in a test tube, add ammonium chloride, shake well, and stand aside for a minute or two. If aluminum is present, it will be precipitated as white aluminum hydrate, but it may take a few moments to collect so that it is readily seen.

2. Render the remainder of the filtrate slightly acid by means of concentrate hydrochloric acid, add a slight excess of ammonium carbonate, boil the solution a moment to expel the liberated carbon dioxide, and allow to settle. If aluminum is present, it will be precipitated as white aluminum hydrate. When the precipitate is first formed, it is almost colorless, and may be overlooked unless the mixture is examined carefully. After standing a while, it is much more easily seen, especially when the tube, or beaker, is moved sufficiently to cause the precipitate to move through the liquid in which it is suspended. .

102. Treatment of Group III, When Phosphoric Acid is Present.—To test for phosphoric acid, remove a little of the original precipitate on the point of a knife blade to a porcelain dish, and dissolve it in a drop or two of nitric acid. Place about two or three cubic centimeters of ammonium-molybdate solution in a test tube, heat it to the boiling point, and add a drop or two of the solution obtained by treating the precipitate with nitric acid. A yellow precipitate proves the presence of phosphoric acid, while the absence of a yellow precipitate proves its absence.

When phosphoric acid is present, the precipitate is removed to a porcelain dish and dissolved in the least necessary quantity of hydrochloric acid, by the aid of heat, an excess of sodium hydrate is added, and the whole is heated to boiling. This dissolves the aluminum hydrate and phosphate, and the other metals remain in the precipitate. Filter, wash once with hot water on the filter, and test the filtrate for aluminum by the methods previously described.

Remove the precipitate to a porcelain dish, dissolve it in concentrate nitric acid, and add an excess of pure tin foil. Heat to boiling, and stir well. The phosphorus and tin

form an insoluble compound, while all the metals are changed to soluble nitrates. Filter, wash with hot water, and then throw away the precipitate, which contains only the tin and phosphorus. Add about 10 cubic centimeters of ammonium chloride to the filtrate, heat it to boiling, and precipitate with a slight excess of ammonia. Filter, wash once with hot water, and add the filtrate to the first filtrate, to be treated for Group IV. Examine the precipitate for iron and chromium, as previously directed.

103. Treatment of Group III, When Oxalic Acid is Present.—To examine the precipitate for the presence of oxalic acid, dissolve a small portion of it in a test tube, in a few drops of concentrate nitric acid, add an excess of sodium carbonate, and boil for a few moments. The metals are precipitated as carbonates and hydrates, and the oxalic acid unites with the sodium, forming soluble sodium oxalate. Filter, acidify the filtrate with acetic acid, boil till all the carbon dioxide is driven off, and add calcium chloride. If oxalic acid is present, the calcium will be precipitated as white calcium oxalate, which is insoluble in acetic acid, but is readily dissolved by hydrochloric acid. In making this test, care must be taken to render the filtrate distinctly acid with acetic acid, and to boil till all carbon dioxide is expelled, otherwise calcium carbonate will be precipitated, and this will be mistaken for calcium oxalate.

If oxalic acid is found to be present, the precipitate is dissolved, and the aluminum removed, just as described in the case where phosphoric acid is present. The precipitate from the sodium hydrate is removed to a porcelain dish, an excess of sodium carbonate added, and boiled for a minute or two. The metals are thus changed to insoluble hydrates and carbonates, and the oxalic acid unites with the sodium, forming soluble sodium oxalate. Filter, and wash two or three times with hot water. The filtrate may be thrown away.

Transfer the precipitate to a beaker, dissolve it in dilute hydrochloric acid, bring to boiling, and precipitate the iron and chromium with a slight excess of ammonia. Filter,

wash once on the filter with hot water, and add the filtrate to the first filtrate from the separation of this group, which is to be treated for the fourth group. The precipitate is examined for iron and chromium by the methods already described.

GROUP IV.

104. The filtrate from Group III, or, in case there were none of the metals of Group III in the solution, the filtrate from Group II, which failed to give a precipitate with ammonia, is next treated for Group IV. But before adding the group reagent to the whole quantity, a small amount is taken out in a test tube and ammonium sulphide added, as this will save boiling off the ammonium sulphide, and filtering from sulphur, in case none of the metals of Group IV are contained in the solution. If this side test yields no precipitate, it is thrown out and the main filtrate is treated for Group V. If we find, by the side test, that metals of the fourth group are present, the filtrate from Group III is heated to boiling and precipitated by ammonium sulphide. It is important to avoid a large excess of this reagent, but a sufficient quantity must be added to precipitate all the metals of this group. It is difficult to tell when just enough of the reagent has been added, but a sufficient quantity is indicated if the solution retains a distinct odor of the reagent after stirring a few moments. As a safeguard, the filtrate must always be tested by adding to it a few drops of the reagent, and if a precipitate is formed, the addition of the reagent is continued till the precipitation is complete, and this precipitate is added to and treated with the first one.

When the precipitation is complete, boil the contents of the beaker for a moment, remove the beaker from the gauze, allow the precipitate to completely settle, decant the clear liquid as completely as possible through the filter, wash the precipitate on to the filter with hot water, and wash twice on the filter with hot water. Care must be taken to expose the precipitate to the air as little as possible, as the air tends to oxidize the sulphides to soluble sulphates. To avoid this, a

drop or two of ammonium sulphide is sometimes added with the water on the filter, but if the whole operation is performed quickly, and with little exposure to the air, this is generally unnecessary.

The filtrate is set aside to be treated for Group V, and the precipitate is examined for the metals of Group IV. By observing the color of the precipitate, we may sometimes avoid useless work. If the precipitate is light colored, only zinc and manganese can be present, and in that case we dissolve the precipitate and proceed at once to separate the zinc and manganese, as directed later. In case the precipitate is black, all the metals of the group may be present, and we must examine the precipitate for all of them. To do this, punch a hole in the apex of the filter with a stirring rod, and wash the precipitate through into a beaker or porcelain dish, using about 30 cubic centimeters of cold water. To this add about 5 cubic centimeters of dilute hydrochloric acid, and stir for a minute or two in the cold. The sulphides of zinc and manganese are dissolved, while the sulphides of cobalt and nickel are not attacked by this dilute acid. Filter, and wash twice on the filter. The precipitate will contain the cobalt and nickel, and the filtrate, the zinc and manganese, if all were present. To learn if cobalt is present in the precipitate, the borax-bead test is used, as described in Art. 59. Nickel also gives some color to the bead; so that, if a distinct blue is not obtained, the result should be rejected and a further examination made. If the bead proves the absence of cobalt, a little of the precipitate is dissolved in a few drops of aqua regia, nearly all the acid driven off, a little water added, and the solution thus made is tested for nickel by adding sodium hydrate. A green precipitate proves the presence of nickel. The other reactions for nickel may also be used to further confirm it.

When cobalt is present, it must be removed before we can test for the nickel. To do this, remove the precipitate to a small porcelain dish—on a small portion of the filter if necessary—and dissolve it in a few drops of aqua regia. Evaporate nearly all the acid, add about 1 cubic centimeter of water,

and filter into a test tube, using a little more water to wash the filter paper, which should be very small. Neutralize this solution with concentrate ammonia, then render it slightly, but distinctly, acid with acetic acid, add a stick of potassium nitrate that will reach nearly to the top of the solution, and allow it to stand for several hours. The cobalt will all be precipitated as a yellow powder, which will settle to the bottom of the tube, and the clear liquid may be examined for nickel by means of sodium hydrate, and by other tests.

The acid filtrate is next examined for zinc and manganese. It is first boiled, to expel all hydrogen sulphide, then rendered strongly alkaline with sodium hydrate, and heated to boiling. Both zinc and manganese are at first precipitated as light-colored hydrates. The manganese is quite rapidly oxidized to a brown compound, while the zinc is dissolved in the excess of sodium hydrate. Filter and test the precipitate for manganese, and the filtrate for zinc. The precipitate may be tested by means of the borax bead, and also by fusing part of it on the foil with sodium carbonate and potassium nitrate. The filtrate may be tested by hydrogen sulphide. If this gives a white precipitate, it is sufficient evidence of zinc.

GROUP V.

105. The filtrate from the fourth group is boiled till the ammonium sulphide is completely decomposed, and filtered from sulphur, if any is deposited during the boiling. In case there were no fourth-group metals in the solution, this boiling will be unnecessary, as there will be no ammonium sulphide in the solution. We can tell when all the sulphide is driven off in this case by the same methods that were used for the purpose when the filtrate from the second group was boiled to expel the hydrogen sulphide.

The clear filtrate is rendered distinctly alkaline with ammonia, heated, and ammonium carbonate is added in sufficient quantity to completely precipitate the barium, strontium, and calcium, as carbonates. The contents of the beaker are boiled for a few moments in order to change any acid carbonates

that may be formed at first, into normal carbonates, but this boiling must not be continued more than a minute at the outside, or the ammonium chloride in the solution will begin to dissolve the carbonates by changing them to chlorides. The precipitate is allowed to settle before filtering. It is washed twice on the filter with hot water, and then examined for the members of this group. The filtrate is set aside to be treated for Group VI.

Remove the precipitate to a beaker and dissolve in a slight excess of acetic acid, by the aid of gentle heat. Remove a little of this solution to a test tube, and add potassium chromate to test for barium. If a yellow precipitate is formed, it shows the presence of barium. In this case, add potassium chromate to the rest of the acetic-acid solution in sufficient quantity to precipitate all the barium. Filter and wash once or twice on the filter. A yellow precipitate at this point is proof of barium, but it may be confirmed by holding a little of it on the loop of a platinum wire in a non-luminous Bunsen flame and noting the color imparted to the flame. It is well, after holding it in the flame for a while, to dip the loop containing the dry precipitate into some dilute hydrochloric acid, and then return it to the flame. The acid will partly dissolve the chromate, forming barium chloride, which is quite volatile, and, therefore, colors the flame much more distinctly. If desired, the rest of the chromate precipitate may now be dissolved in dilute hydrochloric acid, and other tests for barium applied.

The filtrate, which may contain strontium and calcium, is precipitated by ammonia and ammonium carbonate, in exactly the same way that the original group precipitation was made. Filter, and wash the precipitate well to free it from the soluble chromates. Dissolve the precipitate in a little hydrochloric acid, and make a preliminary flame test, by holding a drop of the solution in the flame, on the loop of the platinum wire. If strontium is present, there will be a flash of bright-red light, while calcium imparts a brick-red color to the flame. If the calcium solution is very strong, its flame may be mistaken for the strontium flame.

To separate the strontium and calcium, dilute the solution to from 50 to 75 cubic centimeters, and add ammonium sulphate. Strontium, if present, will be slowly precipitated as white strontium sulphate, while the calcium remains in solution. After letting it stand for some time, for the precipitate to form and settle, filter and test the precipitate for strontium by means of the flame. If the color is not imparted to the flame at once, the precipitate is held in the reducing flame for a time, until the sulphate is partly reduced to sulphide. Then, if it is dipped in dilute hydrochloric acid and quickly withdrawn, the sulphide is partly changed to chloride, which is quite volatile and colors the flame quickly and distinctly.

The filtrate is now rendered distinctly ammoniacal, heated to boiling, and ammonium oxalate added. If calcium is present, a white, crystalline precipitate of calcium oxalate, which is insoluble in acetic acid, is formed. This precipitate proves the presence of calcium, while a failure to obtain this precipitate proves its absence. If the precipitate is obtained, however, it may be further verified by the color it imparts to the flame, as in the case of barium and strontium.

106. Second Method of Separating Strontium and Calcium.—Another method of separating strontium and calcium, based upon the solubility of calcium sulphate in ammonium sulphate, is sometimes used. In this method the barium is removed by potassium chromate, the strontium and calcium precipitated by ammonium carbonate, and washed on the filter to free the precipitate from potassium chromate, as described above. Dissolve this precipitate in the least necessary quantity of hydrochloric acid, and add a little water, but leave the solution quite concentrate. To this solution add dilute sulphuric acid in sufficient quantity to precipitate all the strontium and calcium as sulphates, and allow it to stand for the precipitate to form and settle. Filter, and wash once on the paper. If only a trace of calcium is present, the filtrate should be tested. Otherwise, it may be disregarded.

Remove the precipitate to a porcelain dish, cover it with a concentrate solution of ammonium sulphate,* and heat gently for about 10 minutes, with frequent stirring. This will dissolve the calcium sulphate, while the strontium sulphate is not acted upon. Filter, and wash two or three times, preferably with warm water. Test the precipitate for strontium in the usual manner, and examine the filtrate for calcium by means of ammonium oxalate, as described above.

GROUP VI.

107. If, at the time of the precipitation of the fifth group, the boiling was not continued long enough, or exceeded the proper time, the filtrate may contain traces of barium, strontium, and calcium; so, before treating this filtrate for the sixth group, 2 or 3 drops of sulphuric acid and a like amount of ammonium oxalate are added, and the solution boiled for a few moments, taking care that it remains distinctly alkaline. If a slight precipitate forms, it is filtered off. The filtrate can now only contain the sixth and seventh groups. It should be concentrated to 75 or 100 cubic centimeters before precipitating. Add a few cubic centimeters of concentrate ammonia, and then sodium phosphate; stir well, and let stand for some time for the precipitate to form and settle. If the solution is very dilute, this may require several hours, and, at all events, the solution should stand until it becomes perfectly cold. The presence or absence of a precipitate at this point is proof of the presence or absence of magnesium, but if a precipitate is formed, magnesium may be confirmed by treating a little of it on the charcoal before the blowpipe, as directed in Art. 79.

GROUP VII.

108. As the alkalies have been added to the solution in the form of reagents, we cannot use the filtrate from the sixth group to test for the members of the seventh, but must

* Ammonium-sulphate solution for this purpose is made by dissolving about 15 grams of the solid in 30 cubic centimeters of water.

take small portions of the original solution. We should first test for ammonium. To do this, take a small quantity of the original solution in a test tube, add about an equal amount of sodium hydrate, and boil. Ammonium compounds, when present, are always decomposed, yielding ammonia gas NH_3 , which is recognized by its odor, by the white fumes that are formed when in contact with hydrochloric acid, and by its power of turning red litmus paper blue. The odor is by far the best proof, for nothing else has a similar odor.

A second small quantity of the original solution is now taken, a clean platinum wire that has just been tested in the flame to prove the absence of alkalies, is dipped into it and the drop of solution adhering to the loop is brought into the non-luminous flame.

Sodium is recognized by the intense yellow color that it imparts to the flame, while potassium is recognized by the violet color that is given to the flame by its compounds.

If both sodium and potassium are present in a solution, the violet potassium flame is entirely obscured by the intense yellow flame produced by the sodium. But if the flame is viewed through a thick, blue (cobalt) glass, the yellow rays of the sodium are entirely absorbed and the potassium flame is distinctly seen. A still better method of recognizing sodium and potassium, is by means of the spectroscope, which will be described later.

GENERAL DIRECTIONS.

109. We now have before us a method by which any number of the common metals may be recognized in, and separated from, solutions containing a mixture of metals, *but the student should not expect to become an expert analyst from merely reading directions. He should make up mixtures and separate them according to the scheme given, following directions as closely as possible.*

The operations are described as carefully as possible, but a student must perform each of them, with known solutions,

carefully observing the behavior of each metal or group of metals, before he can be absolutely certain that his results are correct when working on an unknown solution.

The student will also find that he can learn the method much more easily and thoroughly by carrying out each operation as he studies it, using the description given as a guide in his work.

Mixed solutions for practice can easily be prepared by mixing some of the solutions made as described for the reactions of the separate metals. In doing this, certain simple precautions must be taken; as, for example, chlorides must not be introduced into solutions containing first-group metals, or these metals will at once be precipitated as chlorides. Sulphates must not be added to solutions containing lead, mercurous, barium, strontium, or calcium compounds, or these metals will be precipitated as sulphates. Arsenites and arsenates, under certain conditions, precipitate some of the metals, so care should be exercised in making solutions containing these. Much valuable experience will be acquired in making up these solutions, if the work is done thoughtfully.

The student should not make up too complicated a solution at first. In fact, it is best to start with a solution containing only metals of the first group, and after these have been separated, make up more complicated mixtures, but avoiding the more difficult operations until considerable familiarity with the work has been acquired.

Each student is strongly advised to make up and analyze the following list of solutions in their order, using, in making these mixtures, the solutions already made up for the reactions of the separate metals. They should be used as soon as possible after being made up, as some of them decompose upon standing.

1. *Lead, silver, and mercurous.*

This is made by mixing equal parts of the nitrates of the three metals.

2. *Lead, bismuth, and cadmium.*

This is made by mixing solutions of the nitrates of the three metals in equal proportions.

3. *Antimony, arsenic, and tin.*

To prepare this, mix antimony chloride, stannous chloride, and sodium arsenite, in equal amounts. If a precipitate is formed, dissolve it in the least necessary quantity of concentrate hydrochloric acid.

4. *Iron, aluminum, and chromium.*

This is made by mixing equal quantities of the solutions of ferrous sulphate, common alum, and chrome alum. The alums will introduce a little potassium or ammonium, or perhaps both, and the student should examine the solution for these as well as for the constituents that were intentionally introduced.

5. *Aluminum, nickel, and zinc.*

To prepare this, mix equal amounts of the solutions of alum, nickel nitrate, and zinc sulphate. This solution, like the preceding one, should be examined for potassium and ammonium.

6. *Barium, strontium, and calcium.*

This is generally made by mixing barium chloride, strontium nitrate, and calcium chloride, in equal quantities. But either the chlorides or nitrates may be used equally well.

7. *Magnesium, ammonium, potassium, and sodium.*

This solution is generally a mixture of equal parts of the solutions of magnesium sulphate, and ammonium, potassium, and sodium nitrates, but almost any compounds of these metals will answer the purpose.

This list is given as a guide to the student in starting in the group separations, and, after completing it, he should make up and analyze a number of solutions, until he has determined all of the metals, a few at a time, or he can get a friend to make up solutions for him, and thus analyze them before knowing their composition.

The student must never forget to look for the alkalies, whether he finds other metals in the solution or not. A portion of the original solution should first be tested for ammonium with sodium hydrate, and then another portion tested for sodium and potassium in the flame.

The student should never attempt to separate the two

divisions of the second group until he is thoroughly familiar with the separation of the metals of each division, as this is one of the most difficult operations in qualitative analysis.

The sulphides of some of the metals occasionally become slimy at this point and pass through the filter. Boiling, and allowing to settle again, sometimes remedies this, but, as a rule, this portion of the solution must be thrown away, and the analysis begun again with a fresh portion of the original solution. However, after the student gains a little experience in chemical manipulation, this trouble will be very rare.

The separation of Group III, and subsequent groups, in the presence of phosphoric or oxalic acid, should never be attempted until the operator is thoroughly familiar with all the separations when they are absent.

While the main object in this, as in every part of the work, is to become able to analyze substances, it is not the only object. And, although definite directions are given for the separation of the groups, the directions should not be followed blindly and without thought. This system of separating the metals is built upon the properties of their compounds, and their deportment with reagents, as previously described; and the many chemical relations, here brought together in a small space, should be carefully studied. It is only by such study that the student will acquire that knowledge of chemical relations which is essential in all advanced chemical work.

ACIDS.

COMMON INORGANIC ACIDS.

110. Having learned to recognize and separate the metals, the next step is to learn to recognize the acids in a similar manner. As most of the substances that a chemist is called upon to analyze are compounds, he must be able to determine the acid as well as the metal, and, in order to have the conditions as nearly the same in practice as in actual

work, the acids should be determined in compounds rather than to work on free acids.

The reactions for the common inorganic acids will be given first, then the reactions for the common organic acids. These will be followed by the reactions for the less common inorganic and organic acids.

The student should verify and become familiar with the reactions for the common acids, both inorganic and organic. This can only be accomplished by actually performing the operations, as in the case of the metals.

The reactions for the less common acids are given more as a matter of reference, so that if the student is called upon to determine them at any time, he will have directions for doing so.

HYDROCHLORIC ACID.

111. Hydrochloric acid HCl , and all chlorides, except lead, silver, and mercurous chlorides, are soluble in water. Ammonium chloride or sodium chloride may be used for the reactions.

1. *Silver nitrate* precipitates white silver chloride from solutions of hydrochloric acid or chlorides. This precipitate gradually turns to brown upon standing for some time in the light, or is changed much more rapidly by heating. It is soluble in ammonia or potassium cyanide, and is reprecipitated from these solutions by nitric acid.

2. *Lead acetate* precipitates white lead chloride $PbCl_2$ from solutions that are not too dilute. Lead chloride is somewhat soluble in cold water, so it is not completely precipitated. It is soluble in hot water, and, upon cooling, crystallizes from this solution in white needles.

3. *Mercurous nitrate* precipitates white mercurous chloride Hg_2Cl_2 , which is not dissolved by dilute acids, but is soluble in hot concentrate nitric acid. Ammonia changes this precipitate to black amido-mercurous chloride Hg_2NH_2Cl .

4. Solid chlorides, when heated in a test tube with concentrate sulphuric acid, are decomposed, yielding free hydrochloric acid, which may be recognized by its odor. If

a glass rod be dipped in ammonia, and then brought to the mouth of the tube, dense white fumes of ammonium chloride are formed.

HYDROBROMIC ACID.

112. Hydrobromic acid HBr forms compounds similar to those of hydrochloric acid, but they are not so common. All the common bromides, except those of silver, lead, and mercury, are soluble in water. Potassium bromide or sodium bromide may be used for the reactions.

1. *Silver nitrate* precipitates yellowish-white or light-yellow silver bromide $AgBr$ from solutions of bromides or hydrobromic acid. This precipitate is insoluble in dilute acids, dissolves with some difficulty in ammonia, but is easily soluble in potassium cyanide.

2. *Lead acetate* precipitates white lead bromide $PbBr_2$, which is less soluble in water than the corresponding lead chloride, but is dissolved by nitric acid.

3. *Mercurous nitrate* precipitates yellowish-white mercurous bromide Hg_2Br_2 .

4. Most bromides in the solid state, or in concentrate solutions, when heated with concentrate sulphuric acid, are decomposed and give off a brownish-red vapor of free bromine.

5. All bromides, with the exception of silver bromide, are decomposed when heated in a test tube with concentrate nitric acid, yielding free bromine. If a solution of a bromide is treated, it is colored yellow, yellowish red, or brownish red, according to the degree of concentration. If a solid bromide, or a very concentrate solution is treated with the nitric acid, brownish-red vapors are given off, which collect in the upper part of the tube in heavy, reddish globules of free bromine. This is the most characteristic reaction for hydrobromic acid.

HYDRIODIC ACID.

113. The iodides correspond in many respects with the chlorides and bromides, but many more of the iodides of the heavy metals are insoluble in water than is the case with the

chlorides and bromides. The iodides of silver, lead, mercury, bismuth, antimony, tin, and arsenic, are either insoluble, or soluble with difficulty, in water. The others are more or less easily dissolved. Potassium iodide is best used for the reactions.

1. *Silver nitrate* precipitates yellowish-white silver iodide AgI , which becomes dark upon standing in the light. It is insoluble in dilute nitric acid, and only slightly soluble in ammonia, but is dissolved by potassium cyanide.

2. *Lead acetate* precipitates yellow lead iodide PbI_2 , which, like lead chloride, is soluble in hot water.

3. *Mercurous nitrate* precipitates greenish-yellow mercurous iodide Hg_2I_2 , which is soluble in excess of potassium iodide; hence, no permanent precipitate is formed until an excess of mercurous nitrate has been added.

4. *Mercuric chloride*, when added in the proper amount, produces a scarlet precipitate of mercuric iodide HgI_2 , which is soluble in an excess of either the potassium iodide or mercuric chloride, but is insoluble in nitric acid.

5. *Copper sulphate* mixed with *sulphurous acid* gives a dirty-white precipitate of cuprous iodide Cu_2I_2 . Chlorides and bromides are not precipitated by this reagent; hence, it is a convenient method of testing for iodides in their presence. Instead of copper sulphate and sulphurous acid, we may use a solution, made by mixing 1 part of copper sulphate with $2\frac{1}{2}$ parts of ferrous sulphate, and dissolving them in water, as this solution produces the same precipitate.

6. To test for iodine in a very dilute solution, acidify the solution with sulphuric acid, add a few drops of starch solution or starch paste,* and then a few drops of a strong solution of potassium nitrate. If iodine is present, the solution will assume a deep-blue color, owing to the formation of blue starch iodide.

7. All iodides in the solid form, when heated with concentrate sulphuric acid in a test tube, are decomposed,

* Starch paste may be made by grinding up a little pure starch with water, or a solution may be made as described in Art. 80, Experiment 43, *Inorganic Chemistry*, Part 1.

yielding a characteristic violet vapor of iodine, which collects in a solid mass on the sides of the upper part of the tube. Near the edges, where the layer is very thin, this appears violet, but where the layer is thicker it looks black.

SULPHURIC ACID.

114. Sulphuric acid H_2SO_4 is a very strong acid. It forms stable compounds with the metals, and is not replaced in these compounds by any other acid at ordinary temperature. All the normal sulphates, except lead, mercurous, barium, strontium, and calcium sulphates, are readily soluble in water. Sodium sulphate or magnesium sulphate may conveniently be used for the reactions.

1. *Lead acetate* precipitates white lead sulphate $PbSO_4$, which is only slightly attacked by water or dilute acids. It may be dissolved in boiling concentrate hydrochloric acid. It is easily dissolved in alkaline ammonium tartrate, made by treating the precipitate with tartaric acid and ammonia, as described in Art. 20, 8, and from this solution the lead may be precipitated by potassium chromate.

2. *Mercurous nitrate* precipitates white mercurous sulphate Hg_2SO_4 from solutions that are not too dilute. This is much less soluble in water than calcium sulphate; hence, is precipitated from more dilute solutions.

3. *Barium chloride* precipitates white barium sulphate $BaSO_4$, which is insoluble in all dilute, and but slightly attacked by concentrate, acids. The presence of concentrate acids, and of some salts, hinders the immediate formation of the precipitate in very dilute solutions.

4. Some sulphates, when very highly heated in a glass tube, give off sulphurous oxide SO_2 , which is recognized by its penetrating odor.

5. All sulphates in the solid form, when mixed with sodium carbonate and fused on the charcoal before the blow-pipe, are reduced to sulphides by the action of the carbon, and the sulphur, or part of it, unites with the sodium, forming sodium sulphide. If, after cooling, this mass is removed

to a silver coin, or other piece of silver, broken up, and a drop of water added, the solution of sodium sulphide will attack the silver almost immediately, leaving a dark stain of silver sulphide Ag_2S .

This is not characteristic of sulphuric acid, but merely shows the presence of sulphur. The other acids of sulphur give the same reaction. It is very important, however, as it shows that the compound is a salt of one of the acids of sulphur. It is generally spoken of as the *coin test*.

THIOSULPHURIC ACID.

115. Thiosulphuric acid $H_2S_2O_3$ does not exist in the free state, but its salts, the thiosulphates, which are often erroneously called hyposulphites, are stable, and some of them are important. Most of them are soluble in water. Sodium thiosulphate may be used for the reactions.

1. *Silver nitrate* precipitates white silver thiosulphate $Ag_2S_2O_3$, which changes rapidly to yellow, then brown, and finally to black, owing to the formation of silver sulphide Ag_2S . The precipitate is easily soluble in excess of the thiosulphate.

2. *Lead acetate* precipitates white lead thiosulphate PbS_2O_3 , which is soluble in nitric acid.

3. *Barium chloride* precipitates white barium thiosulphate BaS_2O_3 from rather strong solutions. It is decomposed by hydrochloric acid, giving off sulphur dioxide, and throwing out free sulphur in the solution, which it gives a yellowish appearance. The precipitate is slightly soluble in water, so in very dilute solutions no precipitate is formed.

4. *Ferric chloride* imparts a characteristic reddish-violet color to solutions of thiosulphates. The color is not permanent, but, upon standing, ferrous chloride is formed, and the solution becomes colorless.

5. All thiosulphates are decomposed by hydrochloric or sulphuric acid, giving sulphur dioxide and free sulphur. The sulphur thrown out from thiosulphates is yellow, while that from sulphites and sulphides is nearly always white.

6. Thiosulphates give the *coin test* the same as sulphates.

SULPHUROUS ACID.

116. Sulphurous acid H_2SO_3 is a weak, rather unstable acid, and its salts are also rather unstable. The sulphites of the alkalis are soluble in water, but the other sulphites are only soluble with difficulty, or are insoluble. The sulphites, especially in solution, when exposed to the air, are oxidized to sulphates; hence, we generally find sulphates mixed with sulphites. Pure sodium sulphite Na_2SO_3 is a convenient salt to use for the reactions.

1. *Silver nitrate* precipitates white silver sulphite Ag_2SO_3 , which, upon standing, is decomposed into sulphuric acid and metallic silver. This action is hastened by heating.

2. *Lead acetate* precipitates white lead sulphite $PbSO_3$, which is dissolved by nitric acid.

3. *Barium chloride* precipitates white barium sulphite $BaSO_3$ from neutral sulphite solutions. This is soluble in hydrochloric acid; but, as sulphates are nearly always present in sulphites, an insoluble residue of barium sulphate generally remains. By filtering off this residue and adding a few drops of concentrate nitric acid or chlorine water to the clear filtrate, the sulphite will be oxidized to sulphate, and barium sulphate will be precipitated. If this succeeds, it shows that the solution contained sulphite. The oxidation and consequent precipitation is aided by heating.

Barium chloride does not precipitate free sulphurous acid.

4. All sulphites are easily decomposed by strong acids, yielding sulphur dioxide. They are oxidized to sulphates by chlorine or bromine water, and, like all other sulphur compounds, give the coin test.

HYDROSULPHURIC ACID.

117. Hydrogen sulphide H_2S is a weak, unstable acid, and on account of its acid properties is sometimes called *hydrosulphuric acid*. It unites with bases, as we have seen, to form sulphides. The sulphides of the alkalis and alkaline earths are soluble in water. All the others are insoluble. Sodium or ammonium sulphide may be used for the

wet reactions, and any sulphide that has been powdered may be used for the dry ones.

1. *Silver nitrate* precipitates black silver sulphide Ag_2S , which is soluble in warm nitric acid.

2. *Lead acetate* precipitates black lead sulphide PbS , which is soluble in warm nitric acid.

3. *Mercurous nitrate* precipitates black mercuric sulphide HgS , which is not dissolved by any single acid, but is soluble in aqua regia. When treated as directed in Art. 23, 5, this precipitate is changed to a white, insoluble compound by nitric acid.

4. Nearly all the sulphides, either in the solid form or in solution, are decomposed by heating with concentrate sulphuric acid, yielding hydrogen sulphide, which is readily recognized by its odor or by the black color that it imparts to a piece of filter paper moistened with lead solution.

NITRIC ACID.

118. Nitric acid HNO_3 is a strong, stable acid, and forms a large number of salts that are also stable. All the nitrates, with the exception of a few basic ones, are soluble in water; hence, we cannot use precipitation as a means of recognizing nitric acid, and must resort to other reactions. Potassium nitrate is a good salt to use for the reactions.

1. The best test for nitric acid in solution, and, in fact, the only good ordinary test, is performed by mixing about 2 cubic centimeters, of the solution to be tested, with about an equal amount of concentrate sulphuric acid in a test tube, and cooling by holding the tube in water, or by allowing water to run over the outside of it. When the solution has reached about the temperature of the room, carefully pour a solution of ferrous sulphate down the side of the inclined tube, so that the solutions do not mix, but the ferrous sulphate forms a layer on top of the other solution. If the solution contains a nitrate, a ring will be formed where the two solutions meet, which will be variously colored according to the amount of nitric acid present. If but a small

amount of nitrate is present, the ring will be light red, while if the quantity is greater, it will be brown or almost black. The color is caused by nitric oxide NO , which is set free by sulphuric acid, uniting with the ferrous sulphate, forming an unstable compound. If the tube is shaken slightly, the liquids will be mixed slightly at the points where they come in contact, and the ring becomes wider. By heating, the compound is broken up and the liquid becomes clear. At this time, if much nitrate were present, brownish vapors of nitrogen peroxide NO_2 may be seen in the upper part of the tube.

2. As nitrites give the above reaction to a certain extent, it is necessary to distinguish between nitric and nitrous acids. To do this, place a small quantity of the solution in a test tube, and add about half the volume of dilute sulphuric acid, and small amounts of potassium-iodide solution and starch paste. If nitric acid or a nitrate alone is present, no reaction takes place. Now add a little metallic zinc. The hydrogen generated by the action of the sulphuric acid on the zinc, reduces the nitric acid to nitrous acid; this sets free the iodine, which unites with the starch, forming blue starch iodide. If nitrous acid is present, the blue color will be produced at once when the reagents are added.

3. All nitrates are decomposed by heat. The nitrates of the alkalis give off oxygen and are converted into nitrites at first, but are changed to oxides at a higher temperature. The nitrates of the heavy metals give off oxygen and nitric peroxide at once, and are converted into the oxides of these metals. If the nitrates are ignited in a small glass tube that is closed at one end, the oxygen given off will ignite a spark held at the mouth of the tube.

PHOSPHORIC ACID.

119. The phosphates of the alkalis are soluble in water. Nearly all the others are insoluble. A solution of sodium phosphate may be used for the reactions.

1. *Silver nitrate* precipitates light-yellow silver phosphate Ag_3PO_4 , which is soluble in nitric acid and in ammonia.

2. *Lead acetate* precipitates white lead phosphate $Pb_3(PO_4)_2$, which is soluble in nitric acid, but insoluble in acetic acid.

3. *Barium chloride* precipitates white barium phosphate $Ba_3(PO_4)_2$, which is soluble in nitric or hydrochloric acid.

4. *Magnesium sulphate* precipitates white magnesium-ammonium phosphate $MgNH_4PO_4$ from solutions of phosphates containing ammonia and ammonium chloride. In order to avoid mistaking magnesium hydrate for magnesium phosphate, it is best to add an excess of ammonium hydrate to the magnesium sulphate, and then just enough ammonium chloride to dissolve the precipitate thus formed. To this solution add some of the solution to be tested, and shake well. In case of dilute solutions, the precipitate is not formed at once, so it should be allowed to stand for some time. Agitation aids the formation of the precipitate.

5. *Ammonium molybdate* in nitric-acid solution, when added in excess to a solution of phosphoric acid or a phosphate, produces a yellow precipitate of ammonium phosphomolybdate, which varies in composition according to conditions. It is soluble in ammonia, and also in phosphoric acid or phosphates; hence, no precipitate is formed unless there is an excess of ammonium molybdate. The best way to make this test is to place about 2 cubic centimeters of the molybdate solution in a test tube, heat it almost to boiling, and add 2 or 3 drops of the solution to be examined. If phosphoric acid is present in any considerable amount, the yellow precipitate is formed almost at once in this hot solution. Shaking also hastens precipitation. Arsenates also give a yellow precipitate in hot solutions, and silicates sometimes give a yellow color to the solution. But neither arsenates nor silicates are so readily precipitated as are phosphates, and they are easily distinguished by other reactions.

CARBONIC ACID.

120. Carbonic acid H_2CO_3 is a weak acid that has never been obtained in the uncombined state, except in very dilute aqueous solution. Its anhydride, carbon dioxide, and its

salts, the carbonates, are common, and many of the salts are important. The carbonates of the alkalies are soluble in water. All other normal carbonates are insoluble in water. Sodium carbonate is the most convenient salt to use for the reactions.

1. *Silver nitrate* precipitates white silver carbonate Ag_2CO_3 , which changes to brown silver oxide Ag_2O upon boiling.

2. *Lead acetate* precipitates white lead carbonate $PbCO_3$, which is soluble in nitric acid, and also in acetic acid.

3. *Barium chloride* precipitates white barium carbonate $BaCO_3$, which is easily soluble, with effervescence, in hydrochloric acid.

4. All carbonates, either in the solid state or in solutions that are not too dilute, are decomposed by dilute hydrochloric acid, with effervescence, due to the escaping carbon dioxide. A drop of barium hydrate on a glass rod, held at the mouth of the tube where the gas is escaping, will become turbid, owing to the formation of white barium carbonate.

CHROMIC ACID.

121. Chromic acid H_2CrO_4 forms a large number of salts, known as chromates. They are all colored compounds, and are generally either yellow or red. The chromates of the alkalies are soluble in water, while most of the other chromates are insoluble. Potassium chromate serves well for the reactions.

1. *Silver nitrate* precipitates red silver chromate Ag_2CrO_4 , which is soluble in either nitric acid or ammonia.

2. *Lead acetate* precipitates yellow lead chromate $PbCrO_4$, which is soluble in sodium hydrate, and is reprecipitated from this solution by nitric acid.

3. *Mercurous nitrate* precipitates red basic mercurous chromate, which is insoluble in sodium hydrate, but is dissolved by nitric acid.

4. *Barium chloride* precipitates yellow barium chromate

$BaCrO_4$, which is soluble in nitric or hydrochloric acid, and also in chromic acid.

5. Many of the dry chromates, when heated with concentrate hydrochloric acid in a test tube, are changed into chlorides of chromium and the metal that acted as the base, and free chlorine is given off.

6. A yellow normal chromate solution may be changed to a red bichromate by adding an acid, preferably nitric acid. The red bichromate thus formed may be changed back to the yellow normal chromate by adding an excess of ammonia.

7. All chromate solutions containing an excess of hydrochloric acid are reduced to green chromium chloride by heating with sulphurous acid or alcohol. Sulphuric acid serves instead of hydrochloric acid, and solutions in nitric acid can be reduced, though with difficulty.

It is sometimes necessary to reduce chromates of the heavy metals and put the solution thus obtained through the group separations in order to be sure of the results obtained in the dry way.

The chromate is dissolved in an acid that does not precipitate the metal acting as the base, alcohol is added, and the solution is boiled until it becomes a deep green and all alcohol is expelled, which may be determined by the odor. The solution is now diluted to the proper extent and put through the group separations. The chromium, which has been reduced to chromium chloride $CrCl_3$, if hydrochloric acid was used, or chromium sulphate if sulphuric acid was the solvent, will, of course, be precipitated in the third group, while the metal that acted as a base will be precipitated in the group to which it belongs.

8. If insoluble chromates are fused with sodium carbonate to which a little potassium chlorate is added, chromates of the alkalis are formed, which may be dissolved in water, while the metals of the original chromates remain as insoluble carbonates or oxides. The solution will give the reactions for chromates. Or we may dissolve the fusion in acid, reduce the solution, and proceed with the group separations as above.

COMMON ORGANIC ACIDS.

122. Salts of a few of the organic acids are among the most common substances, so the student should become familiar with them. Reactions for four of the most common are given here. If the student becomes thoroughly familiar with these, he will have no trouble in determining the others, if called upon to do so, by following the directions given for their recognition, under the less common acids.

HYDROCYANIC ACID.

123. Hydrocyanic acid HCN is a weak acid that scarcely reddens litmus paper, and its soluble salts have an alkaline reaction. The cyanides of the alkalis and alkaline earths, and mercuric cyanide, are soluble in water. All other single cyanides are insoluble. The acid and its salts are exceedingly poisonous, and should be handled with great care. Potassium cyanide may be used for the reactions.

1. *Silver nitrate* precipitates white silver cyanide $AgCN$, which is soluble in potassium cyanide; hence, no precipitate is formed until silver nitrate is present in excess. The precipitate is soluble in ammonia, and is reprecipitated from this solution by nitric acid.

