INTRODUCTORY QUALITATIVE ANALYSIS

A Duke University Centennial Publication

This book, by a member of the faculty of Duke University, is one of a group appearing in connection with the Duke University Centennial, celebrating in 1938–1939 the anniversary of the origins of Trinity College from which Duke University developed.

INTRODUCTORY QUALITATIVE ANALYSIS

BY

WARREN C. VOSBURGH

Professor of Chemistry at Duke University

Revised Edition

NEW YORK · 1938

THE MACMILLAN COMPANY

Printed in the United States of America.
Published June, 1938.

PREFACE

THIS book is a revision and enlargement of a book of the same title written by Dr. Jacob Cornog and the present author. The present book is adapted to a one-semester course in qualitative analysis, and as before, the chief emphasis is on instruction in chemical principles and the scientific method rather than on the teaching of an immediately practical art.

In the experimental part, the conventional scheme for the separation and detection of the cations is used. This scheme provides many illustrations of important principles, and experience has shown that beginning students can follow it understandingly and with good experimental results. It is defective in failing to include all of the cations with which a student might well become acquainted, but it is doubtful that this could be remedied without too much complication for beginning students. For a similar reason it was not considered essential that all of the more common anions be included. A student properly educated in the principles of analysis should be capable of consulting other books for a more inclusive scheme of analysis and for tests better suited to a particular purpose than the ones given in this book.

The number of preliminary experiments to be carried out previous to the analysis of unknown materials has been kept to a minimum in the belief that too often such experiments are merely isolated experiences in the student's mind and are carried out in purely routine fashion. However, provision is made for the analysis of known mixtures before unknown materials are analyzed.

In the final tests, inorganic reagents are used for the most part. While better experimental results might be obtained with organic reagents, the reactions would not be understood by students who had not studied organic chemistry, and the introduction of very many reactions that the students cannot understand is inadvisable.

For the past five years the qualitative analysis at Duke University has been done on a semi-micro scale. At first the laboratory directions in the first edition of this book were used and the students told to read "one drop" instead of "one cubic centimeter," and to make other alterations in the same proportion, one drop being about one-twentieth of a cubic centimeter. Later, special directions for the semi-micro work were inserted where needed, and the revised directions used in lithoprinted form. At the same time, some improvements were made in the procedures for the ammonium sulfide and ammonium carbonate groups. These revised directions, which are given in the present book, can be used for qualitative analysis either on the ordinary or the semi-micro scale. For ordinary-scale work the regular directions are to be followed, with the omission of the special directions in italics. For semi-micro work the regular directions are to be followed, reading drops for milliliters, except when special directions are given. Experience at Duke University has shown that the latter procedure is satisfactory.

In the theoretical part special attention has been paid to keeping the theory consistent with modern physical chemistry and to presenting it clearly. Care has been taken to prevent any inconsistencies between the electrolyte theory presented and the interionic attraction theory. The newer conception of the ionization of acids and bases has been used. A seeming inconsistency in the occasional use of the term hydrogen ion and the symbol H^+ instead of hydronium ion and H_3O^+ was deliberate. The term hydrogen ion and the symbol H^+ will doubtless be used considerably for some time to come to designate the hydronium ion, and it is well that the student become accustomed to both terms.

The author is indebted to his associates at Duke University for many suggestions and to Dr. Jacob Cornog for reading most of the manuscript and offering valuable criticism.

WARREN C. VOSBURGH

DURHAM, N. C.

CONTENTS

PART I. LABORATORY WORK

PART II. THEORY

APPENDIX

PART I

LABORATORY WORK

Chapter I

GENERAL INFORMATION

QUALITATIVE analysis consists in the separation of a complex substance or mixture into its constituents and the identification of the constituents. For example, by means of qualitative analysis it is possible to learn what things are present in a dime, a brick or a glass windowpane. The word qualitative signifies that the object of the analysis is merely to identify the constituents of the compound or mixture, with no attempt to determine their amounts. If the quantities of the constituents are determined, the process is called quantitative analysis.

Part I of this book gives directions for the practical carrying out of qualitative analysis in the laboratory. In Part II the background of chemical theory necessary for an understanding of the processes of qualitative analysis is laid, and some of the more important features of the experimental procedure are discussed.

1. Preparation for Laboratory Work. Information as to how to obtain a laboratory desk assignment and the necessary chemicals and apparatus may be obtained from the instructor in charge of the course. A list of the apparatus needed is to be found in the appendix of this book, as well as a list of the reagents and solutions that should be available. At the beginning of the course it will be desirable to check the apparatus and see that it is in condition for use.

Before beginning the laboratory work, the remainder of this chapter should be read carefully. Then Chapter II can be consulted for specific directions as to how to proceed with the laboratory work. It should be understood that the directions given there are to be followed unless otherwise ordered by the instructor.

2. Semi-Micro Qualitative Analysis. In the past it has been customary in qualitative analysis to analyze samples of material weighing from 0.5 to 1 g. and to work with volumes of solutions from a few milliliters[1] up to a maximum of somewhat more than 100 ml. There are some decided advantages in working with much smaller quantities than this. Time is saved, since many of the operations are more rapid, the cost of reagents is much less, atmospheric pollution in the laboratory is less and the training in technique is probably superior. The results when working with small quantities are as good as when working with larger quantities.

The laboratory directions in this book are written so that they can be used for either the ordinary scale or what may be called semi-micro qualitative analysis. On the semi-micro scale the quantities dealt with are one-tenth to one-twentieth of those on the ordinary scale. Volumes of solutions in the directions for ordinary-scale qualitative analysis can be converted to the corresponding volumes for semi-micro analysis by reading "drops" in place of "milliliters." Thus 5 ml. on the ordinary scale becomes 5 drops on the semi-micro scale. This follows from the fact that a drop of water or a water solution from an ordinary-sized medicine dropper or pipette has a volume in the neighborhood of one-twentieth of a milliliter. In this way it is possible to convert qualitative analysis directions written for the ordinary scale to the semi-micro scale. When weights of reagents or of unknown materials are given, they are divided by twenty in changing to the semi-micro scale.

In this book most of the directions are given for the ordinary-scale qualitative analysis and for the most part it is expected that if the book is used for semi-micro analysis the appropriate changes will be made as the directions are read. When the change from the one scale to the other involves changes in procedure that might not be obvious, or when special directions for semi-micro analysis are needed, a note in italics introduced by the word "micro" gives the information needed. This is placed immediately following the procedure to be changed. An examination of the directions for Exercises 4 and 5, Chapter II, will make this clear.

3. Use of the Centrifuge for Separations. The methods of qualitative analysis involve many separations of precipitates from solutions. In analysis on the ordinary scale these separa-

---

[1] A milliliter (ml.) is a thousandth part of a liter, and is practically the same as a cubic centimeter; one milliliter is equal to 1.000027 cubic centimeters.

tions are usually made by filtration, the solution being allowed to pass through a porous filter paper which retains the precipitate. On the semi-micro scale it is more convenient to use a centrifuge for such operations, and in some cases probably quite necessary.

To separate a precipitate from a solution, the solution and precipitate are placed in a centrifuge tube, which resembles a test tube, and made to rotate in a horizontal or inclined position at a high rate of speed about a vertical axis. The centrifugal force developed by the rotation throws the precipitate to the bottom of the tube, leaving a clear solution above it. In separations on the semi-micro scale the solution is removed from the precipitate, after centrifuging, by means of a medicine dropper and transferred to another vessel. The precipitate may then be washed with water to complete the separation. The details of these operations are given in Exercise 3, Chapter II.

4. Laboratory Accidents. Laboratory accidents are infrequent, but because they happen sometimes and because the difference of a few seconds in doing the right thing after an accident may make the difference between a trivial incident and a serious injury, the following suggestions are offered. There are three types of laboratory accidents that may result seriously: accidents from fire or explosions, from corrosive chemicals, and fainting.

(*a*) *Fire.* A vessel containing an inflammable substance may be upset and become ignited, resulting in a fire on the desk or even the clothing of those standing near. A small fire is sometimes easily blown out or extinguished by covering it. A larger fire may often be quenched by mopping with a towel. A still larger fire had best be attacked with a fire extinguisher, one or more of which should be located in every laboratory. Some laboratories have a shower bath or other provision for extinguishing fires on clothing. This should be investigated.

(*b*) *Explosions.* Potassium chlorate mixed with certain easily oxidized substances, mixtures of perchloric acid and alcohol, and oxygen under pressure when in contact with oil or other organic matter are violent explosives. Other dangerous oxidizing agents of this type are sodium peroxide, potassium permanganate, chromyl chloride, and chromium trioxide.

Volatile inflammable liquids in closed containers may give an explosive mixture with air; keep flames away from such, and from seemingly empty cans. Substances in this class are ether, carbon disulfide, gasoline, benzene and others.

(*c*) *Chemicals.* Corrosive chemicals often get on the clothing or skin, and if care is not taken damage may result. It is advisable to wear an apron or coat in the laboratory to protect the clothing. As an additional precaution it is well to mop up immediately with a wet sponge any chemicals that are spilled on the desk or on the floor. When a corrosive substance gets on the skin, the first measure is to wash it freely with water. If the skin continues to smart, ask the instructor what to do next, or apply sodium carbonate solution to acid burns and dilute acetic acid to sodium peroxide or hydroxide burns. The acetic acid on the side-shelf is too concentrated. Do not put it on the skin without diluting with about 10 volumes of water.