2. *Lead acetate* precipitates white lead cyanide $Pb(CN)_2$, which is soluble in warm nitric acid.

3. Mix about 2 cubic centimeters of any cyanide solution, about $\frac{1}{2}$ cubic centimeter of ferrous sulphate, and 2 or 3 drops of ferric chloride, in a test tube; add sodium hydrate until the mixture is alkaline, and heat almost to boiling. Now add hydrochloric acid till the solution gives an acid reaction, and a deep-blue precipitate will be formed if the solution contains much cyanide. If the solution is very dilute, a blue coloration will be seen.

4. All cyanides are decomposed, without charring, by heating in a test tube with concentrate sulphuric acid, when

they may be recognized by their characteristic odor, which is similar to that of bitter almonds.

5. Solid cyanides, when heated in the closed tube, decompose without charring.

ACETIC ACID.

124. Acetic acid $C_2H_4O_2$ has a sharp, acid taste, and strong, disagreeable odor, by which it is readily recognized even in dilute solutions. Its salts, the acetates, are nearly all soluble in water. Sodium acetate is a convenient salt to use for the reactions.

1. *Silver nitrate* precipitates white silver acetate $AgC_2H_3O_2$, from rather strong solutions of neutral acetates, or from strong solutions of the acid. This precipitate is dissolved rather easily in water and more readily in ammonia.

2. *Mercurous nitrate* precipitates white mercurous acetate $Hg_2(C_2H_3O_2)_2$ from neutral solutions of acetates that are not too dilute, and from strong solutions of the free acid. The precipitate is somewhat soluble in cold water, and is more readily dissolved if the water is warm. It is also soluble in excess of the reagent.

3. *Ferric chloride* colors a neutral acetate solution red, owing to the formation of ferric acetate $Fe(C_2H_3O_2)_3$. Upon boiling, the iron is precipitated as brown basic acetate $Fe(OH)_3(C_2H_3O_2)_2$, which settles and leaves the supernatant liquid clear.

If the ferric chloride is added to an acetic-acid solution a faint red color is seen, which becomes deeper upon the addition of ammonia. If enough ammonia is added to just neutralize the solution, and this is heated, the same reaction is obtained as with neutral acetates.

4. Any acetate heated with concentrate sulphuric acid, is decomposed, giving off free acetic acid, which is recognized by its odor. If we modify this by adding concentrate sulphuric acid and a little alcohol, and heating, acetic ether is formed during the decomposition. This is recognized by its pleasant odor. In either case, the acetate does not char, as a rule, and never to any great extent.

5. Solid acetates when heated in the closed tube are decomposed without charring, yielding acetone, which may be recognized by its odor, and leaving the oxide or carbonate of the metal in the tube. In cases where the oxide of the metal remains, carbon dioxide also escapes; and in case of some of the weak bases some free acetic acid is driven off.

TARTARIC ACID.

125. Tartaric acid $C_4H_6O_6$ is a colorless, crystalline solid, with rather a pleasant acid taste. It dissolves quite readily in water. Tartrates of the alkali metals, and a few others, are soluble in water. Those that are insoluble in water are easily dissolved by nitric or hydrochloric acid. Sodium-potassium tartrate may be used for the reactions.

1. *Silver nitrate* gives no precipitate with free tartaric acid, but in neutral solutions of tartrates it precipitates white silver tartrate $Ag_2C_4H_4O_6$, which is dissolved by either nitric acid or ammonia. Boiling decomposes the precipitate, and deposits black metallic silver.

2. *Lead acetate* precipitates white lead tartrate $PbC_4H_4O_6$ from solutions of tartaric acid or tartrates. It dissolves easily in nitric acid or ammonia.

3. *Barium chloride* precipitates white barium tartrate $BaC_4H_4O_6$ when added in excess. The precipitate is soluble in nitric, hydrochloric, or acetic acid.

4. When tartaric acid or a tartrate in the solid state is heated with concentrate sulphuric acid, it chars, owing to the separation of carbon, and carbon monoxide is given off. A characteristic odor like that of burned sugar may be noted.

5. Solid tartaric acid and tartrates, when heated in the closed tube, char and give off the characteristic odor resembling that of burned sugar. A black residue of carbon is left in the tube, mixed with the carbonate of the metal, if the substance was a tartrate.

OXALIC ACID.

126. Oxalic acid $C_2H_2O_4$, in the dry state is a white powder. With 2 molecules of water it forms colorless crystals. In either form it dissolves readily in water. The oxalates of the alkalis are soluble, while most of the others are insoluble in water. Ammonium oxalate is common, and serves well for the reactions.

1. *Silver nitrate* precipitates white silver oxalate $Ag_2C_2O_4$, which is readily dissolved by ammonia, or hot concentrate nitric acid. It is dissolved with some difficulty in dilute nitric acid.

2. *Barium chloride* precipitates white barium oxalate BaC_2O_4 from neutral solutions of oxalates. The precipitate is easily dissolved by hydrochloric or nitric acid, and less easily in acetic or oxalic acid, or ammonium chloride, and is slightly soluble in water. Ammonia reprecipitates it from its solutions in nitric or hydrochloric acid.

3. *Calcium chloride*, or any other neutral calcium solution, precipitates white calcium oxalate CaC_2O_4 from even very dilute solutions of oxalates or oxalic acid. The precipitate is almost insoluble in water, and is only very slightly soluble in acetic or oxalic acid, but is easily dissolved in nitric or hydrochloric acid. In very dilute solutions, the precipitate is formed slowly, but is promoted by heating and by the addition of ammonia.

4. Oxalic acid, and all oxalates in the dry state, when heated with concentrate sulphuric acid, are decomposed without charring. The sulphuric acid takes water from them, and carbon monoxide and carbon dioxide are given off. The carbon monoxide may be ignited at the mouth of the tube, and burns with a blue flame, either at the mouth, or down in the tube, depending upon the amount that is given off. The carbon dioxide precipitates the barium from a drop of barium hydrate held at the mouth of the tube on a glass rod, and thus renders it turbid. The student should never fail to get the tests for these two gases, as this is the most characteristic reaction for oxalic acid.

5. In the closed tube the oxalates are all decomposed at

a red heat. If heated carefully, they do not char if pure. Oxalic acid is decomposed into carbon monoxide, carbon dioxide, and water. The oxalates of the alkalies, and of barium, strontium, and calcium, are decomposed into carbon monoxide and carbonates of the metals. The other oxalates give off both carbon monoxide and carbon dioxide, and are reduced to the oxides or to the metallic state, according to the ease with which they are reduced. The carbon monoxide may be ignited, and burns with a blue flame.

127. Remarks.—The four acids given are the most common and important of the organic acids, and if the student makes himself familiar with these, he will experience no difficulty in determining others, should he be called upon to do so.

It will be noted that heating with concentrate sulphuric acid is the most characteristic test for these acids. After a little experience they may be determined with certainty by this reaction alone; but the result thus obtained should always be confirmed by making use of the other reactions given. The reactions for arsenious and arsenic acids, which are quite common, have been given with the reactions for the metals where they are usually found in the course of analysis.

LESS COMMON INORGANIC ACIDS.

BORIC ACID.

128. Boric acid H_3BO_3 is rather weak in all its chemical relations. It is soluble in water, and the solution reddens litmus. It forms but a limited number of salts, and of these, sodium biborate (borax) is the only very important one. The salts of the alkalies are the only ones that are readily soluble in water. Solutions of all the soluble borates in water give an alkaline reaction.

1. *Silver nitrate*, when added to a concentrate solution of a normal borate of an alkali metal, gives a white precipitate of $2AgBO_3 \cdot H_2O$, which has more or less of a yellow tint, owing to the formation of a small quantity of silver

oxide Ag_2O . In concentrate solutions of the acid borates, it gives a white precipitate of $Ag_2B_4O_{11}$. From dilute solutions of the borates of the alkalies, brown silver oxide Ag_2O is precipitated. All of these precipitates are soluble in nitric acid or ammonia.

2. *Lead acetate* precipitates white lead metaborate $Pb(BO_2)_2$ from strong solutions. The precipitate is soluble in an excess of the reagent.

3. *Barium chloride* precipitates white barium metaborate $Ba(BO_2)_2$ from strong solutions of normal borates. In acid borates, the precipitate produced is $Ba_2B_{10}O_{18}$, which is also white. Either precipitate is soluble in an excess of the reagent, in ammonium salts, and in acids.

4. The best, and, in fact, the only reliable, test for boric acid or borates is the characteristic green flame. If boric acid is mixed with alcohol, and the latter ignited, the boric acid will impart a green color to the flame at once; but the borates are not volatile, and, consequently, do not color the flame until we get the boric acid in a volatile form. To do this, mix, in a porcelain dish, a little of the borate to be tested with concentrate sulphuric acid; add some alcohol, heat the contents of the dish, and ignite the alcohol. The sulphuric acid sets boric acid free, and this colors the flame. Boric acid does not usually appear to color the whole flame, but gives to the flame a green border. The delicacy of the reaction is increased by stirring the contents of the dish.

5. If a borate is ground up with a mixture containing about twice its bulk of acid potassium sulphate and about half its bulk of calcium fluoride, a drop or two of water added to form a paste, and this paste held on a platinum wire in the flame of a Bunsen burner, it gives the flame a green color for a moment.

CHLORIC ACID.

129. Chloric acid $HClO_3$, in very concentrate solution, is a slightly yellowish liquid, having an odor similar to that of nitric acid. More dilute solutions are colorless and

odorless. All the chlorates are soluble in water; so no precipitates are obtained.

1. When solutions of chlorates are heated in a test tube with concentrate hydrochloric acid, the liquid assumes a greenish-yellow color, and greenish-yellow vapors of chlorine tetroxide and free chlorine escape.

2. If a solution of a chlorate is colored light blue by a solution of indigo in sulphuric acid, by adding a little dilute sulphuric acid, and then carefully introducing a few drops of a solution of sodium sulphite, the solution is decolorized. The sulphurous acid of the sulphite takes oxygen from the chlorate, setting free chlorine, or a lower oxide of it, which destroys the color of the indigo.

3. Chlorates, when gently heated with concentrate sulphuric acid, are decomposed, yielding greenish-yellow explosive fumes of chlorine tetroxide Cl_2O_2 . Great care must be taken in performing this operation, as the chlorine tetroxide explodes violently at a moderate temperature, often throwing the acid some distance. Very small quantities should be used, and the tube should always be held pointing away from the operator.

4. Nearly all chlorates, when heated in the closed tube, give off oxygen, and are reduced to chlorides. The oxygen will ignite a spark held at the mouth of the tube. The chlorates of barium, strontium, and calcium give off both oxygen and chlorine, and are reduced to oxides.

HYPOCHLOROUS ACID.

130. Hypochlorous acid $HClO$ and the hypochlorites are very unstable. Hypochlorous acid has never been obtained, except in solution, but its salts are known, and calcium hypochlorite, known as chloride of lime, or bleaching powder, is important.

1. *Silver nitrate* precipitates white silver chloride $AgCl$ from solutions of calcium hypochlorite, to which enough nitric acid has been added so that it does not emit an odor

of chlorine. Silver hypochlorite is formed at first, but this decomposes into silver chloride and silver chlorate almost immediately.

2. *Lead acetate* precipitates white lead chloride $PbCl_2$, which soon decomposes, forming oxides of lead, giving the precipitate a yellow color that gradually grows darker until it becomes brown, owing to the formation of lead dioxide.

3. When hydrochlorites are treated with concentrate sulphuric or hydrochloric acid, they are decomposed, giving off free chlorine, which may be recognized by its color and odor.

HYDROFLUORIC ACID.

131. Hydrofluoric acid HF is a colorless, corrosive liquid with a penetrating odor. It fumes strongly in the air, and attacks the tissues, causing sores that are difficult to heal. It is distinguished from all other acids by its power of decomposing silica and silicates that are insoluble in other acids. The fluorides are stable compounds. Those of the alkalis are quite readily dissolved by water, while all the others are either insoluble or are dissolved with more or less difficulty.

1. *Silver nitrate* precipitates white silver fluoride AgF from rather strong solutions. It is somewhat soluble in water, and easily dissolved by nitric acid, but is insoluble in ammonia.

2. *Lead acetate* precipitates white lead fluoride PbF_2 , which is almost insoluble in water, but is dissolved by nitric acid.

3. *Barium chloride* precipitates white barium fluoride BaF_2 from solutions of hydrofluoric acid, but much more readily from solutions of fluorides. The precipitate is almost absolutely insoluble in water, but is dissolved by hydrochloric or nitric acid.

4. *Calcium chloride* precipitates white calcium fluoride CaF_2 , which is so transparent that it is often difficult to see the precipitate at first. It is almost absolutely insoluble in water and is only slightly attacked by acids in the cold. Hot

concentrate hydrochloric acid dissolves it more readily, but only with great difficulty.

5. Nearly all fluorides are decomposed by warm concentrate sulphuric acid, yielding hydrofluoric acid in the gaseous state. If a fluoride is heated with concentrate sulphuric acid in a platinum crucible, covered with a piece of glass, coated with wax through which lines are traced so that the hydrofluoric acid can come in contact with the glass, it attacks the silicon of the glass, forming the volatile fluoride of silicon SiF_4 , and thus etches the glass. After removing the wax, the lines may be plainly seen.

6. A characteristic test for a fluoride may be made by mixing about equal parts of the finely ground fluoride, and powdered silicon dioxide SiO_2 . Place this mixture in a test tube and add about twice its volume of concentrate sulphuric acid. Fit the test tube with a perforated rubber stopper, through which a bent delivery tube passes, as shown in Fig. 9.

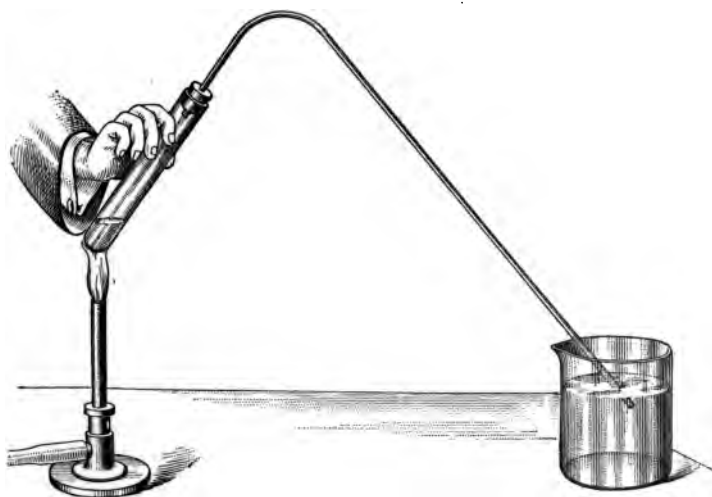


FIG. 9.

The contents of the test tube are now heated, while the end of the delivery tube is held under water. The volatile fluoride of silicon SiF_4 , that is formed passes through the delivery

tube into the water, where it produces a white, gelatinous precipitate of silicic acid. At the end of the operation, first remove the delivery tube from the water, then withdraw the stopper from the test tube, and finally remove the test tube from the flame.

Great care must be taken in performing this experiment. Water must not be allowed to come in contact with the hot sulphuric acid or it will cause an explosion, and the hot acid that will be spattered about may cause much damage. The operation must not be continued too long, or the hydrofluoric acid may dissolve the bottom out of the test tube.

SILICIC ACID.

132. Silicic acid H_4SiO_4 is a gelatinous substance that may be obtained in dilute aqueous solution, from which it shows a great tendency to separate as a gelatinous precipitate. It is a very weak acid in its chemical relations, and will scarcely color litmus paper. The silicates of the alkalis are soluble, but all other silicates are insoluble in water. Some of the silicates are soluble in acids, while others are almost entirely insoluble. Silicic acid and the silicates are not frequently met except in mineral analysis, where they are very common. Most of the silicates are represented by formulas that express their derivation from metasilicic or polysilicic acids, but the reactions are the same for these as for the normal silicic acid.

1. *Lead acetate* precipitates white lead silicate from solutions of the alkali silicates. The precipitate is soluble in nitric acid.

2. *Barium chloride* precipitates white barium silicate from solutions of the silicates of the alkalies. The precipitate is soluble in nitric or hydrochloric acid.

3. *Concentrate hydrochloric acid* precipitates white, gelatinous silicic acid from rather strong solutions of the alkali silicates. If the solution is weak, the precipitate only appears after standing some time, or on being concentrated.

4. *Ammonium-molybdate* solution, when heated with a solution of a silicate, gives the solution a yellow color; and, if the silicate solution is strong, a slight yellow precipitate may be formed.

5. All silicates, when fused with sodium carbonate, yield carbonates of the metal and sodium silicate. The sodium silicate may be dissolved in water, while the carbonate of the metal remains undissolved, or the metallic carbonates may be dissolved in hydrochloric acid, while the silicic acid is partially precipitated. The silicic acid is somewhat soluble in water, but by removing it, or evaporating to dryness and heating, water is driven off, and there is left silicic oxide SiO_2 , which is insoluble in water and all acids except hydrofluoric acid.

If this silicic oxide is separated from the metals by filtration or decantation, and heated in a lead or platinum dish with a concentrate solution of hydrofluoric acid, it will be dissolved, forming volatile silicon tetrafluoride, which will be driven off by the heat, leaving nothing in the dish except traces of metallic compounds that were not perfectly separated from the silicic oxide.

6. A very convenient test for a silicate depends upon the formation of what is known as the *silica skeleton*, in the *microcosmic bead*. A bead is made of microcosmic salt (hydrogen-sodium-ammonium phosphate) in the same manner that a borax bead is made; a little of the silicate is added, and the bead is brought into the hottest part of the blowpipe flame. The metals form part of the fused portion of the bead, while the silicic oxide (silica) remains undissolved and floats in the bead. The bead is sometimes colored with a little copper sulphate, to make the skeleton more easily seen.

NITROUS ACID.

133. Nitrous acid HNO_2 is a blue, unstable liquid that decomposes into nitric acid, nitrous oxide, and water, at ordinary temperatures. It may be preserved at very low

temperatures. Its salts, the nitrites, are also rather unstable. Most of them are soluble in water.

1. *Silver nitrate* gives a white precipitate in rather strong solutions of the alkali nitrites. The precipitate is slightly soluble in cold water, and is much more easily dissolved if the water is heated.

2. *Ferrous sulphate* produces a slight yellowish or greenish-yellow coloration in neutral nitrite solutions. This is changed to a deep-brown color upon the addition of acetic acid. If the ferrous sulphate contains free sulphuric acid, the brown color is produced at once.

3. If a few drops of a mixture of potassium iodide, starch paste, and dilute sulphuric acid, are added to a solution of a nitrite, a deep-blue color is immediately produced, owing to the formation of blue starch iodide. This is a very delicate reaction when properly handled, and shows the presence of nitrites in even very dilute solutions. The potassium iodide must be free from iodate, and the mixture of potassium iodide, starch, and sulphuric acid must remain colorless until added to the nitrite solution, or the reaction shows nothing. The sulphuric acid may be considerably diluted if necessary.

4. Nitrites, when heated with concentrate sulphuric or hydrochloric acid, are decomposed, and brownish-red fumes of nitric oxide are given off.

HYDROSULPHOCYANIC ACID.

134. Hydrosulphocyanic acid *HSCN*, or *hydrothiocyanic acid*, as it is also called, is an oily liquid with a penetrating odor, somewhat similar to that of acetic acid. It mixes with water, forming a very poisonous liquid with an acid reaction. Upon standing, it is gradually dissociated, and hydrocyanic acid is formed during the decomposition. It unites with all bases, forming sulphocyanides, all of which are soluble in water, except those of silver, lead, and mercury.

1. *Silver nitrate* precipitates white, curdy silver sulpho-

cyanide $AgSCN$, which is insoluble in dilute nitric acid, but is soluble in ammonia.

2. *Lead acetate* precipitates yellowish lead sulphocyanide $Pb(SCN)_2$, which is changed to a white basic compound by boiling.

3. *Mercurous nitrate* gives a white precipitate of mercurous sulphocyanide $Hg_2(SCN)_2$, or a gray precipitate of mercuric sulphocyanide $Hg(SCN)_2$ and free mercury, depending upon the degree of concentration and the proportions in which the two liquids are mixed. The white mercurous sulphocyanide may be changed to the gray precipitate of mercuric sulphocyanide and mercury by boiling.

4. *Copper sulphate* precipitates greenish-black copper sulphocyanide $Cu(SCN)_2$ from strong solutions of the alkali sulphocyanides. In dilute solutions, it produces an emerald-green coloration, but no precipitate.

5. *Ferric-chloride* solution, acidulated with hydrochloric acid, imparts a blood-red color to solutions of sulphocyanides, but does not produce a precipitate. The color is due to the formation of red, soluble ferric sulphocyanide $Fe(SCN)_3$. The color is not injured by hydrochloric acid, but is destroyed by mercuric chloride.

6. When a sulphocyanide is heated with nitric acid, a violent decomposition takes place, during which nitric and carbonic oxides are given off, and sulphuric acid is formed.

HYDROFERROCYANIC ACID.

135. Hydroferrocyanic acid $H_4Fe(CN)_6$ is a colorless, crystalline substance that readily dissolves in water, giving a liquid with a strong acid reaction. The ferrocyanides of the alkalies and alkaline earths are soluble, while most of the others are insoluble in water. They are all decomposed by ignition in the closed tube, and if they are not quite dry, hydrocyanic acid, carbon dioxide, and ammonia are given off. If perfectly dry, nitrogen, and sometimes cyanogen, escape.

1. *Silver nitrate* precipitates white silver ferrocyanide $Ag_4Fe(CN)_6$, which is insoluble in nitric acid, and in ammonia in the cold, but is dissolved by potassium cyanide.

2. *Lead acetate* precipitates white lead ferrocyanide, which has the formula $Pb_3Fe(CN)_6$, and is not dissolved by dilute nitric acid.

3. *Copper sulphate* precipitates reddish-brown copper ferrocyanide $Cu_3Fe(CN)_6$, which is insoluble in dilute acids.

4. *Ferric chloride* precipitates dark-blue ferric ferrocyanide $Fe_4^{III}Fe_3^{II}(CN)_{18}$, which is insoluble in dilute mineral acids, but may be dissolved in a large excess of potassium ferrocyanide, giving a deep-blue solution. The precipitate is known as *Prussian blue*.

5. If Prussian blue is heated with an ammoniacal solution of silver, ferric oxide is precipitated, and silver cyanide is formed, and remains in solution. If the ferric oxide is separated, and the solution acidified with nitric acid, white silver cyanide is thrown down.

6. All solid ferrocyanides, when heated with 1 part of water and 3 or 4 parts of concentrate sulphuric acid, are decomposed, yielding hydrocyanic acid, which may be recognized by its odor.

HYDROFERRICYANIC ACID.

136. Hydroferricyanic acid $H_3Fe(CN)_6$ is soluble in water, and many of its salts are also soluble. The ferricyanides, like the ferrocyanides, are all decomposed upon ignition in a closed tube, and in a similar manner.

1. *Silver nitrate* precipitates orange or reddish-brown silver ferricyanide $Ag_3Fe(CN)_6$, which is insoluble in nitric acid, but is dissolved by ammonia or potassium cyanide.

2. *Copper sulphate* precipitates yellowish-green copper ferricyanide $Cu_3Fe_2(CN)_{12}$, which is insoluble in dilute hydrochloric acid.

3. *Ferric chloride* does not produce a precipitate in pure ferricyanide solutions, but gives the solution a dark coloration;

but as ferricyanides often contain ferrocyanides, a precipitate is frequently obtained that is due to impurity. A precipitate will also be formed if the ferric chloride contains ferrous compounds.

4. *Ferrous sulphate* precipitates blue ferrous ferricyanide $Fe_2''Fe_3'''(CN)_{12}$, which is insoluble in dilute inorganic acids. The precipitate is known as *Turnbull's blue*.

5. All ferricyanides are decomposed when heated with 1 part of water and 3 parts of concentrate sulphuric acid, and yield hydrocyanic acid, in the same manner that the ferrocyanides do.*

HYDROFLUOSILICIC ACID.

137. Hydrofluosilicic acid H_2SiF_6 is a white, deliquescent substance that readily dissolves in water, forming a strongly acid liquid. It may be obtained by leading silicon tetrafluoride SiF_4 into water, when hydrofluosilicic and silicic acids are formed. Its salts are called silicofluorides. Most of them are soluble in water.

1. *Lead acetate*, when added in excess to hydrofluosilicic acid or a silicofluoride solution, gives a white precipitate of lead silicofluoride $PbSiF_6$.

2. *Barium chloride* precipitates white barium silicofluoride $BaSiF_6$, which is insoluble in dilute acids.

3. *Ammonium hydrate* added in excess to solutions of hydrofluosilicic acid or its salts, decomposes them, forming insoluble silicic and soluble ammonium fluoride.

4. All solid silicofluorides, when heated with concentrate sulphuric acid, are decomposed with the evolution of silicon tetrafluoride and hydrofluoric acid. If a drop of water on a glass rod is held at the mouth of the tube, it becomes turbid, owing to the formation of silicic acid. Care must be taken

* It will be noticed that hydrocyanic acid was treated as an organic acid, while the other cyanogen acids are treated among the inorganic acids. This is largely an arbitrary division, as all these acids are allied to both organic and inorganic compounds. Hydrocyanic acid seems to have more organic than inorganic properties, while in the other acids the inorganic properties appear to predominate.

not to let the water come in contact with the hot sulphuric acid, and if the operation is performed in a test tube, it must not be continued too long or the hydrofluoric acid may dissolve the tube.

LESS COMMON ORGANIC ACIDS.

CITRIC ACID.

138. Citric acid $C_6H_8O_7$, is obtained in colorless crystals having 1 molecule of water. It dissolves in water readily, forming a liquid with a pleasant acid taste. The citrates of the alkalies, and a number of others, are soluble in water.

1. *Silver nitrate* precipitates white silver citrate $Ag_3C_6H_5O_7$, from solutions of the normal citrates of the alkalies. If rather a large quantity of this precipitate is boiled with a small amount of water, it is decomposed with the separation of metallic silver.

2. *Lead acetate*, when added in excess to a solution of citric acid or a citrate, precipitates white lead citrate $Pb_3(C_6H_5O_7)_2$, which is soluble in ammonia that is free from carbonate.

3. *Barium hydrate*, added in excess to a rather strong citric acid solution, precipitates white barium citrate $Ba_3(C_6H_5O_7)_2$. As this precipitate is somewhat soluble in water, it is not obtained in dilute solutions.

4. Mix about equal parts of citric acid and glycerine, and heat gently until the mixture begins to puff up. Dissolve this mass in ammonia, evaporate off the excess, and add 2 or 3 drops of a solution, consisting of 1 part of red, fuming nitric acid and 4 parts of water. The solution assumes a green color, which is changed to blue by gently heating. A drop or two of hydrogen peroxide may be used instead of nitric acid. This reaction may be used to detect small quantities of citric acid in the presence of oxalic, tartaric, and malic acids.

5. Citric acid, and all citrates in the solid state, when

heated with concentrate sulphuric acid, are decomposed, yielding, at first, carbon monoxide, then carbon dioxide and acetone also, while the solution remains clear; finally the solution blackens, and sulphur dioxide is given off. In order to get these gases in the above order, the mixture should be heated slowly. Carbon monoxide may be recognized by its blue flame, carbon dioxide by its property of rendering turbid a drop of barium hydrate, and acetone and sulphur dioxide by their characteristic odors.

6. Citric acid and citrates, when heated in the closed tube, char, and emit pungent acid fumes that are readily distinguished from those given off by tartaric acid when it carbonizes.

7. *Calcium chloride* does not produce a precipitate in solutions of free citric acid, but if enough ammonium or sodium hydrate is added to neutralize the solution, white calcium citrate $Ca_3(C_6H_5O_7)_2$, is thrown down, provided the solution is not too dilute.

MALIC ACID.

139. Malic acid $C_4H_5O_6$, is a deliquescent, crystalline substance that readily dissolves in water. Most of the malates are also soluble in water.

1. *Silver nitrate* precipitates white silver malate $Ag_2C_4H_4O_6$, from solutions of normal malates of the alkalies. The precipitate becomes slightly gray upon standing for some time, or more readily by boiling.

2. *Lead acetate* precipitates white lead malate $PbC_4H_4O_6$, from solutions of malic acids or malates. If the solution is acid, precipitation is promoted by rendering the solution just neutral, with ammonia, but taking care to avoid an excess, for the precipitate is soluble both in malic acid and in ammonia. It is also soluble in acetic acid. If the solution, in which the precipitate is suspended, is boiled, part of the precipitate is dissolved and the rest will melt into a mass that resembles resin fused under water.

3. If calcium chloride, ammonium chloride, and ammonia are added to a solution of malic acid or a malate, no precipitate is formed even if the solution is boiled. This serves to distinguish between malic acid and citric acid.

4. *Lime water*, prepared with boiling water, gives no precipitate with malic acid or malates even upon boiling.

5. Malic acid, when heated with nitric acid, is decomposed with the evolution of carbon dioxide and formation of oxalic acid.

6. When heated in the closed tube, malic acid is decomposed into fumaric acid, water, and maleic anhydride $C_4H_2O_3$. Water and maleic anhydride are first driven off, and then the fumaric acid is volatilized and condenses upon the upper part of the tube where it is cool, forming a crystalline sublimate. This is a characteristic reaction for malic acid.

7. If a solution of malic acid in a test tube is acidified with a few drops of sulphuric acid, a little potassium bichromate added, and the contents of the tube heated to boiling, an odor resembling that of fresh apples is obtained. This reaction may be used to detect malic acid in the presence of citric acid.

8. If malic acid, or a malate in the solid form, is carefully heated with concentrate sulphuric acid, carbon monoxide and carbon dioxide are given off at first; then the acid turns brown, and finally black, and sulphur dioxide is evolved. The carbon monoxide and carbon dioxide are recognized, in the usual manner, by the blue flame and drop of barium hydrate. The sulphur dioxide is recognized by its characteristic penetrating odor.

FORMIC ACID.

140. Formic acid CH_2O_2 is a colorless, corrosive liquid that fumes slightly in the air and has a very penetrating odor. All formates are soluble in water. One of their most characteristic properties is the power of reducing compounds of the heavy metals, either to the metallic condition or to a lower state of oxidation.

1. *Silver nitrate* gives no immediate precipitate in solutions of free formic acid or dilute solutions of formates. In concentrate solutions of alkali formates, white silver formate $AgCHO_2$ is thrown down. This precipitate rapidly assumes a dark color, owing to its reduction to metallic silver. If the test of formic acid or formate that failed to give a precipitate at first, is allowed to stand, or is heated, metallic silver separates as a gray powder, or as a coating on the sides of the test tube. This reduction is prevented by an excess of ammonia.

2. *Mercurous nitrate* gives no precipitate in solutions of free formic acid, but in strong solutions of alkali formates, white glistening mercurous formate $Hg_2(CHO_2)_2$ separates. This precipitate rapidly becomes gray, owing to the reduction to metallic mercury. The precipitate is completely reduced after standing for some time in the cold, but, by heating, complete reduction is accomplished almost immediately.

3. *Mercuric chloride*, free from hydrochloric acid, when heated with a solution of formic acid or a formate, is reduced, and mercurous chloride Hg_2Cl_2 separates as a white precipitate before the solution reaches the boiling point. This reaction serves to distinguish formic from acetic acid. It is hindered or prevented by the presence of hydrochloric acid or alkali chlorides.

4. *Ferric chloride*, when added to a neutral formate solution imparts a deep-red color to the solution. The same result may be obtained by adding ferric chloride to formic acid, and then just neutralizing with ammonia. This reaction is similar to the reaction of ferric chloride with acetic acid.

5. Formic acid and all solid formates, when heated with concentrate sulphuric acid, are decomposed, the sulphuric acid extracting water, and setting free carbon monoxide, which escapes with effervescence, and, when ignited, burns with a blue flame. The solution does not carbonize, but remains clear, unless some organic impurity is present. When formates or formic acid are heated with concentrate sulphuric

acid and alcohol, ethyl formate is evolved, which is recognized by its peculiar odor, resembling that of rum.

6. All formates, when ignited in the closed tube, char, and give off carbon monoxide, which, when ignited, burns with a blue flame. In many cases carbon dioxide is also given off, which renders the ignition of the carbon monoxide difficult. Carbonates, oxides, or metals are left in the tube.

SALICYLIC ACID.

141. Salicylic acid $C_6H_4O_2$ is a colorless, odorless, crystalline substance that dissolves but slightly in cold water, more readily in hot water, and very freely in alcohol and other organic solvents. It forms two series of salts, known as normal and basic salts. Most of the normal salts are readily dissolved by water, while many of the basic salts are but slightly soluble in that medium.

1. Lead acetate precipitates *white lead salicylate* $Pb(C_6H_4O_2)_2$ from normal alkali salicylate solutions. The precipitate is soluble in an excess of lead acetate or acetic acid, but not in ammonia. It may be dissolved by heating in the solution from which it was precipitated, and, upon cooling, will separate in crystals.

2. *Ferric chloride*, in very dilute solution, when added in small amount to a water solution of salicylic acid or one of its salts, imparts a deep-violet color to the solution. This is a very characteristic reaction, but it is hindered by the presence of some other organic acids, and prevented by hydrochloric acid or ammonia.

3. If a solution of salicylic acid in methyl alcohol (wood alcohol) is heated with about half its volume of concentrate sulphuric acid, methyl salicylate is formed, which is recognized by its characteristic odor of wintergreen oil, of which it is the chief constituent. A solution of salicylic acid in ordinary alcohol, when heated with concentrate sulphuric acid, yields ethyl salicylate, which has an odor similar to that of methyl salicylate.

4. Salicylic acid, when carefully heated in a closed tube, is not decomposed, but sublimes, forming needle-shaped crystals on the cool portion of the tube. If quickly ignited at a high temperature, it is decomposed into phenol and carbon dioxide.

BENZOIC ACID.

142. Benzoic acid $C_7H_6O_2$ is a white, crystalline substance that, when strictly pure, is odorless, but generally has a faint aromatic odor, due to the presence of small quantities of impurity. It is very sparingly soluble in cold water, more freely in hot water, and dissolves readily in alcohol. Most of the benzoates are soluble in water, but a few, having weak bases, are insoluble.

1. *Lead acetate* gives no precipitate with free benzoic acid, but, from rather strong solutions of the alkali benzoates, it precipitates lead benzoate $Pb(C_7H_5O_2)_2$, which is soluble in excess of lead acetate and also in acetic acid.

2. *Ferric-chloride* solution, carefully mixed with a little very dilute ammonia until it takes on a brownish-red color, but remains clear, precipitates flesh-colored basic ferric benzoate $Fe_2(C_7H_5O_2)_3 \cdot Fe_2O_3$, which is decomposed by hydrochloric acid, with separation of benzoic acid. This reaction serves to distinguish between benzoic and salicylic acids.

3. Benzoic acid is dissolved in concentrate sulphuric acid without decomposition. It is precipitated unchanged from its solution in sulphuric acid by the addition of water.

4. Strong mineral acids, when added to concentrate solutions of the soluble benzoates, take the place of the benzoic acid that is thrown out as a glistening, white powder. Benzoic acid may be obtained in the same way from insoluble benzoates, by adding an acid that forms a soluble salt with the base with which it is united.

5. Pure benzoic acid, when heated in a closed tube, volatilizes completely, leaving the tube clean; but there are

generally organic impurities present, which remain in the tube as a charred residue. The acid vapor given off has an irritating effect on the tissues, and when inhaled provokes coughing.

SYSTEMATIC EXAMINATION OF SOLUTIONS FOR ACIDS.

143. It would be a difficult matter to formulate a scheme for the detection and separation of acids in a solution, similar to the one used for the metals, which would be so complete, exact, and practical; and, fortunately, this is unnecessary, for the frequently occurring acids are few in number, and, as a rule, only one, or, at most, but two or three, will be found in any one solution. In a great majority of cases, after determining the metals in a solution—which should always be done first—enough will be known of the composition of the solution so that we may proceed at once to apply special tests for the acids. In this part of the work, more than in any of the preceding, the student must apply all his knowledge of chemistry, and consider carefully the full significance of each reaction, and of each fact which he discovers as he proceeds, or he will make much unnecessary work for himself. For instance, it would be a waste of time and chemicals to examine a neutral or acid solution, in which silver or mercurous compounds had been found, for hydrochloric, hydrobromic, or hydriodic acid, for these compounds cannot exist in such a solution in the presence of these acids. For the same reason, it would be useless to look for sulphuric acid in a solution containing barium or other metals whose sulphates are insoluble, or to examine a neutral solution containing calcium for phosphoric or oxalic acid.

All solutions should be tested with litmus paper before the analysis is commenced, or erroneous conclusions may be drawn. For instance, silver chloride may exist in ammoniacal solution, or phosphates and oxalates of the alkaline earths may exist in acid solution.

It sometimes happens that the separation of the metals

from a solution gives no clue to the acid or acids, and it becomes desirable to pursue a systematic course for their detection. This is accomplished by dividing them into three groups, by means of reagents. The first group is composed of those acids that are precipitated by barium chloride, the second contains those that are not precipitated by barium chloride but are precipitated by silver nitrate, and the third group is made up of those acids that are not precipitated by either of these reagents. Tables 2 and 3 give the color and solubility of the precipitates produced by these reagents, and as lead acetate helps to classify the acids, a table (4) is given showing the color and solubility of precipitates produced by this reagent.

144. Preparation of the Solution.—In many cases, preparation is not required, but if the solution contains metals that would interfere with the reactions, they must be removed by precipitation. The solution should be slightly acid; if it is alkaline or neutral, just enough nitric acid is added to give an acid reaction with test paper. To remove the metals of the first and second groups, lead hydrogen-sulphide gas through the solution until they are all precipitated. Then filter and boil the filtrate until all the hydrogen sulphide is expelled. If metals of the third, fourth, and fifth groups are present, add to the solution a slight excess of sodium carbonate, boil for a moment, and filter. The filtrate will contain the acids, freed from such metals as would interfere with their determination. Render this slightly acid with nitric acid, and boil till all carbon dioxide is expelled; then add dilute ammonia, drop by drop, until a point is reached at which the solution does not give a reaction with either red or blue litmus paper. It is now ready to be examined for the acids. If chromic acid was present, and was reduced by the hydrogen sulphide, this fact must be noted. The solution is now divided into three equal parts. The first portion is treated with barium chloride, the second with silver nitrate, and the third with lead acetate. The precipitates produced in each case are given in the accompanying tables.

TABLE 2.
ACIDS PRECIPITATED BY BARIUM CHLORIDE.

Acid.	Color of Precipitate.	Solubility.
Sulphuric	White.	Insoluble in <i>HCl</i> .
Thiosulphuric.....	White.	Soluble in <i>HCl</i> with evolution of SO_2 and free sulphur.
Sulphurous.....	White.	Soluble in <i>HCl</i> with evolution of SO_2 .
Phosphoric	White.	Soluble in <i>HCl</i> .
Carbonic.....	White.	Soluble in <i>HCl</i> with effervescence.
Chromic.....	Yellow.	Soluble in <i>HCl</i> .
Hydrofluoric	White.	Soluble in <i>HCl</i> .
Boric	White (from concentrate solution).	Soluble in <i>HCl</i> .
Silicic.....	White.	Soluble in <i>HCl</i> .
Hydrofluosilicic....	White.	Insoluble in <i>HCl</i> .
Oxalic.....	White.	Soluble in <i>HCl</i> .
Tartaric.....	White.	Soluble in <i>HCl</i> .

Citric and *malic* acids belong in this group, but must be recognized by special reactions.

145. Grouping the Acids.—In a majority of cases, the precipitates produced by these reagents will indicate the acid present, and it only remains to confirm it by the reactions given for that acid. In some cases, it may be of advantage to have the acids classed in groups, and for this reason the acids that are likely to be met are arranged in three groups, according to the plan before indicated. If the student has done his work thoroughly up to this point, he will experience no difficulty in determining the rarer acids, if called upon to do so, and as they would merely serve to complicate matters, if introduced here, they will be disregarded.

TABLE 3.
ACIDS PRECIPITATED BY SILVER NITRATE.

Acid.	Color of Precipitate.	Solubility.
Hydrochloric	White.	Insoluble in HNO_3 .
Hydrobromic	Yellowish white.	Insoluble in HNO_3 .
Hydriodic	Yellow.	Insoluble in HNO_3 .
Thiosulphuric.	White, turns black on standing.	Soluble in HNO_3 .
Sulphurous.	White, turns gray on boiling.	Soluble in HNO_3 .
Hydrosulphuric.	Black.	Insoluble in cold dilute HNO_3 .
Phosphoric.	Yellow.	Soluble in HNO_3 .
Carbonic	White.	Soluble in HNO_3 , with effervescence.
Chromic.	Red.	Soluble in HNO_3 .
Silicic.	Yellow.	Soluble in HNO_3 .
Nitrous.	White (from concentrate solutions).	Soluble in HNO_3 .
Hypochlorous.	White.	Insoluble in HNO_3 .
Boric.	White (from concentrate solutions).	Soluble in HNO_3 .
Hydrocyanic.	White.	Insoluble in HNO_3 .
Hydrosulphocyanic.	White.	Insoluble in cold dilute HNO_3 .
Hydroferrocyanic ..	White.	Insoluble in HNO_3 .
Hydroferricyanic. ..	Yellow.	Insoluble in HNO_3 .
Oxalic	White.	Soluble in HNO_3 .
Tartaric.	White.	Soluble in HNO_3 . Boiling precipitates gray metallic silver. Precipitates gray metallic silver upon standing for some time in the cold or more readily upon heating.
Formic.		

Benzoic and *salicylic* acids are classed in the second group, but must be recognized by their special reactions.

TABLE 4.
ACIDS PRECIPITATED BY LEAD ACETATE.

Acid.	Color of Precipitate.	Solubility.
Hydrochloric....	White.	Soluble in hot water.
Hydrobromic....	White.	Soluble in HNO_3 .
Hydriodic.....	Yellow.	Soluble in hot water.
Sulphuric.....	White.	Insoluble in HNO_3 .
Thiosulphuric...	White.	Soluble in HNO_3 .
Sulphurous.....	White.	Soluble in HNO_3 .
Hydrosulphuric..	Black.	Soluble in warm HNO_3 .
Phosphoric.....	White.	Soluble in HNO_3 .
Carbonic.....	White.	Soluble in HNO_3 , with effervescence.
Chromic.....	Yellow.	Soluble in concentrate HNO_3 .
Boric.....	White.	Soluble in HNO_3 .
Hydrofluoric....	White.	Soluble in HNO_3 .
Hypochlorous...	White, turning to brown on standing.	
Silicic.....	White.	Soluble in HNO_3 .
Hydrocyanic....	White.	Soluble in HNO_3 .
Hydroferrocyanic	White.	Insoluble in HNO_3 .
Oxalic.....	White.	Soluble in HNO_3 .
Tartaric.....	White.	Soluble in HNO_3 .
Citric.....	White.	
Malic.....	White.	
Salicylic.....	White.	
Benzoic.....	White, from alkali benzoates.	

The four rare organic acids given in this table are precipitated as given if the conditions are right, but other reactions must be depended upon to identify them.

The acids of the first group are those precipitated by barium chloride. They are: *sulphuric, thiosulphuric, sulphurous, chromic, phosphoric, carbonic, boric, hydrofluoric, silicic, oxalic, and tartaric acids.*

The second group is composed of the acids that are not precipitated by barium chloride, but form precipitates with silver nitrate. This group contains: *hydrochloric, hydrobromic, hydriodic, hydrosulphuric, hydrocyanic, hydroferrocyanic, hydroferricyanic, and hydrosulphocyanic acids.*

The third group contains those acids that are not precipitated by either of these reagents. They are: *nitric, chloric, and acetic acids.*

Nitrous acid is also sometimes classed in this group, but generally in the second group. By looking at its reactions it will be seen that its classification is doubtful.

It must be remembered that we cannot use the filtrate from the first group of acids to test for the second group, for in that case the barium chloride, added as the first reagent, will precipitate the silver of the silver nitrate as silver chloride. Separate solutions must always be used, and in applying tests for the acids of the third group, some of the original solution must be used.

SPECIAL TESTS FOR ACIDS.

146. Having now located the acid within very narrow limits, special tests are next applied. One or two of the most characteristic tests for each of the common acids are given in the following list. After determining the acid by one of these tests, it should always be confirmed by the other reactions given for that acid.

1. **Hydrochloric acid**, when treated with silver nitrate, gives a white precipitate of silver chloride $AgCl$, which is easily dissolved by ammonia, and is reprecipitated by nitric acid. Sodium thiosulphate also dissolves the precipitate.

2. **Hydrobromic acid**, treated with silver nitrate, gives yellowish-white silver bromide $AgBr$, which is dissolved with some difficulty in ammonia, but readily by sodium thiosulphate.

The most characteristic test for hydrobromic acid in the case of a solid bromide is made by heating it in a test tube with concentrate nitric acid, when reddish-brown vapors of bromine are given off, and condense in the upper part of the tube, forming red globules. This test may be applied to all solid bromides except the bromide of silver, and can also be applied to concentrate solutions.

3. **Hydriodic acid** gives yellowish silver iodide *AgI* when treated with silver nitrate. The precipitate is almost insoluble in dilute ammonia, but is dissolved somewhat by concentrate ammonia, and is readily soluble in sodium thiosulphate.

A chloride may be recognized in the presence of bromides and iodides by precipitating all of them with an excess of silver nitrate, and dissolving the silver chloride with a mixture of equal parts of dilute ammonia and water. After filtering, the silver chloride may be reprecipitated from the alkaline filtrate by nitric acid. To distinguish bromides and iodides when all three acids are present, place a small quantity of the solution in a test tube, add a few drops of colorless carbon bisulphide, which will form a globule, and then add a saturated solution of chlorine water, drop by drop, and shake the tube frequently. The chlorine water will first set the iodine free, and this will give the globule a violet tint; a few more drops of chlorine water destroys this color, and sets bromine free, imparting a yellow color to the globule, which is in turn destroyed by an excess of the chlorine water.

4. **Sulphuric acid**, when treated with barium chloride, gives white barium sulphate *BaSO₄*, which is insoluble in all acids. Lead acetate precipitates white lead sulphate *PbSO₄*, which may be dissolved by adding tartaric acid, and then rendering alkaline with strong ammonia.

5. **Thiosulphuric acid**, when treated with silver nitrate, gives, at first, a white precipitate that turns brown, and finally

becomes black, owing to its reduction to silver sulphide Ag_2S . All thiosulphates are decomposed by hydrochloric acid, yielding sulphur dioxide and free sulphur.

6. **Sulphurous acid**, when treated with silver nitrate, precipitates white silver sulphite Ag_2SO_3 , which is decomposed into gray metallic silver and sulphuric acid by boiling. All sulphites are decomposed by hydrochloric acid, yielding sulphur dioxide, which is recognized by its odor.

7. **Hydrosulphuric Acid**.—Nearly all sulphides are decomposed when heated with concentrate sulphuric acid, and yield hydrogen sulphide, which is recognized by its odor. All precipitates of acids containing sulphur, when fused on the charcoal with sodium carbonate, form sodium sulphide. If this fusion is placed on a piece of silver, ground up, and a drop or two of water added, it leaves a black stain on the silver, due to the formation of silver sulphide.

8. **Phosphoric Acid**.—If a drop or two of phosphoric acid, or a solution of a phosphate in nitric acid, are added to about 2 cubic centimeters of hot ammonium-molybdate solution in a test tube, a yellow precipitate of ammonium phosphomolybdate is formed at once. This precipitate is soluble in ammonia, and is reprecipitated by nitric acid. Arsenious and arsenic acids, if present, must be removed by hydrogen sulphide before applying this test, as they also give yellow precipitates, though not so readily as phosphoric acid.

9. **Carbonic Acid**.—Hydrochloric acid decomposes all carbonates with effervescence, which is due to escaping carbon dioxide. Effervescence indicates a carbonate, and this conclusion may be confirmed by testing the escaping gas with a drop of barium hydrate on a glass rod. Carbon dioxide renders the barium hydrate turbid.

10. **Chromic Acid**.—Yellow normal chromates are changed to red bichromates by rendering them acid with

nitric or hydrochloric acid. The red bichromates are changed to yellow normal chromates by ammonia. All chromates, in solutions containing free acid, are reduced to green chromium compounds when heated with alcohol or sulphurous acid. The borax-bead test is also a good one; but, when it is applied, it must be remembered that all compounds containing chromium, either in the base or in the acid, give the color to the bead. Compounds containing chromium in the base are green, while the chromates are yellow or red.

11. **Nitric Acid.**—To the solution to be tested for nitric acid, add an equal volume of concentrate sulphuric acid, and cool by allowing water to run over the outside of the test tube. When cool, hold the tube in an inclined position and carefully add 1 or 2 cubic centimeters of ferrous sulphate, in such a manner that the liquids do not mix, but the sulphate forms a separate layer above the solution to be tested. If nitric acid is present, a dark ring will be formed where the two solutions meet. This test is sometimes varied by dropping a crystal of ferrous sulphate into the solution instead of adding the ferrous-sulphate solution. In this case, the crystal is surrounded by a dark color that gradually spreads to the rest of the solution.

12. **Boric Acid.**—Mix the substance to be tested for boric acid with concentrate sulphuric acid, in a porcelain dish; add alcohol, stir, and heat the contents of the dish, and then ignite the alcohol. The characteristic green flame is conclusive proof of boric acid. The free acid gives the flame without being mixed with sulphuric acid, but nearly all the borates are non-volatile.

13. **Silicic Acid.**—Solutions to be tested for silicic acid may be rendered distinctly acid with hydrochloric acid, and evaporated to dryness in a porcelain dish. The residue is treated with hydrochloric acid to dissolve any metals present, and silicic oxide will remain as an undissolved residue. This may be separated from the solution, removed to a platinum

crucible, and dissolved in hydrofluoric acid. Upon heating, the silicon tetrafluoride formed is volatilized, leaving the crucible empty.

For solid silicates, the *silica skeleton* in the microcosmic bead, described in Art. 132, 6, gives an easy means of recognizing the acid. This reaction may be performed, using any precipitate obtained from silicic acid.

14. Arsenious and Arsenic Acids.—These acids have been treated among the metals where they are always found in the course of analysis. Arsenious acid is precipitated at once from acid solutions by hydrogen sulphide, as yellow arsenious sulphide. Arsenic acid is first reduced to arsenious by the hydrogen sulphide, and is then precipitated. Heat promotes the reduction and precipitation. They may be further identified by their reactions with silver nitrate. Neutral solutions of arsenites produce a yellow, and arsenates a red, precipitate.

15. Hydrocyanic Acid.—To test a solution of hydrocyanic acid, mix about 2 cubic centimeters of it in a test tube with from half a dozen to a dozen drops of ferrous sulphate and 2 or 3 drops of ferric chloride, add sodium hydrate till the mixture is distinctly alkaline, and heat nearly to boiling. Then add hydrochloric acid in sufficient quantity to produce a distinctly acid reaction. If much hydrocyanic acid is present, a deep-blue precipitate will be formed, and if but little of the acid is present, it will give a blue coloration. This test may be applied to insoluble cyanides by first fusing them with sodium carbonate. During the fusing, the hydrocyanic acid unites with sodium, forming soluble sodium cyanide. This is dissolved in about 2 cubic centimeters of water and the solution treated as described above. The reaction with silver nitrate, which is similar to that of hydrochloric acid, is quick and simple, and may serve to identify this acid in many cases.

16. Hydrosulphocyanic acid imparts an intense red coloration to a dilute solution of ferric chloride. The color

is not injured by hydrochloric acid, but is destroyed by mercuric chloride.

17. Hydroferrocyanic Acid.—In acid solutions of hydroferrocyanic acid or ferrocyanides, ferric chloride produces a dark-blue precipitate of ferric ferrocyanide $Fe_4'''Fe_2''(CN)_{12}$, known as Prussian blue.

18. Hydroferricyanic acid, and solutions of ferricyanides, when treated with ferrous sulphate, yield a blue precipitate of ferrous ferricyanide $Fe_2'''Fe_4''(CN)_{12}$, which is insoluble in dilute acids. This precipitate is known as Turnbull's blue.

147. Writing Reports.—In reporting analyses, the student should adopt a neat and uniform system of writing his results. In commercial work, the exact form adopted is a matter of personal preference, but in sending analyses of the substances, sent with the Question Paper, to the Schools, the following forms should always be followed. In order to illustrate the method of using these blanks, analyses are reported on the forms.

1. *Where one metal is to be determined in a solution.*

QUESTION No. __

Reagent.	Precipitate.	Conclusion.
1. H_2S .	Black.	$Ag, Pb, Hg(ous), Hg(ic)$, or Cu . Possibly Bi or Sn .
2. $NaOH$.	Yellow.	$Hg(ic)$.

REMARKS.—Mercury in the mercuric condition was indicated as above, and confirmed by the usual reactions. Therefore, No. __ is a solution of a mercuric compound.

[Signature, etc.]

2. *Determination of several metals in a solution.*

QUESTION No. —

Group.	Precipitate.	Conclusion.
I.	White.	{ Possible metals— <i>Ag, Pb, Hg(ous)</i> . { Metals found— <i>Ag</i> .
II.	Black.	{ Possible metals—All of the group. { Metals found— <i>Bi, Cu</i> .
III.	None.	{ Possible metals—None. { Metals found—None.
IV.	Light colored.	{ Possible metals— <i>Mn, Zn</i> . { Metals found— <i>Zn</i> .
V.	None.	{ Possible metals—None. { Metals found—None.
VI.	None.	{ Possible metals—None. { Metals found—None.
VII.	Odor of NH_3 . No flame test.	{ Ammonium is present, but sodium { and potassium are not.

REMARKS.—The above metals were found and confirmed in the usual manner. The solution contains a mixture of compounds of silver, bismuth, copper, zinc, and ammonium.

[Signature, etc.]

3. *When metal and acid are both determined.*

QUESTION No. —

METAL.

Reagent.	Precipitate.	Conclusion.
1. H_2S .	Black.	<i>Ag, Pb, Hg(ous), Hg(ic), Cu</i> . Possibly <i>Bi</i> or <i>Su</i> .
2. $NaOH$.	Blue, black on boiling.	<i>Cu</i> .

REMARKS.—Copper was determined as shown above, and confirmed by the other reactions for copper.

ACID.

Reagent.	Precipitate.	Conclusion.
1. $BaCl_2$.	White, insoluble in acids.	Acid of the first group. Probably H_2SO_4 .
2. $Pb(C_2H_3O_2)_2$.	White, soluble in tartaric acid and ammonia.	H_2SO_4 .

REMARKS.—Sulphuric acid was found as above, and confirmed by the *coin test* and other reactions.

CONCLUSION.—The compound is copper sulphate $CuSO_4$.

[Signature, etc.]

QUALITATIVE ANALYSIS.

(PART 2.)

EXAMINATION OF DRY SUBSTANCES.

PRELIMINARY REMARKS.

1. As we now have before us all the information necessary for the analysis of any common inorganic substance in solution, the next step will be the analysis of dry substances. The dry reactions are short and simple, and in many cases yield positive results very quickly. In case of some complex substances that do not give positive results by this method, clues are obtained that render their analysis by the wet method much easier, after putting them into solution by one of the methods given later.

In this, as in every part of the work, the student should not merely follow directions, but should make use of all of his knowledge of chemistry, and study carefully the cause of each phenomenon that he observes. Physical properties, such as the color and form of many substances, give valuable indications in regard to their composition, and in some cases the substances are so strongly indicated in this way that it is only necessary to confirm them by a few reactions. But as a rule, a systematic course of treatment should be pursued. The most common operations are six in number, and are generally applied in the following order:

§ 11

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1. *Heat the substance in a closed tube.*
2. *Heat the substance on the charcoal before the blowpipe.*
3. *Heat the substance in the non-luminous flame on a loop of platinum wire.*
4. *Heat the substance in the borax or microcosmic bead.*
5. *Fuse the substance on the platinum foil with sodium carbonate and potassium nitrate.*
6. *Heat the substance with concentrate sulphuric acid in a test tube.*

One of these tests will show that the substance is one of a number of compounds. The next will reduce the possible number, or perhaps indicate the compound, and each succeeding test reduces the number, until we arrive at a result. It seldom happens that all six tests are applied to any one substance, for, when a previous test has shown that a certain operation will not yield any information, it is, of course, omitted.

The above scheme is based upon the supposition that the substance is *not* a metal or an alloy. If its appearance indicates that it *is* one of these, it is treated by a method to be given later.

EXAMINATION IN THE CLOSED TUBE.

2. If the substance is in the form of a powder, or in small crystals, it is ready for analysis; if in lumps or large crystals, it must first be pulverized. A small quantity of it is introduced into the tube and shaken down into the closed end. The quantity should not exceed half an inch in the bottom of the tube. This is heated gently at first, and finally at the highest temperature of the Bunsen flame. The points to be observed are:

1. *If water is driven off and condenses in the upper part of the tube.*
2. *If any gas escapes.*
3. *If there is any change of color.*
4. *If sublimation takes place.*

5. *If the substance fuses.*
6. *If the substance carbonizes.*

3. Water is Expelled.—If water is driven off, it shows that the substance belongs to one of the following classes:

1. *Substances containing water of crystallization.* Many of these fuse at first, and solidify as the water is driven off. Some of them, especially alums, borates, and phosphates, swell up as the water is being driven off.

2. *Hydrates, or compounds containing chemically combined water.*

3. *Salts that contain mechanically enclosed water, in which case they usually decrepitate.**

4. *Deliquescent substances.*

5. *Ammonium salts that are decomposed with the formation of water.* Ammonium nitrate is the most common of these, and in its case nitrous oxide N_2O is formed at the same time, and will ignite a spark on the end of a splinter held at the mouth of the tube. The reaction of the water that condenses in the tube should always be tested with litmus paper. An alkaline reaction indicates the presence of ammonium compounds, and an acid reaction indicates a salt of a volatile acid.

Certain minerals possess the property of decrepitating without giving off water, when heated.

4. A Gas or Vapor is Evolved.—If a gas or vapor is given off, the color, odor, and reaction with litmus paper should be observed. It should also be tested to see if it is combustible, and if it will rekindle a spark on the end of a splinter.

The most common gases given off at this point are the following:

1. *Oxygen* is recognized by its power of reigniting a glowing spark on the end of a splinter of wood, when it is

* By saying that a substance *decrepitates* is meant that when heated it breaks up violently into small pieces, which tend, if not confined, to fly some distance. This is usually accompanied with a crackling sound.

held at the mouth of the tube. It indicates nitrates, chlorates, metallic peroxides, or oxides of the noble metals.

2. *Sulphur dioxide* is recognized by its odor and its acid reaction. It is produced when sulphites and some sulphates are decomposed by heat, and also when some sulphates and sulphides are mixed and ignited.

3. *Nitrogen peroxide* is known by its brownish-red color and peculiar odor, and indicates nitrates or nitrites—especially those of the heavy metals.

4. *Carbon dioxide* indicates carbonates or oxalates of metals that are reducible. The gas is odorless, colorless, and non-combustible. It is recognized by its property of rendering turbid a drop of barium hydrate, and by extinguishing a spark held in the mouth of the tube.

5. *Carbon monoxide* indicates oxalates or formates. It is recognized by the blue flame with which it burns when ignited. In the case of formates of easily reducible metals, and of a number of oxalates, carbon dioxide is also given off, and this makes it difficult to ignite the carbon monoxide. Formates often char to a considerable extent in the closed tube, while this is very rare with oxalates. When mixed with a little manganese dioxide and a few drops of water on a watch glass, and a little concentrate sulphuric acid is added, oxalates give off carbon dioxide, while formates do not. This gives us a convenient method of distinguishing between these two acids.

6. *Chlorine, bromine, and iodine* indicate certain chlorides, hypochlorites, bromides, and iodides, which are broken up by heat. They may be recognized by their odor and color. Chlorine is yellowish green; bromine, brownish red; and iodine, violet. If given off in any considerable quantity, iodine forms a black sublimate in the upper part of the tube.

7. *Hydrogen sulphide* indicates sulphides that contain water, or thiosulphates. It is readily recognized by its odor, and, if evolved in sufficient quantity, when ignited, burns with a pale-blue flame having a red mantle, forming sulphur dioxide and water.

8. *Cyanogen and hydrocyanic acid* indicate cyanides that

are decomposed by heat. They are known by their peculiar odor, similar to that of bitter almonds. Cyanogen, when free from other gases, will burn with a crimson flame, if ignited.

9. *Ammonia*, which is recognized by its odor and alkaline reaction, indicates ammonium salts. Nitrogenous organic matter or cyanides containing water may also give it off; but in this case the substance usually chars, and the ammonia is generally mixed with other vapors having disagreeable odors.

10. *Nitrous oxide* indicates ammonium nitrate, or an ammonium salt mixed with a nitrate. It is recognized by its power of supporting combustion, which is almost as great as that of oxygen. If ammonium nitrate alone is present, its decomposition products will be completely volatilized, leaving the tube clean.

5. A Change of Color.—If the substance changes color, the colors before heating, while hot, and after cooling, should be observed.

1. If the substance changes from white to yellow when hot, and becomes white again upon cooling, it indicates zinc oxide ZnO , or a compound of zinc, like the carbonate, which is readily reduced to oxide when heated.

2. A change from white or light yellow to yellowish brown when hot, turning to dirty light yellow upon cooling, indicates stannic oxide SnO_2 .

3. If the substance changes from light yellow to yellowish red or brownish red when hot, returning to yellow on cooling, and fuses at a high temperature, it indicates lead oxide PbO .

4. A change from red to brown when hot, turning red again on cooling, indicates red lead oxide Pb_3O_4 . Intense heat expels part of the oxygen from this, forming the yellow oxide PbO .

5. A change from white or light yellow to orange yellow or reddish brown when hot, turning to pale yellow on cooling, indicates bismuth oxide Bi_2O_3 .

6. A change from a light yellowish color to dark brown,

remaining dark brown after cooling, indicates manganous oxide MnO , or a compound, as the carbonate, which is readily reduced to oxide by heat.

7. A change from yellow to dark brown, turning light reddish brown on cooling, indicates cadmium oxide CdO , or a compound, such as the carbonate, that is reduced to the oxide by heat.

8. A change from light blue or light green to black, with the evolution of water, when hot, remaining black when cold, indicates a hydrate or carbonate of copper, changing to oxide, or a similar change in the corresponding compounds of nickel.

9. A change from brownish red to black when hot, turning to brownish red again upon cooling, indicates ferric oxide Fe_2O_3 .

10. A change from grayish white to black when hot indicates ferrous carbonate $FeCO_3$.

11. A change from yellow to dark orange, the substance fusing at an intense heat, indicates potassium or sodium chromate.

12. A change from light red to dark red, and then almost black upon raising the temperature, turning light red again upon cooling, indicates mercuric oxide HgO . In this case, intense ignition decomposes the compound, with the evolution of oxygen and the formation of a sublimate of metallic mercury in the upper part of the tube.

6. A Sublimate is Formed.—If a sublimate forms, it shows the presence of a volatile body. By observing the color and other properties of the sublimate, many substances may be recognized.

The most common substances giving a white sublimate are as follows:

1. *Ammonium salts*, which may be verified by the characteristic odor of ammonia given off when the substance is heated with a few drops of sodium hydrate.

2. *Mercurous chloride*, which sublimes without fusing, is yellow when hot, but turns to white on cooling.

3. *Mercuric chloride* first fuses, then fills the tube with dense white fumes that condense in the upper part of the tube in the form of a white crystalline sublimate.

4. *Lead chloride* fuses to a yellow liquid and then volatilizes, forming a white sublimate that is volatilized with difficulty.

5. *Arsenious oxide* volatilizes without fusing, and forms a white crystalline sublimate. If a little powdered charcoal is introduced into the tube, and heat applied, it reduces the oxide, and a dark arsenic mirror is produced.

6. *Antimonious oxide* fuses to a yellow liquid, and sublimes at a bright-red heat in the form of brilliant, white, needle-shaped crystals.

7. *Oxalic acid* gives off thick fumes that are irritating, and provoke coughing when inhaled. They condense in the upper part of the tube, forming a white crystalline sublimate.

8. *Salicylic acid*, when gently heated, volatilizes without decomposition, forming a white crystalline sublimate. It may be recognized by the odor of phenol, which is given off when it is quickly and intensely heated.

9. *Benzoic acid* is volatilized by heat, without decomposition, giving off irritating fumes that induce coughing when inhaled. The fumes condense in the upper portion of the tube, forming a white crystalline sublimate.

The most common substances giving a yellow sublimate are as follows:

1. *Sulphur* is dark red when hot, but becomes yellow again on cooling. When heated to rather a high temperature in the presence of air, it burns to sulphur dioxide. It may indicate free sulphur, or may result from the decomposition of a metallic persulphide, such as FeS_2 , Sb_2S_5 , etc.

2. *Arsenious sulphide* gives a sublimate that is red while hot, but usually turns to yellow upon cooling.

3. *Mercuric iodide* forms a yellow crystalline sublimate, that turns red when rubbed with a glass rod, probably owing to a change in crystalline form.

The common substances giving a dark-colored sublimate are as follows:

1. *Iodine* gives off violet vapors that condense on the sides of the tube, forming a black sublimate that often appears to have a violet tinge at the edges, where the sublimate is very thin.

2. *Mercury* and *amalgams* form globules in the tube. In many cases these globules are very minute, and give the sublimate the appearance of a gray mirror.

3. *Mercuric sulphide* yields a black sublimate that becomes red when rubbed with a glass rod.

4. *Arsenic* and arsenides give a brownish-black shining mirror, but no globules are formed. The vapors that are given off have the characteristic garlic odor by which arsenic may always be recognized.

7. The Substance May Fuse Without Apparent Decomposition.—This indicates some compound of one of the alkalis, or one of a few compounds of the alkaline earths, such as a nitrate, a chloride, or a bromide. If, upon intense ignition, a gas is given off, and small fragments of charcoal dropped in the tube are energetically attacked when they come in contact with the fused mass, a nitrate or chlorate is indicated. The gas evolved in this case is oxygen.

8. The Substance Carbonizes.—If the substance carbonizes, or chars, it shows the presence of organic matter. This is always accompanied by the evolution of gases, and by water that is usually either acid or alkaline to litmus paper. If the substance is entirely composed of organic matter, it will be completely consumed when ignited on the platinum foil. Much may be learned of the composition of a substance by noting the odor of the evolved gas. An odor like that of burning hair indicates an organic compound containing nitrogen. The odor of acetone indicates an acetate. An odor like that of burnt sugar indicates a tartrate. If the residue in the tube effervesces when treated with dilute acid, and the original substance did not effervesce when similarly treated, it shows that the substance was composed of an

organic acid combined with an alkali, or alkaline-earth metal, and that this has been reduced to a carbonate by the heat. If this carbonate is soluble in water and gives an alkaline reaction with litmus paper, we may assume that the organic acid was combined with an alkali metal. If the carbonate is insoluble in water, it indicates that the acid was united to an alkaline-earth metal.

Compounds containing an organic acid combined with a metal that is easily reduced, often leave the uncombined metal in the tube. In this case the oxygen of the oxide is removed by the carbon that is thrown out during the reaction, leaving the metal, and much or all of the carbon unites with the oxygen, leaving little or none in the tube.

9. The Substance Remains Unchanged.—If the substance is not altered by the heat, it shows the absence of organic matter, salts containing water of crystallization or constitution, compounds that are easily fused, those that change color when heated, and volatile compounds, except carbon dioxide, which may be given off without being observed in any way except by applying a test at the mouth of the tube.

EXAMINATION ON THE CHARCOAL.

10. Place a little of the substance to be tested in a small cavity that has been made for the purpose in a piece of fine-grained, soft-wood charcoal, and by means of the blowpipe, direct the flame upon it, heating gently at first, and afterwards to the highest temperature obtainable. One of the objects of this treatment is to see if the substance is fusible, and it should be noted whether the substance fuses easily, with difficulty, or is infusible. After trying this, the substance should be exposed to the inner, or reducing, flame, to see if it can be reduced to the metallic state by the combined action of the inner blowpipe flame and the carbon of the charcoal. Most of the reactions observed in the closed tube will be repeated on the charcoal, and a number of others

added. The phenomena here observed may lead to the direct detection of the composition of the substance, or reduce the number of possible compounds within very narrow limits.

11. The Substance Decrepitates.—This indicates one of a number of crystalline substances, some of which contain water of crystallization, or substances containing water mechanically enclosed. Of the crystalline substances that decrepitate, sodium chloride (common salt) is probably the most common.

12. The Substance Deflagrates.—If the substance deflagrates (i. e., burns violently), a nitrate or chlorate is indicated, and more particularly nitrates and chlorates of the alkalis. Deflagration is caused by the carbon of the charcoal uniting with the oxygen set free when chlorates or nitrates are decomposed by the heat. The residue left on the charcoal should be tested. If the substance was a nitrate, a carbonate will be left on the charcoal, and may be recognized by treating part of it with dilute hydrochloric acid, when it will effervesce. If the substance was a chlorate, a residue of chloride will be left on the charcoal, and may be identified by one of the tests for hydrochloric acid.

13. The Substance Fuses.—If the substance fuses and penetrates the charcoal, or forms a bead in the cavity, without giving an incrustation, gas, or odor, and without changing color, a salt of an alkali, or one of a few compounds of the alkaline earths, is indicated. To distinguish between these, first place a small quantity of the substance in a test tube, add a little strong solution of sodium hydrate, and heat. If an ammonium compound is present, ammonia will be evolved, and is recognized by its odor. Next, bring a little of the substance into the flame on the loop of a platinum wire, and observe the color imparted to the flame, both with and without the blue glass. After holding it in the flame for a short time, dip it into hydrochloric acid, and again bring it into the flame. The colors imparted to the flame by the metals

are: sodium, yellow; potassium, violet; barium, green; strontium, crimson; and calcium, brick red.

14. The Substance Volatilizes.—If the substance volatilizes, it indicates one of the compounds of mercury, arsenic, antimony, or ammonium, or organic substances.

The student should be very careful not to inhale much of the vapors given off by these compounds, as they are very injurious. It is a good plan to make it a rule not to breathe any of the vapors produced by substances that give sublimates in the closed tube; or, if we do so in order to detect the odor in the case of arsenic, to be very careful not to inhale much.

15. A Metallic Globule is Formed.—1. If, upon the sustained application of a strong flame for some time, a metallic globule is obtained, and no incrustation is formed, it indicates that the substance was a compound of gold, copper, silver, or tin. If the globule is yellow, gold is indicated; if red, it indicates copper; and silver or tin is indicated if a white globule is formed. In the case of tin and silver, incrustations are formed, but they are often so slight as to be overlooked, and so are mentioned here. The compounds of platinum, iron, cobalt, and nickel are also reduced; but, if pure, these metals cannot be fused into globules by the blowpipe flame.

2. A white, soft, and malleable metallic globule, with a yellow volatile incrustation that becomes lighter colored upon cooling, indicates a compound of lead. In this case the flame is usually colored blue when the incrustation is volatilized, especially if the reducing flame is used.

3. If the metallic globule is white, hard, and brittle, and fuses easily, and the incrustation is dark orange yellow when hot, but changes to lighter yellow upon cooling, and is volatile, but does not color the flame, a compound of bismuth is indicated.

4. A metallic globule that is easily fused and slowly volatilized, together with a reddish-brown incrustation that

volatilizes without coloring the flame, indicates a compound of cadmium.

5. If the metallic globule is white, hard, and brittle, and the incrustation is white and volatile, a compound of antimony is indicated.

6. If a white, rather hard, but malleable globule is formed and a very slight, dark-red incrustation is deposited, silver compounds are indicated. If small quantities of lead and antimony are present, the incrustation will be crimson.

7. A bright, readily fusible metallic globule that is malleable, together with an incrustation that closely surrounds the globule and is faint yellow while hot, but becomes white upon cooling, indicates a compound of tin. The incrustation is often very slight, and the metallic globule is only obtained by persistent heating in the reducing flame, or by special treatment to be described later.

16. An Incrustation is Formed Without a Metallic Globule.—It will be noted that some of the metals that were mentioned as giving metallic globules are also mentioned here. The reason for this is that some of the compounds of these metals may yield a metallic globule, while it is impossible to obtain it from others by ordinary means; hence, they must be treated under both heads.

1. A white incrustation that forms on the charcoal at some distance from the test, and volatilizes very easily when heated, giving a garlic odor, indicates a compound of arsenic.

2. A reddish-brown incrustation that volatilizes easily before the flame without imparting a color to it, indicates a compound of cadmium.

3. A white incrustation that forms rather near the test, and is so volatile that it may be driven from place to place on the charcoal, indicates a compound of antimony.

4. A dark reddish-yellow incrustation that becomes lemon yellow on cooling, and may be volatilized without coloring the flame, indicates a compound of bismuth.

In the case of antimony and bismuth, metallic globules are usually—though not always—formed.

5. An incrustation that is deposited rather near the test, is yellow while hot, but turns to white upon cooling, and is volatilized with difficulty, indicates a compound of zinc.

6. An incrustation that surrounds the test closely, is yellowish white while hot, and white when cold, and is not volatile, indicates a compound of tin.

7. A reddish-brown incrustation that imparts a deep-green color to the flame indicates a compound of thallium.

17. An Infusible Metal.—If the substance does not give an incrustation, but is reduced to the metallic state without forming a globule, owing to the infusibility of the metal, a compound of platinum, iron, chromium, cobalt, nickel, or manganese is indicated. By heating a little of the metal in the borax or microcosmic bead, chromium, cobalt, and manganese may be identified, and the others more or less clearly indicated.

18. A White, Luminous, Infusible Mass.—If a white mass that is infusible, and is incandescent when highly heated, is formed on the charcoal, either at once or after water is expelled, it indicates a compound of tin, aluminum, zinc, barium, strontium, calcium, magnesium, silicic oxide, or, possibly, a silicate. A drop or two of cobalt-nitrate solution should be added, and the mass again heated in the oxidizing blowpipe flame to the highest temperature obtainable. By this means the test is generally given a characteristic color.

1. *Blue* indicates aluminum oxide, or a compound that has been reduced to the oxide, a phosphate of an alkaline-earth metal, or possibly silicic oxide, or a silicate.

2. *Green* indicates an oxide of zinc or tin, or one of their compounds that has been reduced to the oxide. Stannic oxide is colored rather a bluish green.

3. *Rose color* indicates magnesium oxide that may have been formed by the reduction of some other compound on the charcoal. Magnesium phosphate gives a violet-colored residue.

4. *Gray* indicates an oxide of barium, strontium, calcium,

one of their compounds that has been reduced to the oxide, or, possibly, silica, or a silicate. If a small piece of the test, placed on a piece of red litmus paper, and moistened with a drop of water, colors the paper blue, it indicates barium, strontium, or calcium, as the oxides of these metals give an alkaline reaction. The same test may be applied in the case of magnesium, as its oxide is also alkaline. To distinguish between barium, strontium, and calcium, moisten a small piece of the test on a platinum wire with hydrochloric acid, dry it carefully near the flame, moisten again with hydrochloric acid, and bring it into the outer flame, when the metal will impart its characteristic color to the flame. The colors imparted by strontium and calcium are very similar under certain circumstances, and care should be taken to distinguish between them.

Silicic oxide (silica) and silicates may be recognized by heating a small portion of the substance in a microcosmic bead, when the silica skeleton will be formed if silicon is present.

19. A Colored Mass.—If a colored residue that is only slightly luminous when heated is left on the charcoal, it indicates a compound of copper, iron, chromium, cobalt, nickel, or manganese, or some compound of sulphur. The metals named may be distinguished from one another with a fair degree of accuracy by means of the borax or microcosmic bead, and by fusing on the platinum foil with sodium carbonate and potassium nitrate, as previously described.

If a compound of sulphur is present, it may be recognized by mixing some of the substance with sodium carbonate and fusing it on the charcoal, when sodium sulphide is formed, which, when ground up on a piece of silver and moistened with a drop or two of water, will deposit a black stain of silver sulphide. In performing this operation, it is sometimes necessary to heat the mixture, at the highest temperature obtainable, with the reducing blowpipe flame for some time, in order to reduce the compound and form sodium sulphide.

20. In the case of oxides and other easily reducible compounds, such as nitrates, the substance will be reduced to the metallic state when heated alone on the charcoal, in the reducing blowpipe flame, if it is a compound of a reducible metal; but, in case of compounds that are difficult to reduce, such as sulphates, sulphides, chlorides, phosphates, etc., the reduction is greatly facilitated by adding sodium carbonate. By this means double decomposition is induced, and the oxide is formed, and from this we may be able to obtain the metal. In many cases reduction is greatly aided by mixing the substance with about twice its volume of potassium cyanide, and heating this mixture in the reducing blowpipe flame on the charcoal, or by heating the substance with a mixture of sodium carbonate and potassium cyanide. If a metallic globule is obtained by any of these methods, it should be examined as to its color, hardness, brittleness, and malleability. In case the globule is sufficiently large, it may be removed from the charcoal with the forceps, placed on a smooth piece of steel, and examined with the aid of a hammer. If the globules are small, they should be scraped out, together with the adhering charcoal, into a small mortar, a little water added, and the charcoal loosened from the metal by gently rubbing with a pestle. The charcoal is then carefully washed out by means of water, and the metal left in the mortar, where it may be examined by means of the pestle, or it may be removed to the smooth steel and a hammer used, as in the case of large globules. If the metal is yellow, gold is indicated; copper is indicated if the metal is red; silver is white; tin, grayish white; cadmium, bluish white; lead, whitish gray; bismuth, reddish gray; and antimony, gray. Lead and tin are soft and malleable; gold and cadmium are harder than lead and tin, but not very hard, and are malleable; copper and silver are rather hard, but are malleable, and bismuth and antimony are hard and brittle. After examining the globule in this way, it is best to dissolve it in acid, and apply the wet reactions. It is impossible to reduce the alkalis and alkaline-earth metals to the metallic state by any treatment on the charcoal.

Many of the reactions observed in the closed tube will also appear when the substance is heated on the charcoal, and indicate the same things here that they do in the closed tube. Thus, ammonia, which is always recognized by its odor, indicates a compound of ammonium, etc.

EXAMINATION IN THE FLAME.