Chemical burns should be treated by a physician; there is more danger of infection than with ordinary burns, and they often heal slowly.

Chemicals in the eye require special mention. When a person gets a chemical in the eye he may be so blinded as to be unable to help himself. Do not hesitate to lead such a person to the sink and apply copious quantities of water to the eyes. If the chemical is a strong one, like concentrated sulfuric acid, place the person under the water tap face up and open the tap. Prompt action here may save a person from blindness. Do not put anything in the eye except water unless told to do so by a competent authority. If the eye still smarts or burns after the first treatment, a drop of castor oil in the eye will often bring relief.

(*d*) *Poisons.* Many of the reagents employed in chemical laboratories are poisons; see that they are never taken into the mouth. Avoid drinking from beakers.

(*e*) *Breathing Irritating Gases.* Accidents sometimes occur that make it necessary to breathe irritating gases for longer or shorter periods. Breathing through a moist or even dry handkerchief or towel will often lessen the irritation. After the accident, if fresh air does not relieve the irritation in the nasal passages, try smelling denatured alcohol. If this does not bring relief, try *cautiously* smelling 3 or 6 *M* ammonium hydroxide.

(*f*) *Fainting.* People occasionally faint in the laboratory as well as elsewhere. In the laboratory the chief danger arises from the possibility of striking the head against a desk-top or concrete floor in falling. A person who has fainted should be placed flat on the back wherever he is and let alone for as much as five minutes, after which time restorative measures may be employed. If you feel yourself fainting in time, tell your neighbor and lay yourself flat on the floor or a clean desk-top, assisted by your neighbor. If you see one of your neighbors turn pale and begin to totter, assist him to lay himself out flat on his back, avoiding contacts between head and stone desk-tops on the way down.

(*g*) *Cuts.* In trying to push a glass tube through a cork or rubber stopper there is danger of the tube breaking and causing a severe cut. This danger can be nearly eliminated by proper procedure; take hold of the tube *near the stopper* and if much resistance is offered to the passage of the tube, lubricate both tube and stopper with water. Always avoid putting much strain on glass. Smooth the cut-off ends of glass tubing by heating in a flame until the rough edges are fire-polished.

(*h*) *Small-Scale Work.* Work on as small a scale as possible. Small-scale work not only involves smaller quantities of dangerous materials than large-scale work, but is likely to effect a worth-while saving of time and materials.

In handling larger quantities of dangerous materials than usual (*i.e.*, larger than called for in the usual laboratory manuals), one should consult the instructor as to procedure and precautions, and have him check the apparatus to be used.

5. Ventilation in the Laboratory. (*a*) *Polluted Air.* The air in laboratories devoted to qualitative analysis sometimes becomes badly polluted. Breathing such air may cause fainting, headaches, dizziness, colds, bronchitis, or mental and physical fatigue at the conclusion of the laboratory period. Instructors and students should cooperate in trying to keep the laboratory a healthy place in which to work.

Laboratories should be maintained at a relatively low temperature. The quantity of heat generated by the use of a large number of Bunsen burners is surprising, as is also the quantity of pollution contributed by the gaseous products of combustion. Turning down or extinguishing burners when not in use minimizes pollution.

(*b*) *Fumes.* Laboratory directions for qualitative analysis often require that solutions containing acids or ammonium salts be evaporated to a smaller volume or to dryness, with the result that quantities of corrosive vapors are liberated. Such an evaporation should be conducted so that fumes are not liberated in the room, that is, before a fume duct or in a hood. Fume ducts or hoods are of little use if the fans or other mechanical ventilating devices are not in operation. Report to your instructor whenever the ventilating devices fail to remove the fumes. Also remonstrate with your neighbors whenever they do anything to pollute the air of the laboratory.

(*c*) *Hydrogen Sulfide.* Another source of pollution of laboratory air is hydrogen sulfide gas. This gas, which is necessarily much used in qualitative analysis, is a dangerous poison. Breathing it in high concentration will cause death in ten minutes or less. Its concentration in the air in the laboratory never gets high, but even in low concentrations it contributes to or causes many of the physiological effects of breathing bad air previously mentioned. The one precaution in the use of hydrogen sulfide is to use it in such a way that little escapes into the air of the room. It is a good idea to have a nearby window open while using hydrogen sulfide. Fresh air is the antidote for hydrogen sulfide poisoning.

6. Miscellaneous Suggestions and Directions. Burned matches, broken glass, used filters, and other solid waste material should not be placed in the sink unless you wish to flood the laboratory. Such materials should be placed in waste jars. The waste jar may be placed at some distance from where you work and running to it each time you use a match may be inconvenient. It is suggested that while doing laboratory work you keep a beaker or other vessel on your desk and place in it all the solid waste during the laboratory period. At the end of the period make a trip to the waste jar and empty it.

Many steps can be saved in using reagents located on side shelves. There are two ways in which a portion of a reagent can be transported from the side shelf to your desk. You can take a vessel, go to the side shelf, pour out the required quantity of reagent, and return to your desk, walking twice the distance from your desk to the side shelf. Or, you can go to the side shelf, bring the reagent bottle to your desk, use it and return it to the side shelf, walking four times the distance between your desk and the side shelf. The latter method will not only take extra steps and time, but will inconvenience others who need to use the same reagent.

When heating a solution in a test tube do not aim the opening toward yourself or toward a neighbor.

When mixing two liquids, particularly when diluting concentrated sulfuric acid, always pour the heavier (sulfuric acid) into the lighter (water), thus lessening the chance for spattering, which in some cases is dangerous.

When too much of a solid or liquid has been poured from a reagent bottle, never pour the excess back into the bottle. Either save it until you need it or throw it away. This lessens the chance of introducing impurities into the reagent in the bottle.

While a material is being removed from a reagent bottle, do not lay the stopper down in such a manner that the part of the stopper that enters the neck of the bottle comes in contact with the desk top or shelf. Replace stoppers when through using reagent bottles.

Chapter II

LABORATORY EXERCISES

THE laboratory exercises in this chapter constitute a course of instruction in the technique of qualitative analysis. The first exercise gives directions for the preparation of certain necessary pieces of apparatus, involving some simple glass working, which every laboratory worker should learn. The directions in part *a* of Exercise 1 are for ordinary-scale qualitative analysis and those in part *b* for semi-micro analysis. Exercises 2, 3, and 4 illustrate some of the methods of qualitative analysis that need special attention. Exercise 2 is for ordinary-scale work, Exercise 3 for semi-micro work and Exercise 4 for both. Exercises 5–8, 10–11 and 13 give practice in the systematic methods of analysis; analyses are carried out on known mixtures in which all of the ions are present for which tests are to be made. These exercises are important, because experience with the procedure is necessary before the procedure can be used with confidence for the analysis of unknown materials. Finally, Exercises 9, 12 and 13–15 are on the analysis of materials of unknown composition.

In the directions for the laboratory work as well as in the theoretical part of the book, the theory of ionization is used. This is done because it makes possible greater clarity of expression and greater simplicity than would otherwise be the case. Anyone who is placed at a disadvantage by a lack of understanding of the theory of ionization is urged to review the subject in a textbook of elementary chemistry, or to read Chapters VI, VII and VIII of this book as a preparation for the laboratory work.

EXERCISE 1

PREPARATION OF APPARATUS

(*a*) *Ordinary-Scale Apparatus.* Make two wash bottles, and a precipitation flask. Make one of the wash bottles from a Florence flask of 500-ml. or 1-liter capacity as shown in Fig. 1 A. Make the other wash bottle and the precipitation flask from Erlenmeyer (conical) flasks of about 250-ml. capacity, as shown in Fig. 1 B and Fig. 1 C, respectively. Use rubber stoppers. See that each stopper fits the opening for which it is intended before inserting the glass tubing.

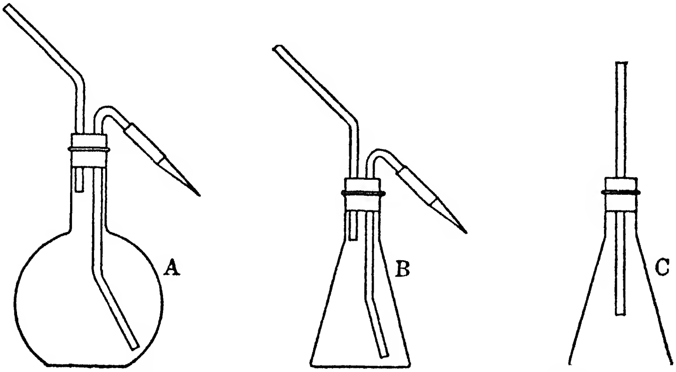


FIG. 1. A. Wash bottle for distilled water, 500 or 1000-ml. capacity. B. Wash bottle for various wash solutions, 250-ml. capacity. C. Precipitation flask, 250-ml. capacity.

After the various pieces of glass tubing have been bent to the desired shapes and cut to the right lengths, fire-polish the ends. To do this, hold the ends in the flame until the edges of the glass begin to soften. After this, allow the glass to cool. Fire-polishing is important, not only because fire-polished tubes are more easily thrust through rubber stoppers, but also because there is much less danger of cutting oneself or the rubber in the process.

Before starting to push a glass tube through the hole of a stopper, wet the tube and the inside of the hole with water. When pushing the tube through, *take hold of the tube near the stopper.* This greatly reduces the danger of the tube breaking and cutting your hand.