21. As we have already seen, a number of substances impart characteristic colors to the flame when heated in it; and, as the operation is simple and quickly performed, it gives us a good method of determining these substances. In performing this operation, be sure that the platinum wire is perfectly clean, by burning it off till it does not color the flame, after it has been suspended in hydrochloric acid; and, while hot, bring the loop in contact with some small particles of the substance to be tested. They will adhere to the hot wire, and may be brought into the outer flame, when they will impart the characteristic color to the flame, if the substance is one that colors the flame. If the substance does not color the flame, it should be dipped in hydrochloric acid, and brought into the flame again. If it does not color the flame now, dip it into sulphuric acid, and again bring it into the outer flame, as this is necessary in order to set free phosphoric or boric acid. When compounds of sodium are present, they give such an intense color as to often obscure the colors of the other substances, so that it is very often necessary to view the flame through a blue glass. The following colors when obtained are quite characteristic:

1. *Yellow* indicates a compound of sodium. It is often so intense that it is impossible to see the colors imparted to the flame by other substances that may be present; so, when a flame is colored an intense yellow, it should be viewed through a blue glass, when the yellow rays will be absorbed and other shades will appear.

2. *Violet* indicates a compound of potassium.

3. *Bright red* or *crimson* indicates a compound of

strontium or lithium. There is a slight difference in these flames, which serves to indicate more or less clearly to the experienced chemist which metal is present; but this reaction alone cannot be depended on to identify either of these metals with certainty; they may, however, be distinguished easily by other means, as lithium forms no compounds insoluble in water, while strontium forms many.

4. *Brick red* indicates a compound of calcium. Under certain conditions, the color imparted to the flame by calcium compounds is almost as bright a red as that given by strontium or lithium, but this is rather unusual.

5. *Blue* indicates a compound of lead, antimony, arsenic, or copper chloride CuCl_2 . All compounds of copper, except the chloride, impart a green color to the flame.

6. *Green* indicates a compound of barium, copper, thallium, molybdenum, manganese chloride, boric acid, or phosphoric acid. Molybdenum gives a rather yellowish-green color to the flame; volatile compounds of boric acid impart a bright green, which often lasts but a moment, and phosphoric acid a rather pale green. Borates and phosphates must be treated with sulphuric acid before trying the flame reaction. Phosphates may sometimes fail to color the flame, but borates always impart a green color, especially if treated with sulphuric acid and alcohol and ignited in a porcelain dish, as described in treating the reactions of boric acid.

EXAMINATION IN THE BEAD.

22. Compounds of many of the metals, when heated in the borax or microcosmic bead, impart a color to the bead by which these metals are indicated. The colors imparted by three of these metals—chromium, cobalt, and manganese—are so distinctive as to be conclusive proof of the presence of these metals, and the others may be recognized with tolerable certainty by this test, after the operator has become familiar with them. In making this test, first be sure the wire is perfectly clean; then, while it is hot, dip the loop

into powdered borax, or microcosmic salt, and heat the portion that adheres to the hot wire until it fuses into a clear, transparent bead; and while this is hot bring it in contact with a few small particles of the substance to be tested, which will adhere to the soft, hot bead. Only a very small quantity of the substance should be taken for this purpose. Now heat the bead containing the substance, in the oxidizing flame, until it is thoroughly fused, and observe the color of the bead when hot, while cooling, and after it is cold. Then hold the bead in the reducing flame for some time, and note any change that may take place either while the bead is hot or after it cools. The following are the most important metals that give colored beads, with the colors which they impart.

A blue bead in both the oxidizing and the reducing flame, that appears more clearly colored upon cooling, indicates cobalt.

An amethyst-red bead showing the color much better after cooling, and becoming colorless, but not quite clear, when heated in the reducing flame, indicates manganese.

A green bead, in both the oxidizing and the reducing flame, that becomes particularly clear and distinct upon cooling, indicates chromium.

A bead that in the oxidizing flame is bluish green when hot, and blue when cold, and becomes red in the reducing flame after considerable of the substance has been added, indicates copper.

A bead that in the oxidizing flame is brownish red, and changes to yellow or becomes colorless upon cooling, and in the reducing flame is red while hot, yellow while cooling, and yellowish green when cold, indicates iron.

A bead that in the oxidizing flame is red when hot, but becomes yellowish brown, yellow, or even colorless upon cooling, and in the reducing flame is reddish brown when hot, and becomes gray and opaque when cool, indicates nickel.

A bead that in the oxidizing flame is yellow when hot and becomes lighter colored—sometimes almost colorless—on cooling, and in the reducing flame is yellow or almost

colorless when hot, and gray and opaque when cold, indicates bismuth.

An infusible skeleton floating in the fused bead indicates silicic oxide or a silicate. For the silicates, a microcosmic bead must be used.

A bead that, when heated in the oxidizing flame, is light yellow or opal while hot, and turbid when cold, and becomes whitish gray in the reducing flame, indicates silver.

In the case of sulphides and arsenides, the substance should be heated on the charcoal with the blowpipe until the sulphur or arsenic is driven off, as these may interfere with the bead reaction to a certain extent, and a little of the residue is used in the bead.

The most important of the bead reactions may be given in the form of a table for convenience:

TABLE 1.

<i>O. F.</i>	<i>Metal.</i>	<i>R. F.</i>
Blue	<i>Co</i>	Blue
Amethyst	<i>Mn</i>	Colorless
Green	<i>Cr</i>	Green
<i>Hot.</i> —Bluish green } <i>Cold.</i> —Blue }	<i>Cu</i>	Red when cold
<i>Hot.</i> —Brownish red } <i>Cold.</i> —Yellow or colorless }	<i>Fe</i>	{ <i>Hot.</i> —Red <i>Cold.</i> —Yellowish green
<i>Hot.</i> —Red } <i>Cold.</i> —Yellow }	<i>Ni</i>	{ <i>Hot.</i> —Red <i>Cold.</i> —Gray and opaque
<i>Hot.</i> —Yellow } <i>Cold.</i> —Light yellow }	<i>Bi</i>	{ <i>Hot.</i> —Light yellow <i>Cold.</i> —Gray and opaque

EXAMINATION ON THE PLATINUM FOIL.

23. Examination on the foil is only resorted to in cases where chromium or manganese has been indicated by some of the preceding tests, when it is used to confirm these metals. Care must be taken not to fuse compounds of such metals as lead or mercury on the foil, or they will alloy with the

platinum and destroy the foil. To perform this operation, mix a little of the substance with about its own volume of potassium nitrate, and three times its volume of sodium carbonate, on the foil, and heat till it is thoroughly fused. If manganese is present, it is oxidized to manganate and gives the fusion a deep-green color, which is a very characteristic reaction for manganese. When the fusion is dissolved in boiling water, the manganese is precipitated as a brown oxide. If a chromium compound is present, it will be oxidized to chromate of sodium or potassium, and will give the fusion more or less of a yellow tint. In this case the fusion should be dissolved in equal parts of acetic acid and water, the solution boiled until all carbon dioxide is expelled, and lead acetate added. If chromium is present, yellow lead chromate will be precipitated. The precipitate is soluble in sodium hydrate, and is reprecipitated from this solution by nitric acid. The fusion is dissolved in acetic acid and water, rather than water alone, in order to break up the carbonate and expel the carbon dioxide, which, if present, would precipitate the lead as carbonate, and obscure the reaction with the chromate.

EXAMINATION WITH SULPHURIC ACID.

24. Treatment with sulphuric acid is for the purpose of detecting the acid present, and much may be learned of the composition of a substance by this means. To make this test, place a small amount of the substance in a test tube, add about 2 or 3 cubic centimeters of concentrate sulphuric acid; heat gently at first, then gradually raise the heat to the boiling point. During this heating, some of the following gases may be liberated, which will lead to the identification of the acid.

1. *A colored gas is given off.* It may be:

Chlorine, which is recognized by its yellowish-green color and peculiar, penetrating odor, indicates a hypochlorite, a mixture of a chloride and a nitrate, or a chloride and a

peroxide. These latter may suffer double decomposition, during which chlorine is liberated. A greenish-yellow explosive mixture of chlorine and chlorine tetroxide indicates a chlorate. In case a chlorate has been indicated by a previous reaction, only a very little of the sample should be taken, as a larger quantity is likely to cause a violent explosion, which is dangerous, as it may spatter the hot concentrate acid.

Yellowish vapors of *bromine*, which are generally mixed with some hydrobromic acid, may be recognized by their color and odor, and indicate a bromide. In case a bromide is thus indicated, a small quantity of the substance should be heated with concentrate nitric acid, which decomposes all bromides, except the bromide of silver, giving off reddish vapors that condense in red globules in the upper part of the tube.

Dark-red vapors of *chromium oxychloride* CrO_2Cl_2 indicate a mixture of a chloride and a chromate.

Reddish-brown fumes of *nitrogen tetroxide* N_2O_4 , which are recognized by their color and odor, and which indicate a nitrite. Nitrites are decomposed in the same way when heated with dilute sulphuric acid.

Violet vapors of *iodine*, which condense, forming a black solid in the upper part of the tube, and show the presence of an iodide.

2. *A colorless gas with an odor may be given off.* The most common are:

Hydrochloric, or, possibly, *hydrobromic*, acid. These are recognized by their odors, and by the white fumes that are produced when they come in contact with a drop of ammonia held at the mouth of the tube on a glass rod. They indicate salts of these acids. Hydrobromic acid is always more or less decomposed by the heat of the reaction, and brownish vapors of bromine may be seen.

Hydrofluoric acid, known by its penetrating odor and white fumes, but especially by its power of etching glass, shows the presence of a fluoride.

Sulphur dioxide, known by its penetrating odor, like that

of burning sulphur matches, indicates a sulphite or thiosulphate.

Hydrogen sulphide, recognized by its disagreeable odor, and its property of blackening a piece of filter paper that has been moistened with a solution of lead or silver, indicates a sulphide.

Nitric acid, which is indicated by its odor, and by the brown fumes that are given off when a small crystal of ferrous sulphate is dropped into the tube, indicates a nitrate. In this case the contents of the tube should be cooled, and ferrous-sulphate solution cautiously added, when the characteristic brown ring will be formed where the two solutions meet.

Hydrocyanic acid, which is recognized by its peculiar odor, similar to that of bitter almonds, indicates a cyanide.

Acetic acid, which is recognized by its odor, indicates an acetate. In this case a little of the substance should be heated with concentrate sulphuric acid and alcohol, when acetic ether, having an agreeable odor somewhat like that of ripe apples, is evolved.

A gas having an odor like that of burnt sugar, accompanied by a charring of the substance, indicates *tartaric acid* or one of its compounds.

3. *A colorless, odorless gas may be evolved.* It may be:

Oxygen, which is recognized by its power of igniting a spark on the end of a splinter when held in the mouth of the tube, indicates a peroxide, a chromate, or a permanganate.

Carbon dioxide, which is evolved with effervescence, and renders turbid a drop of barium hydrate or of lime water, held at the mouth of the tube on a glass rod, indicates a carbonate. In this case a little of the substance should be treated in a test tube with hydrochloric acid, as all carbonates are decomposed by hydrochloric acid, with effervescence. A few of the mineral carbonates, however, show but slight effervescence if the acid is dilute.

Carbon monoxide, which is recognized by its burning with a blue flame when ignited at the mouth of the tube, indicates

an organic compound or a ferrocyanide. Oxalic acid or an oxalate gives both carbon monoxide and carbon dioxide, without any charring of the substance. Both of these gases should be identified in the case of an oxalate, by the blue flame, and the reaction with a drop of barium hydrate. Tartrates give off first carbon monoxide, then begin to char and give off a mixture of carbon monoxide and sulphur dioxide, and, finally, the contents of the tube become thick and black, and yield an odor like that of burnt sugar. Formic acid and formates, when heated with concentrate sulphuric acid, are decomposed with the formation of water and carbon monoxide; the latter escapes with effervescence, and burns with a blue flame. If heated with concentrate sulphuric acid and alcohol, ethyl formate is evolved, and is recognized by its peculiar rum-like odor. Citric acid at first yields carbon monoxide, then carbon monoxide mixed with carbon dioxide, which is recognized by its reaction with barium hydrate, and acetone, indicated by its odor. During this time the solution remains clear; but, upon continued heating it assumes a dark color, and sulphur dioxide is given off.

If a white insoluble precipitate is formed during the treatment with sulphuric acid, lead, mercurous, barium, strontium, or calcium compounds are indicated.

25. Metals and Alloys.—If the appearance of the substance indicates that it is a metal or an alloy, it should be examined as to color, hardness, and malleability, and then small portions of it tested with hydrochloric acid, to see if hydrogen is liberated, and with nitric acid, to see if nitrogen dioxide is evolved. If these gases are given off, they prove the substance to be a metal or an alloy. A small portion of the metal should next be heated on the charcoal before the blowpipe. Its behavior here may lead directly to its recognition, or suggest some special test by which it may be identified.

After these preliminary tests, a small portion of the metal is treated in a test tube with a mixture of equal quantities of concentrate nitric acid and water, and heat is applied, if

necessary. By this means all the metals may be classified as follows:

1. Metals that are not acted on by nitric acid, consisting of gold and platinum.

2. Metals that are oxidized by nitric acid, but whose oxides are not soluble to any considerable extent in an excess of the acid, or in water. This group consists of tin and antimony; and, in the presence of these metals, arsenic, and sometimes bismuth, form compounds that are insoluble in nitric acid and water.

3. Metals that, when treated with nitric acid, form nitrates that are soluble in an excess of the acid, or in water. This class includes all the metals, except those mentioned above.

In any case, evaporate most of the excess of acid, and dilute the substance remaining in the tube with about four times its volume of water. If a clear solution is formed, it may be subjected at once to treatment for the group separations. If a metal remains unattacked by the acid, it is filtered off, and the filtrate tested for metals that may have been dissolved; the metal on the filter is then dissolved in aqua regia, and the solution tested for gold and platinum, as directed in the next section, after most of the excess of acid has been driven off by heating carefully, and the solution has been diluted with about four times its volume of water. If a white insoluble mass is formed, it must be filtered off, and the filtrate examined for metals that may have gone into solution. The precipitate will probably be the oxide of tin or antimony, or possibly one or both of these, together with arsenic or bismuth. And, in addition to these, the precipitate may contain undissolved gold or platinum. After washing it two or three times on the filter, it is removed to a porcelain dish and heated with yellow ammonium sulphide. If not all dissolved, filter, wash well on the filter, and treat the filtrate for the separation of tin, antimony, and arsenic, as described in Art. 97, *Qualitative Analysis*, Part 1. The precipitate may contain gold, platinum, and bismuth. Dissolve it in aqua regia, drive off most of the excess of acid, dilute with water, heat almost to boiling, and lead a current

of hydrogen sulphide through the hot solution until the metals are completely precipitated as sulphides. Filter, remove the precipitate to a porcelain dish, and heat some time with a mixture of equal parts of concentrate nitric acid and water. This will dissolve the bismuth sulphide, and leave the sulphides of gold and platinum unattacked. Filter, and test the filtrate for bismuth. Then dissolve the precipitate in aqua regia, and test for gold and platinum, as directed in Art. 39, *et seq.* If both gold and platinum are present, they are separated by means of oxalic acid.

SOLUTION OF SOLID SUBSTANCES.

26. As all solid substances, except simple ones that yield positive results in the dry way, should be dissolved, and the solutions subjected to wet analysis, to confirm the results obtained by the dry method, the means of getting them into solution becomes a matter of importance. The method to be pursued will depend on the dry reactions, and it is impossible in a work of this kind to consider every possible case separately, but a general outline may be given from which the student may select the method suited to any particular case. All substances may be divided into three classes, as follows:

1. *Substances soluble in water.*
2. *Substances insoluble in water, but soluble in an acid.*
3. *Substances decomposed by fusing with carbonates.*

As complex substances may contain compounds belonging to each of these classes, a small portion should be heated in a test tube with water, the filtrate tested for compounds that may have gone into solution, and the residue treated with acids. The excess of acid should be driven off after this operation, the substance diluted with water, filtered, the filtrate tested for substances that may have been dissolved, and the residue, if any remains, fused with carbonates of sodium and potassium. By this treatment, all compounds may be dissolved.

As the treatment of metals and alloys has already been described, they will not be considered here.

27. Substances Soluble in Water.—Unless the dry reactions have clearly shown that such treatment would be useless, the first operation should be to boil a little of the substance thoroughly in a test tube with water. All substances that have been fused, must be ground to a fine powder before treatment. If an undissolved residue remains, it should be filtered off, and the clear filtrate examined for compounds that may have been dissolved. The principal substances dissolved by water are:

1. All chlorates, hypochlorites, acetates, and formates.
2. All chlorides, bromides, and iodides, except those of silver, lead, and mercury in the mercurous condition.*
3. All nitrates and nitrites, except a few basic nitrates.
4. All sulphates, with the exception of lead, mercurous, barium, strontium, and calcium sulphates.
5. The alkalis and all their compounds, except metantimonate of sodium and potassium silicofluoride.
6. The chromates of copper, zinc, manganese, ferric iron, and mercury in the mercuric condition.
7. Oxalates of chromium, aluminum, antimony, ferric iron, and tin in the stannic condition.
8. Sulphides of the alkaline earths. The sulphides of calcium and magnesium sometimes dissolve with difficulty.

In addition to these, the cyanides, arsenites, arsenates, acid carbonates, and oxides of the alkaline earths are partially dissolved in water. Calcium sulphate may also be partly dissolved in a large quantity of water.

28. Substances Insoluble in Water.—If the substance is insoluble in water, a portion should be placed in a test tube, concentrate hydrochloric acid added, and the contents of the tube boiled, if necessary. By this means many substances insoluble in water are changed to soluble chlorides,

* Cuprous chloride, bromide, and iodide are insoluble in water; but, as they are not common, and are rapidly oxidized to soluble cupric compounds, they may generally be disregarded.

and water is formed, or the acid, if volatile, is driven off, or, if non-volatile, remains in solution.

If this treatment fails to decompose the substance, a small quantity of it should be heated in a test tube with concentrate nitric acid. This will oxidize some insoluble compounds, forming soluble ones; as, mercurous chloride is oxidized to mercuric, etc.

If the substance is not dissolved by either of these acids separately, it should be boiled with aqua regia. If this fails to dissolve the substance, it must be fused with a carbonate or subjected to some special treatment in order to get it into solution. In each case the excess of acid should be driven off, water added, the substance filtered, and the clear filtrate tested to see if a part of the substance has been dissolved.

In case the substance is dissolved by one of these acids, the excess of acid is driven off, the substance diluted with four or five times its volume of water, and subjected to examination for the metals in the wet way.

29. Substances Fused With Carbonates.—Most substances are decomposed by acids, but a few—including anhydrous silicates, and sulphates of barium, strontium, and, possibly, calcium, although the latter is usually dissolved, partly by water and partly by acids—remain undissolved, and must be put into solution by some other means. The most general method of doing this is to fuse the substance with about six times its weight of a mixture of equal parts of sodium and potassium carbonates. By this means the substances are decomposed, the acid of the substance unites with sodium or potassium, forming soluble alkali salts, and the metal is changed to carbonate. The fusion is made in a platinum vessel, usually the foil, and must be continued until chemical action ceases and the fusion becomes quiet. Substances that would alloy with platinum must not be treated in this manner.

The fusion after cooling is transferred to a test tube or a small beaker, and boiled with water until it is thoroughly disintegrated. The acid, which is combined with an alkali,

will now be in solution, and the carbonate or oxide of the metal will remain undissolved. Filter, and test the filtrate for the acid; then dissolve, in hydrochloric acid, the residue that remains on the filter, and test this solution for the metal.

Pulverized silicates that are insoluble in the acids used may be decomposed by hydrofluoric acid, and this method must be resorted to when the alkalies are to be determined.

Insoluble cyanides, ferrocyanides, and ferricyanides are best dissolved by fusing in a porcelain crucible, with about five times their weight of a mixture of equal parts of sodium and potassium carbonates. The acid unites with the alkalies, forming soluble cyanide, ferrocyanide, or ferricyanide of sodium and potassium, and carbonates or oxides of the metals are formed. After disintegrating the fusion in hot water, and filtering, the acid may be determined in the filtrate. Then the precipitate is dissolved in nitric acid, and the metals determined in this solution.

30. We now have before us all the principal dry reactions, and the general methods of dissolving solid substances. After this has been done, the results obtained in the dry way should always be confirmed by the wet reactions. When an acid is used in dissolving a substance, this solution cannot be used in testing for the acid, for the reactions for the acid used in dissolving the substance will, of course, be obtained.

THE RARE ELEMENTS.

31. The rare elements arrange themselves in the same groups as the common metals, but the distinction between the groups is not so sharp as in the case of the common metals; and, as their treatment at that point would have greatly complicated the work, they were reserved for special treatment in a separate section. The most important reactions, by which these elements may readily be recognized, are given here.

GROUP I.

*Thallium Tl**Tungsten W*

32. Thallium.—Thallium is a soft white metal, and is often found in minute quantities associated with sulphides of the other metals, as in copper and iron pyrites. It forms two series of compounds—thallous and thallic—but the latter are very unstable, and are readily reduced to thallous compounds. It is readily dissolved by dilute nitric or sulphuric acid, but is only slightly acted upon by hydrochloric acid. Thallium is not completely embraced in this group, as thallous chloride is slightly, and thallic chloride easily, soluble in water, so that, in dilute solutions of thallous, or ordinary solutions of thallic, compounds, the metal passes on to the fourth group, where it is completely precipitated by ammonium sulphide.

1. Thallic compounds are reduced to thallous compounds with the separation of free sulphur when treated with hydrogen sulphide.

2. *Sodium and ammonium hydrates and carbonates* precipitate brown, gelatinous compounds from thallic solutions, but give no precipitates with ordinary thallous solutions. The carbonates give white precipitates with very strong thallous solutions.

3. *Potassium iodide* precipitates light-yellow thallous iodide TlI from thallous solutions. In thallic solutions the same precipitate is formed, and iodine is set free.

4. *Hydrochloric acid* precipitates white thallous chloride from thallous solutions that are not very dilute, but gives no precipitate with thallic compounds.

5. *Ammonium sulphide* precipitates black thallous sulphide Tl_2S from thallium solutions. Hydrogen sulphide produces the same precipitate from solutions that do not contain inorganic acids, but the presence of inorganic acids prevents this precipitate.

6. All thallium compounds are readily reduced when heated on the charcoal before the blowpipe, and deposit a

dark-violet or black incrustation that is volatile and imparts a green color to the flame.

7. Thallium compounds are best recognized by the deep emerald-green color that they impart to the flame, or by means of the spectroscope. The thallium spectrum consists of one green line. In many cases the flame or the line can only be seen for a short time.

33. Tungsten.—Tungsten is a white, hard, brittle element that is classed with the metals principally on account of its weight and some other physical properties. In nearly all its chemical relations it acts as a non-metal. Its oxygen compounds are all acid. Magnesium tungstate and the alkali tungstates are soluble. All the others are insoluble in water, and many of them in acids. The insoluble tungstates are best decomposed by fusing with carbonates of sodium and potassium, when soluble tungstates of the alkalies are formed.

1. *Hydrochloric acid* precipitates white H_2WO_4 , H_2O from cold solutions, and yellow H_2WO_3 from hot solutions. These precipitates are insoluble in an excess of acid, but soluble in ammonia.

2. *Hydrogen sulphide*, when led through a solution of a tungstate that is rendered distinctly acid, reduces the tungstate to a lower oxide, and gives the solution a blue color.

3. *Ammonium sulphide* gives no precipitate in neutral or alkaline solutions of tungstates, but, if an excess of the sulphide is added and then the solution is rendered acid, a light-brown precipitate of tungsten trisulphide WS_3 , is formed.

4. *Stannous chloride* gives a yellow precipitate that changes to a fine blue color when hydrochloric acid is added and heat is applied. This is a very characteristic reaction for tungsten.

5. *Metallic zinc* and hydrochloric acid added to a tungstate solution produce a blue color, owing to reduction of the tungsten to a lower oxide W_2O_3 .

6. All tungsten compounds, when heated for some time

in the reducing flame, in the microcosmic bead, impart a blue color to the bead. If iron is introduced, the bead assumes a blood-red color; but the blue color is restored by adding a little tin foil, and heating again.

GROUP II.

DIVISION A.

Palladium Pd
Osmium Os

Rhodium Rh
Ruthenium Ru

34. These rare elements occur associated with platinum almost exclusively. They are all completely precipitated by hydrogen sulphide, and are insoluble in ammonium sulphide and alkaline hydrates, hence they are completely comprehended in this group.

35. Palladium.—Palladium always occurs associated with platinum, and is nearly always present, in small quantities, in platinum ores. It is obtained from the residue that is left when platinum is extracted from its ores. It is lighter than platinum, is white, malleable, and ductile, and only fuses at very high temperatures. It is more easily oxidized, and is less dense than platinum. It has both divalent and tetravalent relations, but the compounds in which it acts as a divalent element are much more common and stable. It is not dissolved by hydrochloric acid, and is only slightly acted on by nitric acid, but is readily dissolved to $PdCl_2$ by aqua regia.

1. *Ammonium hydrate* precipitates, from palladium solutions, flesh-colored palladammonium chloride $Pd(NH_4)_2Cl_2$, which dissolves in an excess of ammonia, especially when heated, forming a colorless solution from which it is reprecipitated in yellow crystals by hydrochloric acid.

2. *Sodium hydrate* precipitates a brown basic salt that is slightly soluble in an excess of the reagent.

3. *Hydrogen sulphide* precipitates black palladious sulphide PdS from slightly acid solutions of palladium. The precipitate is insoluble in ammonium sulphide, but dissolves slowly in hot concentrate hydrochloric acid, and readily in aqua regia.

4. *Ammonium sulphide* gives the same reaction as hydrogen sulphide.

5. *Mercuric cyanide* precipitates yellowish-white palladious cyanide $Pd(CN)_2$ from neutral or slightly acid solutions. The precipitate is slightly soluble in hydrochloric acid, and is readily dissolved by ammonia. This reaction is very characteristic, and it is important as the means of separating palladium from the residuary solution in the platinum process. The cyanide is decomposed by heat, leaving the palladium in the spongy form. This is known as *palladium sponge*.

6. *Stannous chloride* in the presence of free hydrochloric acid gives the solution at first a red color, which quickly changes to brown, and finally becomes greenish. Upon the addition of considerable water, this changes to reddish brown.

7. *Potassium iodide* precipitates black palladious iodide PdI_2 , which is soluble in considerable excess of the precipitant, forming a dark-brown solution. This reaction is very characteristic.

8. *Potassium sulphocyanide* does not precipitate palladium, even after the addition of sulphurous acid. This gives us the best means of separating palladium from copper.

36. Osmium.—Osmium is a very rare element, but it occasionally occurs in platinum ores alloyed with iridium. It is usually obtained as a black or gray powder, with metallic luster, and is the most infusible metal known. Metallic osmium, osmium oxide OsO , osmium trioxide Os_2O_3 , and osmic oxide OsO_2 , are all readily oxidized to osmium tetroxide OsO_4 when heated in the air. This is a very volatile compound, with an exceedingly irritating and offensive odor, similar to that of chlorine and bromine, and gives us the best means of recognizing osmium.

If a little osmium is held in the outer non-luminous flame on a platinum wire, it makes the flame exceedingly luminous. By this means the presence of osmium is indicated in alloys of osmium and iridium. If only minute quantities of osmium are present, the flame is only rendered highly luminous for a very short time; but, by holding the alloy in the reducing flame for a time, and then returning it to the outer flame, this may be repeated.

Fuming nitric acid and aqua regia dissolve osmium, forming the tetroxide. The application of heat hastens the solution, and volatilizes the tetroxide, which is recognized by its odor.

Osmium tetroxide, when heated with water, first fuses, and then slowly dissolves to a colorless liquid, with an unpleasant, irritating odor.

1. *Hydrogen sulphide* gives this solution a dark-brown color; and when an acid is added, a dark-brown precipitate of osmium sulphide OsS_4 is formed. This is insoluble in ammonium sulphide and alkali hydrates.

2. *Sulphurous acid* produces at first a yellow color, which, upon the addition of more of the reagent, changes to reddish brown, then green, and finally blue.

3. *Zinc*, added to an acid solution, precipitates metallic osmium.

4. All compounds of osmium, when ignited in hydrogen, yield the metal, but, when ignited on the charcoal in the oxidizing flame, yield volatile osmium tetroxide, which is recognized by its odor.

37. Rhodium.—Rhodium occurs in very small quantities in platinum ores. In the compact form it is a silver-white, malleable metal, which fuses with great difficulty, and is insoluble in all acids. When precipitated from solution it is a gray powder, dissolving somewhat in concentrate nitric acid. A solution of rhodium is best obtained by fusing the metal or one of its salts in acid potassium sulphate, and dissolving the fusion in water or hydrochloric acid. The solution in water is yellow, and the hydrochloric-acid solution is red.

1. *Sodium hydrate* precipitates yellow rhodium hydrate $Rh(OH)_3 \cdot H_2O$, which is changed to dark brown or black $Rh(OH)_3$ by boiling.

2. *Hydrogen sulphide*, when led through a hot rhodium solution for some time, precipitates brown rhodium sulphohydrate $Rh_2(SH)_4$, which is insoluble in alkali sulphides and in single acids, but is dissolved by aqua regia. When this precipitate is boiled with considerable water, it is decomposed into hydrogen sulphide H_2S and rhodium sulphide Rh_2S_3 .

3. *Zinc*, added to an acid solution, precipitates black metallic rhodium.

38. Ruthenium.—Ruthenium, like the other rare metals of this group, is chiefly found associated with platinum. In the compact form it is a grayish-white brittle metal that is exceedingly difficult to fuse. When precipitated, it is a grayish-black powder. It is scarcely acted upon by aqua regia, and is unaffected when fused with acid potassium sulphate. A solution of ruthenium is best obtained by fusing for some time with a large excess of potassium nitrate. After cooling, the fused mass dissolves in water to an orange-colored solution of potassium ruthenate K_2RuO_4 . A few drops of nitric acid precipitate dark-brown ruthenium trioxide Ru_2O_3 , which is dissolved in hot concentrate hydrochloric acid. This solution is used for the following reactions:

1. *Hydrogen sulphide*, when led through this solution for some time, produces a light-colored precipitate of unknown composition. Upon continued treatment, the precipitate becomes darker, and when nearly black, if the precipitate is filtered off, a deep sky-blue filtrate is obtained.

2. *Ammonium sulphide* precipitates brownish-black ruthenium trisulphide Ru_2S_3 , which is almost insoluble in an excess of the reagent.

3. *Potassium iodide*, added to a cold solution, slowly precipitates black ruthenic iodide RuI_4 . If added to a hot solution, the black precipitate is formed at once.

4. *Zinc*, added to the acid solution of the chloride, at first imparts a blue color to the solution, owing to the reduction to ruthenious chloride, and finally precipitates black metallic ruthenium.

DIVISION B.

*Gold Au**Platinum Pt**Iridium Ir**Molybdenum Mo**Selenium Se**Tellurium Te*

39. Gold.—Gold is usually found in the metallic state. In this condition it is recognized by its yellow color, malleability, and insolubility. It is insoluble in any single acid, but is readily dissolved by aqua regia, forming $AuCl_3$. It acts both as a monovalent and as a trivalent element, but in most of its compounds it is trivalent.

1. *Hydrogen sulphide* precipitates brownish-black gold sulphide Au_2S_3 from a cold solution of the trichloride. The precipitate dissolves slowly in colorless ammonium sulphide, but more readily in yellow ammonium sulphide, and the solution is promoted by heating. It is not dissolved by any single acid, but dissolves readily in aqua regia.

2. *Ammonium sulphide* precipitates brownish-black gold sulphide Au_2S_3 , which dissolves in an excess of the reagent, especially when heated. It dissolves more readily in yellow ammonium sulphide, and is still more easily dissolved by yellow sodium sulphide.

3. *Ferrous sulphate* reduces the gold chloride, and precipitates metallic gold, in a very finely divided reddish-brown powder. When held up and looked at towards the light, the liquid in which the gold is suspended appears bluish by the transmitted light.

4. *Stannous chloride*, which contains some stannic chloride, produces a purple precipitate, known as "purple of Cassius." This precipitate is decomposed, with the separation of metallic gold, by hydrochloric acid. The mixture of stannous and stannic chlorides is obtained by adding a few drops of chlorine water to stannous chloride.

5. *Sulphurous acid* reduces the chloride, and finely divided

metallic gold separates, and is suspended in the solution. Upon boiling, this settles to the bottom of the tube as a black powder.

6. *Oxalic acid*, when heated with a solution of gold chloride that does not contain too much free acid, reduces the gold to the metallic state, and gives off carbon dioxide, sometimes with effervescence. After decanting the liquid, the gold may be fused into a metallic globule. This is best done in a porcelain crucible. The reaction with oxalic acid affords the best means of separating gold from other metals, especially platinum.

40. Platinum.—Platinum in the compact form is a rather hard, very malleable and ductile, steel-gray metal that fuses only at very high temperatures, and is insoluble in any single acid, but dissolves in aqua regia. Platinum sponge is dull gray, and precipitated platinum is a black powder, known as *platinum black*. When platinum is dissolved in aqua regia, if an excess of hydrochloric acid is present, platinum chloride $PtCl_4$ is formed. After driving off the excess of acid by gentle heat, and diluting with water, a solution is obtained that is suitable for the following reactions:

1. *Hydrogen sulphide*, when led into a cold platinum solution, at first colors the solution brown, and then slowly precipitates brownish-black platinum sulphide PtS_2 . If the solution is heated, the precipitate forms at once. Ammonium and sodium sulphides, especially when heated, dissolve this precipitate, but the solution is slow, and it is difficult to dissolve it completely. Hot concentrate nitric acid slowly dissolves the precipitate that is formed in the cold, but scarcely acts on the sulphide precipitated from hot solutions. It dissolves in aqua regia.

2. *Ammonium sulphide* precipitates brownish-black platinum sulphide PtS_2 , which is slightly soluble in an excess of the reagent, and more easily dissolved by yellow ammonium or sodium sulphide. Heat aids the solution.

3. *Ferrous sulphate* does not produce a precipitate in

solutions of platinum chloride, except upon long-continued boiling, in which case platinum finally separates.

4. *Stannous chloride* does not precipitate platinum from its solutions, but imparts a dark-red or reddish-brown color to the solution.

5. *Potassium iodide*, when added in excess to an ordinary platinum solution, produces a dark-red coloration. If the solution is very dilute, a rose-red color is obtained.

6. *Oxalic acid* does not precipitate platinum from its solutions. This gives us the best means of separating gold and platinum. If, to a solution of these metals that contains a slight excess of hydrochloric acid, oxalic acid is added and the solution boiled, all the gold will be precipitated and the platinum will remain in the solution. After the gold is filtered off, the platinum may be precipitated as sulphide, or we may add ferrous sulphate to the solution, render it alkaline with sodium hydrate, then add hydrochloric acid, and heat, when the platinum will be precipitated as platinum black.

41. Iridium.—Iridium is found associated with other metals in platinum ores, especially with osmium as an alloy of osmium and iridium known as *osmiridium*. In the compact condition it is a heavy, steel-gray, brittle metal that fuses only at very high temperatures. In compact form, or when reduced from its compounds by hydrogen at a red heat, all acids, even aqua regia, fail to dissolve it—a fact that serves to distinguish it from gold and platinum. When precipitated from a solution, or when alloyed with a large amount of platinum, aqua regia dissolves it, forming the tetrachloride $IrCl_4$. Acid potassium sulphate oxidizes, but does not dissolve it, thus serving to distinguish it from rhodium. When fused with potassium nitrate, it is oxidized, and may be partially dissolved in water. If the fusion is heated with aqua regia, the iridium is completely dissolved, forming a dark-red solution of iridic chloride $IrCl_3$.

1. *Hydrogen sulphide* at first reduces the iridic chloride to iridious chloride Ir_2Cl_6 , and sulphur is thrown out. The

solution assumes an olive-green color. But, upon continued treatment, brown iridious sulphide Ir_2S_3 is precipitated.

2. *Ammonium sulphide* precipitates brown iridious sulphide Ir_2S_3 , which is easily dissolved in an excess of the reagent.

3. *Zinc*, added to a solution of iridic chloride containing free hydrochloric acid, reduces it and deposits metallic iridium as a black powder.

4. *Ferrous sulphate*, *sulphurous acid*, and *oxalic acid* do not precipitate iridium.

42. Molybdenum.—Molybdenum is found in small quantities as molybdenum sulphide and as lead molybdate. All its compounds when heated in the air are changed to molybdic oxide MoO_3 , which is soluble in ammonia. If hydrochloric acid is added to this solution, it precipitates the white oxide, which dissolves in more of the acid. This solution gives the following reactions:

1. *Hydrogen sulphide* at first gives the solution a blue color, and then precipitates dark-brown molybdenum sulphide MoS_3 , while the supernatant liquid becomes green. The precipitation is not complete in the cold, but, by heating the solution and treating for some time with hydrogen-sulphide gas, the molybdenum is all precipitated. The precipitate dissolves in alkali sulphides, and is reprecipitated from this solution by hydrochloric acid.

2. *Zinc*, when added to the hydrochloric-acid solution, soon develops a blue, green, or brown color, depending on the degree of concentration of the solution.

3. *Stannous chloride* imparts a blue, green, or brown color to the solution, depending on the amount of the reagent added, and the concentration of the solution.

4. *Ferrous sulphate*, containing free sulphuric acid, gives the solution a blue color that is permanent.

5. *Sodium phosphate*, added to a molybdate solution containing a little free nitric acid, produces at once, or upon gently heating, a yellow precipitate of phosphomolybdate, which is insoluble in nitric acid, but is soluble in an excess

of the reagent. Ammonia also readily dissolves the precipitate, and from this solution it is reprecipitated by nitric acid.

6. All molybdenum compounds, when heated in the oxidizing blowpipe flame on the charcoal, deposit an incrustation of molybdic oxide, which is yellow when hot, and white or yellowish white when cold.

43. Selenium.—Selenium is classed with the non-metals. It occurs principally as lead selenide $PbSe$. In many respects it resembles sulphur. Selenium and most of its compounds are soluble in nitric acid or aqua regia, but the selenides of lead and silver dissolve with difficulty. All selenium compounds, when fused with a mixture of sodium carbonate and potassium nitrate, form alkaline selenates that are soluble in water, and the solution remains clear when acidified with hydrochloric acid. If the solution is boiled with hydrochloric acid, chlorine is given off, and selenic acid is reduced to selenious acid. This solution gives the following reactions:

1. *Hydrogen sulphide*, conducted into a cold solution, produces a yellow precipitate that is probably a mixture of finely divided selenium and free sulphur. If led into a hot solution, a reddish-yellow precipitate of selenium sulphide Se_2S_3 is obtained. This is soluble in ammonium sulphide.

2. *Stannous chloride* precipitates finely divided selenium, which remains suspended in the liquid for some time, giving the solution a reddish color. It finally settles to the bottom in the form of a reddish-gray powder.

3. *Sulphurous acid* gives the same reaction as stannous chloride.

4. *Barium chloride*, added to a selenious acid or a selenite solution in which the excess of hydrochloric acid has been neutralized, precipitates white barium selenite $BaSeO_3$, which is soluble in nitric and in hydrochloric acid.

5. Selenium is most readily recognized by heating any of its compounds on the charcoal in the reducing blowpipe flame, when a red incrustation is formed, and a putrid odor

similar to that of decaying horseradish is observed. The incrustation is volatilized by the blowpipe flame, and gives off the characteristic putrid odor.

44. Tellurium.—Tellurium has many of the physical properties of the metals, and on this account is sometimes classed with them. But, chemically, it acts as a non-metal, and is generally classed as such. It resembles sulphur and selenium, and belongs to this group of elements. It occurs in small quantities in nature, combined with gold, silver, or lead. It is white and brittle, fuses easily, and may be sublimed in the closed tube. Tellurium is insoluble in hydrochloric acid, but dissolves readily in nitric acid, forming tellurous acid H_2TeO_3 . If this solution is poured into water, the tellurous acid is precipitated. Tellurous acid H_2TeO_3 , and its anhydride TeO_2 , are readily dissolved by hydrochloric acid, and this solution gives the following reactions:

1. *Hydrogen sulphide* precipitates dark-brown tellurous sulphide TeS_2 , which dissolves readily in ammonium sulphide.

2. *Stannous chloride, sulphurous acid, or zinc*, added to a rather strongly acid solution, precipitates the tellurium as a black powder. This action is aided by warming the solution.

3. *Sodium hydrate or carbonate* precipitates white tellurium hydrate, which is soluble in an excess of the reagent.

4. Solid tellurium compounds, when heated on the charcoal before the blowpipe, deposit a white incrustation of tellurous oxide TeO_2 , which has a yellowish color when hot.

5. Tellurium compounds, when fused on the charcoal with sodium carbonate, form soluble sodium telluride, which, when placed on a piece of silver and moistened, gives a black stain, similar to that produced by sulphur compounds.

6. When held in the flame on a loop of platinum wire, tellurium imparts a bluish-green color to the flame.

7. If a little finely pulverized telluride ore is covered with water in a porcelain dish, a little mercury added, and then some sodium amalgam, the water is given a violet color by sodium telluride going into solution.

GROUPS III AND IV.

45. As the distinction between the third and the fourth group is not sharp, it is much better to disregard it entirely and treat the two groups as one. This is rendered more practicable in this case by the fact that it is seldom necessary to make a general separation of the rare elements. In a great majority of cases, it is only necessary to determine the presence of one or a very few of them, which may be done by applying the reactions given for the separate elements. This division includes:

<i>Titanium Ti</i>	<i>Vanadium V</i>	<i>Uranium U</i>
<i>Beryllium Be</i>	<i>Indium In</i>	<i>Gallium Ga</i>
<i>Zirconium Zr</i>	<i>Cerium Ce</i>	<i>Yttrium Y</i>
<i>Didymium Di</i>	<i>Thorium Th</i>	

46. Titanium.--Titanium occurs in quite large quantities in nature, in clay and some iron ores, and in a number of minerals. It is not used in commerce, and, consequently, is not frequently met in the laboratory. It is most frequently met in the form of titanic oxide TiO_2 . Titanic oxide is not dissolved by any acid except hydrofluoric acid, and somewhat in concentrate sulphuric acid. When the solution in hydrofluoric acid is evaporated with sulphuric acid, it is neither decomposed nor volatilized. The best means of obtaining a solution of titanium is to fuse the oxide for some time with acid potassium sulphate. The fused mass will dissolve in moderately warm water, but, if the solution is boiled, metatitanic acid is precipitated. The solution as obtained above may be used for the following reactions.

1. *Ammonium hydrate* precipitates white, flocculent titanic acid H_2TiO_3 , which is insoluble in excess, but is dissolved by hydrochloric or dilute sulphuric acid.
2. *Sodium hydrate* gives the same reaction as ammonia.
3. *Sodium thiosulphate*, when boiled with rather a dilute solution of titanium, precipitates it completely as metatitanic acid.

4. *Ammonium sulphide* precipitates white titanic acid H_2TiO_3 , which is insoluble in excess of the reagent, but is dissolved by hydrochloric or sulphuric acid.

5. *Zinc*, added to an acid solution of titanium, produces a blue or violet coloration, and, after standing for some time, a blue precipitate separates. Upon standing, this precipitate gradually changes to white. If sodium hydrate is added to the blue solution before the precipitate begins to separate, blue titanium hydrate is precipitated, and on standing gradually changes to white titanic acid.

6. *Potassium ferrocyanide* gives a reddish-yellow precipitate.

7. *Potassium ferricyanide* produces a yellow precipitate.

8. Titanic acid dissolves quite readily in the microcosmic bead, when held in the outer flame near the point of the inner flame, forming a clear colorless bead, that becomes opaque when held at the point of the outer flame. If, instead of holding the bead at the point of the outer flame, it is held for some time in the reducing flame, it is colored yellow while hot, red while cooling, and violet when cold.

47. Vanadium.—Vanadium occurs chiefly combined with lead, and in some iron and copper ores. It is known in several stages of oxidation. VO , V_2O_3 , and VO_2 are known, but vanadic oxide V_2O_5 , the anhydride of vanadic acid, is the principal oxide. All the lower oxides are oxidized to vanadic oxide, or vanadic acid, by nitric acid or aqua regia, or when fused with potassium nitrate or heated in the air. Vanadic oxide, or acid, dissolves in a large amount of water to a red liquid, or in sulphuric acid to a red or yellow liquid. Moderately dilute sulphuric acid dissolves all of the oxides. In this acid, vanadous oxide VO dissolves to a blue solution, vanadium trioxide V_2O_3 to a green solution, and the dioxide VO_2 to a blue solution. The reddish or yellow solution of vanadic acid in sulphuric acid gives the following reactions:

1. *Ammonium hydrate* produces a brown precipitate that dissolves in an excess of the reagent to a yellowish-brown solution.

2. *Sodium hydrate* gives the same reaction as ammonia.
3. *Hydrogen sulphide* reduces the vanadic acid to vanadium dioxide, and thus colors the solution blue, while free sulphur separates.
4. *Ammonium sulphide* precipitates brown vanadium sulphide V_2S_5 , which dissolves with some difficulty in an excess of the reagent to a reddish-brown liquid. From this solution sulphuric acid reprecipitates the brown vanadium sulphide.
5. *Zinc*, added to the acid solution, which is warmed, reduces the vanadic acid, forming at first a blue solution that changes to green, and finally to violet or blue.
6. *Sulphurous acid* reduces the vanadic acid to vanadium dioxide, which imparts a blue color to the solution.
7. *Potassium ferrocyanide* produces a green, flocculent precipitate that is insoluble in acids.
8. Vanadium compounds dissolve in the borax bead in both the oxidizing and the reducing flame, forming clear beads. When a small quantity is heated in the oxidizing flame, a colorless bead is produced, but if much vanadium is present the bead will have a yellow color. If a bead containing a small quantity of vanadium is heated in the reducing flame, a green bead is obtained, while, if more vanadium is present, the bead will be brown when hot, and turn green upon cooling.

48. Uranium.—Uranium occurs in small quantities in nature, principally in pitchblende. There are two oxides, uranous oxide UO_2 and uranic oxide UO_3 , and two series of salts. The uranous salts are green, and the uranic compounds are yellow. The latter are by far the more common. Most of the uranic salts are soluble in water, and those that are insoluble in water dissolve in hydrochloric or sulphuric acid.

1. *Ammonium hydrate*, added to uranic solutions, produces a yellow precipitate of ammonium uranate $(NH_4)_2U_2O_7$, which is insoluble in an excess of the reagent.
2. *Sodium hydrate* precipitates yellow sodium uranate $Na_2U_2O_7$, which is insoluble in excess of the reagent.

3. In uranous solutions, ammonium and sodium hydrates give reddish-brown precipitates.

4. *Ammonium sulphide* precipitates, from neutral solutions or acid solutions after neutralizing, brown uranic oxy-sulphide, which is insoluble in pure colorless ammonium sulphide, but dissolves in yellow ammonium sulphide to a brown solution. The precipitate is dissolved by ammonium carbonate, or by acids. Even acetic acid dissolves it. If the precipitate is boiled in the liquid from which it was precipitated, the oxysulphide is decomposed into uranous sulphide US_2 and free sulphur.

5. *Ammonium carbonate* precipitates yellow ammonium-uranium carbonate $(NH_4)_2UO_2(CO_3)_2$, which readily dissolves in an excess of the reagent. From this solution the uranium is completely precipitated by sodium hydrate, especially when boiled.

6. *Potassium ferrocyanide* produces a reddish-brown precipitate that looks much like copper ferrocyanide, but is distinguished from it by being soluble in ammonia, forming a yellow solution.

7. *Zinc*, added to an acid solution, imparts a green color to the liquid, especially when it is heated. This color is due to the reduction of the uranic to a green uranous compound.

8. Uranium compounds, heated in the borax bead in the reducing flame, impart a green color to the bead that is seen best after the bead cools. Heated in the oxidizing flame, the bead is colored yellow when hot, and assumes a fine yellowish-green color when cold.

49. Beryllium.—Beryllium occurs in nature almost entirely as a silicate. It is associated with aluminum in beryl and emerald. In many respects the compounds of beryllium resemble those of aluminum, but it is divalent, and, therefore, cannot form alums. The soluble beryllium compounds have a sweetish, astringent taste, and give an acid reaction with litmus paper. Most of the silicates are decomposed when heated with concentrate sulphuric acid, and all are readily decomposed when fused with four or five

times their weight of mixed carbonates of sodium and potassium. From solutions of beryllium salts the following reactions are obtained:

1. *Ammonium hydrate* precipitates white, flocculent beryllium hydrate $Be(OH)_2$, which is only slightly soluble in an excess of the reagent. The precipitate looks very much like aluminum hydrate.

2. *Sodium hydrate* precipitates white beryllium hydrate $Be(OH)_2$, which dissolves readily in an excess of the reagent, and the solution remains clear upon boiling, but if considerable water is added, and the boiling continued, beryllium hydrate separates. In this respect it differs from aluminum.

3. *Ammonium carbonate* precipitates white beryllium carbonate $BeCO_3$, which dissolves in a considerable excess of the reagent. This is one of the best methods of distinguishing between beryllium and aluminum. If this solution is diluted with water, and boiled for some time, the beryllium is precipitated as a basic carbonate.

4. *Sodium carbonate* precipitates white beryllium carbonate $BeCO_3$, which is slightly soluble in excess.

5. *Ammonium sulphide* precipitates white beryllium hydrate $Be(OH)_2$.

6. *Oxalic acid* and oxalates do not precipitate beryllium from its solutions, which fact distinguishes it from a number of the other rare metals.

7. Beryllium is separated from aluminum by fusing the mixture with twice its weight of hydrogen-potassium fluoride, and treating the fusion with hydrofluoric acid and water. The beryllium dissolves in this, while the aluminum remains as insoluble potassium-aluminum fluoride.

8. Beryllium compounds, when heated on the charcoal before the blowpipe, yield a mass that is somewhat luminous. When this is moistened with cobalt nitrate, and reignited, it assumes a gray color. In this it differs from aluminum, whose compounds, when similarly treated, are colored blue.

50. Indium.—Indium is found in small quantities, associated with tungsten, and in the blende obtained in certain

localities. It is soft, ductile, fuses easily, and resembles platinum in color. In the air, or in contact with water, it oxidizes, but not quite so rapidly as zinc. The metal dissolves slowly in cold dilute hydrochloric or sulphuric acid, but much more readily if heat is applied. It dissolves readily in cold dilute nitric acid. It is trivalent in all its compounds, and its salts are nearly all colorless. They dissolve in water or acids, forming colorless solutions.

1. *Ammonium hydrate* precipitates white indium hydrate $In(OH)_3$, which is insoluble in excess of the reagent.

2. *Sodium hydrate* precipitates white indium hydrate $In(OH)_3$, which dissolves in an excess of the reagent. From this solution the indium hydrate slowly separates when it is boiled, or when ammonium chloride is added.

3. *Ammonium carbonate* precipitates white indium carbonate $In_2(CO_3)_3$, which is soluble in excess of the reagent, and is reprecipitated from this solution by boiling.

4. *Sodium carbonate* gives the same precipitate as ammonium carbonate, but it is insoluble in excess of the sodium carbonate.

5. *Hydrogen sulphide* precipitates, from neutral solutions or those containing only acetic acid, yellow indium sulphide In_2S_3 . The presence of free inorganic acids prevents the precipitation.

6. *Ammonium sulphide* produces a white precipitate of unknown composition. If the yellow indium sulphide is boiled with yellow ammonium sulphide, it becomes white, and partly dissolves. Upon cooling, a white precipitate separates from this solution.

7. *Zinc*, added to an acid solution, precipitates the metal in white shining scales.

8. Indium, when heated on the charcoal, fuses to a bright metallic globule, and deposits an incrustation that is dark yellow when hot, and light yellow when cold, and is only volatilized with difficulty.

9. Indium compounds, held in the colorless flame on a loop of platinum wire, impart a violet-blue color to the flame. Viewed through the spectroscope, this flame gives

two characteristic blue lines. These are the brightest when the chloride is used, but in this case they only last a short time. The lines given by the sulphide are less bright, but are much more persistent.

51. Gallium.—Gallium occurs in very small quantities in some zinc ores. It is a white, hard, slightly malleable metal that dissolves slowly in hot nitric acid, and readily in hydrochloric acid. Its salts are colorless, and the nitrate, chloride, and sulphate readily dissolve in water to colorless solutions.

1. *Ammonium hydrate* precipitates white gallium hydrate $Ga(OH)_3$, which is soluble in excess of the precipitant.

2. *Sodium hydrate* gives the same reaction as ammonium hydrate.

3. *Ammonium carbonate* produces a white precipitate that is soluble in excess of the reagent.

4. *Hydrogen sulphide* does not give a precipitate in solutions containing free mineral acids, but precipitates white gallium sulphide Ga_2S_3 from acetic-acid solutions.

5. *Ammonium sulphide* precipitates white gallium sulphide, which is insoluble in an excess of the reagent.

6. *Potassium ferrocyanide* produces a light, bluish colored precipitate that dissolves more easily in water than in hydrochloric acid.

7. When gallium compounds are held in the Bunsen flame, they give a spectrum consisting of one rather indistinct violet line; but when a spark passes from the positive terminal of an induction coil to the surface of a gallium solution, under which the negative terminal is dipped, the spectrum produced consists of two distinct violet lines. This is the most distinctive reaction for gallium, and the one that led to its discovery.

52. Zirconium.—Zirconium occurs as a silicate in a few rare minerals. It is tetravalent, and forms a white infusible oxide ZrO_2 , which is luminous when heated. The native minerals are decomposed by fusing, in powdered form, for

some time, with four or five times their weight of sodium carbonate, forming sodium zirconate. The zirconium is dissolved by treating the fused mass with hydrochloric acid, leaving insoluble silicic acid, which may be filtered off. With this solution the following reactions may be obtained:

1. *Ammonium hydrate* precipitates white zirconium hydrate $Zr(OH)_4$, which is insoluble in an excess of the reagent.

2. *Sodium hydrate* gives the same reaction as ammonium hydrate.

3. *Ammonium carbonate* precipitates a white basic carbonate that is soluble in considerable excess of the precipitant. Upon boiling this solution, white, gelatinous zirconium hydrate separates.

4. *Sodium carbonate* gradually precipitates a white basic carbonate that is slightly soluble in an excess of the reagent.

5. *Ammonium sulphide* precipitates white, flocculent zirconium hydrate, which is not dissolved by an excess of the reagent, nor by alkali hydrates.

6. *Oxalic acid* or ammonium oxalate precipitates white, crystalline zirconium oxalate, which is soluble in an excess of the reagent. From this solution, ammonium hydrate reprecipitates the zirconium oxalate.

7. *Sodium thiosulphate*, when boiled with a zirconium solution, precipitates white zirconium thiosulphate, even from dilute solutions.

8. *Hydrogen peroxide* precipitates zirconium in the form of a white, bulky hydrate, probably $Zr(OH)_4$.

9. *Hydrofluoric acid* does not precipitate zirconium from its solutions, which fact serves to distinguish it from yttrium and thorium.

53. Cerium.—Cerium occurs in small quantities in nature, principally as cerous silicate in cerite, and as cerous phosphate in monazite. It exhibits two degrees of valence, forming, with oxygen, cerous oxide Ce_2O_3 , and ceric oxide CeO_2 . The cerous salts are stable, but ceric salts are readily decomposed, forming cerous compounds. The cerous salts

and their solutions are white or colorless, while ceric compounds and solutions are yellow or red.

Most compounds of cerium may be dissolved by treating the finely powdered compound for some time with concentrate hydrochloric acid. All of its compounds may be decomposed by fusing the pulverized compound with about five times its weight of sodium carbonate. Upon treating the fusion with hydrochloric acid, the cerium dissolves to a colorless solution of cerium chloride $CeCl_3$.

1. *Ammonium hydrate* precipitates a white basic compound that is insoluble in an excess of the reagent.

2. *Sodium hydrate* gives a white precipitate, probably $Ce(OH)_3$.

3. *Ammonium carbonate* precipitates white cerous carbonate $Ce_2(CO_3)_3$, which is only slightly soluble in an excess of the reagent.

4. *Oxalic acid*, added to a solution that does not contain too much free acid, precipitates white cerous oxalate, which is insoluble in an excess of the reagent, but dissolves in a large excess of hydrochloric acid.

5. *Sodium thiosulphate* does not precipitate cerous solutions, even when heated with the concentrate solution, but does form a precipitate with ceric-nitrate solutions.

6. Ceric solutions have a yellow color, but are reduced to cerous compounds by sulphurous acid, and the color is thus destroyed.

7. Cerium oxides are dissolved in the borax bead. In the oxidizing flame the bead is colored yellowish red while hot, and gets lighter colored upon cooling, and sometimes becomes colorless. In the reducing flame the bead is colorless.

54. Yttrium.—Yttrium occurs as a silicate in gadolinite and a few other rare minerals. A solution of yttrium may be obtained by fusing the silicate with sodium and potassium carbonates, and dissolving the fusion in hydrochloric acid. Yttrium forms the oxide Y_2O_3 , known as *yttria*. It is slightly soluble in cold nitric, hydrochloric, or sulphuric

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acid, and dissolves completely in these acids when heated for some time. Its salts and solutions are colorless. Yttrium solutions give the following reactions:

1. *Ammonium hydrate* precipitates white yttrium hydrate $Y(OH)_3$, which is insoluble in an excess of the reagent, but dissolves in mineral acids. The precipitate also dissolves slowly in ammonium carbonate, and from this solution it is reprecipitated by boiling.

2. *Sodium hydrate* gives the same reaction as ammonium hydrate.

3. *Ammonium carbonate* produces a white precipitate that is somewhat soluble in an excess of the reagent. From this solution it is reprecipitated by boiling.

4. *Sodium carbonate* gives a white precipitate that is slightly soluble in an excess of the precipitant, but dissolves more readily in ammonium carbonate, and is reprecipitated from this solution by boiling.

5. *Ammonium sulphide* precipitates white yttrium hydrate $Y(OH)_3$, which is insoluble in an excess of the reagent, but dissolves in ammonium carbonate or in strong mineral acids.

6. *Oxalic acid* precipitates white yttrium oxalate $Y_2(C_2O_4)_3$, which is insoluble in excess of the reagent, but is partly dissolved by heating with ammonium oxalate. If this solution is diluted and cooled, the oxalate again separates almost completely. The precipitate also dissolves with some difficulty in hydrochloric acid.

7. *Hydrofluoric acid* produces a white gelatinous precipitate that is insoluble in excess of the reagent, and in water. Before it has been heated it dissolves in mineral acids, but after heating it can only be decomposed by concentrate sulphuric acid.

8. When heated on the charcoal before the blowpipe, yttrium oxide is luminous, and emits a white light without fusing.

55. Didymium.—Didymium is found associated with cerium in cerite. It may be separated from cerium by precipitating both the metals as oxalates from a solution obtained

as described under cerium, and heating the precipitate, after it is dry, until the oxalates are broken up, forming oxides; then, by treating the mixed oxides with nitric acid, the didymium is dissolved to a rose-colored solution, while the cerium remains as an insoluble residue.

1. *Ammonium hydrate* precipitates a white basic salt that is insoluble in excess of the reagent, but is dissolved by hydrochloric acid.

2. *Sodium hydrate* gives the same reaction as ammonium hydrate.

3. *Ammonium carbonate* produces a white precipitate that is insoluble in an excess of the reagent, but is soluble in hydrochloric acid.

4. *Sodium carbonate* gives the same reaction as ammonium carbonate.

5. *Oxalic acid* precipitates white didymium oxalate $Di_2(C_2O_4)_3$, which is slightly soluble in cold hydrochloric acid, and dissolves quite readily when the acid is heated.

6. Didymium oxide, when ignited on the charcoal before the blowpipe, appears pure white; but, if a few drops of concentrate nitric acid are added, and it is again ignited at a rather low temperature, it becomes dark brown, owing to the formation of the peroxide DiO_2 . If this is again intensely ignited, it changes to the white oxide Di_2O_3 .

7. In the oxidizing flame, didymium oxide dissolves in the microcosmic bead, giving it an amethyst color. The color disappears when the bead is held in the reducing flame. It scarcely colors the borax bead, unless large quantities are added.

56. Thorium.—Thorium is a rare metal, and is found in nature, principally as a silicate, in thorite, monazite, etc. The oxide ThO_2 , commonly called *thoria*, is important, as it is the chief constituent used in the mantle of the Welsbach light. The native minerals and the artificial compounds are decomposed by treating with rather concentrate sulphuric acid.

1. *Ammonium hydrate* precipitates white thorium hydrate $Th(OH)_4$, which is insoluble in an excess of the reagent. The precipitate is soluble in all inorganic acids while it is

moist, but after heating it is only decomposed by rather concentrate sulphuric acid.

2. *Sodium hydrate* gives the same reaction as ammonium hydrate.

3. *Ammonium carbonate* precipitates a white basic thorium carbonate, which dissolves readily in an excess of the reagent, in a strong solution, but with difficulty if the solution is dilute. Upon heating this solution, the basic carbonate is reprecipitated.

4. *Sodium carbonate* precipitates a white basic carbonate, which is soluble in an excess of the reagent, especially if the solution is strong.

5. *Oxalic acid* precipitates white thorium oxalate $Th(C_2O_4)_2$, which is insoluble in an excess of the reagent, but dissolves in a boiling concentrate solution of ammonium oxalate, and is not reprecipitated when the solution is diluted and cooled. The precipitate also dissolves slightly in dilute inorganic acids, and readily in ammonium acetate containing free acetic acid.

6. *Hydrofluoric acid* precipitates white thorium fluoride ThF_4 , which is gelatinous at first, but upon standing changes to a powder. It is insoluble in an excess of the reagent and in water.

7. *Ammonium sulphide* precipitates white thorium hydrate $Th(OH)_4$, which is insoluble in an excess of the reagent, but is dissolved by mineral acids, if treated while still moist.

8. *Sodium thiosulphate*, when boiled with a rather strong solution of thorium, precipitates white thorium thiosulphate, mixed with free sulphur, but the precipitation is not complete, and the precipitate may be colored by the sulphur.

9. *Potassium sulphate*, in concentrate solution, when boiled with a solution of thorium, precipitates the thorium completely as white potassium-thorium sulphate, which is insoluble in an excess of the reagent, and dissolves with difficulty in cold water, but easily in hot water.

10. Thoria is white or gray. When heated on the charcoal before the blowpipe, it is incandescent, and emits an exceedingly brilliant white light.

GROUP VII.

*Lithium Li**Cæsium Cs**Rubidium Rb*

57. Lithium.—Lithium occurs quite widely distributed in nature, but in very small quantities. It is found in many mineral waters, in the ashes of some plants, and in several minerals. In some ways it acts like a fifth, and in some ways like a sixth, group metal, but a majority of its chemical relations place it in this group. The hydrate and the carbonate of lithium dissolve with some difficulty in cold water, but more readily in warm water. Hydrates and carbonates, however, do not precipitate lithium from ordinary solutions. Acid sodium tartrate and platinum chloride do not precipitate lithium from its solutions.

1. *Sodium phosphate*, when boiled with a rather strong lithium solution that has been rendered alkaline with sodium hydrate, precipitates white crystalline lithium phosphate Li_3PO_4 , which settles quickly. The precipitate dissolves readily in hydrochloric acid, and when this solution is rendered alkaline by ammonia, no precipitate is formed when cold, but when heated the lithium phosphate again separates. In this, lithium differs from the alkaline earths, and also differs from them in that, when the phosphate is heated on the charcoal before the blowpipe, it fuses and is absorbed into the pores of the charcoal.

2. *Ammonium fluoride*, when added to a rather strong lithium solution, together with an excess of ammonia, gradually precipitates white lithium fluoride LiF . As fluorides of the other alkalies are easily soluble in a mixture of equal parts of ammonium hydrate and water, while it requires 3,500 parts of this mixture to dissolve lithium fluoride, this method may be employed in separating lithium from the other alkalies.

3. All volatile lithium compounds (especially the chloride) impart a bright-red color to the flame, and this is probably the most used of any method in determining lithium. In the presence of large quantities of sodium, the color imparted to the flame by a small amount of lithium is masked by the

yellow sodium flame, and a blue glass must be used to absorb the yellow rays, as in the case of potassium.

4. The best method of detecting small quantities of lithium is by means of the spectroscope. The lithium spectrum consists of a bright-red line and a faint-yellow line.

58. Cæsium and Rubidium.—Cæsium and rubidium are quite widely distributed in nature, but in very minute quantities. They are very closely allied, and resemble potassium, both in compounds and in the color that they impart to the flame.

1. *Platinum chloride* precipitates these metals in the form of double chlorides of the metals and platinum, similar to potassium-platinum chlorides. These precipitates are not nearly so soluble in water as the corresponding double salt of potassium.

2. Cæsium carbonate is soluble in absolute alcohol, while rubidium carbonate is insoluble in that medium, but they cannot be completely separated by this means.

3. Probably the best method of separating these metals is by means of stannic chloride. To do this, add stannic chloride to the hot concentrate solution containing considerable strong hydrochloric acid. The cæsium is precipitated as cæsium-stannic chloride, while the rubidium remains in solution. The precipitate is washed with concentrate hydrochloric acid.

4. Volatile compounds of cæsium and rubidium impart a violet color, similar to that of potassium, to the non-luminous flame; but, when this is viewed through the spectroscope, the spectra of the two metals are very distinct. Cæsium gives two brilliant sky-blue lines and a less distinct red line. Rubidium gives two indigo-blue lines and two bright-red lines. As the flames (and consequently the lines) produced by the chlorides of these metals are more distinct than those produced by the other compounds, the chlorides should always be used.

59. There are a number of rare elements that are not treated here. As many of the rare elements have only

lately been discovered, and their reactions have not been thoroughly studied, it is impossible to treat them in a Paper of this kind at the present. It has lately been discovered that some of the substances here treated as elements are really composed of two or more closely related elements; but, as they have not yet been separated and studied, it is only possible at the present time to treat them as elements. It is altogether probable that the chemistry of the rare elements will be changed very materially within the next few years.

THE SPECTROSCOPE.

ITS USE IN ANALYSIS.

60. In studying the reactions of the metals, the color that is imparted to the flame by the vapors of many of them is made use of in recognizing them; and in several cases in this Paper the spectrum of the metal is spoken of. In every case where a color is imparted to a flame, the reaction becomes much more distinctive if the spectroscope is used. The spectroscope is made in several forms, but the principle is the same in all. We have seen, in Art. **145**, *et seq.*, *Physics*, that, when light passes through a glass prism, it is separated into its primary colors, and each color is refracted, forming a certain angle with the incident ray. Upon this principle, which is explained in Art. **150**, *et seq.*, *Physics*, the spectroscope is constructed. A common form of spectroscope is shown in Fig. 1. It consists of a tube *a*, at the end of which there is a narrow slit through which the light passes to a lens in the tube, which throws it on the flint-glass prism *b* in the form of a narrow band, owing to the narrow slit through which it has passed. This prism refracts the light at a certain angle, depending on its color, and this line of refracted light is viewed through the tube *c*, which contains a lens and acts as a telescope. The spectroscope is usually supplied with a tube *d*, containing a scale that may

be thrown into the spectrum by the light *c* at the end of the tube. By this means, the spectrum, when viewed through the tube *c*, appears in connection with the scale, so that the exact position of the lines may be noted. The lines produced by any metal always appear in exactly the same place

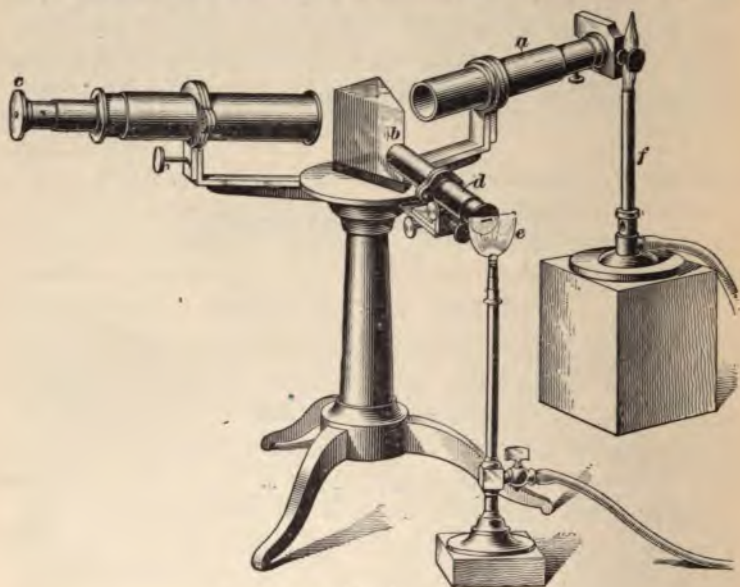


FIG. 1.

when the same instrument is used. The instrument is generally mounted on a brass support, as shown in the figure. The whole of the spectrum cannot be seen at once; hence, the tube *c* is made so that it may be turned, bringing the different parts of the spectrum successively into view. In some instruments the tube *c* is made stationary, and the prism is so arranged that it may be rotated, thus accomplishing the same object. The prism is usually enclosed in a metal covering, through which the ends of the tube *a*, *c*, and *d* pass.

If the Bunsen burner *f* is burning with a non-luminous flame, the spectrum appears blank and is devoid of lines, but if a little sodium compound is brought into the flame it at once assumes a yellow color, and a bright-yellow line is

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seen in the spectrum. This is such an extremely delicate reaction that $\frac{1}{8000000}$ part of a milligram of sodium may be detected with accuracy by this means. It is such a delicate reaction that it is difficult to obtain a flame that will not give this yellow line, owing to the sodium floating in the air in the form of dust. The colors imparted to the flame by most of the metals are not single colors, but combinations of different colors. Thus, the violet flame of potassium contains red and violet rays, and produces a dark-red line near one end of the spectrum and a violet line near the other. The red line is much the stronger of the two, and if only a very little potassium is present, the violet line is very faint or may not be seen at all. In the same way the lithium flame, which appears bright red, contains some yellow rays, and its spectrum consists of a bright-red line and a faint-yellow line. As the tube *c* contains a lens and acts as a telescope, it should always be focused before using, so that the lines of the spectrum appear perfectly clear and distinct. No two metals impart exactly the same color to the flame; hence, the spectrum of each is absolutely distinct, as regards the position of its lines. For this reason, when several metals are brought into the flame at once, either in the solid form or in solution, the spectra in no wise interfere with one another, provided the slit in the tube *a* is made narrow enough for the colors to appear as mere lines rather than as bands; in this way, several metals may be detected at once with absolute certainty. For instance, sodium, potassium, and lithium often occur in very small quantities in mineral waters, and the spectroscope is used in detecting them. For this purpose a little pure hydrochloric acid is added, and the water is evaporated nearly to dryness. A drop of this concentrated solution is held in the flame on the loop of a clean platinum wire, and the flame examined by the spectroscope. If the water contains these three metals alone, the spectra will appear as shown in Plate I. If only these three metals are present in the solution, their spectra will appear as shown in the illustration, and no other lines will be seen; but usually the water contains other metals, and these may be determined

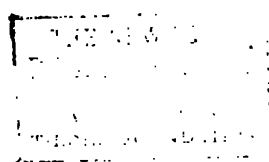
at the same time, by comparing the lines observed with those produced by other metals, as shown in Plate II.

It has been stated that the colors imparted to the flame are due to highly heated vapors; hence, volatile compounds must be used in working with the spectroscope. The chlorides of the metals are generally the most volatile, and nitrates rank next. Carbonates are usually difficult to volatilize, but are easily changed to chlorides by means of hydrochloric acid. Silicates must be decomposed by means of a flux, usually sodium carbonate, and some substances should be held in the reducing flame and then dipped in hydrochloric acid, thus forming chlorides. In the case of very volatile compounds, such as lithium and thallium chlorides, the spectrum, although lasting only a short time, is very brilliant.

61. In Plate II the spectra of the metals that are often determined by means of the spectroscope are given. As the flame is colored by highly heated luminous vapors, metals that do not ordinarily color the flame, if heated to a temperature high enough to volatilize them, impart colors to the flame and consequently produce spectra by which they may be recognized. But in all such cases the wet reactions suffice for the determination of these metals, and it is much easier and simpler to determine them in this way than it is to get the heat necessary to volatilize them. Hence, the use of the spectroscope in analysis is usually restricted to the determination of the alkalies, a few of the rare elements that are easily volatilized, and, in some cases, barium, strontium, and calcium.

ANALYSIS OF WATER.

62. As water is never pure, unless specially prepared, but always contains some substances in solution, the quality of the water depends upon the quantity of these substances contained in it; hence, a quantitative analysis is usually required to determine the fitness of a water for drinking and cooking purposes. But for many purposes all that is required is a qualitative examination, and by this means we



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can learn much of the fitness of a water for drinking purposes by noting whether much or little of the various constituents are present, as indicated by the production of a mere coloration, a slight, or a copious, precipitate, when the reagents are added. In this way, after some practice, quite an accurate opinion can be formed in regard to the amounts of substances present, and the consequent character of the water. In the case of poisonous substances, whose mere presence is sufficient to condemn the water, their qualitative determination alone is required.

63. Treatment of the Sample.—There are several methods of proceeding with the analysis of water, and all methods are modified to suit the particular case. In choosing his mode of procedure, the chemist should be governed largely by circumstances. If something is known of the source and character of the water, the method of analysis should be made to suit the particular case. A method that is very commonly employed is as follows: If the water is clear, about 1 liter is taken for the analysis, and is evaporated in a large, perfectly clean porcelain dish, adding in successive portions, if necessary, until all is in the dish, and then evaporating until the bulk is reduced to about 250 cubic centimeters. During this evaporation, as a rule, a precipitate will be formed, consisting of the metals that were held in solution by free carbonic acid, or in the form of bicarbonates. Allow the dish and contents to cool, and filter through a perfectly pure filter, bringing as much of the precipitate as possible on to the paper. Add a small amount of pure, recently distilled water to the dish, and, after washing out the dish with it, pour it on to the filter, thus washing the part of the precipitate that has been brought on to the paper. Repeat this two or three times, and then proceed to examine the precipitate and the filtrate.

64. Examination of the Precipitate.—The precipitate usually contains some of the following constituents: calcium carbonate, magnesium carbonate, ferric hydrate which is precipitated by boiling a solution of ferrous carbonate,

silica, calcium phosphate, ferric phosphate, ferric silicate, and, sometimes, calcium sulphate, if the water contains much of this substance.

Place the porcelain dish, which still contains much of the precipitate, under the funnel, break the point of the filter with a clean glass rod or platinum wire, and wash the precipitate into the dish with a small quantity of hot, dilute hydrochloric acid. At this point, effervescence is usually observed, due to the escape of carbon dioxide, when the carbonates are decomposed by the acid. Heat the dish and contents to complete the solution as far as possible, and proceed as follows:

1. Take a small portion of the solution, which often is not quite clear, in a test tube or on the lid of a porcelain crucible, and add a few drops of potassium sulphocyanide. A red coloration shows the presence of iron.

2. Evaporate the rest of the solution to dryness on a water



FIG. 2.

bath, in a small porcelain dish. A water bath for this purpose may be made by placing the porcelain dish on a beaker, or other suitable vessel, containing water, as shown in Fig. 2, and heating the water to boiling. The steam from the boiling water, coming against the bottom of the dish, evaporates the solution quite rapidly. A piece of folded paper or some other substance should be placed over the edge of the beaker, to make a small space between the beaker and the dish, for the escape of steam, and the water in the beaker must be replenished as it

evaporates. When the solution in the dish is evaporated

to dryness, moisten the residue with hydrochloric acid, heat it gently, add water, and continue the heating until the soluble portion is dissolved. If an insoluble residue remains, it can only be silica, but may be further tested with hydrofluoric acid, if desired.

3. Evaporate a few cubic centimeters of the filtrate nearly to dryness in a test tube, add a few drops of nitric acid, and test for phosphoric acid with ammonium molybdate.

4. To another small portion in a test tube, add a few drops of hydrochloric acid, boil, and then add a little barium-chloride solution. A white insoluble precipitate shows the presence of sulphuric acid.

5. Heat the remainder of the solution to boiling, and add ammonia in sufficient quantity to render the solution alkaline, but avoid a large excess. If a precipitate is formed, filter, and examine the precipitate for iron and aluminum by methods previously described. Heat the clear filtrate to boiling, add from 3 to 5 cubic centimeters of ammonium oxalate, and a like amount of ammonium hydrate; boil for a few seconds, and stand aside for 4 or 6 hours. A white precipitate shows the presence of calcium, which was present in the water in the form of bicarbonate, or also of sulphate, if the portion just tested contained sulphuric acid.

6. Filter off the calcium oxalate, and evaporate the filtrate to a small bulk, if necessary, after making sure that all the calcium was precipitated. To the concentrated filtrate, add about 5 cubic centimeters of a solution of sodium-ammonium phosphate (microcosmic salt), and then about half its volume of ammonia; stir well, and stand in a cool place for 10 or 12 hours. A white precipitate shows the presence of magnesium, which was in the water in the form of carbonate or bicarbonate. The precipitate sometimes adheres to the sides of the beaker in the form of colorless crystals that cannot be seen until the liquid is poured out.

65. Examination of the Filtrate.—1. To about 10 cubic centimeters of the filtrate, add 1 or 2 cubic centimeters of nitric acid, and, after mixing thoroughly, add silver

nitrate, when chlorine, if present, will be precipitated as white silver chloride. This is sufficient proof of chlorine, but, if any considerable precipitate is formed, it may be confirmed by dissolving in ammonia, and reprecipitating with nitric acid.

2. To another portion of about 10 cubic centimeters, add 1 cubic centimeter of nitric acid, evaporate the whole to about one-half cubic centimeter, and test for phosphoric acid with ammonium molybdate.

3. Evaporate about 30 cubic centimeters of the filtrate to a small bulk, and test its reaction with litmus paper. If the reaction is alkaline, and a drop or two of it, placed on a watch glass, effervesces when brought in contact with a drop of acid, and, if calcium carbonate is precipitated when calcium chloride is cautiously added to a portion of the alkaline solution, the water contains a carbonate of an alkali metal. Evaporate the rest of this test to dryness on the water bath, boil the residue with alcohol, filter, evaporate the filtrate to dryness, dissolve the residue in a very little water, and test this solution for nitric acid with diphenylamine or aniline sulphate.

A diphenylamine solution is made by treating about 2 milligrams of the crystals with 5 cubic centimeters of concentrate sulphuric acid, adding an equal volume of water, and mixing the solution thus formed with about 5 cubic centimeters of concentrate sulphuric acid. To test for nitric acid, place about half a cubic centimeter of this solution on a watch glass, and add a drop or two of the liquid to be tested. If nitric acid is present, a blue line will be formed where the liquids meet.