The larger wash bottle is to be used for distilled water only. Whenever the directions call for water, distilled water should be used. The smaller wash bottle is to be used for specially prepared wash solutions. The precipitation flask is to be used when precipitation by hydrogen sulfide gas is required.

When the wash bottles and the precipitation flask are finished, make three stirring rods, each 15 to 18 cm. (6 to 7 inches) long. These are merely solid glass rods with the ends fire-polished.

(*b*) *Apparatus and Reagents for Semi-Micro Work.* Make a wash bottle like B of Fig. 1 from a 200 or 250-ml. flask. Read the directions for this in part *a* of this exercise. The tip of the delivery tube should be drawn out to a fine point so that very small quantities of water can be delivered. This wash bottle is to be used for distilled water only. Whenever the directions call for water, distilled water should be used.

For the piece of apparatus shown in Fig. 2 A, cut a piece of 5 mm. (outside diameter) glass tube about 15 cm. (6 inches) long and fire-polish both ends. Push the tube through a one-hole rubber stopper that fits an 18 × 150 mm. test tube (capacity 30 ml.). Read the precautions given in part *a* for avoiding cuts. Adjust the tube in the stopper so that 5 to 7 cm. (2 to 3 in.) of the tube projects beyond the small end of the stopper. When the stopper is placed in a 30-ml. test tube, a piece of apparatus like that shown in Fig. 2 A is obtained. This is used in the semi-micro work in place of the precipitation flask of Fig. 1 C.

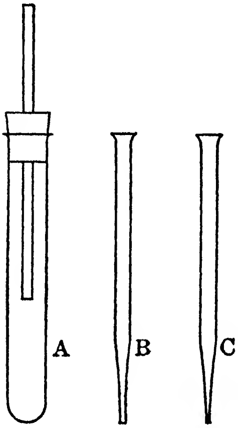


FIG. 2. Apparatus for semi-micro analysis.

In addition to the wash bottle and precipitation apparatus, make 4 dropping pipettes, or droppers, with medicine-dropper bulbs attached, the glass parts of which are shown in Figs. 2 B and 2 C. The glass parts of the droppers should be about 15 cm. (6 inches) long. To make the glass parts take a piece of 7 mm. (outside diameter) glass tube at least 25 cm. (10 inches) long and heat a broad band of it 12 to 15 cm. (5 or 6 inches) from one end with the fishtail top on the burner, holding the tube at both ends and rotating it continuously so that it will be heated equally on all sides. When the heated glass becomes soft, remove it from the flame and draw it out carefully by pulling gently on the ends. The tube should be narrowed down to about the diameter of the tip of an ordinary medicine dropper. If the tube is not narrowed down enough, heat again and repeat the drawing out. Cut the glass at the proper point or points of the drawn-out portion, by scratching with a file and breaking, making two dropper tubes. Heat the ends of the tubes in the flame for an instant to fire-polish them. Make two droppers (Fig. 2 B) with tips as near like those of the droppers furnished in the apparatus outfit as possible and two with much smaller tips, like Fig. 2 C. The bulb ends of the droppers can be flared out to hold rubber bulbs by softening in the flame and pressing the glass outward with the narrow end of a file. When the glass is cool attach medicine-dropper bulbs.

Make three or four stirring rods each 10 to 12 cm. (4 to 5 inches) long, of glass rod 3 mm. in diameter. Fire-polish the ends of the rods.

Measure the volume of the drops given by each of the two droppers having the larger tips in the following manner. First learn to measure 1 ml. of water by means of a measuring pipette. Draw up water in the pipette until the level is above the zero mark, then quickly cover the end of the pipette with the first finger (not the thumb) of the right (or left) hand. By relieving the pressure slightly, allow the water column to fall until the bottom of the meniscus (the curved surface of the water) is even with the zero mark. Hold the meniscus at this point, touch the tip of the pipette to the surface of the water, or to a glass wall (to remove any portion of a drop that may be hanging to it) and then insert the lower end of the pipette in a dry, 3-ml. test tube. Allow the water to flow from the pipette until the meniscus is on the 1-ml. mark; then touch the tip of the pipette to the surface of the water and remove the pipette from the test tube. Make a light scratch with a file on the test tube at the level of the surface of the water. This makes the test tube a rough measuring vessel for measuring 1 ml. Now pour out the water as well as possible and drop some water into the tube from one of the larger-tipped droppers, counting the drops, until 1 ml. of water has been delivered. Record the number of drops in your notebook. Check the other dropper similarly. If it takes less than 16 drops or more than 24 to make 1 ml., adjust the tip in such a way as to bring the number within these limits. It is to be assumed later that a drop is 0.05 ml. and that all drops are alike. Compare the size of the drop from a pipette with a very small tip with that of a drop from a larger tip.

After the use of a dropper, it must be washed before it is used for another solution. To wash a dropper, take some distilled water in a test tube and draw up a portion of it and expel it into the sink. If it is known that a solution has been drawn into the upper part of the dropper, or into the bulb, remove the bulb and use the wash bottle for washing out the glass part of the dropper and the bulb if necessary.

It is desirable to have at least twelve bottles of reagents for a desk set. The reagents needed most frequently are the following:[1]

HCl	3 *M*	CH_3COONH_4	3 *M*
HCl	12 *M*	CH_3COOH	6 *M*
HNO_3	6 *M*	Na_2S_x	2.5 *M*
H_2SO_4	3 *M*	$(NH_4)_2CO_3$	3 *M*
K_2CrO_4	1 *M*	$NaOH$	3 *M*
NH_4OH	3 *M*	$AgNO_3$	0.2 *M*

The bottles for the 3 *M* HCl, 6 *M* HNO_3 and 3 *M* NH_4OH should be larger than the others. Each reagent bottle should be provided with a stopper carrying a medicine dropper. Pass the glass tube of a medicine dropper through a short piece of rubber tube that fits like a stopper in the neck of a 30-ml. bottle, or for a 60-ml. bottle (or larger) a cork with a hole bored in it. Now test each dropper to find out how many drops are equal to one milliliter. Use the droppers that deviate the most from 20 drops per milliliter for the concentrated acid, sodium hydroxide and sodium polysulfide bottles.

---

[1] The ordinary-scale directions call for 6 *M* solutions of hydrochloric acid and ammonium and sodium hydroxides. It is better on the semi-micro scale to use 3 *M* solutions of these reagents. For semi-micro work, the 3 *M* solutions should be used when the directions specify 6 *M*, and the volumes specified should be doubled.

7. Notebooks. It is recomended that a bound notebook be used for recording notes on the laboratory work. Information as to what to write in the notebook is given along with the directions for the exercises, and this may be supplemented by directions from the instructor. Whenever a question is asked in the directions for the exercises, it is intended that the answer be written in the notebook. The notes must be kept in such a manner that the instructor will be able to understand them without difficulty.

EXERCISE 2

SEPARATION BY PRECIPITATION. FILTRATION

The object of Exercise 2 is to show how two metallic ions in a solution can be separated from each other and from the solution.

Mix together in an Erlenmeyer flask 5 ml. of 0.2 *M* $AgNO_3$ and 2 ml. of 0.5 *M* $Cu(NO_3)_2$. Dilute the solution with about 25 ml. of distilled water.

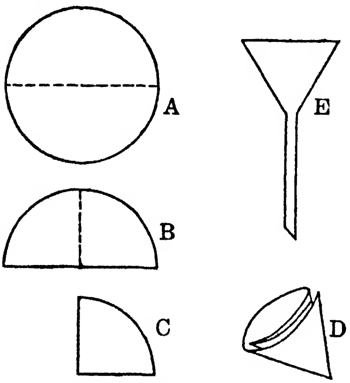


FIG. 3. Making a filter.

The silver ion can be removed from the solution in the following manner. Add slowly, with constant shaking, 2 ml. of 6 *M* HCl. Observe what happens. Shake the flask until the precipitate coagulates and settles quickly to the bottom when the shaking is stopped. The precipitate is next separated from the solution by filtration, which is accomplished in the following manner. Fold a circular piece of filter paper, A in Fig. 3, along a diameter as indicated by the dotted line, obtaining B. Fold B along the dotted line, obtaining C. Open one side of the folded paper as indicated in D, obtaining a folded paper that will fit snugly in the glass funnel E. Put it in the funnel and wet it with distilled water. Support the funnel by means of a funnel support or in the top of an Erlenmeyer flask if the stem is not too long. Pour into the filter as much clear solution as possible without having the liquid on the filter rise above the edge of the filter paper. When most of the clear solution has been filtered, pour the rest of the solution and the precipitate into the filter. The time required for filtration will generally be shortened if most of the clear solution is poured through the filter before much of the solid precipitate is allowed to get on the filter. Pouring off the solution without disturbing the precipitate is often called "decantation." The solution that has passed through the filter into the flask under the funnel is called the "filtrate."

When filtration is complete, replace the flask containing the filtrate by an empty flask and wash the precipitate by playing on it a stream of water from the wash bottle, letting the water run through the filter. The wash water can be rejected. Record the color of the precipitate and the filtrate in your notebook. Where are the silver and copper? How can you tell? Write the answers to these questions in your notebook.

Now add 5 ml. of 6 *M* sodium hydroxide to the filtrate and mix well. What do you observe? Filter part of the mixture, using a fresh filter paper, and record the color of the precipitate and filtrate. Keep part of the mixture for later use. Where is the copper? Has the copper been separated from the solution? Separations like this one are the basis of qualitative analysis.