The aniline-sulphate solution is made by adding about half a dozen drops of aniline to 15 cubic centimeters of dilute sulphuric acid, and then adding this solution drop by drop to about 40 cubic centimeters of concentrate sulphuric acid. If about 1 cubic centimeter of this solution is placed on a watch glass, and a drop or two of a liquid containing nitric acid is added, a red color is produced.

Very often a drop or two of the original water, or of a

somewhat concentrated solution, is added to one of these reagents, to test for nitric acid; but the method described, although rather long, is usually to be recommended on account of its greater accuracy.

4. To the remainder of the original filtrate, add about 5 cubic centimeters of hydrochloric acid, and evaporate at first over the Bunsen flame, and finally to dryness on the water bath. Moisten the residue with hydrochloric acid, warm gently, add water, bring into solution by the aid of heat, and filter off the insoluble silica, which is nearly always present. To a little of this filtrate in a test tube, add a few drops of hydrochloric acid and then barium chloride. A white insoluble precipitate shows the presence of sulphuric acid. Render the rest of the filtrate distinctly alkaline with ammonia, add about 5 cubic centimeters of ammonium oxalate, bring to boiling, add 1 or 2 cubic centimeters of ammonia, and stand in a warm place for about 5 hours for the precipitate to collect and settle. A white precipitate shows the presence of calcium. Filter, and test a portion of the filtrate for magnesium, by ammonia and sodium-ammonium phosphate, as previously described. The rest of the solution is tested for the alkalis. This may be done in several ways. The shortest, and probably the most satisfactory, method of testing is to evaporate the solution nearly to dryness, holding a drop of it in the non-luminous flame, and noting the color imparted by the solution, using the blue glass, or, still better, examining the flame by means of the spectroscope. In case a spectroscope is not accessible, it may be necessary to adopt another method for potassium. Sodium is always recognized by the yellow color it imparts to the flame, but, in the presence of large quantities of sodium, a small amount of potassium may be overlooked, even when the flame is examined through a blue glass; hence, in the presence of much sodium, if no potassium is found by the flame reaction, the following method should be employed:

Evaporate the test to dryness, and heat it carefully over the flame until all ammonium compounds are volatilized. Heat the residue with from 10 to 30 cubic centimeters of

water, depending upon the amount of residue, and to this solution add a few drops of barium chloride. If this produces a precipitate, continue the addition drop by drop as long as a precipitate is formed, apply heat, add a little pure barium or calcium hydrate, bring to boiling, and filter off the precipitate. To the filtrate, add a few drops of ammonia and then pure ammonium carbonate drop by drop as long as a precipitate forms; heat gently, filter off the precipitate, evaporate the filtrate to dryness, and ignite gently until all ammonium compounds are expelled. Dissolve the residue in a few cubic centimeters of water, add 2 or 3 drops of ammonia and a few drops of ammonium carbonate, and heat gently to precipitate small quantities of the alkaline earths that may still be present. Filter off any precipitate that may be formed, evaporate the filtrate to dryness, and carefully ignite till the last traces of ammonium salts are driven off. If the work has been properly done up to this point, the residue can contain only sodium and potassium, and will completely dissolve in 1 or 2 cubic centimeters of water to a clear solution. If this fails, the alkaline earths have not been completely removed, and the treatment with ammonia and ammonium carbonate must be repeated. If the solution in a very small amount of water is clear, add to it a few drops of platinum chloride, and heat gently on the water bath until the mixture is almost syrupy; then add about 20 cubic centimeters of alcohol, and continue the heat over the water bath for a minute or two. If a heavy yellow powder remains undissolved, it shows the presence of potassium.

5. If a spectroscope is available, a very good method of testing for the alkalies is to evaporate from 200 to 500 cubic centimeters of the water, with the addition of a little hydrochloric acid, almost to dryness, and examine this concentrated solution by means of the spectroscope. In this way we avoid the chance of introducing alkalies into the water with the reagents.

66. Examination for Ammonia.—In testing for ammonia, place a fresh sample, consisting of about 300 cubic

centimeters of the original water, in a flask or glass cylinder, add 2 cubic centimeters of a saturated solution of sodium carbonate, and 1 cubic centimeter of a solution of sodium hydrate, made by dissolving 1 part of dry sodium hydrate in 2 parts of water. Stopper the flask, shake well, and allow the precipitate to settle. Pour from 50 to 100 cubic centimeters of the clear liquid through a clean filter into a glass cylinder or large test tube, and add 1 cubic centimeter of Nessler's solution.* A yellow coloration, or, perhaps, a slight reddish-brown turbidity upon the addition of another cubic centimeter of the solution, shows the presence of ammonia. This operation must be carried on in a room free from ammonia vapors, for this is so delicate a reaction that the small amount of ammonia in the air would be sufficient to give the reaction.

67. Separation of Ammonia in Different Conditions.

In many cases the determination of ammonia as just described is all that is required, but in a large number of cases it is a matter of importance to know in what condition the ammonia exists in the water. It occurs in water in two conditions, (1) as ammonia that is merely dissolved in the water and is known as *free ammonia*; and (2) ammonia that is being formed by the decomposition of nitrogenous organic matter, known as *albuminoid ammonia*.

To distinguish between these, place 500 cubic centimeters of the water to be tested in a perfectly clean retort or flask, and connect it with a condenser, as shown in Fig. 25, *Theoretical Chemistry*. Heat the water in the retort or flask to boiling, and receive the distillate in a glass cylinder. When

*To make Nessler's solution, add about 800 cubic centimeters of water to 35 grams of potassium iodide and 13 grams of mercuric chloride; heat to boiling, and continue the heat till solution is complete. Remove the solution from the heat, and when quite cold, add a saturated solution of mercuric chloride, drop by drop, until a precipitate begins to form that does not dissolve when stirred. Now add 160 grams of potassium hydrate, or 120 grams of sodium hydrate, and water enough to make the solution up to 1 liter. When the hydrate is all dissolved, add a few more drops of mercuric chloride, and allow the precipitate to settle. The clear liquid should have a slight yellowish color, and if colorless, a little more mercuric chloride must be added.

about 50 cubic centimeters have passed over, remove the cylinder and add 1 or 2 cubic centimeters of Nessler's solution. A yellow color at this point shows the presence of free ammonia. Continue the distillation until about 200 cubic centimeters of the water have passed over. Then remove the light and add 50 cubic centimeters of a solution of potassium hydrate and potassium permanganate.* Return the burner, and continue the distillation. When 50 cubic centimeters of the water have passed over, add 2 cubic centimeters of Nessler's solution. A yellow color shows the presence of albuminoid ammonia, but the absence of a yellow color does not prove its absence. If albuminoid ammonia is present, some of it nearly always comes over with the first 50 cubic centimeters of the distillate, but we cannot state positively that the water contains no albuminoid ammonia until three portions of the distillate, of 50 cubic centimeters each, have been tested in this manner.

68. Nitrous Acid.—To test for nitrous acid, it is usually sufficient to measure 50 cubic centimeters of the water into a suitable vessel, add 1 cubic centimeter of dilute sulphuric acid, 1 cubic centimeter of potassium-iodide solution, and a little starch solution. The formation of a blue color, either at once or after a few moments, indicates a relatively large amount of nitrous acid, but, if the color does not appear for some time, it indicates that only a small quantity is present, while a failure to obtain a blue color, even after several hours, indicates that the water is free from nitrous acid.

In performing this operation, bright daylight, and especially direct sunlight, should be avoided, or a blue color will probably be produced even if no nitrous acid is present. And it is best to treat 50 cubic centimeters of a water, known to be free from nitrous acid, in the same manner and at the

* To make this solution, dissolve 50 grams of potassium hydrate and 2 grams of potassium permanganate in 250 cubic centimeters of water. Boil until about one-fourth of the liquid is evaporated, in order to drive off any ammonia that may be present, and then add enough water, which is strictly pure and free from ammonia, to make 250 cubic centimeters of solution.

same time that the water to be tested is treated. This method is very simple, and its results are quite reliable, but not absolutely certain, as the water may contain substances that interfere with the reaction. To avoid this source of error, we may place about 300 cubic centimeters of the water to be examined in a retort or flask, add a little acetic acid, and distil it as in the preceding article, in testing for ammonia. Nitrous acid, if present, will come over in the first 50 cubic centimeters of the distillate, and this may be tested with potassium iodide and starch solution as just described, or still better with a solution of sulphanilic acid and naphthylamine in acetic acid. To make this solution, dissolve one-half a gram of sulphanilic acid in 150 cubic centimeters of acetic acid. Then boil one-tenth of a gram of naphthylamine with 20 cubic centimeters of water, and decant the colorless liquid, from the violet-colored residue, into 150 cubic centimeters of acetic acid. Mix these two solutions, and, if the resulting mixture is colored, add zinc dust, and shake till the color is destroyed. Allow the solution to settle, decant the clear liquid, and keep it in a well stoppered bottle.

If a little of this solution is added to the distillate, and the mixture heated to 70° or 80°, it will assume a rose color if nitrous acid is present.

69. Organic Matter.—To test for organic matter in water, it is usually sufficient to evaporate about 200 cubic centimeters of the original sample to dryness on the water bath, and heat the residue over the Bunsen burner, gently at first, and gradually increasing the temperature. If there is any considerable amount of organic matter present, the residue will become brown or black, and a burnt odor is generally observed. If the water contains carbonates, and the residue has not been heated too strongly, carbon dioxide with a burnt odor will generally be given off when the residue is treated with dilute hydrochloric acid.

70. Decaying Matter.—A simple test for decaying organic matter may be made by filling a rather large bottle

to two-thirds its capacity with the water to be tested, covering it with the hand, shaking it well, and noting if any odor is evolved. If hydrogen sulphide is present, it will probably mask any other odor. In this case place a fresh sample of the water in the bottle, add a little copper sulphate, cover with the hand, shake well, and note the odor.

If hydrogen sulphide is found in applying this test, we should seek to confirm it by means of reagents, although it often happens that the odor evolved is a more delicate test than any of the wet reactions. To test water in the wet way for hydrogen sulphide, nearly fill a rather large white bottle with the water to be tested, and add a few drops of a strong solution of lead acetate in sodium hydrate. If this produces a white precipitate, a few drops of a strong solution of copper chloride in water must be substituted. Place the bottle on a sheet of white paper, and look down through it towards the white surface. If a black precipitate or a brown coloration is produced by either of these reagents, it shows the presence of hydrogen sulphide in greater or less amount.

This coloration may be produced either by free hydrogen sulphide dissolved in the water or by the sulphide of an alkali; hence, if the water is alkaline, indicating the probable presence of an alkaline sulphide, the following method of distinguishing between the two should be employed: Close a rather large bottle, half filled with the water, with a cork, to the bottom of which is fastened a piece of filter paper that has been saturated with a solution of lead acetate and then moistened with a drop or two of ammonium carbonate. Allow the bottle thus stoppered to stand for several hours, and shake at frequent intervals, taking care not to allow any of the water to spatter on to the paper. Hydrogen sulphide will give the paper a brown color, but the sulphide of an alkali will not affect it unless it comes in contact with the water.

71. Carbonic Acid and Bicarbonates.—To a rather large sample of the freshly drawn water, add a little lime water, a drop at a time. If the water contains free carbonic

acid, a white precipitate of calcium carbonate will be formed at first, and upon stirring will be dissolved by the free carbonic acid, forming calcium bicarbonate; but, upon the addition of a few more drops of the lime water, a permanent precipitate of calcium carbonate will be formed. If the water does not contain free carbonic acid, but does contain bicarbonates, a permanent precipitate will be formed at once.

72. Poisonous Metals.—The poisonous metals most frequently found in water are lead, copper, and zinc. To examine the water for these, place about 1 liter of the water in a tubulated retort, and add about 10 cubic centimeters of dilute hydrochloric acid; direct the neck of the retort steeply upwards, leave the tubulure open, and evaporate the water to about 100 cubic centimeters. If a precipitate forms during this concentration, it is filtered off. As it may contain lead, add to it a little tartaric acid, then a slight excess of ammonia, boil, filter, and test the filtrate for lead with hydrogen sulphide. Lead hydrogen sulphide through the first filtrate, to precipitate copper and lead, filter, and, if any considerable precipitate is formed, treat it for the separation of these metals, as described in the separation of the metals of Group II. If only a slight precipitate is formed, more of the water must be evaporated and treated in the same way, in order to get enough of the precipitate, so that it can be separated. Boil the filtrate, or the solution if no precipitate was formed, to expel all traces of hydrogen sulphide, and, if sulphur separates during the boiling, filter it off. To the clear liquid, add a few drops of concentrate nitric acid and 3 or 4 cubic centimeters of ammonium chloride, heat to boiling, and add a slight excess of ammonia. If a precipitate forms, filter it off, and if of any considerable size, examine it for iron and chromium, for iron, if present in any considerable quantity, is injurious to the health, and chromium is quite poisonous.

Add just enough acetic acid to the filtrate to render it acid, and lead a current of hydrogen sulphide through it. A white

precipitate shows the presence of zinc. Or the usual method of analysis may be followed, and ammonium sulphide added instead of acetic acid and hydrogen sulphide.

Arsenic sometimes occurs dissolved in water, and when present should never be overlooked. Marsh's test is nearly always used in examining water for arsenic. It may be performed as described in Art. 74, *Inorganic Chemistry*, Part 2. Or, a somewhat simpler form of apparatus may be used, as shown in Fig. 3. To test the water for arsenic,

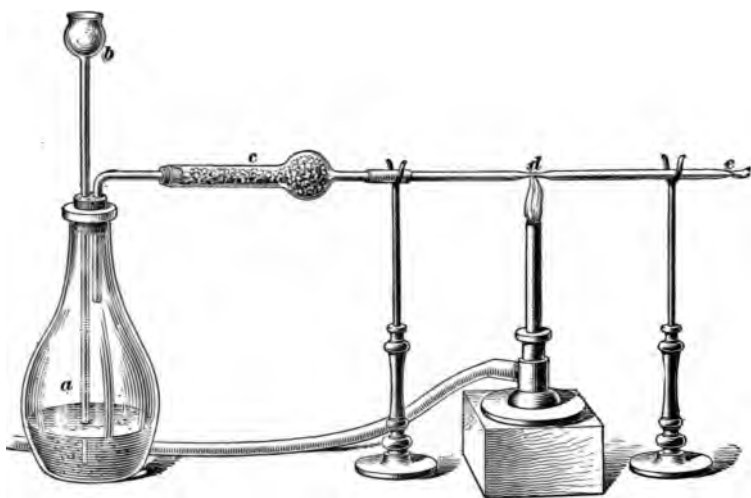


FIG. 3.

pure zinc is placed in the evolution flask *a* and covered with pure water. Connect the apparatus, and pour about half as much concentrate sulphuric acid through the funnel tube *b* as there is water in the flask. The hydrogen evolved passes out through the drying tube *c*, which is filled with granulated calcium chloride, and thence through a hard-glass tube that has been drawn out at a point *d*. After enough hydrogen has been evolved to drive all the air out of the apparatus, so that there is no danger of its containing an explosive mixture of air and hydrogen, bring a Bunsen burner under the tube at *d*, and ignite the hydrogen at *e*. If, after several trials, no

black spot is deposited on a piece of cold porcelain by the flame *e*, and no mirror is deposited on the tube between *d* and *e*, we may assume that our materials are free from arsenic. Now through the funnel tube *b* add a few cubic centimeters of the water that has been concentrated as just described, taking care not to introduce any air with the water, and after a few moments test the flame *e* with a piece of cold porcelain. The tube must be kept at a red heat at *d*, and the flame at *e* must be repeatedly tested for several minutes. If, at the end of fifteen minutes, the flame has not deposited a black spot on the cold porcelain, and no mirror has been formed between *d* and *e*, we can safely assume that the water is free from arsenic, but if either of these phenomena is observed, it shows the presence of arsenic.

If antimony were present in the water, it would give the mirror in the tube and a black stain on the porcelain, but, as antimony is not likely to occur in water, and as its compounds are also poisonous, it is not necessary as a rule to distinguish between antimony and arsenic. If it is desired to learn which is present, this is easily done, for the stain produced by arsenic is brownish black and has a bright luster, while the stain produced by antimony is a dull deep black. The stain produced by arsenic is immediately dissolved by a solution containing a mixture of sodium hypochlorite and sodium chloride, while the stain deposited by antimony is only dissolved very slowly, or not at all, by this solution.

73. The Water is Turbid.—In case the water to be examined is not clear, part of the tests must be made on the water in its original condition and part after it has cleared. Fill a large bottle with the water, stopper it tightly, and stand it aside in a cool, dark place until perfectly clear. Draw off the necessary quantity of the clear water by means of a siphon, and treat it as described in Arts. **63, 64, 65, 69, and 71.** Then, using fresh samples of the water in its original turbid condition, test for ammonia as described in Art. **66**, for nitrous acid according to Art. **68**, for decaying matter according to Art. **70**, and for

poisonous metals according to Art. 72. In the case of turbid waters, the distillation method must be used for nitrous acid.

It is often desirable to know the character of the solid matter in water. In order to learn this, filter off the sediment that remained in the bottle in which the water was set aside to become clear, treat it with hydrochloric acid, filter off the insoluble matter, which nearly always remains, and subject the filtrate to treatment for the group separations. Fuse the insoluble residue with sodium carbonate, dissolve the fusion in hydrochloric acid, and put this solution also through the group separations.

EXAMINATION OF URINE.

74. Urine is the most important vehicle through which waste matter escapes from the body; hence, it always contains salts and organic matter. The constituents of normal urine vary considerably, both in character and quantity, so that, to obtain complete information in regard to the character of a sample of urine, a quantitative examination is required. But certain constituents that are never present in health are found in urine in case of disease; hence, we may learn much from a qualitative examination. The composition of the urine varies at different times in the day; hence, a sample representing the average for twenty-four hours should be taken for analysis. The quantity of urine passed in twenty-four hours varies considerably, but averages from 1,200 to 1,500 cubic centimeters.

75. **Color.**—The first step in the examination of urine is usually to note its color. In health the color may be light yellow, lemon yellow, or amber. As, in health, the quantity of coloring matter passed remains comparatively constant, while the total amount of urine passed varies greatly, it necessarily follows that the less urine passed, the darker will be its color, owing to the strong solution of

coloring matter that is thus obtained. Hence, normal urine may vary considerably in color, but, if very light or very dark colored, disease is indicated. To determine the color of a sample of urine, it is merely necessary to place some of it in a colorless-glass vessel and compare the shade with the colors given in *Vogel's scale of urine tints* in Plate III.

76. Reaction.—Usually the second operation in the examination of urine is to test its reaction with litmus paper. Normal urine should be slightly acid, but shortly after a meal it may be neutral or even slightly alkaline. The total urine passed in twenty-four hours should surely have an acid reaction; if alkaline, it shows that the urine has decomposed before passing, and consequently indicates a deranged condition of the system. Urine containing much albumin is often alkaline; hence, if a sample of urine is alkaline, this is taken as an indication of Bright's disease. To test the reaction of urine, two pieces of litmus paper should be used, one red and the other blue. As the reaction is usually only faintly acid or alkaline, the paper should not be strongly colored, or the urine may not be strong enough to change the color. With paper that is only faintly colored the reaction is much more delicate. The urine should not be allowed to stand longer than necessary before taking its reaction, as it is likely to decompose, especially if it stands in a warm place, and a urine that is originally acid may thus become alkaline.

77. Specific Gravity.—As urine is a solution of solid substances in water, it is always heavier than water. The specific gravity depends on the amount and character of the solid matter passed, and upon the quantity of urine. The amount of solid matter will be the same whether a large or a small amount of urine is passed; hence, if the quantity of urine is small, the solution will be concentrate, and the specific gravity high, while, if the quantity of urine is large, the solution will be dilute, and the specific gravity will consequently be low. In health the specific gravity of urine may vary from 1.005 to 1.025; while in case of disease it

varies from 1.002 to 1.060. Sugar, which is present in the urine in case of diabetes, gives it a high specific gravity. Hence, if the specific gravity is more than about 1.028, the urine should at once be tested for sugar. The test for specific gravity is usually made with a hydrometer, which

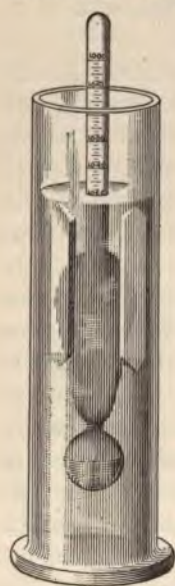


FIG. 4.

is graduated from 1.000 to 1.060, known as a *urinometer*. To make this test, a sample of urine is placed in a cylinder, and the urinometer is lowered into it, as shown in Fig. 4. The urinometer will sink into the urine up to some point on the graduated stem, and the reading on the stem at the surface of the liquid is the specific gravity. The urinometer is just like the hydrometer described in Art. 42, *Physics*, except that it is graduated from 1.000 to 1.060, and many urinometers contain a thermometer in the stem. All of them are made to take the specific gravity of the urine at a certain temperature, generally 15°, and, as the urine is usually warmer

than this, it must be cooled to this temperature before it is tested. This may readily be done by holding the cylinder containing the urine in cold water, or by allowing cold water to run over the outside of the cylinder; but care must be taken not to allow any water to get into the urine, or its specific gravity will be reduced. The urinometer is nearly always used in taking the specific gravity of urine, on account of the ease and rapidity with which it yields a result; but if there should be an error in the graduation of the urinometer, all results obtained with it would be erroneous; hence, when great accuracy is desired, the specific gravity is also taken by means of a bulb, or specific-gravity bottle, as described in Art. 36, *Physics*.

From the specific gravity of urine, the approximate quantity of solid matter that it contains may be calculated. The last two figures of the specific gravity multiplied by $2\frac{1}{3}$ gives the approximate weight, in grams, of solid matter in 1 liter of the urine.

ILLUSTRATION.—The specific gravity of a sample of urine is 1.010. To find how much solid matter it contains, multiply 10 by $2\frac{1}{3}$; thus, $10 \times 2\frac{1}{3} = 23\frac{1}{3}$ grams in 1 liter. If the amount of urine passed in 24 hours is known, the approximate quantity of solid matter passed may readily be found from this result, by a simple calculation.

78. Sugar.—Sugar is found in the urine of patients suffering from diabetes, and urine containing sugar is frequently spoken of as diabetic urine. Sugar occurs in urine in the form of *glucose*, or *grape sugar*. It probably never occurs in normal urine, and certainly never in any considerable amount; hence, if sugar enough to give a distinct reaction is found in urine, it is a certain indication of disease. There are several methods of testing for sugar in urine, but probably Fehling's solution is most commonly employed for this purpose.

1. *Determination by Fehling's Solution.*—Fehling's solution is an alkaline solution of copper. To make it, dissolve 34.652 grams of pure crystallized copper sulphate in sufficient water to make 500 cubic centimeters of solution, and keep in a well stoppered bottle. Then dissolve 173 grams of pure crystallized neutral sodium tartrate in 480 grams of a solution of sodium hydrate, having a specific gravity of 1.14; dilute to 500 cubic centimeters, and keep this solution also in a well stoppered bottle. These solutions are mixed in equal proportions just before using, but must be kept in separate bottles until they are to be used, as decomposition takes place when they are mixed and allowed to stand. To use the Fehling solution, pour 1 cubic centimeter of the solution of sodium tartrate and sodium hydrate into a rather large test tube, add an equal amount of the copper-sulphate solution, dilute this to 10 cubic centimeters, and heat to boiling. If the solution has been prepared according to the directions given, it should remain clear; if a precipitate

forms, the solution is useless, and a new one must be made up. If the chemicals used in preparing the solution are pure, and it is prepared as directed, it will remain clear. After boiling the solution for a few seconds, remove it from the flame, and at once add the urine to be tested, a few drops at a time. When about 1 cubic centimeter of the urine has been added, the mixture should again be heated to boiling, but the boiling must not be continued more than a few seconds. Continue the gradual addition of the urine, keeping the solution as near the boiling point as practicable, until 10 cubic centimeters have been added, and again boil the solution for a few seconds. If the solution remains unchanged after this treatment, it is quite safe to assume that the urine is free from sugar, for sugar when present acts as a reducing agent, destroying the color of the solution, and precipitating red cuprous oxide Cu_2O . If any considerable amount of the red cuprous oxide is precipitated, it is proof of the presence of sugar. In experienced hands this is a very accurate test, but, like other tests for sugar in urine, it only yields reliable results when properly performed. Hence, the beginner should always confirm his results, by repeating the determination or by another test.

2. *Trommer's Test*.—To 8 or 10 cubic centimeters of the urine in a large test tube, add one-third of its bulk of sodium hydrate, made by dissolving 10 grams of solid sodium hydrate in 30 cubic centimeters of water, and then add, a drop at a time, a solution of copper sulphate, made by dissolving 5 grams of the pure crystals in 50 cubic centimeters of water. After the addition of each drop of the copper sulphate, the solution should be shaken, and if the precipitate at first formed dissolves, this is evidence of sugar, but is not conclusive. Continue the addition of copper sulphate until a slight permanent precipitate is formed, and then heat the solution just to the boiling point, and remove it at once from the flame. If sugar is present, a precipitate of yellow cuprous hydrate is formed. This soon changes to red cuprous oxide, which settles to the bottom or sides of the tube.

One of these methods is nearly always used in testing for

sugar in urine, but care must be taken in using them, or erroneous results will be obtained. If the boiling is continued long when the copper solution is added, it may be decolorized, or a slight precipitate may even be formed when the urine does not contain sugar, as other constituents of the urine have the power of reducing copper sulphate, when boiled with it for some time. Albumin, if present, interferes with the reduction of copper; hence, it must be removed, by one of the methods given later, before one of these methods can be employed. To avoid these sources of error, the following exact method is sometimes used:

3. *Brücke's Method*.—To 50 cubic centimeters of the urine in a beaker, add 60 cubic centimeters of a solution of neutral lead acetate, made by dissolving 6 grams of the solid lead acetate in sufficient water to make 60 cubic centimeters of solution. This precipitates most of the substances that would interfere with the reaction, and leaves the sugar in solution. Filter, wash the precipitate on the filter once or twice with cold water, and to the filtrate add ammonia, in slight, but distinct, excess. This precipitates the sugar as lead saccharate $(PbO)_2(C_6H_{12}O_6)_2$. Allow the precipitate to settle, wash twice by decantation with cold water, then filter and wash on the filter with cold water until the washings give no reaction with red litmus paper. Wash the precipitate from the filter into a beaker, using about 75 cubic centimeters of water, and pass a current of hydrogen sulphide through the liquid in which the precipitate is suspended, as long as a black precipitate of lead sulphide is formed. The hydrogen sulphide breaks up the lead saccharate, precipitating the lead as sulphide, and the sugar goes into solution. Filter off the lead sulphide, and wash the precipitate two or three times with cold water. Boil the filtrate until all hydrogen sulphide is expelled, and the volume of the liquid is reduced to about 50 cubic centimeters. If any sulphur separates in the solution during the boiling, filter it off, and stand the clear liquid aside for at least twenty-four hours for any uric acid that it may contain to separate in crystals. A little of the clear liquid, which is now freed from substances that

would interfere with the reaction, is decanted, or filtered off, and tested with Fehling's solution, as previously described.

79. Albumin.—Whether albumin ever occurs in strictly normal urine or not, is a question that has not been settled. But if present in normal urine, it is only in minute quantities, while in case of some diseases, especially Bright's disease, the urine may contain large quantities of it. In testing for albumin, the sample should be perfectly clear, and if the urine is cloudy or contains a sediment, it should be filtered before testing. There are several methods of testing for albumin in urine. Those most frequently used are here given.

1. *Testing by Heat.*—To test for albumin by means of heat, half fill a test tube with perfectly clear urine, and gently heat the upper part of the liquid to a temperature of 75° or 80°, and examine the sample in a good light to see if any difference in transparency between the upper and lower parts of the sample can be observed. If much albumin is present, it is usually precipitated by the heat in the upper part of the tube, while in the lower part, where the sample is still comparatively cool, but little or no precipitation is observed. Now continue heating until it boils, and finally bring the whole sample to boiling. If a precipitate is formed, or the sample becomes turbid, it is due to the presence of albumin or phosphates of the alkaline earths. To distinguish between these, add about half a cubic centimeter of nitric acid, drop by drop, when the precipitate, if it is a phosphate, will dissolve, while albumin is unchanged or may become more distinct.

If the sample of urine tested is strongly alkaline, probably no precipitate will be formed until the nitric acid is added, even though it contains considerable albumin; and, if it is strongly acid, a soluble modification of albumin may be formed that will not be precipitated until the sample is neutralized with sodium hydrate. Hence, we must be governed in our mode of procedure by the reaction of the urine. If the urine is acid to litmus paper, and a sample, when treated

as just described, gives no precipitate, a second quantity, in a test tube, should be neutralized with sodium hydrate, and then treated as directed above.

2. *Heller's Test*.—Heller's test depends upon the coagulation of albumin by nitric acid, when the two liquids are brought in contact without mixing. To make this test, place a few cubic centimeters of strong, colorless nitric acid in a test tube, and add an equal amount of the clear urine to be tested, allowing it to run down the side of the inclined tube, so that it will not mix with the nitric acid. If much albumin is present, a white band will be formed at the point where the two liquids meet, which varies in thickness according to the quantity of albumin present. If a precipitate is not formed at once, the tube and contents should be set aside for several hours.

Some chemists prefer to place the urine in the tube first, and add the acid to it, and this may be done by inclining the tube containing the urine, and pouring the nitric acid carefully down the side of the tube, when the two liquids will form separate layers, and the white ring or band will be formed where they meet. This test is sometimes modified, by getting the two layers as described, and then heating cautiously, taking care not to allow the liquids to mix more than is necessary. As in the case of the test by heat, if the urine is strongly acid, the test by nitric acid may fail to produce a precipitate, even though the urine contains considerable albumin, on account of the formation of so called acid albumin, which is soluble in acids. Consequently, if the urine is acid to litmus paper, and gives no reaction for albumin by Heller's test, as just described, a fresh sample of it should be neutralized with sodium hydrate, and the test repeated on this neutral sample.

When nitric acid stands in contact with urine, it acts on the coloring matter, forming a dark ring that grows darker on standing, and if albumin is present, and coagulated by the nitric acid, it is often colored more or less by these coloring matters, which have been rendered dark by the acid.

3. These tests have been modified in a number of ways

by different chemists. A very good method is as follows: Fill a test tube to about one-third its capacity with the clear urine to be tested, and heat it to the boiling point; remove it from the flame, and, without allowing it to cool, pour about 1 cubic centimeter of colorless nitric acid down the side of the inclined tube, so that it forms a separate layer. If a white band does not form after standing for some time, heat the solution carefully at first, so that the two liquids remain separate, and finally shake them up so that the acid is thoroughly mixed with the urine, and allow the tube to stand for several hours.

As albumin is rather difficult to determine, and in many cases is very important, a single test should never be relied on; but, if two of the tests given are used, and the reaction of the urine taken into account, it is scarcely possible to make a mistake.

The determinations given are the principal qualitative tests applied to urine, but it occasionally happens that qualitative determinations of sulphuric, hydrochloric, and phosphoric acids are required. For these constituents the following tests are recommended:

80. Sulphuric Acid.—Sulphuric acid occurs in normal urine combined with sodium and potassium, forming sulphates of these metals. Normally, about 2 grams of sulphuric acid are passed daily. To determine sulphuric acid, place about 25 cubic centimeters of the urine to be tested in a small beaker, add about 1 cubic centimeter of concentrate hydrochloric acid, and then 8 or 10 cubic centimeters of barium-chloride solution, and stir well. A white precipitate shows the presence of sulphuric acid. Something may be learned of the quantity of sulphuric acid present by this reaction. If the solution becomes milky, it shows that the urine contains about the normal amount of sulphuric acid, while a creamy appearance and consistency shows an increase, and a mere cloudiness a decrease, in the quantity. Hydrochloric acid must always be added before the barium chloride, or barium phosphate may also be formed. If the urine is

not clear, or if a precipitate is formed when the hydrochloric acid is added, it must be filtered and the clear filtrate tested for sulphuric acid.

81. Hydrochloric Acid.—Hydrochloric acid occurs in urine chiefly combined with sodium, in the form of sodium chloride, but also in smaller quantities, combined with potassium and ammonium. In normal urine, the amount passed in 24 hours should contain from 10 to 16 grams of chlorides. To test for hydrochloric acid, place about 25 cubic centimeters of the clear urine in a small beaker, add about half a cubic centimeter of dilute nitric acid to keep the phosphates in solution, and then 2 or 3 drops of silver-nitrate solution. If the urine contains from $\frac{1}{2}$ to 1 per cent. of chlorides, this will form curdy lumps of white silver chloride which do not readily break up, or else give the solution a milky appearance when it is gently agitated. If curdy lumps of precipitate are not formed, but the solution becomes equally milky throughout, it shows that the urine contains less than the normal amount of chlorides, while a failure to get a precipitate shows the absence of chlorides.

A small amount of albumin in the urine does not usually interfere with the determination of the normal quantity of hydrochloric acid, but if much albumin is present, or if the quantity of hydrochloric acid is small, it is necessary to remove the albumin before testing for hydrochloric acid. To do this, heat the sample of urine to boiling, add a few drops of nitric acid, allow the albumin thus precipitated to settle, and filter it off. To the clear filtrate add a little more nitric acid, and then silver nitrate, as just directed. This determination is sometimes important in the case of certain acute diseases. In these cases the disappearance of chlorides from the urine indicates a change for the worse, while their reappearance always denotes improvement. In the case of acute pneumonia, the appearance of chlorides in the urine is frequently the first indication of recovery.

82. Phosphoric Acid.—Phosphoric acid is contained in urine in the form of calcium and magnesium phosphates

(known as earthy phosphates), and alkaline phosphates, principally acid sodium phosphate. There are two common methods of determining the phosphates:

1. Place in a small beaker about 25 cubic centimeters of the urine to be tested, render it slightly, but distinctly, alkaline with ammonia, heat gently until a precipitate begins to form, stir well, and stand aside for an hour or so, for the precipitate to collect and settle, taking care that the solution remains alkaline. If earthy phosphates are present, they will be precipitated from this alkaline solution. If the urine is normal, the precipitate will be white; but if abnormal coloring matters are present, they will be precipitated with the phosphates, and give their color to the precipitate. The precipitate of earthy phosphates is filtered off, and the filtrate is tested for alkaline phosphates. To do this, add from 5 to 8 cubic centimeters of magnesium solution,* stir well, and stand aside for a few moments. Then stir again, and note the appearance of the sample. The phosphoric acid of the alkaline phosphates is precipitated as pure white magnesium-ammonium phosphate; and, if the liquid has a milky appearance, a normal amount of phosphoric acid is present. If the liquid is more creamy in appearance, it shows an excess of phosphoric acid, while a mere cloudiness shows a decreased amount. If no precipitate or only a slight one is formed, the solution should be allowed to stand for several hours and then be again examined.

It frequently happens that the total phosphoric acid is all that is required. In this case, place about 25 cubic centimeters of the urine in a small beaker, render it alkaline with ammonia, heat gently, and slowly add about 8 cubic centimeters of magnesium solution, with constant stirring.

2. We have seen that silver nitrate precipitates phosphoric acid from neutral solutions, and this fact is sometimes made use of in determining phosphoric acid. This is done

* To make magnesium solution for this purpose, dissolve 1 gram of magnesium sulphate in 8 cubic centimeters of water, add 1 gram of ammonium chloride, and, when all is dissolved, add 1 cubic centimeter of concentrate ammonia.

as follows: Place about 25 cubic centimeters of the sample in a beaker, add about 1 cubic centimeter of nitric acid, and precipitate the hydrochloric acid with an excess of silver nitrate. Stir well, and filter off the silver chloride. The filtrate contains the phosphoric acid in acid solution, together with the excess of silver nitrate added to precipitate the hydrochloric acid. To the clear filtrate, add ammonia, drop by drop, with constant stirring, until the neutral point is just reached, when silver phosphate is precipitated. As silver phosphate is soluble in ammonia, a few more drops will dissolve it, and from this solution it may be reprecipitated by adding nitric acid, a drop at a time, until the solution is just neutral. If it is desired to do so, the earthy phosphates may be removed by heat and ammonia. The filtrate is rendered acid, and the alkaline phosphates determined by this method. As this test only yields good results when carefully and properly applied, the first method is recommended, especially for beginners, but it is a good plan to confirm the results thus obtained by the second method.

83. Samples for Practice.—In examining urine for sugar and albumin, only negative results are ordinarily obtained; hence, the student is advised to make up samples containing these substances, in order to become familiar with their reactions. This may be done by dissolving small quantities of these substances in water, and adding these solutions to samples of normal urine. A solution containing sugar may readily be made by dissolving about 1 gram of grape sugar, or glucose (the kind of sugar that occurs in urine), in 50 cubic centimeters of water, and adding this to an equal amount of urine. A solution containing albumin is not quite so easily prepared, but may be made quite readily as follows: Add the white of an egg to about 100 cubic centimeters of cold water, stir it well for some time, and allow the part that does not dissolve to settle. After the undissolved portion has completely subsided, pour the clear liquid, which contains albumin in solution, into an equal volume of urine.

COMMON INORGANIC POISONS.

84. The chemist is often called upon to determine if a substance contains a certain poison, and this section is designed to enable the student to answer such a question, and to give him a certain familiarity with the methods employed in such cases. Obviously, an exhaustive treatment of the subject of poisons would be out of place in a Paper of this character, hence, only the common poisons will be treated. But, if the student makes himself familiar with the determination of the poisons treated in this Paper, he will be able to determine any of the less common ones, by referring to one of the books on this subject. The most common inorganic poisons are arsenic, phosphorus, and hydrocyanic acid, or a cyanide.

ARSENIC.

85. Preliminary Examination.—Arsenic is the most frequently used of the poisons, and generally in the form of arsenious oxide (white arsenic), which is very dangerous, as small doses are fatal, and it is almost tasteless, so that its presence cannot be detected in this way. The sample for analysis may be almost any ordinary substance—a food, vomit, or even a stomach. In case wilful poisoning is suspected, it is desirable to learn, if possible, in what form the arsenic was administered.

1. If food, vomit, or some similar substance is submitted for analysis, mix it well, set aside from one-third to one-half for further examination, or to confirm the results obtained, and mix the rest in a rather large, perfectly clean porcelain dish, with two or three times its volume of water. Stir well with a glass rod, allow the heavy solid matter to settle, and pour the liquid, together with the light suspended matter, into a second porcelain dish. Stir the solid matter with a glass rod, and feel over the bottom of the dish with the rod

for any gritty particles of solid matter. Pour the liquid from the second dish back into the first, stir well, allow it to settle, and again pour the liquid into the second porcelain dish. To the solid matter in the first dish add an equal volume of water, stir well, allow it to stand a moment for any heavy grains of solid matter to settle, pour the rest of the contents of the dish, as completely as possible without disturbing such grains, into the second dish, and examine the bottom of the dish that has just been emptied, for white grains of arsenious oxide, or black grains or scales of metallic arsenic.

If such grains are found, remove a few of them, and dry them between folds of filter paper. If black grains are found, introduce them into a closed tube and heat over the Bunsen burner, when a black mirror on the cool part of the tube shows the presence of metallic arsenic. If white grains are found, introduce them into a closed tube that is drawn out to a point, as shown in Fig. 5, so that they fall to the point *a*, and drop in a splinter of freshly ignited charcoal, which will be held at the point *b*. Now heat the charcoal to redness, and then change the position of the tube so that the white grains are heated at the same time, when, if arsenious oxide is present, a black mirror will be formed at *c*.