Filtration by Suction. Sometimes filtration can be carried out more rapidly by the use of a suction filter than in the manner described above. A suction filter is a device for applying suction to the lower end of a filter, and its use is described in the next four paragraphs. As an exercise in the use of this apparatus, filter by suction the remainder of the mixture of copper hydroxide and the solution from which it was precipitated. The precipitate and filtrate can then be rejected.

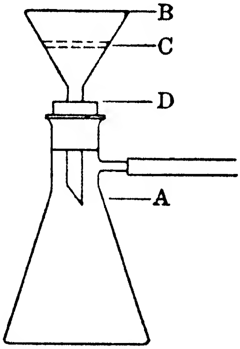


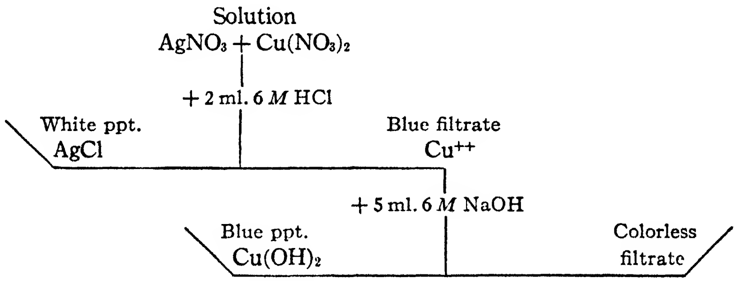
FIG. 4. Suction filter.

One type of apparatus for filtering by suction is illustrated in Fig. 4. It consists of a thick-walled flask A, called a filter flask, having a side-arm for connecting to the suction and a porcelain funnel B, sometimes called a Hirsch funnel, with a perforated diaphragm at C. The stem of the Hirsch funnel is put through a hole in the rubber stopper D and the stopper fits tightly in the neck of the flask. The suction, or partial vacuum, is often produced by a so-called filter pump operated by water power. The filter pump can be attached to a water faucet and is connected to the filter flask by means of a rubber tube. Some laboratories have large vacuum pumps to supply the whole laboratory, with pipes leading from it to the laboratory desks.

To prepare a suction filter, assemble the apparatus as shown in Fig. 4, connecting the filter flask to the filter pump or vacuum line by rubber tubing. Place on the diaphragm of the funnel a piece of filter paper that is slightly smaller than the diaphragm, but which covers all the holes. Wet the filter paper and turn on the suction. Now pour some water on the filter to see that there are no leaks and that the filter is working satisfactorily. Press down with the finger any portions of the paper that are not tight against the diaphragm. If the filter seems to work satisfactorily, break the suction, best by pulling the rubber tube off the side-arm of the filter flask, and pour the water out of the flask. Reassemble the apparatus, apply the suction, and proceed with the filtration much as with an ordinary filter. The same directions for washing apply to a precipitate on a suction filter as apply to a precipitate on an ordinary filter. At the end of a filtration break the suction before turning off the filter pump.

Fine-grained precipitates are sometimes drawn through a suction filter. When this happens, the filtrate may be poured through the filter a second time. Usually enough of the precipitate is retained in the first filtration to make a filter bed that will hold a finer precipitate than will the filter paper alone. Sometimes only a small amount of precipitate passes through, and time can be saved by refiltering through an ordinary folded paper without suction and throwing away the small precipitate.

8. Outlines for Qualitative Analysis Procedure. In connection with the directions given below, a diagrammatic or outline method for recording the processes of qualitative analysis is used. Outlines are useful both in giving laboratory directions and in stating experimental results. As an example, Outline 1 is given for the separation and precipitation of silver and copper ions as carried out in Exercise 2. The meaning of the outline will be apparent if the procedure of Exercise 2 is recalled. The original solution, containing silver and copper nitrates, is treated with 2 ml. of 6 *M* HCl. This causes the precipitation of silver chloride. The equation for this reaction is



OUTLINE 1. Separation of silver and copper ions.

$$AgNO_3 + HCl \longrightarrow AgCl + HNO_3$$

or, written in the ionic form,

$$Ag^+ + Cl^- \longrightarrow AgCl$$

Copper nitrate remains in solution. Copper nitrate is an ionized salt and in solution consists of copper ions, Cu^{++}, and nitrate ions, NO_3^-. The mixture is then filtered to separate the solid from the liquid portion. Filtration is indicated in the outline by the junction of a vertical line with a horizontal line. The part of the horizontal line to the left of the junction always represents the precipitate (solid) and the part to the right always represents the filtrate (liquid). Whenever a mixture is filtered, both precipitate and filtrate must be accounted for. In this case the precipitate is silver chloride. It is rejected, as indicated by the end of the line being turned up. The filtrate is blue in color and contains the copper in the form of cupric ion. Sodium hydroxide solution is added to the filtrate. This causes the precipitation of copper hydroxide.

$$Cu(NO_3)_2 + 2\,NaOH \longrightarrow Cu(OH)_2 + 2\,NaNO_3$$

$$Cu^{++} + 2\,OH^- \longrightarrow Cu(OH)_2$$

The colorless solution is now separated from the blue copper hydroxide precipitate, and both are rejected.

In making outlines, the conventions for representing filtration and rejection and the indication of treatment other than filtration by a vertical line progressing in a downward direction should be followed carefully. On the other hand considerable latitude is permissible in what is recorded as observations, explanations and conclusions. There is one more convention not shown in the outline given. When a final test is made and a particular ion is found present, the record of the final test in the outline is enclosed in a rectangle to call attention to it. If an outline is used to record a particular analysis and an ion is found absent, no rectangle should be put around the record of the test.

EXERCISE 3

PRECIPITATION ON THE SEMI-MICRO SCALE. SEPARATION OF PRECIPITATE AND MOTHER-LIQUOR BY MEANS OF A CENTRIFUGE

In a centrifuge tube place 2 drops of 0.5 *M* $FeCl_3$ and dilute with 0.9 ml. of water measured by means of a measuring pipette. Stir with a small stirring rod to mix thoroughly. Test with litmus paper; this is best accomplished by laying out a strip of blue litmus paper on a clean watch glass, removing a small drop of the solution on the end of the stirring rod and touching to the paper. Now add 3 *M* NH_4OH a drop at a time, stirring well and testing with red litmus after each drop, until a brown precipitate is formed and the solution is decidedly alkaline. Place the centrifuge tube in a centrifuge and place a similar tube containing about 1 ml. of water in the opposite tube-holder of the centrifuge as a counterbalance. Run the centrifuge for 30 seconds or more and remove the tubes. The ferric hydroxide precipitate should have settled to the bottom of the centrifuge tube and a clear solution should be left above it. By means of a dropping pipette with a small tip remove to a small test tube as much as possible of the clear solution (filtrate), without including any of the precipitate. Acidify the solution by adding 3 *M* HCl a drop at a time, testing with litmus after each drop. Add one drop of 0.1 *M* $K_4Fe(CN)_6$ and observe the color of the solution. A blue coloration is caused by the formation of colloidal potassium ferric ferrocyanide, $KFe[Fe(CN)_6]$, which shows that a small quantity of ferric ion was present in the solution. A larger quantity of ferric ion gives a blue precipitate of Prussian (or Berlin) blue, $Fe_4[Fe(CN)_6]_3$. Record the results in your notebook. Since the solubility of ferric hydroxide is extremely small, the presence of ferric ion in the acidified solution indicates either incomplete precipitation or incomplete separation of the solution from the precipitate. If the presence of ferric ion is shown, repeat the experiment to see if a better separation can be made. This time, in removing the solution from the precipitate place a small piece of cotton over the end of the dropper and draw the solution through it.

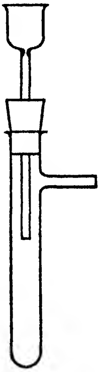


FIG. 5. Semimicro suction filter.

When as good a separation as possible has been made by means of the centrifuge, repeat the precipitation with another sample of ferric chloride solution. This time filter by suction instead of centrifuging. Insert the delivery tube of a small glass Büchner funnel into a one-hole rubber stopper that fits a side-arm test tube, taking care to avoid breaking the funnel. Place the stopper bearing the funnel in the side-arm test tube as shown in Fig. 5 and place a small disc of filter paper in the funnel over the opening into the stem. Connect the side-arm of the test tube to a filter pump or to a vacuum outlet by means of a rubber tube. Wet the filter paper, turn on the suction and pour the solution and precipitate from the test tube to the funnel. When the solution has run through the filter, rinse the test tube with a little water and pour the rinsings into the filter. Acidify the filtrate with 3 *M* HCl and test for ferric ion as before. Record the result in your notebook.

Write in your notebook equations in both molecular and ionic forms for the reaction of ferric chloride with ammonium hydroxide and for the reaction of ferric chloride with potassium ferrocyanide.

9. Application of Directions Written for the Ordinary Scale to Work on the Semi-Micro Scale. The directions in the following exercises are given for work on the ordinary scale with notes in italics where necessary to show how the directions should be modified for the semi-micro scale. Unless otherwise stated, the volumes which are given in milliliters for ordinary-scale work are converted to the semi-micro scale by reading "drops" for "milliliters." If the concentration of a reagent specified is different from the concentration of the solution available, the appropriate change in the quantity should be made, unless otherwise directed. For example, if 5 ml. of 6 *M* HCl is specified and only 3 *M* HCl is available, 10 ml. should be used. It should also be understood that the centrifuge is to be used for separations on the semi-micro scale when the directions call for filtration, unless otherwise directed.

EXERCISE 4

WASHING PRECIPITATES

Mix in a small flask (*micro: in a centrifuge tube*) 2 ml. of 0.5 *M* $FeCl_3$, 2 ml. of 0.5 *M* $Ni(NO_3)_2$ and 16 ml. of water. To this solution add 1 ml. of 6 *M* NH_4OH. Ferric hydroxide should be formed as a brown precipitate.

$$FeCl_3 + 3\,NH_4OH \longrightarrow \underline{Fe(OH)_3} + 3\,NH_4Cl$$

$$Fe^{+++} + 3\,OH^- \longrightarrow \underline{Fe(OH)_3}$$

The line under the ferric hydroxide formula in the equation indicates that ferric hydroxide is precipitated.

Filter and reject the filtrate. (*Micro: centrifuge for 30 seconds or more, remove the clear solution by means of a dropper and reject it.*) Now wash the precipitate on the filter by means of a fine stream of water from the wash bottle and catch the wash solution in a clean test tube. (*Micro: add to the precipitate in the centrifuge tube 1 ml. of water, stir to mix the precipitate and wash water thoroughly, centrifuge again and transfer the clear wash water to a small test tube.*) This solution is to be tested to see how much nickel ion it contains.

Prepare a very dilute nickel nitrate solution as follows. Dilute 1 ml. of 0.5 *M* $Ni(NO_3)_2$ with 98 ml. of water and mix well. (*Micro: dilute two drops of 0.5 M* $Ni(NO_3)_2$ *to 10 ml. in a graduate and pour out into a beaker or 30 ml. test tube for mixing.*) Now dilute 1 ml. of this 0.005 *M* $Ni(NO_3)_2$ with 19 ml. of water (*micro: dilute 1 drop of the 0.005 M solution to 1 ml. in a 3-ml. test tube*) and add a drop or two of 6 *M* NH_4OH (*micro: 1 drop of 3 M* NH_4OH) and about 1 ml. of dimethyl glyoxime solution. A red precipitate should be formed and its quantity is a measure of the quantity of nickel ion present. Dimethyl glyoxime is a very weak acid with the formula $C_4H_6N_2O_2H_2$. One of the hydrogen atoms is replaceable by a metal.

$$Ni^{++} + 2\,C_4H_6N_2O_2H_2 \longrightarrow \underline{(C_4H_6N_2O_2H)_2Ni}$$

Test the wash solution from the ferric hydroxide for nickel ion by adding ammonium hydroxide and dimethyl glyoxime solutions just as in testing the known solution. Compare the quantity of the red precipitate in the wash-water with the quantity in the diluted nickel chloride solution. Record the result in your notebook.

Wash the ferric hydroxide precipitate again with about the same quantity of water as before, and test the wash water for nickel. Repeat the washing and testing until it is found out how many washings are necessary before a wash water is obtained that contains less nickel ion than the very dilute known nickel nitrate solution tested. Record the results in your notebook.

What was the concentration of nickel ion in the very dilute nickel chloride solution that was tested? Approximately what weight in milligrams of nickel ion is contained in 10 ml. (*micro: 1 ml.*) of the nickel chloride solution tested? The atomic weight of nickel may be taken as 59 for this calculation.

10. The General Methods Used in Qualitative Analysis. In Exercise 2 a method is described for separating silver and copper ions from each other when they are present together in a solution. Separation is possible by virtue of the fact that silver ion forms a precipitate by uniting with chloride ion while copper ion does not. One ion possesses a property not possessed by the other. By an extension of this idea very complex substances can be separated into their constituent parts. Of course the larger the number of different substances composing a mixture, the more complicated the matter of analysis becomes. In elementary qualitative analysis courses the number of substances to be sought in any mixture is usually limited to about twenty-four of the commonly occurring cations (metallic ions) and a somewhat smaller number of anions (negative ions.) Methods for the systematic analysis of cations are found in Chapter III, and directions for the detection of anions are found in Chapter IV.

In the analysis of a solution that may contain any or all of twenty to twenty-four cations, the ions are separated on the basis of certain properties into five different groups. Then each group is analyzed separately for the individual ions that it contains. Exercise 5 is devoted to the separation of the groups, while Exercise 6, 7, 8, 10 and 11 deal with the analysis of group precipitates. The directions for the analytical procedures are given both in outline form and in the printed text. The text should be followed carefully while the work is being done, as many details are given there that are not in the outlines. The outlines will serve to give an idea of the process as a whole and should be consulted frequently during the work. In the outlines most of the filtrates and precipitates are numbered. For example, in Outline 2 page 22 hydrochloric acid is added to the original solution and a precipitate is formed. The precipitate is numbered (1) and the filtrate is numbered (2). The filtrate is treated with hydrogen sulfide and another precipitate is formed which is numbered (3), while the filtrate from precipitate (3) is numbered (4), and so on. The purpose of the numbers is to aid in identifying filtrates and precipitates. When a precipitate or filtrate is to be set aside, even if only for a short time, it should be labeled for later identification. Marking the container with the number of the corresponding precipitate or filtrate as given in the outline is a convenient method of labeling.

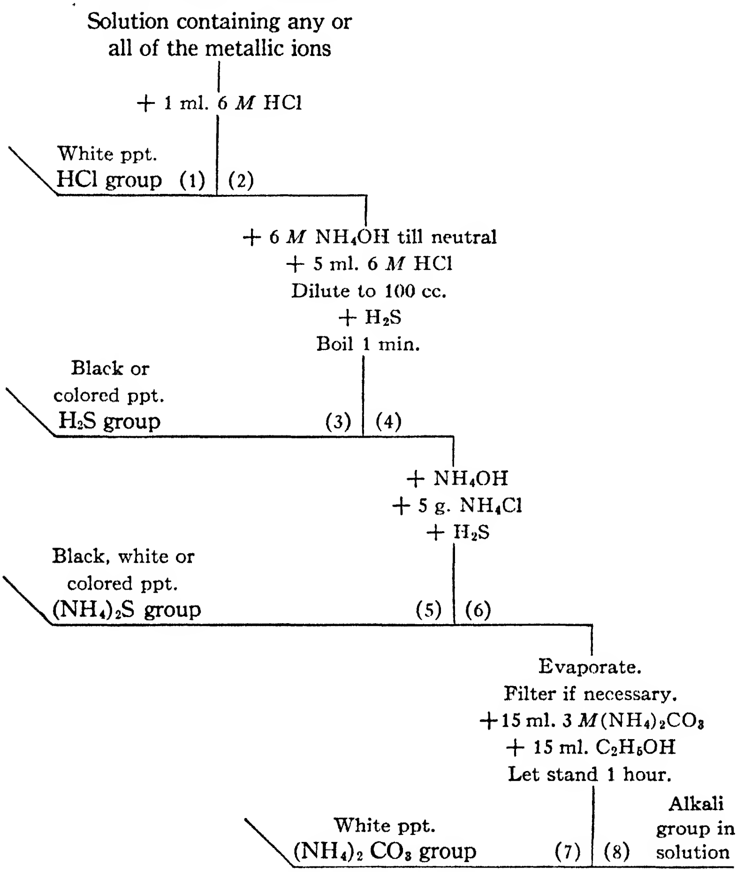
Twenty-four cations can be separated and detected by the procedure given in this book. These ions are separated into the five groups shown in Table I.

TABLE I

GROUPING OF THE CATIONS

HCl *Group*	H_2S *Group*	$(NH_4)_2S$ *Group*	$(NH_4)_2CO_3$ *Group*	*Alkali Group*
Pb^{++}	Hg^{++}	Ni^{++}	Ba^{++}	Na^+
Hg_2^{++}	Pb^{++}	Co^{++}	Sr^{++}	K^+
Ag^+	Bi^{+++}	Zn^{++}	Ca^{++}	NH_4^+
	Cu^{++}	Mn^{++}	Mg^{++}	
	Cd^{++}	Fe^{++}		
	As^{+++}	Al^{+++}		
	Sb^{+++}	Cr^{+++}		
	Sn^{++}			

Exercise 5 shows how the separation into groups is carried out. In Exercise 5 a solution is prepared containing one representative of each group, and the procedure for the separation is carried out as if all of the ions were present. The method of separation of the groups is shown in Outline 2.



OUTLINE 2. Separation of the metallic ions into groups.

EXERCISE 5

SEPARATION OF THE GROUPS

Mix in a small flask (*micro: centrifuge tube*) 3 ml. each of the following solutions:

$0.2\ M\ AgNO_3$
$0.5\ M\ Cu(NO_3)_2$
$0.5\ M\ Ni(NO_3)_2$
$0.5\ M\ Ca(NO_3)_2$
$1\ M\ KNO_3$

Add 1 ml. of 6 M HCl and stir the solution. A white precipitate of silver chloride is formed. This is representative of the hydrochloric acid group.