FIG. 5.

Whether such grains are found or not, wash the contents of the first dish into the second, and treat as directed in Art. 86.

2. If a stomach is to be analyzed, empty the contents into a porcelain dish, turn the stomach inside out, and search the lining for white or black grains or scales, which are often found adhering to, or embedded in, the membrane, and are frequently indicated by red spots. If such grains are found, examine them for arsenic and arsenious oxide, as just described. Then cut the stomach into small pieces, mix it thoroughly with the contents in the dish, and proceed as directed in examination No. 1.

86. Method for the Determination of Arsenic in Any Form.—The reaction of the mixture in the porcelain dish is next ascertained by means of litmus paper, and, if acid, just enough pure sodium carbonate is added to render it neutral, and the whole is evaporated to a pasty consistence over the water bath. If the sample contained alcohol, the evaporation must be continued until this is completely driven off. A quantity of hydrochloric acid, of about 1.12 Sp. Gr., about equal in weight to the amount of solid substance taken for analysis, is added, together with distilled water, if necessary, in order that the hydrochloric acid shall not exceed one-third of the total liquid present. Add about 2 grams of potassium chlorate, and heat the mixture on the water bath. When the liquid has attained the temperature of the water bath, add more potassium chlorate at intervals of 5 or 10 minutes, in portions of $\frac{1}{2}$ gram to 2 grams, and stir it well. Replace the water that has evaporated from time to time. Continue this treatment until the contents of the dish have become nearly homogeneous and fluid, and have assumed a light-yellow color that is retained when the substance is heated for 20 or 30 minutes longer, without the further addition of potassium chlorate.

When this point is reached, add about 1 gram of potassium chlorate, stir, and immediately remove the dish from the water bath. When the dish and contents have become perfectly cold, filter, and wash the residue well with hot water. The residue may contain metallic mercury, albuminate of mercury, lead sulphate, and possibly lead chloride, basic bismuth chloride, and stannic oxide. It should be marked Ppt. 1, and set aside to be examined for these metals, as described in Art. 87. The filtrate and washings are usually kept separate. Heat the filtrate on the water bath, with the renewal of the water as it evaporates, until the odor given off by the chlorate has disappeared. Evaporate the washings on the water bath to about 100 cubic centimeters, and add this to the filtrate, which has been evaporated so that the total amount of liquid is from three to four times the volume of the hydrochloric acid added. Transfer the liquid to a

flask, heat it to about 70° on the water bath, and while at this temperature, conduct a slow stream of hydrogen sulphide through it for about 12 hours. Then remove the flask from the water bath, and allow the mixture to cool while the gas is still passing through it. When the contents of the flask have become cool, withdraw the delivery tube from the flask, and wash it with ammonia, allowing the washings to run into a beaker. Acidulate the ammoniacal washings with hydrochloric acid, and add this to the contents of the flask. Cover the flask loosely with filter paper, and stand it in a moderately warm place for from 6 to 12 hours. Collect the precipitate on a small filter, and wash thoroughly with water containing a little hydrogen sulphide. Saturate the filtrate and washings with hydrogen sulphide, and evaporate to a small bulk over the water bath. If any precipitate is formed during the evaporation, filter it off, wash well, and add it to the main precipitate. The filtrate should be examined for the metals of the third, fourth, and fifth groups. The precipitate contains the arsenic, together with any other metals of the first and second groups that may be present, and generally some organic matter. Remove the precipitate and filter to a small porcelain dish, and heat it on the water bath until perfectly dry. Add pure fuming nitric acid (which must be free from chlorine), drop by drop, until the precipitate is thoroughly moistened, and again evaporate to dryness on the water bath. Moisten the precipitate with pure concentrate sulphuric acid, heat for about 2 hours on the water bath, and then on the sand bath at a moderate temperature, gradually raising the temperature until white fumes begin to escape. The mass should now be easily broken up, and a small portion of it when stirred with a little water should not impart any considerable color to the fluid. If it gives a brown color to the water, or if the mass should have a brown, oily appearance, add some small pieces of pure dry filter paper, and heat the mass till white fumes again begin to come off, and then allow the dish and contents to become nearly cold. Add a mixture of 1 part of concentrate hydrochloric acid and 8 parts of water, and heat on the water bath

for about 1 hour, stirring occasionally. Filter, wash well with hot water containing a little hydrochloric acid, and finally with boiling water. The undissolved portion on the filter, which may contain lead, mercury, tin, bismuth, and antimony, should be marked Ppt. 2, and set aside for examination according to Art. 87.

The filtrate is removed to a flask, and hydrogen sulphide again conducted through it, exactly as described in the first precipitation, by hydrogen sulphide. The precipitate, which is now free from organic matter, is collected on a small filter and washed. It will contain all the arsenic, and perhaps some other metals as sulphides. If the precipitate is yellow, and a small portion of it, when shaken in a test tube with ammonium carbonate, completely dissolves, arsenic alone is present. In this case, dissolve it in ammonia, evaporate the solution to dryness on the water bath, add a little fuming nitric acid, heat, then add concentrate sulphuric acid, and evaporate on the sand bath until all nitric acid is expelled, and white fumes begin to come off. Allow the residue to cool, add from 5 to 10 cubic centimeters of sulphurous acid, evaporate the excess on the water bath, and examine the resulting solution for arsenic by one of the methods to be given later.

If the precipitate contains other metals than arsenic, remove the filter, together with the precipitate, to a small porcelain dish, pour ammonia over the precipitate, add a few drops of ammonium sulphide, and remove the filter, washing it thoroughly with as little water as possible. Heat the dish and contents on the water bath while stirring the mixture. Filter, wash, and mark the residue Ppt. 3, to be examined according to Art. 87. Evaporate the filtrate to dryness on the water bath, add a little pure fuming nitric acid, and again evaporate until nearly dry. To the residue add a little sodium hydrate, and then sodium-carbonate solution in slight excess. Now add a mixture of 1 part of sodium carbonate and 2 parts of sodium nitrate; evaporate to dryness over the water bath, remove to a Bunsen flame, and gradually increase the heat until the substance fuses. Allow the fusion to cool, add cold water, and stir frequently until the

mass is thoroughly disintegrated, when all the arsenic will be dissolved. If a residue remains undissolved, filter it off, wash, and examine it for antimony and tin. To the filtrate add pure dilute sulphuric acid until the reaction is strongly acid, evaporate nearly to dryness on the water bath, add a little more dilute sulphuric acid, and heat on the sand bath until heavy white fumes begin to come off. Cool the residue, add from 5 to 10 cubic centimeters of sulphurous acid, and heat on the water bath till most of the excess of sulphurous acid is driven off. Add a little water to make a clear solution, and test for arsenic by one of the following methods:

1. *Marsh's Test*.—This test is applied in exactly the same manner as described in Art. 72. The solution prepared as directed above is added in the same way as the water is added, and the black mirror or stain shows the presence of arsenic. Only a little of the arsenic solution should be added at a time, for, if much is added, it may cause violent action, which would interfere with the test, or perhaps cause its loss, through foaming over. In many cases a solution of arsenic may be tested directly by this method, without the long preparation above described, but when absolutely accurate results are desired, and organic matter is present, the above directions should be carefully followed.

2. *Fresenius' and von Babo's Method*.—Add a little water to the solution obtained as described above, transfer it to a small flask, heat to 70° , and precipitate the arsenic by a current of hydrogen sulphide, as previously directed, except that in this case all the arsenic will be precipitated in 6 hours. Filter, wash well, and, if much is present, dry the filter and precipitate, remove the thoroughly dry precipitate to a porcelain boat, and proceed directly with its reduction. If the precipitate is too small to be removed from the filter, dissolve it while wet with a little ammonia; allow the solution to run into a porcelain crucible, add from $\frac{1}{5}$ to $\frac{1}{2}$ gram of dry sodium carbonate, evaporate to dryness on the water bath, and remove the dry residue, or the precipitate as obtained above, to a porcelain boat *c*, Fig. 6, mix it with about twice its weight of pure potassium cyanide and 5 or

6 times its weight of pure dry sodium carbonate, and place the boat and contents in a hard-glass tube, drawn out at one end. Connect the apparatus as shown in Fig. 6, and after the tube is thoroughly filled with carbon dioxide—generated by the action of hydrochloric acid on marble, in the Kipp apparatus *a*, and washed by concentrate sulphuric acid in the

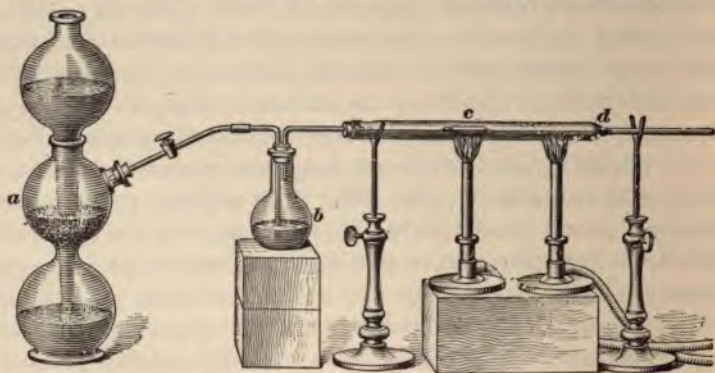


FIG. 6.

flask *b*—gently heat the tube throughout its entire length, to be sure all moisture is driven off. Then regulate the flow of carbon dioxide so that it passes through the flask *b* at the rate of about one bubble per second, gradually heat the tube to redness near the point *d*, where it begins to narrow, then place a second burner under the boat at *c*, gradually increasing the heat until the tube is bright red and the contents of the boat are thoroughly fused, continuing the heat until all the arsenic is driven off. The arsenic will be deposited on the tube just beyond the burner at the point *d*, and in the narrow part of the tube, forming a metallic mirror. If any arsenic is not deposited on the tube, but escapes, it may be detected by its garlic odor. In this determination the carbon dioxide should always be generated in Kipp's, or some similar generator, so that its flow may be properly regulated.

87. Examination of the Residues or Precipitates. Although the main object of this process is the determination of arsenic, the insoluble residues obtained while carrying it

out should be examined for other poisonous metals. This may be done as follows:

1. *Examination of Ppt. 1.*—This residue may contain lead, mercury, bismuth, and tin. When dry, remove it to a porcelain dish, add red fuming nitric acid, and evaporate almost to dryness on the water bath. Add water and a little common nitric acid, and continue the heating for some time; then filter, dilute the filtrate, precipitate with a current of hydrogen sulphide, and examine the precipitate for the metals mentioned above, as directed under the group separations in *Qualitative Analysis*, Part 1. The precipitate may contain a little lead, and should be examined for it.

2. *Examination of Ppt. 2.*—This residue may contain lead, mercury, antimony, and possibly tin and bismuth. Remove it to a small porcelain dish, add an excess of aqua regia, heat for some time on the water bath, and finally boil down to a small bulk on the sand bath or over the flame. Add water and a little hydrochloric acid, bring the solution to boiling, and if an insoluble residue remains, filter it off. Precipitate the metals from the filtrate by a current of hydrogen sulphide, and examine the precipitate as directed under the group separations in *Qualitative Analysis*, Part 1.

3. *Examination of Ppt. 3.*—This residue may contain lead, mercury, and possibly copper. Remove it to a porcelain dish, and heat on the water bath with a mixture of equal parts of concentrate and dilute nitric acid, for half an hour, and then bring to boiling on the sand bath or over the flame. Mercury will not be attacked by this acid, but other metals that may be present will be dissolved. Dilute, filter, and examine the precipitate and filtrate, as directed under the separation of the metals of the second group in *Qualitative Analysis*, Part 1.

PHOSPHORUS.

88. Preliminary Examination for Phosphorus.—Phosphorus has been quite largely used in poisoning mice, etc., and its poisonous properties have become quite

generally known. Consequently, the chemist is occasionally called upon to examine the contents of a stomach, an article of food, or some similar substance, for phosphorus. In such cases the chemist should direct his attention exclusively to the detection of phosphorus in the free state. Merely finding phosphoric acid would not prove anything, for this is a constituent of nearly all animal and vegetable bodies. In examining a substance for phosphorus, there should be no unnecessary delay, for in the air the phosphorus is oxidized to phosphorous acid, and finally to phosphoric acid.

The first step in the examination of a substance for unoxidized phosphorus is to ascertain if its presence is indicated by the odor of the substance, or by phosphorescence when the sample is stirred in a perfectly dark room. These tests furnish strong indications, but cannot be depended on, as the odor and phosphorescence may both be due to other substances. Next, place a little of the sample in a small flask, and, if dry, moisten it with water. In the mouth of the flask, loosely fit a cork to which is fastened a strip of filter paper saturated with a neutral solution of silver nitrate; and heat the flask and contents to about 40°. If the paper is not colored after an hour of this treatment, it is scarcely possible that free phosphorus is present, and it is hardly necessary to proceed further with the examination, but the result may be confirmed by one of the following methods. If the paper is blackened, phosphorus is indicated but not proved, as the blackening may be caused by other substances. Consequently, in this case, the substance must be further examined by one of the following methods.

89. Examination by Means of Distillation With Water.—Mix a rather large portion of the sample with water and a little dilute sulphuric acid in the flask *a*, Fig. 7, and connect it with a Liebig condenser *b c*. Place a screen *e f* of some opaque material between the flask and the condenser to prevent the light of the lamp falling upon the condenser, and distil the contents of the flask, receiving the distillate in a flask *d*. This experiment must be performed

in a dark room. If the substance contains free phosphorus, there will be seen a strong luminous ring that usually moves up and down near the point *b* where the steam enters the cooled part of the tube. Samples that contain only very small quantities of phosphorus usually produce a luminous ring that may be seen continuously for half an hour. If much phosphorus is present, it will collect in small globules in the bottom of the flask *d* and may be further examined. If phosphorus has been introduced into the substance in the form of phosphorus matches, an oxidizing agent will always be present. In this case a little ferrous sulphate should be

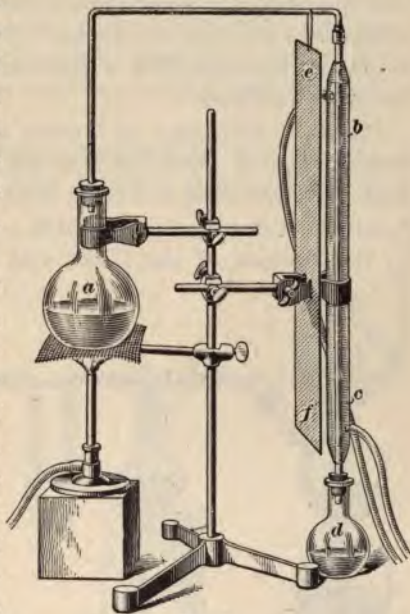


FIG. 7.

added with the sulphuric acid, in order to destroy the oxidizing agent; and if hydrogen sulphide is present, a little ferric chloride should also be added. Ether, alcohol, oil of turpentine, and many other ethereal oils prevent the luminosity so long as they are present. Ether and alcohol are soon distilled over, and the luminosity will then appear, but many of the ethereal oils prevent it permanently, and when they are present the method described in Art. 90 should be employed.

Instead of the apparatus shown in Fig. 7, the ordinary form of distilling apparatus shown in Fig. 25, *Theoretical Chemistry*, may be used; but the form shown in Fig. 7 is better for this purpose.

90. Examination by Driving Off Phosphorus in a Current of Carbon Dioxide.—The method just described

in Art. 89 is easily carried out, and yields conclusive results even with minute quantities of phosphorus, when substances that prevent the reaction are absent. But as a number of substances prevent the formation of a luminous ring, whenever this reaction fails a portion of the sample should be treated as follows:

Place the substance in a flask, add water, and then dilute sulphuric acid until the reaction of the liquid is distinctly acid. Fit the flask *d*, Fig. 8, with a stopper having two perforations, through one of which a glass tube *c* passes nearly to the bottom of the flask; and through this tube pass a

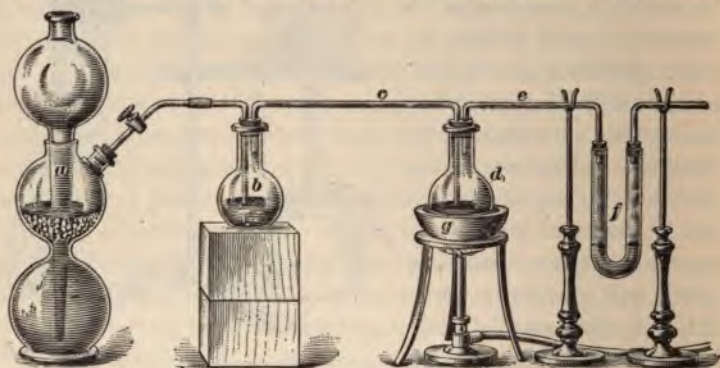


FIG. 8.

slow current of carbon dioxide, which has been generated in the Kipp apparatus *a*, and washed in the flask *b* containing concentrate sulphuric acid. Connect the tube *e*, which passes through the other perforation, and through which the gas passes from the flask *d*, with a U tube *f* containing a neutral solution of silver nitrate, so that the gas passes through this solution. When the flask *d* is thoroughly filled with carbon dioxide, place it on the water bath *g*, and, while heated on the bath, pass a slow current of carbon dioxide through it for several hours. If the substance contains phosphorus, it will be carried over unoxidized, by the carbon dioxide, and form a black precipitate of silver phosphide and metallic silver, when it comes in contact with the silver-nitrate solution. If no precipitate is formed in the U tube

after several hours, free phosphorus is not present, and the operation need not be carried further. If a black precipitate is formed, it is an indication of phosphorus, but is not conclusive, as it may be formed by other substances, and must be further examined. In this case, filter the contents of the tube, wash the precipitate well with water, and proceed as follows:

Place some zinc in the two-necked Woulff bottle *a*, Fig. 9, and add dilute sulphuric acid through the funnel tube *b*,

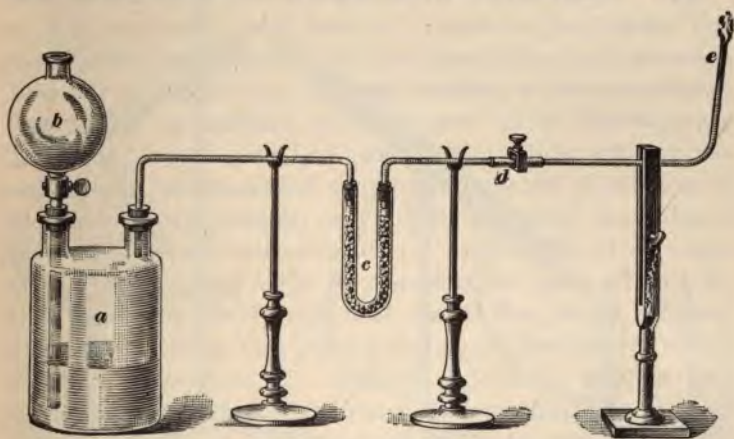


FIG. 9.

which must be large enough to hold more than the total amount of acid added. Lead the hydrogen thus generated through the U tube *c*, which contains pumice stone saturated with a concentrate solution of potassium hydrate, to absorb any hydrogen sulphide that may be present. Connect the tube leading from the U tube with a tube having a platinum tip at *e*, by means of a piece of rubber tubing over which a screw pinch cock *d* is fitted, and by means of this pinch cock regulate the flow of hydrogen so that it will burn at *e* with a steady flame. If this flame is colorless, and does not produce a green coloration when allowed to impinge on a piece of cold porcelain, the gas is free from hydrogen phosphide. Now wash the precipitate, supposed to contain

silver phosphide, into the generator *a*, through the funnel tube *b*. If this precipitate contains phosphorus, hydrogen phosphide will be formed in the generator, and in a few moments the inner cone of the flame will become green, and an emerald-green coloration will be imparted to the cold porcelain.

HYDROCYANIC ACID.

91. Preliminary Examination.—If an article of food, the contents of a stomach, or some other substance is to be examined for hydrocyanic acid or a cyanide—most frequently potassium cyanide—which has the same effect as the acid, there should be as little delay as possible, as hydrocyanic acid is quite readily decomposed and may be lost, and it has been claimed, but not thoroughly demonstrated, that hydrocyanic acid is formed during the decomposition of animal matter. If the sample for examination does not have an odor of its own, the presence of hydrocyanic acid will be revealed by its well known odor; but, if the substance with which it is mixed has a strong odor, that of the hydrocyanic acid may be completely hidden. In any event, the odor alone cannot be depended on, as nitrobenzol and benzaldehyde have odors somewhat similar to that of hydrocyanic acid.

Mix a small portion of the sample with water, filter, and test part of the filtrate with ferric chloride for ferrocyanides and sulphocyanides, and the other part with ferrous sulphate for ferricyanides. Then proceed with the examination according to the information obtained by these tests.

92. Examination for Hydrocyanic Acid When Ferrocyanides, Ferricyanides, and Sulphocyanides Are Absent.—If the preliminary examination has shown that ferrocyanogen, ferricyanogen, and sulphocyanogen compounds are absent, mix the substance with water, add a solution of tartaric acid until the substance has a strong acid reaction, and introduce it into the retort *a*, Fig. 10, through the tubulure *b*. Tightly stopper the tubulure, and lower the retort into a vessel *c* containing a solution of calcium

chloride, so that it does not touch the bottom of the vessel. Slant the neck of the retort upwards, and heat the calcium-chloride bath until the contents of the retort begin to boil. Lead the vapors through a Liebig condenser, the lower end of which is connected with a tube that passes through one of the perforations of a doubly perforated stopper that is closely fitted into the top of the cylinder *d*. Through the other perforation of this stopper pass a tube that leads to the U tube *e*, containing a dilute solution of pure sodium hydrate, to

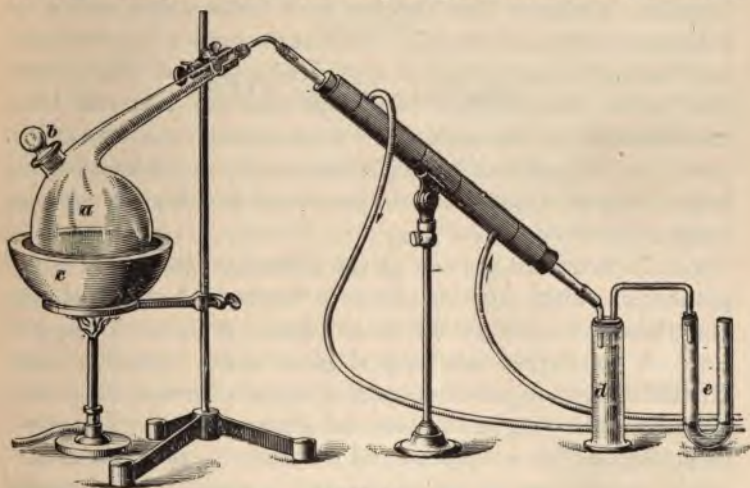


FIG. 10.

absorb any hydrocyanic acid that may pass over. When about 10 cubic centimeters of distillate have collected in the cylinder *d*, replace it with another cylinder, divide the distillate into three parts, and test them as follows:

1. To one-third of the distillate in a test tube, add a little ferrous-sulphate solution, a drop of ferric-chloride solution, and then enough sodium hydrate to give the liquid an alkaline reaction, when, if hydrocyanic acid is present, a greenish-blue precipitate will be formed that consists of a mixture of ferric ferrocyanide and the hydrates of iron. Now add hydrochloric acid, which will dissolve the hydrates of iron, and leave a blue precipitate of ferric ferrocyanide, or, if only

a minute quantity of hydrocyanic acid is present, a greenish solution will be left in the tube, from which a slight blue precipitate will settle upon standing.

2. Place a second portion of the distillate in a porcelain dish, add a drop of sodium-hydrate solution, then sufficient yellow ammonium sulphide to impart a yellowish color to the solution, and slowly evaporate to dryness on the water bath. If the solution contained hydrocyanic acid or a cyanide, the residue in the dish will contain sodium sulphocyanide. Dissolve this residue in a little water, add 4 or 5 drops of hydrochloric acid, allow it to stand a few minutes, and then add a few drops of ferric chloride. A red coloration shows the presence of a sulphocyanide that has been formed from hydrocyanic acid by the above treatment. In case the red color is not permanent, or a violet color is formed, more of the ferric chloride must be added to produce a permanent red color.

3. To the third portion of the filtrate, add a few drops of potassium-nitrite solution, about 3 drops of ferric chloride, and then just enough dilute sulphuric acid to change the color of the ferric salt formed from brown to light yellow. Heat the solution carefully, until it just commences to boil, and, after allowing it to cool, add ammonia in slight excess, to precipitate the excess of iron. Filter off the precipitate, and to the filtrate, which should still contain free ammonia, add a few drops of hydrogen sulphide. If the solution contained hydrocyanic acid, potassium nitroprusside will be formed, and the hydrogen sulphide acting upon this imparts a violet color to the solution.

The second filtrate that collects in the cylinder should be tested in the same manner, and finally the contents of the U tube should be subjected to the same tests.

93. Determination of Hydrocyanic Acid When Ferrocyanides, Ferricyanides, or Sulphocyanides Are Present.—If the preliminary examination has shown the presence of ferrocyanogen, ferricyanogen, or sulphocyanogen compounds, mix the sample with water, add a little tartaric

acid, and then sodium carbonate until the sample is slightly alkaline. Introduce the sample into a retort, and heat over the water bath to about (but not exceeding) 60° , while leading a slow current of washed carbon dioxide through the tubulure, nearly to the bottom of the retort. The carbon dioxide should be generated in a Kipp apparatus, and washed in concentrate sulphuric acid. Collect the distillate in a cylinder to which a U tube containing sodium hydrate is attached, as shown in Fig. 10, and subject the distillate to the tests described in Art. 92.

THE ALKALOIDS.

94. The detection and separation of the alkaloids is much more difficult than the detection and separation of the metals. This is due to several causes. Reagents do not give the same sharp distinction between the alkaloids that is seen in the case of the metals, and, as the alkaloids form a comparatively new field of chemistry, and have not been thoroughly studied, in many cases the reactions are not understood, and only the outward appearance known, so that the conditions that may modify these reactions are not known.

As new alkaloids, of whose reaction nothing is known, are continually being discovered, anything like a complete treatment of this subject is impossible at the present time. Only a few of the most common alkaloids, therefore, will be treated in this course. This will be sufficient for the average student, but if a student wishes to know more of this subject, after making himself familiar with the alkaloids treated in this Paper, he will be in a position to widen his range of knowledge in this field, by reading and investigation.

VOLATILE ALKALOIDS.

95. The volatile alkaloids are liquids at ordinary temperatures. They may be volatilized either in the pure state or when mixed with water, and, consequently, are obtained

in the distillate when their salts are distilled with strong fixed bases and water. When their vapors come in contact with the vapor of a volatile acid, they form a white cloud, similar to that formed by ammonia and hydrochloric acid. The most common volatile alkaloids are *nicotine* and *conine*. They are most easily detected when in the pure state, and, consequently, should be obtained as nearly as possible in that condition before applying tests for them. To do this, add sodium-hydrate solution to the aqueous solution of the alkaloids, and distil them in a current of hydrogen, which has been generated in a Kipp apparatus, and lead into the retort containing the solution. Neutralize the distillate with oxalic acid, and evaporate slowly. Dissolve the oxalate of the alkaloid in alcohol, filter off any residue that may be present, and evaporate the solution. Treat the residue with water, add sodium-hydrate solution, shake this mixture with ether, separate the ethereal solution, and allow the ether to evaporate at about 20°, leaving the pure alkaloid.

96. Nicotine.—Nicotine in the pure state is a colorless, oily liquid, with a disagreeable odor. It is found in the tobacco plant, especially in the leaves and seeds. When allowed to stand in the air, it assumes a yellowish or brownish color. When heated to boiling (247°) in the air, it partially decomposes, but may be distilled in an atmosphere of hydrogen without decomposition. It mixes with water in all proportions, and dissolves easily in alcohol or ether.

Nicotine has a pungent taste, and is very poisonous. It acts as a moderately strong base, precipitating metals as hydrates, and forming salts with acids. Most of these salts are non-volatile, and easily soluble in water or alcohol, but insoluble in ether. They are odorless, but have a strong taste of tobacco.

1. A solution of nicotine in water, or a nicotine salt mixed with sodium hydrate, when shaken with ether, forms a solution of nicotine in ether. If this ethereal solution is removed to a watch glass, and the ether evaporated at a temperature of about 20°, the nicotine will remain on the

watch glass in drops or streaks. If this is now heated, the nicotine will be volatilized, forming white fumes, with a strong, disagreeable odor.

2. *Platinum chloride*, when added to a rather strong solution of nicotine or one of its salts, produces a light-yellow, flocculent precipitate that dissolves upon heating; but, if the heat is continued, an orange-yellow crystalline precipitate soon separates from this solution. If the solution is rather weak and contains free hydrochloric acid, the precipitate may not form for some time, and from a rather strong solution in alcohol, containing a little free hydrochloric acid, a yellow precipitate forms at once.

3. *Gold chloride*, when added to a solution of nicotine or one of its salts, in water, forms a reddish-yellow precipitate that is slightly soluble in hydrochloric acid.

4. *Iodine solution*,* when added in small quantity to a solution of nicotine in water, produces a yellow precipitate that, upon standing, dissolves in the solution. If a little more of the iodine solution is added to this solution, a bright reddish-brown precipitate is formed that also disappears upon standing. If iodine solution is added to a solution of a nicotine salt, the reddish-brown precipitate is formed at once.

5. *Picric acid*, when added in excess to a solution of nicotine in water, or to a neutral solution of a nicotine salt, produces a yellow precipitate that is soluble in hydrochloric acid.

6. *Tannic acid*, added to an aqueous solution of nicotine, produces a white precipitate that is soluble in hydrochloric or sulphuric acid.

7. *Silver nitrate*, when added to a solution of nicotine in water or alcohol, slowly imparts a brown color to the solution, and finally a black precipitate separates.

8. *Concentrate sulphuric acid*, or *nitric acid* of 1.2 Sp. Gr., dissolves nicotine in the cold to a colorless solution, but nitric acid of 1.3 Sp. Gr. forms a red solution.

* To make this solution, dissolve about 20 grams of potassium iodide in water, add 13 grams of iodine, stir, and dilute to 1 liter.

9. When a drop of nicotine is gently warmed with 4 or 5 drops of hydrochloric acid of 1.12 Sp. Gr., it forms a brown solution. If to this a drop of nitric acid of 1.4 Sp. Gr. is added, after the solution has become cool, it gives the solution a reddish-violet color that gradually changes to red.

10. If a few drops of a solution of nicotine in water, or of a neutral solution of nicotine hydrochloride, are added to an excess of mercuric-chloride solution, a white, flocculent precipitate is produced that is soluble in ammonium chloride or hydrochloric acid.

97. Conine.—Conine is a colorless, oily liquid that becomes brown when exposed to the air. It occurs in the spotted hemlock, especially in the green seed. When heated in the air to the boiling point (about 168°), it partly decomposes and becomes brown, but may be distilled unaltered in an atmosphere of hydrogen. It is only slightly soluble in water, but dissolves readily in alcohol or ether, and its solutions have a strong alkaline reaction. Conine is a strong base. It slowly volatilizes at ordinary temperatures, giving off poisonous vapors with a pungent, stupefying odor, which give dense white fumes with the vapor of a volatile acid. It precipitates metals as hydrates in a manner similar to ammonia, and with the acids it forms salts that are soluble in water or alcohol, but are insoluble, or nearly so, in ether.

1. When an aqueous solution of a conine salt is mixed with sodium hydrate, and this mixture is shaken with ether, the conine dissolves in the ether. If this ethereal solution is now evaporated on a watch glass at about 25°, the conine will remain on the watch glass in yellowish, oily drops.

2. *Platinum chloride* does not produce a precipitate in solutions of conine salts, even when concentrate.

3. *Gold chloride*, when added to a rather strong solution of conine hydrochloride, produces a light, yellowish precipitate that is insoluble in hydrochloric acid.

4. *Iodine solution* acts in the same way with a conine solution that it does with nicotine.

5. *Picric acid*, in concentrate solution, when added to

conine that is covered with a little water, produces a yellow precipitate; but, if the solution is at all dilute, no precipitate is formed.

6. *Silver nitrate*, when added to a solution of conine in alcohol, yields a grayish-brown precipitate at once.

7. *Mercuric chloride*, when added in excess to a conine solution, produces a white precipitate that is soluble in hydrochloric acid.

8. *Chlorine water*, when added to conine that is covered with a little water, produces a white precipitate that dissolves easily in hydrochloric acid.

9. *Concentrate sulphuric acid*, or *nitric acid* of 1.4 Sp. Gr., dissolves conine in the cold without coloration.

NON-VOLATILE ALKALOIDS.

Solid alkaloids that cannot be distilled with water.

GROUP I.

Non-volatile alkaloids that are precipitated from solutions of their salts by sodium hydrate, and dissolve in an excess of the reagent.

Morphine

Cocaine

98. Morphine.—Morphine is a white crystalline substance obtained from opium, the dried juice of the seed capsules of the poppy. It is very slightly soluble in cold water, but dissolves somewhat more freely in hot water; it dissolves somewhat more readily in alcohol, but is most readily dissolved by amyl alcohol, especially when hot. Its solutions have a bitter taste and an alkaline reaction. It unites with acids, neutralizing them and forming salts that are easily soluble in water and most of them also in alcohol. Morphine and its salts are poisonous.

1. *Sodium hydrate* or ammonia precipitates morphine from solutions of its salts, in the form of a white crystalline powder. Shaking promotes the formation of this precipitate, which is generally slow in separating. It dissolves very readily in an excess of sodium hydrate, less easily in

ammonia, and with difficulty in ammonium carbonate. If the solution in sodium hydrate is shaken with ether, but very little of the morphine will be taken up; it is all dissolved, however, when shaken with warm amyl alcohol.

2. *Sodium carbonate* precipitates morphine as a white powder that is insoluble in an excess of the reagent. Consequently, if carbon dioxide is led into the solution of morphine in sodium hydrate, it will precipitate the morphine by changing the sodium hydrate to carbonate.

3. *Sodium bicarbonate* precipitates morphine, in the form of a white powder, from neutral solutions of its salts, but does not form a precipitate in acid solutions.

4. *Picric acid*, when added to a concentrate neutral solution of a morphine salt, produces a yellow precipitate that dissolves quite readily in water. Hence, no precipitate is formed in neutral solutions.

5. *Tannic acid*, when added to an aqueous solution of a morphine salt, produces a white precipitate that dissolves readily in acids.

6. *Concentrate nitric acid*, when added to morphine or one of its salts, in the dry state or in concentrate solution, produces a reddish-yellow color that is not changed by the addition of stannous chloride. Nitric acid does not impart a color to dilute solutions in the cold, but if heated, they assume a yellowish color.

7. If morphine is dissolved in pure, concentrate sulphuric acid in the cold, and a small fragment of potassium nitrate is added, a brown coloration is produced at the point of contact. Sometimes the color is reddish at first, but rapidly changes to brown. If the sulphuric-acid solution of the morphine is allowed to stand for 15 hours in the cold, or is heated for half an hour at 100°, before adding the potassium nitrate, and is then cooled and a small piece of potassium nitrate added, it imparts a blood-red color to the solution. Sometimes the potassium nitrate gives the solution a violet color at first, but this rapidly changes to red.

8. If a little morphine is dissolved in concentrate sulphuric acid, a little sodium arsenate added, and the solution

heated, it assumes a reddish-brown color. If this solution is cooled, and water is slowly added, the color changes first to red and then to green. If this green solution is shaken with ether, it gives the ethereal solution a reddish-violet color. If shaken with chloroform, a deep-violet color is produced.

9. If a small quantity of morphine is dissolved in about 1 cubic centimeter of concentrate hydrochloric acid, a drop of concentrate sulphuric acid added, and the solution is placed on a watch glass and evaporated over the water bath, a purple residue remains on the glass. If, to this residue, a few drops of hydrochloric acid are added, and then enough saturated solution of sodium bicarbonate to render it neutral or slightly alkaline, a drop or two of a solution of iodine in alcohol will impart a green color to the solution. Ether, when shaken with this solution, dissolves the coloring matter, forming a layer of solution with a reddish-violet color.

10. A simple test for morphine may be made by mixing a little of the morphine with about six times its weight of white sugar, and adding a few drops of concentrate sulphuric acid to this mixture. The solution thus obtained will have a red color that changes to green, and finally to brownish yellow. If a morphine solution is to be tested, to a small portion add as much white sugar as it will dissolve, and then a few drops of concentrate sulphuric acid. The addition of a drop or two of bromine water is said to increase the delicacy of this reaction.

11. If a small fragment of morphine or a morphine salt is added to a small quantity of a solution, containing about 1 gram of ammonium molybdate in 10 cubic centimeters of concentrate sulphuric acid, in a porcelain dish, and broken up with a stirring rod, it gives the solution a violet color that gradually changes to green, while the edge of the solution appears blue. If this is now stirred, the color changes to a brownish green, and finally to deep blue. If a drop of rather dilute solution of a morphine salt is added to the molybdate solution, a blue ring is formed that gradually extends to the whole of the solution. The solution of ammonium molybdate in sulphuric acid must be freshly prepared, as it rapidly decomposes.

99. Cocaine.—Cocaine is a white crystalline substance obtained from coca leaves. It has a bitter taste, and possesses the property of destroying the sense of feeling. It dissolves slightly in water, more easily in alcohol, and still more readily in ether. Its solutions have an alkaline reaction. It dissolves readily in acids, forming salts, most of which are soluble in water and alcohol, but insoluble, or nearly so, in ether.

1. *Sodium hydrate*, when added to a solution of a cocaine salt, produces a white precipitate that is slightly soluble in an excess of the reagent.

2. *Ammonium hydrate* gives a reaction similar to sodium hydrate, but the precipitate dissolves much more readily in an excess of the ammonia. If a little ether is shaken with the solution in ammonia, it takes up the cocaine, which will be deposited in needles when this ethereal solution is evaporated in the air.

3. *Sodium carbonate*, added to a solution of a cocaine salt, produces a white precipitate that is insoluble in an excess of the reagent.

4. *Tannic acid*, added to a solution of cocaine that contains hydrochloric acid, produces a yellow precipitate that forms a resinous mass when shaken, or upon standing.

5. *Mercuric chloride*, when mixed with a solution of a cocaine salt, produces a white precipitate that is soluble in hydrochloric acid, ammonium chloride, or alcohol.

6. *Stannous chloride*, when added to a concentrate solution of a cocaine salt, produces a curdy, white precipitate that is soluble in nitric acid.

7. *Concentrate sulphuric acid* dissolves cocaine to a colorless solution that is not colored by nitric acid or nitrates. Molybdic acid and white sugar also fail to produce characteristic colors.

8. *Nitric acid* of 1.4 Sp. Gr. dissolves cocaine or its salts to a colorless solution. If this solution is evaporated on the water bath, and a few drops of a solution of potassium hydrate in alcohol are added to the residue, the whole being stirred, a characteristic odor, similar to that of peppermint, is given off.

9. *Potassium chromate*, when added to a rather strong solution of cocaine that contains a very little free hydrochloric acid, precipitates yellow cocaine chromate, which is soluble in an excess of hydrochloric acid, or in a large quantity of water.