Separate the silver chloride precipitate from the solution by filtration as in Exercise 2. (*Micro: centrifuge for about 30 seconds, then remove the clear solution by means of a dropper and place it in a 3-ml. test tube.*) Reject the precipitate. Neutralize the acid in the filtrate by adding 6 M NH_4OH, 2 ml. at first and then a few drops at a time, shaking or stirring after each addition and testing with the indicator methyl orange to determine when enough has been added. Methyl orange is pink in color in acid solutions that are not too dilute, but turns yellow when the hydrogen-ion concentration has been reduced to between 10^{-4} and 10^{-5} M. When the solution to be tested is colorless, or has only a faint color, a few drops of a solution of methyl orange can be added to the solution to be tested, if desired. In the present colored solution it is better to use methyl orange paper. Remove a very small portion of the solution on the end of a stirring rod and touch it to the paper. If the solution is acid to methyl orange, the spot touched will be turned pink. Continue the addition of the ammonia until the methyl orange paper just fails to be turned pink, then add 5 ml. of 6 M HCl, dilute the solution to 100 ml. and place in a precipitation flask. (*Micro: add 0.5 ml. of 3 M HCl measured by means of a measuring pipette. Next, measure carefully by means of the measuring pipette five 1-ml. portions of water and deliver them into a 30-ml. test tube. Make a light file mark on the test tube at the level of the surface of the 5 ml. of water. Now empty the tube and transfer the acidified solution from the small test tube to the large one. Rinse the small test tube and add the rinsings to the large one. Finally dilute the solution in the large tube with water until the volume is just 5 ml. as measured by the file mark on the tube.*) Stopper the precipitation flask (*micro: 30-ml. test tube*) with a one-hole rubber stopper bearing a glass tube reaching to a point inside the tube not less than 4 to 5 cm. (1.5 to 2 inches) above the surface of the solution and projecting 3 to 5 cm. (1 to 2 inches) on the outside, as shown in Fig. 1, page 11 (*micro: Fig. 2, page 12.*) Attach the glass tube to the source of hydrogen sulfide gas and pass the gas into the flask with the stopper loosened until it is thought that the air has been displaced by hydrogen sulfide.[1] Then push in the stopper tightly without disconnecting from the source of hydrogen sulfide and shake vigorously to aid the solution

---

[1] **Caution.** When using hydrogen sulfide remember that it is an actively poisonous gas. It will cause headaches even if breathed in low concentrations. However, its effects are immediate, that is, breathing it today will not affect one tomorrow. It is well to have a window at least partly open near the source of hydrogen sulfide gas and to avoid as far as possible getting any quantity of it in the air of the room. The smaller quantity of hydrogen sulfide required for semi-micro qualitative analysis is one of the advantages of work on this scale.

in absorbing the gas. A black precipitate is copper sulfide, CuS, which is representative of the hydrogen sulfide group.

$$Cu^{++} + S^{--} \longrightarrow \underline{CuS}$$

Filter by suction and reject the precipitate of copper sulfide. (*Micro: pour the solution and precipitate into two centrifuge tubes, half in each. Place one on each side of the centrifuge and run the centrifuge for 30 seconds. Rinse the large test tube, rejecting the rinsings. When the centrifuging is complete, draw off the clear solution from above the copper sulfide and place it in the large test tube, rejecting the copper sulfide.*)

Pass more hydrogen sulfide into the filtrate to see if any more precipitate can be formed. If so, precipitation was incomplete and the saturation with hydrogen sulfide and filtration must be repeated until precipitation can be shown to be complete.

When precipitation of the copper sulfide is shown to be complete, add to the filtrate 4 ml. of 6 M NH_4OH and test with red litmus paper. The solution should still be acid; if it is not, add a little 6 M HCl and test again. Weigh 5 g. of solid ammonium chloride, NH_4Cl (*micro: 0.25 g. of* NH_4Cl) and dissolve it in the solution. Then add 6 M NH_4OH a few drops at a time (*micro: one drop at a time from a dropper having a very small tip*), stirring and testing after each addition, until the litmus changes to a violet color. Then add hydrogen sulfide in the same manner as in the precipitation of the copper sulfide. A black precipitate is nickel sulfide, NiS, and is representative of the ammonium sulfide group.

$$Ni^{++} + S^{--} \longrightarrow \underline{NiS}$$

Filter, and transfer the filtrate to the precipitation flask. Reject the precipitate of nickel sulfide. Add 1 ml. of 6 M NH_4OH to the filtrate and pass in hydrogen sulfide again to test the filtrate for completeness of precipitation. If any further precipitate is formed, filter again to remove it from the solution and test the filtrate again by adding ammonia and hydrogen sulfide. When precipitation has been shown to be complete, transfer the solution to a pyrex beaker or porcelain casserole (*micro: porcelain crucible*) and set it over a low flame or on a hot plate and allow it to evaporate until the volume is less than 10 ml. (*micro: 0.5 ml.*).[1] Dilute the solution to 10 ml. (*micro: 0.5 ml.*), stir well, and if there is any undissolved matter filter and reject it. Calcium and potassium ions should remain in the solution.

To the 10 ml. of solution containing calcium and potassium ions add 15 ml. of 3 M $(NH_4)_2CO_3$ and 15 ml. of denatured alcohol (*micro: 1 ml. of each*) and mix well by shaking or stirring. A white precipitate is calcium carbonate, $CaCO_3$, which represents the ammonium carbonate group precipitate. Filter and reject the precipitate.

---

[1] While this evaporation is going on, Exercise 6 may be started.

Transfer the filtrate from the calcium carbonate to a porcelain casserole, or pyrex beaker (*micro: porcelain crucible*), support the casserole by means of a ring or tripod with a wire gauze under it (*micro: support on a triangle*) and evaporate to dryness. When only a little water remains, and considerable solid matter, spattering may occur. If this happens, remove the flame until the spattering stops. Then heat very carefully until the mass is dry and does not spatter when strongly heated. Now place the casserole under a hood or in such a position that the top of the casserole is as high as the opening in a fume duct and not more than one inch away. This is to avoid polluting the laboratory with fumes of sublimed ammonium salts which are copiously given off when the casserole is heated.

Continue heating carefully, increasing the temperature when spattering ceases and finally heat until the smoke of ammonium salts stops coming off. See that no ammonium salts remain on the upper part of the container. If desired, the burner can be inverted and the mass can be heated from above. This minimizes spattering and makes the process more rapid. The process of evaporating the liquid of a solution and then heating the residue is implied by the words "evaporate to dryness and bake."

Dissolve the residue in 2 to 3 ml. of water and transfer to a test tube (*micro: centrifuge tube*). In another test tube dissolve a small quantity of solid sodium cobaltinitrite, $Na_3Co(NO_2)_6$, in 1 or 2 ml. of water. Add the latter solution to the solution of the residue. A yellow precipitate is potassium sodium cobaltinitrite, $K_2NaCo(NO_2)_6$.

In your notebook write molecular and ionic equations for all of the reactions that take place in this exercise.

EXERCISE 6

ANALYSIS OF THE HYDROCHLORIC ACID GROUP

Mix in a centrifuge tube 2 ml. each of the following solutions:

$0.2\ M\ AgNO_3$
$0.05\ M\ Hg_2(NO_3)_2$
$0.1\ M\ Pb(NO_3)_2$

and analyze according to the directions in Chapter III, Sections 11 to 13.

Note that tests are to be made only for the ions of the hydrochloric acid group at this time, as it is known that the solution contains no others. Therefore, modify the directions of the systematic analysis accordingly.

In your notebook calculate the quantities in milligrams of each of the three cations contained in the sample. Calculate also the volume of 6 M HCl (*micro: 3 M*) required to precipitate the three chlorides, when the sample is taken as specified above, and calculate the volume of the hydrochloric acid solution that would be required if the sample analyzed were 250 mg. (*micro: 25 mg.*) of silver metal. In such a case the metal would be converted to silver nitrate by the action of nitric acid, to prepare it for analysis. Would more acid or less be required if the sample were 250 mg. (*micro: 25 mg.*) of lead metal? Atomic weights are given on the inside front cover of the book.

EXERCISE 7

ANALYSIS OF THE HYDROGEN SULFIDE GROUP

Mix 3 ml. of 6 M HCl and 2 ml. each of the following:

0.1 M $HgCl_2$
0.1 M $Pb(NO_3)_2$
0.1 M $Bi(NO_3)_3$
0.5 M $Cu(NO_3)_2$
0.2 M $Cd(NO_3)_2$
0.2 M $AsCl_3$
0.2 M $SbCl_3$
0.2 M $SnCl_4$ (stannic chloride)

A precipitate of lead chloride may be formed. In this case filter and receive the clear solution in a precipitation flask (*micro: transfer the solution to a 30-ml. test tube*), rejecting the lead chloride. The solution so prepared is to be considered as the filtrate from the hydrochloric acid group and analyzed according to the directions in Chapter III, Sections 14 to 24, page 37. The results of the analysis are to be considered satisfactory only if the final tests show the presence of each of the cations known to have been present in the original solution and the tests come out as described in the text.

It is probable that the analysis will have to be interrupted at one or more points between laboratory periods. It is to be understood that qualitative analysis procedures may be interrupted and taken up again later at any points except where the directions specifically indicate that the procedure must not be interrupted. To keep a filtrate between laboratory periods, it should be placed in a flask or test tube, tightly stoppered and labelled. It will be found less easy to remember the identity of a solution than one would expect when putting it away. A precipitate should be kept moist. It may be kept in a stoppered flask, test tube, or centrifuge tube, and if necessary a little water may be added to insure the presence of sufficient moisture. A precipitate on a filter paper may be preserved by placing paper and precipitate in a test tube, adding a few drops of water and stoppering tightly.

When the analysis of the group has been finished, place in separate test tubes one-milliliter samples of each of the solutions of which the group sample was composed. Add to each a few milliliters of water and then some hydrogen sulfide. Observe the colors of the various sulfides and record them in your notebook. Observation of the color of a group precipitate can give useful information as to its composition, if the colors of the possible components are known. Conclusions based on color need to be confirmed by further tests before being accepted as final.