10. If a little cocaine is dissolved in about 1 cubic centimeter of concentrate sulphuric acid, a quantity of potassium iodate, amounting to about three times the weight of the cocaine, is added, and the whole is heated on the water bath; it first assumes a yellow color, then green streaks appear that grow darker, and gradually spread to the whole of the liquid, and finally the whole solution becomes brown.

11. If cocaine and concentrate hydrochloric acid are sealed in a strong glass tube, and heated on the water bath for 3 or 4 hours, the cocaine will be decomposed, and methyl alcohol and benzoic acid will be formed. If considerable cocaine was present, white crystals of benzoic acid will separate when the tube is allowed to cool.

12. If a little cocaine solution is added to 2 or 3 cubic centimeters of chlorine water, and to this a few drops of palladium chloride are added, a red precipitate is formed.

100. Separation of Morphine and Cocaine.—Cocaine may be separated from morphine by rendering a solution of their salts just alkaline with ammonia, and shaking with petroleum ether. This extracts the cocaine, but does not dissolve the morphine. The cocaine is obtained by evaporating the petroleum-ether solution.

GROUP II.

Non-volatile alkaloids that are precipitated by sodium hydrate, and are insoluble in an excess of the reagent, and are also precipitated by sodium bicarbonate, even from acid solutions.

Quinine Cinchonine Narcotine

101. Quinine.—Quinine is a white crystalline substance found in cinchona bark. It is slightly soluble in water, but dissolves more readily in alcohol or ether. It is exceedingly

bitter, and its solutions are alkaline. It unites with acids, forming neutral and acid salts. The neutral salts are sparingly soluble in cold water, but more readily soluble in hot water or alcohol, while the acid salts dissolve readily in water.

1. *Sodium hydrate* precipitates quinine from solutions of its salts, in the form of a white powder, which is insoluble in an excess of the reagent.

2. *Ammonium hydrate* produces a white precipitate that is slightly soluble in an excess of the reagent. If the mixture containing the precipitate formed by ammonia is shaken with ether, to which about 2 per cent. of alcohol is added, the precipitate is dissolved and two clear layers of liquid are formed.

3. *Sodium carbonate* precipitates quinine in the form of a white powder that is insoluble, or but slightly soluble, in an excess of the reagent.

4. *Sodium bicarbonate*, when added to a rather strong neutral or acid solution of a quinine salt, produces a white precipitate that is very slightly soluble in an excess of the reagent.

5. *Tannic acid*, when added to an aqueous solution of a quinine salt, produces a white precipitate that is soluble in a little hydrochloric acid, and is reprecipitated by the addition of more hydrochloric acid. The precipitate is also soluble in acetic acid.

6. *Concentrate sulphuric acid* dissolves quinine and its salts to a colorless or faintly-yellowish solution. If this solution is cautiously heated, it becomes yellow, and finally brown.

7. *Nitric acid* of 1.4 Sp. Gr. dissolves quinine and its salts to a colorless solution that generally has a bluish opalescence, and turns yellow when heated.

8. If, to a solution of a quinine salt, about one-sixth its volume of strong chlorine water is added, and then ammonia is added slowly until the reaction of the solution is alkaline, an emerald-green coloration is produced. This test may be varied by adding chlorine water, then potassium ferrocyanide,

and finally ammonia, when the solution will assume a deep-red color that rapidly changes to brown. The addition of acetic acid to the red solution destroys the color, but it may be restored by the careful addition of ammonia. This is a delicate and characteristic reaction, but is prevented by the presence of morphine.

9. If a drop of water is added to a small piece of potassium hydrate and this is fused, and, while still warm, a solution of quinine in alcohol is added, the alcohol evaporated off, and the residue gently heated, a green color is imparted to the mass. Other alkaloids give similar, but not the same, colors.

10. A characteristic test for quinine may be made by dissolving a little of the sulphate in acetic acid, adding a little alcohol, and then a solution of iodine in alcohol until the solution has a brownish-yellow color, when a black precipitate will separate, either at once or after standing a few minutes.

102. Cinchonine.—Cinchonine is a white crystalline substance, found in cinchona bark, together with quinine and other bases. It is almost insoluble in water, and but slightly soluble in alcohol containing water, but somewhat more readily in absolute alcohol, especially when hot. It is most readily dissolved in a mixture consisting of 3 parts of chloroform and 1 part of alcohol. Its solutions have a bitter taste and an alkaline reaction. Cinchonine neutralizes acids completely, forming salts that have a bitter taste, are soluble in water and alcohol, but insoluble, or nearly so, in ether.

1. *Sodium hydrate* precipitates cinchonine from solutions of its salts, in the form of a white powder that is insoluble in an excess of the reagent.

2. *Ammonium hydrate* gives the same reaction as sodium hydrate.

3. *Sodium carbonate*, when added to a solution of a cinchonine salt, produces a white precipitate that is insoluble in an excess of the reagent.

4. *Sodium bicarbonate* precipitates cinchonine, in the

form of a white powder, from moderately strong solutions of its salts.

5. *Tannic acid*, when added to an aqueous solution of a cinchonine salt, produces a white precipitate that dissolves in a little hydrochloric acid, and is reprecipitated if more hydrochloric acid is added. It is also soluble in acetic acid. (Compare Art. 101, 5.)

6. *Concentrate sulphuric acid* dissolves cinchonine to a colorless solution that becomes brown, and finally black, when heated.

7. If cinchonine is dissolved in concentrate sulphuric acid, and a little concentrate nitric acid is added, the solution remains colorless in the cold; but, when heated, it first becomes yellowish, then brown, and finally black.

8. If, to a solution of a cinchonine salt, about one-fifth its volume of strong chlorine water is added, and then ammonia, until the reaction of the liquid is alkaline, a yellowish-white precipitate is formed.

9. If a little potassium hydrate is fused, with the addition of a drop of water, a little solution of cinchonine in alcohol is added, and the residue is carefully heated, after evaporating the alcohol, a reddish-brown or violet color is at first imparted to the mass, which, upon the continued application of heat, changes to bluish green, and vapors with a pungent odor are evolved.

10. *Potassium ferrocyanide*, when added to a neutral solution of a cinchonine salt, or one containing but little free acid; precipitates yellow, flocculent cinchonine ferrocyanide. If an excess of the reagent is added and the mixture is gently heated, the precipitate dissolves, but, upon cooling, it separates again in golden-yellow crystals.

103. Narcotine.—Narcotine is a white crystalline substance obtained from opium. It is almost insoluble in water, and only sparingly soluble in alcohol and ether, but dissolves readily in chloroform. Narcotine is tasteless, but its solutions are exceedingly bitter, and do not color litmus paper. It dissolves readily in acids, forming salts that have an acid

reaction and are bitter. Most of the salts are soluble in water, alcohol, and ether. When solutions of the salts are shaken with chloroform, the narcotine is dissolved in it, even in the presence of a free acid.

1. *Sodium hydrate* precipitates narcotine from solutions of its salts, in the form of a white crystalline powder that is insoluble in an excess of the reagent.

2. *Ammonium hydrate* precipitates narcotine in the form of a white powder that is insoluble in an excess of the reagent. If the liquid containing this precipitate is shaken with considerable ether, the ether dissolves the precipitate, and two clear layers of liquid are formed. If some of the ethereal solution is allowed to evaporate on a watch glass, the narcotine will remain as a white crystalline powder.

3. *Sodium carbonate* precipitates narcotine from its solutions in the form of a white crystalline powder that is insoluble in an excess of the reagent.

4. *Sodium bicarbonate* gives the same reaction as sodium carbonate.

5. *Tannic acid* does not produce a precipitate in neutral solutions of narcotine salts, but sometimes gives the solution a milky appearance. If a drop of hydrochloric acid is added, a precipitate is formed that dissolves when heated, and separates again when the solution is cooled.

6. *Chlorine water* imparts a greenish-yellow color to solutions of narcotine salts. If ammonia is now added, the color is changed to reddish yellow, and becomes stronger.

7. *Concentrate sulphuric acid* dissolves narcotine, forming a solution with a greenish-yellow color that soon changes to pure yellow. If this solution is heated, various colors are produced, depending on the amount of narcotine present. If considerable narcotine is present, the solution at first assumes an orange color, then becomes blue, and sometimes purple streaks form. If the solution is now allowed to cool, it assumes a red color, but if heated nearly to boiling, it becomes reddish violet. If the sulphuric acid contains but very little narcotine, a crimson color is seen instead of blue.

8. If a little narcotine is dissolved in concentrate sulphuric

acid, and heated until it assumes a reddish color, and, after cooling, a drop of ferric chloride is added, at the point where the ferric chloride enters the liquid a red color is formed that shades off to violet; after about 10 minutes, the red color spreads to the rest of the liquid.

9. *Nitric acid* of 1.4 Sp. Gr. dissolves narcotine to a reddish-yellow solution. During the solution, heat is generated and reddish fumes are evolved. If the solution is now heated over the Bunsen flame, more fumes are given off, and the solution becomes clear yellow.

10. A solution containing 10 milligrams of ammonium molybdate in 1 cubic centimeter of concentrate sulphuric acid dissolves narcotine to a green solution that rapidly changes to red.

104. Separation of Quinine, Cinchonine, and Narcotine.—If an acid solution of these alkaloids is shaken with chloroform, the narcotine will be dissolved in the chloroform and form a separate layer of clear liquid, while the quinine and cinchonine remain in the acid solution. If the chloroform solution is removed and evaporated in the air, the narcotine remains as a white powder. Now render the solution, containing quinine and cinchonine, alkaline with ammonia, and shake it with ether that contains about 2 per cent. of alcohol. This will precipitate the cinchonine, and dissolve the quinine, which may be obtained in the same manner as the narcotine. The precipitated cinchonine may then be obtained from the liquid.

GROUP III.

Non-volatile alkaloids that are precipitated by sodium hydrate, and are insoluble in an excess of the reagent, but are not precipitated from acid solutions by sodium bicarbonate.

Strychnine

Brucine

Atropine

105. Strychnine.—Strychnine is an exceedingly poisonous, white crystalline substance found in various varieties of strychnos, but especially in the beans of the strychnos nux

vomica. It has an alkaline reaction, and is very bitter. It is almost insoluble in water, alcohol, or ether, but dissolves in chloroform and acetic ether. It neutralizes acids, forming salts, most of which are soluble in water and alcohol, but are insoluble in ether and chloroform. They all have an extremely bitter taste, and are exceedingly poisonous.

1. *Sodium hydrate* precipitates strychnine from solutions of its salts, in the form of a white crystalline powder that is insoluble in an excess of the reagent. If the solution is very dilute, the precipitate only separates after some time.

2. *Ammonium hydrate* precipitates strychnine in the form of a white powder that is soluble in an excess of the reagent. But if this solution is allowed to stand for some time, it again separates, in the form of white needles.

3. *Sodium carbonate* gives the same reaction as sodium hydrate.

4. *Sodium bicarbonate* slowly precipitates strychnine from neutral solutions, in the form of fine white needles that are insoluble in an excess of the reagent. But, if a drop of acid is added, the precipitate dissolves in the carbonic acid that is liberated, even if the solution remains alkaline. In acid solutions, sodium bicarbonate produces no precipitate.

5. *Tannic acid*, when added to a solution of a strychnine salt, produces a white precipitate that is insoluble in hydrochloric acid.

6. *Chlorine water*, when added to a solution of a strychnine salt, produces a white precipitate that dissolves in ammonia to a colorless solution.

7. *Mercuric chloride*, added to a solution of a strychnine salt, produces a white precipitate that dissolves when heated, and is reprecipitated in white needles upon cooling.

8. *Potassium sulphocyanide*, when added to a strong solution of a strychnine salt, produces a white crystalline precipitate that is only slightly soluble in an excess of the reagent. In dilute solutions this precipitate is only formed after standing for some time.

9. *Cerium dioxide*, when added to a solution of strychnine

in concentrate sulphuric acid, produces a deep-blue color that slowly changes to violet, and finally to red.

10. *Concentrate sulphuric acid* dissolves strychnine to a colorless solution. If, to a little of this solution in a porcelain dish, a little dry potassium chromate is added, it imparts a blue color to the solution that changes to red, and finally to reddish yellow. The same reaction is produced by manganese dioxide, but, in this case, it takes place more slowly. This reaction may be varied in several ways. If a solution, made by dissolving 10 milligrams of potassium chromate in 5 cubic centimeters of water, and adding 15 grams of concentrate sulphuric acid, is placed in a test tube, and a solution of strychnine is added, so that it forms a separate layer, a bluish-violet band will be formed where the two liquids come in contact. The same reaction is obtained if a little solid strychnine or one of its salts is sprinkled on the acid-chromate solution. Morphine, if present, interferes with this reaction. This may be partly overcome by placing a few small particles of the strychnine on a watch glass, covering with a dilute solution of potassium dichromate, and stirring well. By this means the strychnine is slowly converted into strychnine chromate, which is almost insoluble. Pour off the liquid, wash the residue once with water, pour off as much of this as possible, and absorb the rest with a piece of filter paper. By this treatment the strychnine chromate is obtained as a solid in the dish, and most of the morphine is removed, if only a small amount was present. Now, if a little concentrate sulphuric acid is brought into the dish, bluish-violet streaks are formed. The best method of obtaining this reaction when morphine is present is to treat the concentrate aqueous solution of the salts with potassium chromate, when the strychnine will be precipitated as strychnine chromate, and the morphine will remain in solution. Filter the strychnine chromate, wash at once with cold water, and dry it. If the dry precipitate is rubbed off the paper into a porcelain dish, and treated with concentrate sulphuric acid, a bluish-violet color is produced at once.

11. *Nitric acid* of 1.4 Sp. Gr. dissolves strychnine to a

colorless solution that turns yellow when heated. A little potassium chlorate added to the cold colorless solution gives it a purple color.

106. Brucine.—Brucine is a white crystalline substance found associated with strychnine in the *strychnos nux vomica*. It is but slightly soluble in water or ether, but dissolves readily in alcohol. It is very poisonous, and is extremely bitter. It neutralizes acids completely, forming salts that dissolve readily in water. Like the free alkaloid, the salts are poisonous and very bitter.

1. *Sodium hydrate* precipitates brucine from solutions of its salts in the form of a white, granular, or crystalline precipitate that is insoluble in an excess of the reagent.

2. *Ammonium hydrate* produces a white precipitate that at first has an oily appearance, but becomes crystalline upon standing. When first precipitated this is soluble in an excess of the reagent, but if the solution thus obtained is allowed to stand for some time, the precipitate again separates in the form of crystals that do not dissolve in more of the reagent.

3. *Sodium carbonate* produces the same reaction as sodium hydrate.

4. *Sodium bicarbonate* produces a white, silky precipitate of brucine, which is insoluble in an excess of the reagent, but is dissolved by a drop of acid.

5. *Tannic acid* produces a dirty white precipitate that is insoluble in hydrochloric acid, but dissolves in acetic acid.

6. *Chlorine water*, when carefully added to the solution of a brucine salt, imparts a bright-red color to the solution. If ammonia is now added, the color changes to brownish yellow. If a little chlorine water is added to solid brucine, it dissolves to a red liquid that becomes colorless if more chlorine water is added. If this colorless solution is evaporated to dryness on the water bath, it deposits a red residue.

7. *Mercuric chloride*, added to a solution of a brucine salt, produces a white, granular precipitate.

8. *Mercurous nitrate* that contains as little free acid as possible, when added to the solution of a brucine salt, leaves

the solution colorless. But if this is now gently heated on the water bath, it gradually assumes a red color. This reaction serves well to detect brucine in the presence of strychnine, which is not colored by mercurous nitrate.

9. *Potassium sulphocyanide*, when added to a strong solution of a brucine salt, produces a white, granular precipitate. The same precipitate separates from more dilute solutions after standing some time.

10. *Concentrate sulphuric acid*, when added in small amounts to a little brucine, dissolves it, forming a rose-colored solution that soon changes to yellow. If a little sulphuric acid containing nitric acid* is added, the liquid at first assumes a red color that soon changes to yellow.

11. *Concentrate nitric acid* dissolves brucine and its salts to bright-red solutions that soon change to yellowish red, and, when heated, become yellow. If stannous chloride is added to a solution that has been heated until it is yellow, it assumes a deep-violet color, and, if the solution is concentrate, a violet precipitate separates. The violet color will be imparted to solutions that have been quite largely diluted with water. Colorless ammonium sulphide produces the same reaction as stannous chloride, and hydrogen sulphide produces a violet color at first, but, upon continued treatment, the solution finally becomes green.

12. If a little brucine is dissolved in acetic acid, the solution diluted with water, and lead dioxide added, a rose color is imparted to the liquid.

107. Atropine.—Atropine is a white crystalline substance found in the deadly nightshade. It is only slightly soluble in water or ether, but dissolves readily in alcohol and chloroform. It is poisonous, has a bitter taste that is very persistent, and an alkaline reaction. It unites with acids, forming salts that are easily soluble in water or alcohol, but insoluble, or nearly so, in ether.

* This mixture of acids, known as *Erdmann's acid mixture*, is made by mixing 6 drops of strong nitric acid with 100 cubic centimeters of water, and adding 10 drops of this mixture to 20 grams of concentrate sulphuric acid.

1. *Sodium hydrate* precipitates part of the atropine from strong aqueous solutions of its salts, in the form of a white powder, that is insoluble in an excess of the reagent.

2. *Ammonium hydrate*, added to a rather strong solution of an atropine salt, produces a white precipitate that is soluble in an excess of the reagent.

3. *Sodium carbonate* gives the same reaction as sodium hydrate.

4. *Sodium bicarbonate* does not produce a precipitate in a solution of an atropine salt.

5. *Gold chloride*, when added to an aqueous solution of an atropine salt, produces a yellow precipitate that gradually becomes crystalline upon standing.

6. *Tannic acid*, added to an aqueous solution of an atropine salt, produces a white, curdy precipitate that is soluble in hydrochloric acid and in ammonia.

7. *Mercuric chloride*, dissolved in water, when added to a solution of atropine in alcohol, produces a yellow precipitate that changes to orange red when gently heated.

8. If a little atropine in a porcelain dish is covered with concentrate sulphuric acid, and heated until it begins to froth and turn brown, an odor similar to that of wild-plum blossoms is given off. If a small piece of potassium dichromate is now added, the odor becomes similar to that of the wild rose, and if the heating is continued, an odor similar to that of bitter almonds is given off. The odor of flowers may also be obtained by bringing a little atropine in contact with a few chromic-acid crystals, and gently heating until the chromic acid begins to turn green.

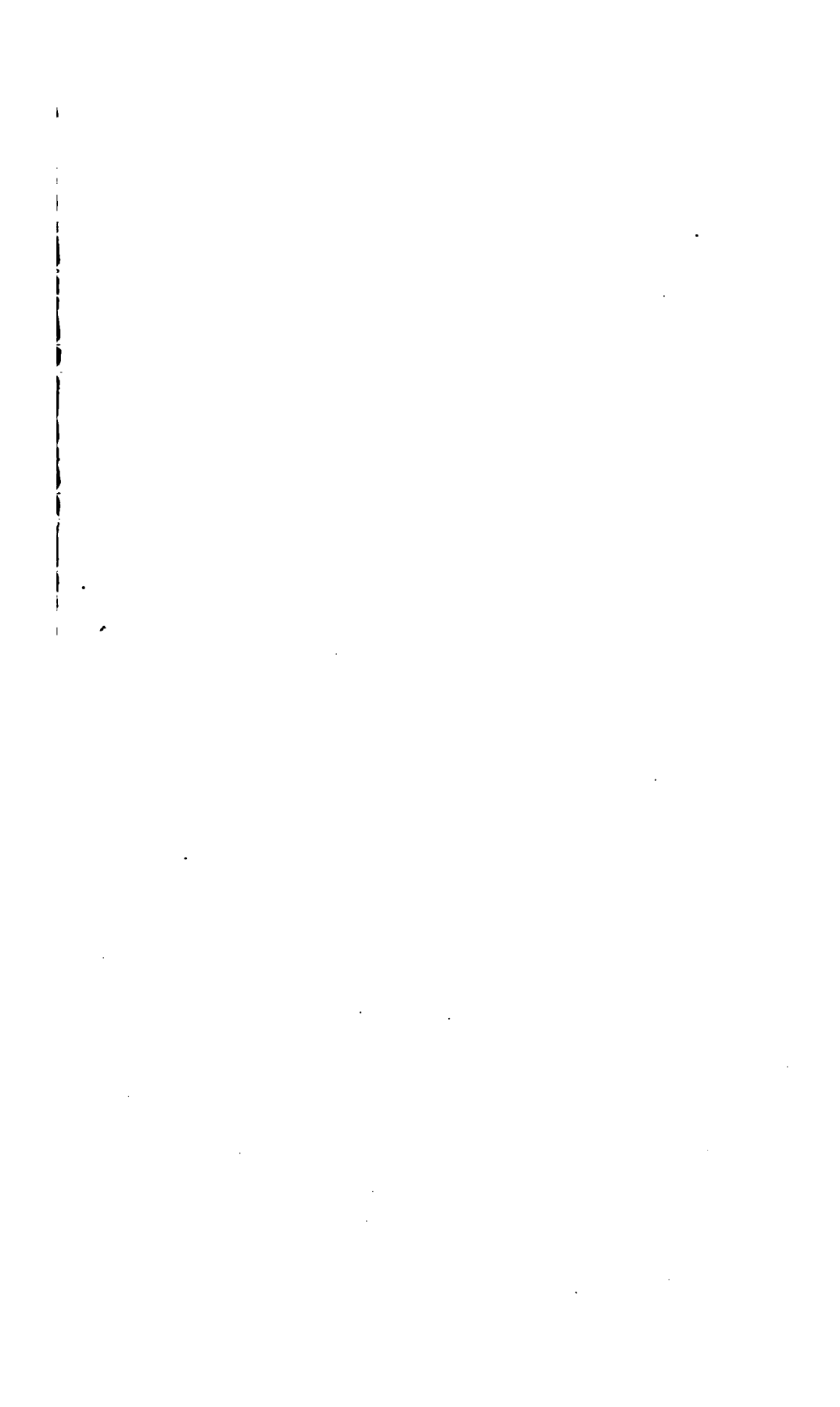
9. If atropine is mixed with concentrate sulphuric acid in a porcelain dish, and a little solid potassium nitrite is stirred into this mixture, it assumes a yellow or orange color. If a few drops of a solution of potassium hydrate in absolute alcohol are now added, the mixture assumes a reddish-violet color that soon changes to pink.

10. If a little atropine or an atropine salt in a porcelain dish is covered with fuming nitric acid, and the mixture is evaporated to dryness on the water bath, a colorless residue

remains, which assumes a violet color that changes to red, if a drop of potassium hydrate dissolved in absolute alcohol is added to the residue after it becomes cold. Strychnine and some other compounds give similar reactions, but not the same.

108. Separation of Strychnine, Brucine, and Atropine.—Strychnine may be separated from brucine and atropine by shaking these alkaloids with cold absolute alcohol, when the brucine and atropine will be dissolved, and the strychnine, which is insoluble in cold absolute alcohol, may be filtered off. Brucine and atropine may be separated by shaking an alkaline solution containing them with petroleum ether, which dissolves the brucine, and leaves the atropine. The brucine may be obtained by separating the layer of petroleum ether, and evaporating it at a rather low temperature. If the solution, separated from the petroleum ether, which contains the atropine, is shaken with ether, the atropine will be dissolved, and may be obtained by separating the ethereal solution and evaporating it in the air.

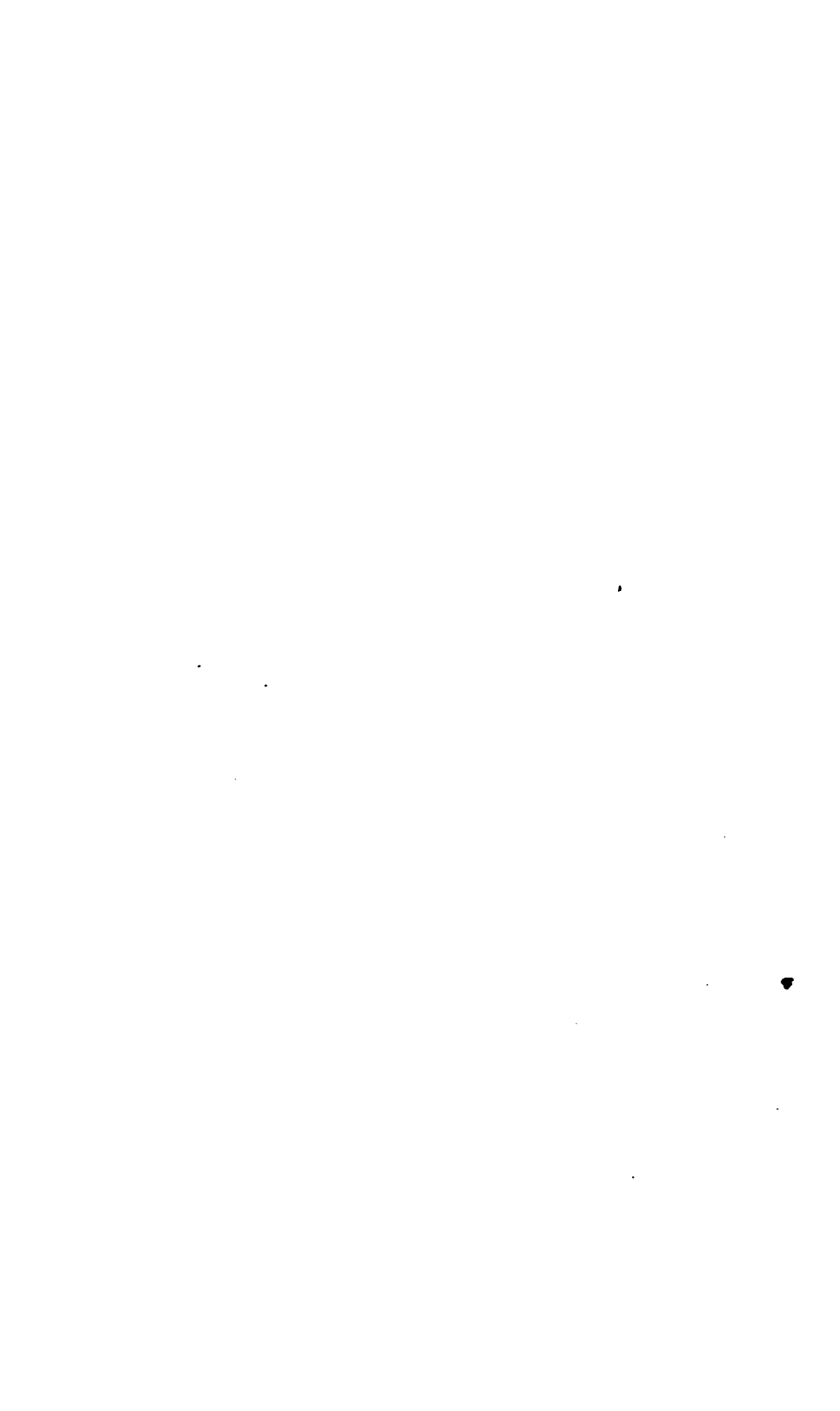
Strychnine and brucine occur together in nature, and are often found together in commerce. When only these two alkaloids are present, they may be separated by placing the dry substance in a porcelain dish, and covering it with strong chlorine water, when brucine will be dissolved to a red solution, and the strychnine will remain unchanged.



A SERIES
OF
QUESTIONS AND EXAMPLES

RELATING TO THE SUBJECTS
TREATED OF IN THIS VOLUME.

It will be noticed that the various Question Papers that follow have been given the same section numbers as the Instruction Papers to which they refer. No attempt should be made to answer any of the questions or to solve any of the examples until the Instruction Paper, having the same section number as the Question Paper in which the questions or examples occur, has been carefully studied.



QUALITATIVE ANALYSIS.

(PART 1.)

- (1) Define qualitative analysis.
- (2) What metals impart the following colors to the borax bead: (*a*) green, (*b*) blue, and (*c*) amethyst in the oxidizing flame, and colorless in the reducing flame?
- (3) What is aqua regia, and how is it made?
- (4) What are the two methods of qualitative analysis?
- (5) Express, in the form of an equation, the reaction that takes place when silver nitrate is precipitated by hydrochloric acid.
- (6) Describe the separation of the metals of the third group when phosphoric and oxalic acids are absent.
- (7) What metals are precipitated by hydrochloric acid?
- (8) What part of the flame of a Bunsen burner acts (*a*) as an oxidizing flame? (*b*) as a reducing flame?
- (9) How are (*a*) oxidation and (*b*) reduction accomplished by the flame of a Bunsen burner?
- (10) What metal imparts a crimson color to the flame?
- (11) What metals give black precipitates when their solutions are treated with hydrogen sulphide?
- (12) Describe the method of determining the members of the seventh group.

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(13) What metal, when fused with sodium carbonate and potassium nitrate, imparts a deep-green color to the fusion?

(14) Name the metals that are not precipitated from acid solutions by hydrogen sulphide, but are precipitated by ammonium sulphide, giving the color of the precipitate formed in each case.

(15) What metals are precipitated by sulphuric acid?

(16) Describe briefly the best method of distinguishing between solutions of zinc and aluminum.

(17) Express, in the form of an equation, the reaction that takes place when sulphuric acid is added to a solution of barium chloride.

(18) How are precipitates washed?

(19) Define (*a*) reagent and (*b*) reaction.

(20) Name the *group reagents* in the order in which they are used.

(21) What is the most characteristic test for the common organic acids?

(22) When hydrogen sulphide produces a precipitate in the solution of a metal, what compound of the metal is formed?

(23) What metals are precipitated as hydrates by ammonium sulphide?

(24) What is the most characteristic test for bromides?

(25) How are solutions concentrated?

(26) What metals are precipitated in the form of hydrates by sodium carbonate?

(27) What is the best test for ammonium compounds?

(28) What metals are precipitated from their solutions by a large excess of water?

(29) What metals are precipitated as yellow sulphides by hydrogen sulphide?

(30) Give a list of the metals composing each of the groups.

(31) How are the acids divided into groups?

(32) How are cobalt and nickel separated?

(33) (a) What is the color of the precipitate formed when a solution of antimony chloride is treated with hydrogen sulphide? (b) Express this reaction by an equation.

(34) If a compound is fused with sodium carbonate on the charcoal, and the fusion when placed on a piece of silver and moistened with water produces a black stain on the silver, what is learned of the composition of the compound?

(35) How would you distinguish between barium, strontium, and calcium in solutions?

(36) Briefly describe the most characteristic test for phosphoric acid.

(37) What is indicated when the original fourth-group precipitate is light colored?

(38) Complete the following equation, and name the factors and products of the reaction:



(39) What is the color and composition of the precipitates formed when sodium hydrate is added to the following solutions: (a) silver? (b) lead? (c) mercurous? (d) mercuric? (e) copper?

(40) What color is imparted to the flame by volatile barium compounds?

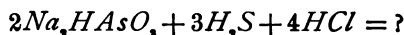
(41) Describe the precipitate formed when hydrogen sulphide is slowly added to a mercuric solution.

(42) If a compound, when heated with concentrate sulphuric acid, gives off carbon monoxide and carbon dioxide, and does not char, what acid is indicated?

(43) Solutions of copper and nickel have similar colors. What is the simplest way to distinguish between them?

(44) How would you test for nitric acid in a solution?

(45) Complete the following equation, and name the factors and products of the reaction:



(46) What metals form white precipitates when ammonium sulphide is added to their solutions?

(47) How may ferrous solutions be changed to ferric?

(48) Why is ammonium chloride added to the solution before precipitating the third group with ammonia?

(49) What metals are not precipitated by ammonium sulphide?

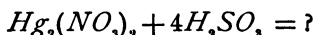
(50) What common metals form two series of salts?

(51) What odor is given off when acetates are heated
(a) with concentrate sulphuric acid? (b) with concentrate sulphuric acid and alcohol?

(52) What metals, when their solutions are treated with hydrogen sulphide, produce black precipitates that are changed to white, insoluble compounds by heating with concentrate nitric acid?

(53) (a) When hydrogen sulphide is added to an acid solution of an arsenious compound, what precipitate is formed? (b) In what is this precipitate soluble?

(54) Complete the following equation:



(55) How does lead behave when heated on the charcoal before the blowpipe?

(56) What metal is precipitated from its solutions by hydrogen sulphide, in the form of a yellow sulphide that is insoluble in ammonium sulphide?

(57) Briefly describe the most characteristic test for hydrochloric acid.

(58) If a substance, when heated on the charcoal before

the blowpipe, gives off white fumes with a garlic odor, what is indicated?

(59) What precipitates are obtained when the following solutions are treated with barium chloride: (a) a sulphate? (b) a thiosulphate? (c) a sulphite?

(60) If the precipitates obtained as described in the last question are pure, how do they act when treated with hydrochloric acid?

(61) How may chromates be reduced?

(62) When hydrogen sulphide is added to a mercurous solution, (a) what is the color and composition of the precipitate? (b) In what is it soluble?

(63) Describe a blowpipe.

ACTUAL ANALYSIS.

NOTE.—With this Question Paper the student receives twelve 2-ounce bottles of solutions for analysis. About one-third the contents of each bottle should be sufficient for the analysis, but more is given in order that the work may be verified. The student should not attempt to analyze these samples until he is thoroughly familiar with the Instruction Paper, and has analyzed a number of solutions that he has made up himself, for these samples can only be duplicated at the student's expense.

SINGLE METALS.

(64) What metal, in solution, is contained in bottle labeled "Qualitative Analysis, Part 1, Question 64"?

(65) What metal is contained in bottle labeled "Qualitative Analysis, Part 1, Question 65"?

(66) What metal is contained in bottle labeled "Qualitative Analysis, Part 1, Question 66"?

(67) What metal is contained in bottle labeled "Qualitative Analysis, Part 1, Question 67"?

MIXTURES.

(68) What metals are contained in bottle labeled "Qualitative Analysis, Part 1, Question 68"?

(69) What metals are contained in bottle labeled "Qualitative Analysis, Part 1, Question 69"?

(70) What metals are contained in bottle labeled "Qualitative Analysis, Part 1, Question 70"?

COMPOUNDS.

(71) What compound (metal and acid) is contained in bottle labeled "Qualitative Analysis, Part 1, Question 71"?

(72) What compound is contained in bottle labeled "Qualitative Analysis, Part 1, Question 72"?

(73) What compound is contained in bottle labeled "Qualitative Analysis, Part 1, Question 73"?

(74) What compound is contained in bottle labeled "Qualitative Analysis, Part 1, Question 74"?

(75) What compound is contained in bottle labeled "Qualitative Analysis, Part 1, Question 75"?

QUALITATIVE ANALYSIS.

(PART 2.)

(1) What are the principal operations performed in the analysis of substances by the dry method?

(2) If a white, luminous, infusible mass is obtained when a substance is heated on the charcoal, (*a*) what does this indicate? (*b*) What should be the next step in the analysis?

(3) If the infusible mass mentioned in the last question assumes a rose color when ignited with cobalt nitrate, what is indicated?

(4) (*a*) What is the first step in the examination of urine? (*b*) How is this accomplished?

(5) (*a*) What odor is observed when an acetate is heated with concentrate sulphuric acid? (*b*) What should be the next step in this case?

(6) How are the alkaloids divided into groups?

(7) In what form should a substance be, when analyzed by the dry method?

(8) If a substance heated on the charcoal fuses and penetrates the charcoal, (*a*) what is indicated? (*b*) How would you distinguish the bases that may be present?

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(9) If a substance is fused on the charcoal with sodium carbonate, and the fusion when placed on a piece of silver and moistened with water produces a black stain, what is indicated?

(10) How may we obtain a solution of a substance that is insoluble in water and acids?

(11) Into what two classes are the phosphates that occur in urine divided?

(12) Name the common volatile alkaloids.

(13) What points should be observed when a substance is heated in the closed tube?

(14) (a) What is indicated if a substance deflagrates when heated on the charcoal before the blowpipe? (b) What further information is obtained if a residue of chloride is deposited on the charcoal?

(15) What are the principal points to be observed when a substance is heated on the charcoal before the blowpipe?

(16) What metals may be recognized by fusing their compounds on the platinum foil with sodium carbonate and potassium nitrate?

(17) If a substance effervesces when treated with concentrate sulphuric acid, (a) what is indicated? (b) What should be the next step in the examination in this case?

(18) For what is thorium important?

(19) (a) What is the principle of the spectroscope? (b) In what cases is it used?

(20) If a substance when heated in the closed tube gives off a gas having the odor of bitter almonds, what is indicated?

(21) What is indicated if a gas having an alkaline reaction and the odor of ammonia is evolved when a substance is heated in the closed tube?

(22) If a substance volatilizes when heated on charcoal, giving off fumes with a garlic odor, (*a*) what is indicated? (*b*) If the substance is yellow, and the odor of burning sulphur is also given off, what additional information is obtained?

(23) If a solid heated with concentrate sulphuric acid gives off a mixture of gases that give a blue flame when ignited, and render a drop of barium hydrate turbid when held at the mouth of the tube, what is indicated?

(24) How are the metals classified with regard to their solubility?

(25) What rare elements belong to Group VII?

(26) Briefly describe the method of determining arsenic in water?

(27) (*a*) What is the reaction of normal urine, and (*b*) how is it determined?

(28) How may strychnine and brucine be separated?

(29) (*a*) What compounds yield carbon monoxide when heated with concentrate sulphuric acid, and (*b*) how is the carbon monoxide recognized?

(30) What rare elements are found in Division B of Group II?

(31) What poisonous metals are most frequently found in water?

(32) How would you test for nitric acid or nitrates in drinking water?

(33) Of what common non-volatile alkaloids is Group II composed?

(34) If a substance, when heated in the closed tube, changes color from white to yellow when hot, and becomes white again upon cooling, what is indicated?

(35) If a substance when heated on the charcoal yields a white, malleable, metallic globule, surrounded with a

(64) Describe the phenomena observed when brucine is treated (a) with concentrate nitric acid and stannous chloride; (b) with concentrate nitric acid and hydrogen sulphide.

(65) What rare elements belong in Group I?

(66) Between what limits does the specific gravity of urine vary (a) in health? (b) in disease?

(67) (a) Where is titanium found in nature? (b) Give a characteristic test by which it may be recognized.

(68) In a case where poisoning by phosphorus is suspected, why would it not be sufficient to treat the sample with an oxidizing agent, and then test for phosphoric acid?

ACTUAL ANALYSIS.

(69) What metal is contained in the box labeled "Qualitative Analysis, Part 2, Question 69"?

(70) What compound is contained in the box labeled "Qualitative Analysis, Part 2, Question 70"?

(71) What metal is contained in the box labeled "Qualitative Analysis, Part 2, Question 71"?

(72) What compound is contained in the box labeled "Qualitative Analysis, Part 2, Question 72"?

(73) What compound is contained in the box labeled "Qualitative Analysis, Part 2, Question 73"?

(74) What compound is contained in the box labeled "Qualitative Analysis, Part 2, Question 74"?

(75) What compound is contained in the box labeled "Qualitative Analysis, Part 2, Question 75"?

(76) What compound is contained in the box labeled "Qualitative Analysis, Part 2, Question 76"?

(77) What double salt is contained in the box labeled "Qualitative Analysis, Part 2, Question 77"?

(78) What powdered mineral is contained in the box labeled "Qualitative Analysis, Part 2, Question 78"?

(79) What fertilizer is contained in the box labeled "Qualitative Analysis, Part 2, Question 79"?

(80) What pigment is contained in the box labeled "Qualitative Analysis, Part 2, Question 80"?





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