Write in your notebook an ionic equation for the precipitation of each of the sulfides of the hydrogen sulfide group. Also, calculate the volume of hydrogen sulfide gas at 0° and 760 mm. pressure that would be required to precipitate the copper ion resulting from the action of nitric acid on 0.25 g. (*micro: 25 mg.*) of copper. This is the largest quantity of copper ion that could be present in a sample taken for analysis if the directions given in Exercise 9 with respect to the sizes of samples are followed.

EXERCISE 8

ANALYSIS OF THE AMMONIUM SULFIDE GROUP

Mix in a test tube 2 ml. each of the following solutions:

$0.5\ M\ Ni(NO_3)_2$
$0.5\ M\ CoCl_2$
$0.5\ M\ Zn(NO_3)_2$
$0.5\ M\ MnCl_2$
$0.5\ M\ FeCl_3$
$1\ M\ Al(NO_3)_3$
$0.5\ M\ Cr(NO_3)_3$

Start at the beginning of the systematic analysis, beginning with Chapter III, Section 11, page 35, and continue through the analysis of the ammonium sulfide group. No members of the first two groups are present; nevertheless test for these groups in order to experience the negative results. Notice that the iron is present in the beginning as ferric ion, Fe^{+++}, which is an oxidizing agent. Hydrogen sulfide is a reducing agent capable of reducing ferric ion. The hydrogen sulfide is oxidized by the ferric ion to sulfur. Does this account for the precipitate that you observe in testing for the hydrogen sulfide group? To get rid of a finely divided sulfur precipitate, boil the solution to coagulate the precipitate; then it can be removed by filtering or centrifuging.

Determine experimentally the colors of the various compounds in the group precipitate and record them in your notebook. For the sample of an iron compound use ferrous sulfate, $FeSO_4$, instead of ferric chloride.

Write in your notebook an equation for the reaction of ferric ion and hydrogen sulfide, also ionic equations for the reaction of ammonium hydroxide on aluminum and chromium nitrates.

EXERCISE 9

THE ANALYSIS OF AN ALLOY

It will be assumed that the alloy to be analyzed is composed of metals whose ions are members of the first three groups, which is true of many alloys. The first step in the analysis is to convert the metals of the alloy to the corresponding metallic ions and bring the ions into solution. The solution is then analyzed for the ions of the first three groups by the methods illustrated in Exercises 6, 7 and 8.

(*a*) *Dissolving the Alloy.* To find how to dissolve the alloy, try tests on some small portions. Add to a 0.05 to 0.1 g. portion (*micro: 5 to 10 mg.*) in a test tube a little 6 M HNO_3 and heat. If this treatment fails to convert the alloy into soluble compounds, try 16 M HNO_3 in the same way. If neither dilute nor concentrated nitric acid dissolves the alloy, some suggestions as to what to try next may be found in Chapter V.

When the most satisfactory method of dissolving the alloy has been ascertained by experiments on small portions, weigh on a rough balance a sample of between 0.2 and 0.25 g. (*micro: 20 to 25 mg.*) of the alloy, place it in a porcelain casserole (*micro: in a crucible*) and dissolve it, warming, if necessary, to hasten the reaction. When the reaction with acid is complete, evaporate (under the hood or near an opening in the fume duct, because of the acid fumes) until most of the excess acid has been driven off. Avoid evaporating to dryness. Then dissolve in the smallest possible quantity of water, heating and adding a little acid if necessary.

(*b*) *Analysis of the Solution.* If nitric acid was used to dissolve the alloy and a clear solution was obtained, start the analysis of the solution at Section 11, Chapter III, page 35. If hydrochloric and nitric acids were used and a clear solution obtained, the hydrochloric acid group must be absent. In this case start the analysis with the hydrogen sulfide group, Section 14, Chapter III, page 37.

If hydrochloric acid together with a little nitric acid was used and a white residue remained undissolved, filter and treat the residue as the hydrochloric acid group precipitate and the filtrate as the filtrate from the hydrochloric acid group; but before doing this read the next section.

(*c*) *Residue from Hydrolysis.* A residue remaining undissolved after treatment with concentrated hydrochloric acid should not be confused with a precipitate resulting from the hydrolysis of a soluble chloride or nitrate. If the solution should be clear before evaporation, but a precipitate remain undissolved when water is added after evaporation, the precipitate is probably the result of hydrolysis. Bismuth, antimony and tin chlorides and nitrates are hydrolyzed to give compounds that are only slightly soluble in water, but are dissolved by acids. For example, bismuth chloride is hydrolyzed in accordance with the following equation:

$$\mathrm{BiCl_3 + H_2O \rightleftarrows \underset{\text{Bismuth oxychloride}}{\underline{BiOCl}} + 2\,HCl}$$

A decrease in the hydrochloric acid concentration favors hydrolysis, while an increase is unfavorable. When a precipitate is formed by hydrolysis, therefore, the addition of more acid will get it into solution. If the hydrochloric acid group is absent and hydrolysis occurs with formation of a precipitate, the precipitate need not be dissolved. The oxychlorides react with hydrogen sulfide to give sulfides in the same way that the chlorides do.

(*d*) *Control and Blank Tests.* It may happen in the course of the analysis that one or more of the tests will be indecisive. In such a case the best plan is to take from the side shelf a sample of a solution containing the ion in question, add any reagents required to make it like the unknown solution, and then make the test on the known solution so prepared. It may be necessary to repeat the test on a known solution with a larger or smaller quantity of the ion under test to imitate the unknown better. If the results for the known solution still do not resemble those for the unknown, it is advisable to make a test on a solution to which none of the ion in question has been added, but which is in other respects a good imitation of the unknown solution. A "blank test" like this last one shows what a negative test looks like. It may also show that a small positive test can be obtained for the ion in question from the reagents alone.

(*e*) *Quantities of the Components.* Try to form an opinion as to the relative quantities of the components of the alloy. By observing the sizes of the precipitates, the components can probably be grouped in three classes: (1) those present in moderate or small proportion, (2) those present in large proportion and (3) those present only in traces. The latter are components present in such small quantities that positive tests can just barely be obtained. Iron is present in traces in quite a variety of materials.

(*f*) *Notebook Record.* Record in your notebook the treatment used to dissolve the sample, describing any treatments that failed, and give the components of the alloy and your estimate of the proportions.

EXERCISE 10

ANALYSIS OF THE AMMONIUM CARBONATE GROUP

Mix in a test tube 2 ml. each of the following solutions:

0.2 *M* $\mathrm{BaCl_2}$
0.2 *M* $\mathrm{SrCl_2}$
0.5 *M* $\mathrm{Ca(NO_3)_2}$
1 *M* $\mathrm{Mg(NO_3)_2}$

Turn to the analysis of the ammonium carbonate group, Section 35, Chapter III, page 62, and, omitting Section 34 on the preliminary treatment, start with the precipitation of the group and continue through the analysis of the group.

Barium and strontium chromates are both precipitated readily. Under what conditions can barium chromate alone be precipitated from a solution containing both barium and strontium ions when an excess of chromate ion is added? What condition is necessary for the precipitation of strontium chromate? Is barium chromate precipitated under the conditions favorable for strontium chromate? Devise experiments to aid in answering these questions, if necessary, and describe the experiments in your notebook and give the conclusions.

EXERCISE 11

THE ALKALI GROUP

The alkali group is not precipitated as a group, because no cations other than sodium, potassium and ammonium ions are present in the filtrate from the ammonium carbonate group. Before testing for sodium and potassium ions, the ammonium salts that have been added to the solution in the precipitation of the ammonium sulfide and ammonium carbonate groups must be completely removed. The reason for their removal is that ammonium ion resembles potassium ion chemically and could easily be mistaken for it.

Mix in a porcelain casserole (*micro: porcelain crucible*) 2 ml. of 1 M KCl, 2 ml. of 1 M NaCl and 5 ml. of 3 M $(NH_4)_2CO_3$. This is an imitation of the filtrate from the ammonium carbonate group. Add 2 ml. of 3 M HCl and evaporate carefully to dryness.

Heat the casserole containing the dry residue until the ammonium salts have been volatilized completely and no more white smoke is evolved on heating either the bottom or the upper parts of the vessel. Dissolve the residue in about 4 ml. of water and transfer to a test tube. If any undissolved residue is present, filter and reject it. Remove about half of the clear solution to another test tube. Use one portion of the solution for the potassium ion test and another for the sodium ion test as described in Sections 41 and 42, Chapter III, page 69.

Test small portions of a solid ammonium salt for ammonium ion by the two tests described in Section 43, Chapter III, page 69, first by the recognition of ammonia liberated from the salt by its odor and second by the chemical test. For the latter, use a sample of between 5 and 10 mg.

EXERCISE 12

ANALYSIS OF A SECOND ALLOY

Analyze an alloy that may contain metals whose ions belong to any of the first four groups, but not the alkali group. The alkali metals are seldom present in practical alloys. The same is true of the alkaline earth metals, barium, strontium and calcium, but magnesium is often present in small quantities and in a few alloys is one of the chief components. Before trying to learn how to dissolve the alloy read the section on dissolving alloys in Chapter V, and also review Exercise 9. It may be expected that this alloy will be more difficult to get into solution than the first, although this will not always be the case.

EXERCISE 13

THE DETECTION OF ANIONS

Read Chapter IV as far as the section headed "Analysis of the Halogen Group," page 78.

Mix in a test tube (*micro: centrifuge tube*) 2 ml. each of the following solutions:

$1\ M$ NaCl
$0.5\ M$ KBr
$0.2\ M$ KI
$0.1\ M$ $K_4Fe(CN)_6$
$0.2\ M$ NH_4SCN

The anions of these salts belong to Group 1 of the anions. Ferricyanide ion, which also belongs to Group 1, is omitted because it oxidizes iodide ion to iodine. Bore a hole through a cork that fits the test tube and pass a piece of glass tubing through it. This makes a stopper through which hydrogen sulfide can be passed. Pass some hydrogen sulfide into the solution to add sulfide ion to the others. Remove about 2 ml. of the solution to another test tube and add one ml. of $0.2\ M$ $AgNO_3$. A precipitate shows the presence of the halogen group of the anions.

Analyze the remainder of the solution by the method described in Section 51 of Chapter IV, page 78.

When this has been finished, practice similarly the analysis of group 2 of the anions. Mix in a test tube the following solutions, (sulfite ion being omitted because it reduces dichromate ion):

$0.2\ M$ Na_2SO_4, 3 ml.
$1\ M$ K_2CrO_4, 1 ml.
$1\ M$ KF, 3 ml.

Test for the group in the manner described on page 76, using 2 ml. of the solution, then use the remainder for practicing the analysis of Group 2, page 82.

As an example of the oxidizing group (page 77) take 5 ml. of $0.2\ M$ $NaNO_2$. It is not necessary to include the other ions of Group 3. Make a test for the presence of the group (page 77) and then make tests for arsenate and arsenite ions, nitrate and nitrite ions together, and finally for nitrite ion alone, page 84.

Mix a small quantity of solid sodium carbonate with about an equal quantity of solid antimony sulfide. Test this material for carbonate and sulfide ions as described on page 87.

EXERCISE 14

DETECTION OF ANIONS IN AN UNKNOWN MIXTURE OF SODIUM AND POTASSIUM SALTS

Analyze an unknown mixture of soluble sodium and potassium salts for anions only. The treatment with sodium carbonate solution as described on page 74, Chapter IV, is unnecessary and should be omitted.

EXERCISE 15

ANALYSIS OF A MIXTURE OF SALTS

Analyze for both cations and anions a mixture of salts that is not necessarily soluble in water, but which should be capable of being brought into solution by acids. Weigh a 0.5 g. portion (*micro: 50 mg.*) for analysis for the cations. See Chapter V for suggestions as to the procedure for dissolving solids. The sample for anions should be given the sodium carbonate treatment as described on page 74, Chapter IV.

EXERCISE 16

ANALYSIS OF AN INDUSTRIAL PRODUCT OR A MINERAL

Analyze for both cations and anions a material that may be either an industrial product or a mineral. Weigh a 0.5 sample (*micro: 50 mg.*) for analysis for the cations. It may be possible to dissolve the material by means of acids, but in some cases a carbonate fusion will be necessary. For directions for this see Chapter V. Before carrying out the fusion of the sample, it is advisable to try a fusion with only a mixture of sodium and potassium carbonates and no sample present. When this has been brought to the liquid state successfully, the fusion of a mixture containing the sample can be undertaken. The sample for the anion analysis should be given the usual sodium carbonate treatment even if a fusion is necessary for the sample for cations.

Chapter III

SYSTEMATIC ANALYSIS FOR THE CATIONS

In the directions for the systematic analysis it is assumed that the material to be analyzed has been brought into solution. If this has not already been done, Chapter V may be consulted as to methods for getting solid materials into solution. It is further assumed that organic matter, including oxalate and tartrate ions, is absent and that fluoride, silicate, cyanide, ferrocyanide and ferricyanide ions are absent.[1] The quantities of reagents specified in the directions are calculated on the assumption that the samples taken for analysis will contain not more than 0.25 g. of an alloy or 0.5 g. of a material that consists only partly of metallic elements (*or 25 mg.* and *50 mg. respectively on the semi-micro scale*). If the material to be analyzed is a solution, the volume taken should be such as to contain not more than 0.25 g. of metallic ions.

As indicated in connection with Exercise 5, the method of analysis consists in the separation of the cations into five groups on the basis of certain precipitation reactions, then further separation of each of the groups into the separate ions and finally identification of these. The groups of cations must be precipitated from the solution in a certain definite order, and it is usually best to analyze each precipitate as soon as it is obtained, reserving the filtrate containing the groups not yet precipitated for future analysis.

Absence of a group precipitate when a test for the group has been properly made may be taken as proving the absence of all members of the group. On the other hand, when a group precipitate is obtained, no definite conclusions may be drawn except that one or more of the ions of the group must be present. Analysis of the precipitate then gives further evidence and leads to definite conclusions.

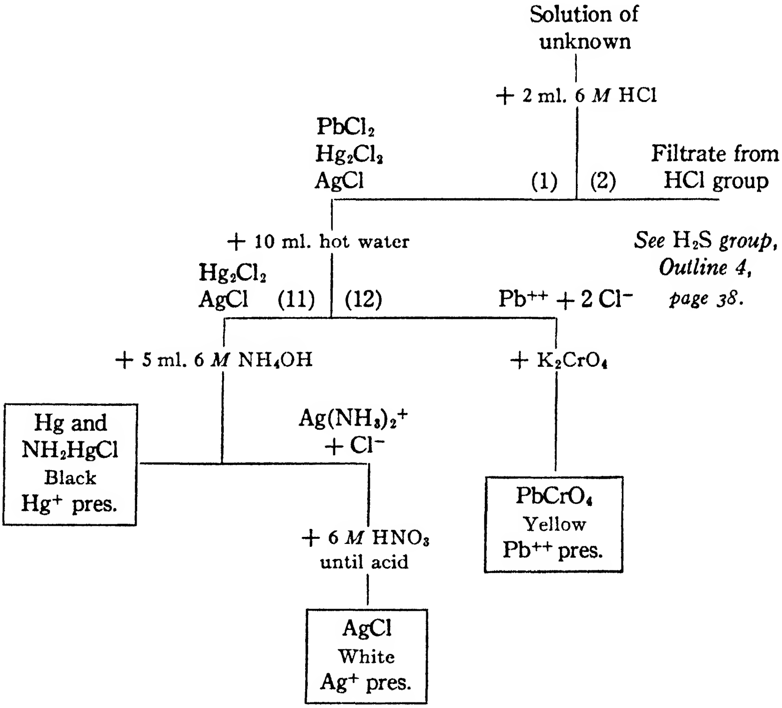
---

[1] It is presumed that in an elementary course *soluble* unknown materials containing these anions will not be given for *cation* analysis. Materials requiring carbonate fusion may contain some of these anions.

It should be emphasized that the directions below must be followed carefully if conclusive results are to be obtained. Carelessness and attempted short-cuts are likely to result in inconclusive tests and either erroneous conclusions or loss of time.

THE HYDROCHLORIC ACID GROUP

The first group to be precipitated is the hydrochloric acid group, which consists of ions that unite with chloride ion to form slightly soluble chlorides, namely lead, silver and mercurous ions. The group is precipitated by the addition of hydrochloric acid to a solution containing any or all of the cations. Outline 3 shows the procedure for precipitating and analyzing the hydrochloric acid group, and Sections 11 to 13 give the procedure in detail.



OUTLINE 3. Precipitation and analysis of the hydrochloric acid group.

11. Precipitation of the Group. Test the solution containing the cations of the unknown material with litmus and if basic, acidify with 6 *M* HNO_3. Then add 2 ml. of 6 *M* hydrochloric acid to precipitate the group. Stir well and, if there is a precipitate, filter. Reserve the filtrate for the precipitation of the other groups, or if there is no precipitate, consider the entire solution as the filtrate from the hydrochloric acid group and pass on to the hydrogen sulfide group.[1] Wash the precipitate with two 5-ml. portions of 1 *M* hydrochloric acid,[2] and reject the wash solution.

12. Lead Ion. Wash the precipitate on the filter with about 10 ml. of hot water, allowing the water to run through the filter into a test tube. (*Micro: add about 10 drops of water to the precipitate in a centrifuge tube, heat by immersing the lower part of the tube in boiling water,[3] stir well, centrifuge immediately on taking the tube from the hot water and remove the solution to a 3-ml. test tube while still hot.*) Add to the filtrate in the test tube a few drops of 1 *M* K_2CrO_4 to test for lead ion. A yellow precipitate of lead chromate indicates the presence of lead ion. (*Micro: centrifuge if it is desired to estimate the quantity of the precipitate.*) Absence of a precipitate indicates the absence of lead ion, although it may still be found present in the hydrogen sulfide group. The lead chromate precipitate may be rejected.

13. Mercurous and Silver Ions. A residue remaining on the filter paper (*micro: in the centrifuge tube*) after the hot water treatment may be mercurous chloride or silver chloride or undissolved lead chloride or any combination of these. Repeat the treatment with hot water until no more lead chloride is dissolved, as shown by testing the hot water for lead ion. If the precipitate is completely dissolved by this treatment, mercurous and silver ions are absent. Pour over the residue, if any remains, 6 ml. of 6 *M* NH_4OH and catch the filtrate in a test tube. Blackening of the residue on the filter indicates the presence of mercurous ion.

Acidify the filtrate containing the ammonium hydroxide with

---

[1] See Note 2 following Section 13.

[2] See Note 3 for the preparation of the diluted acid and Note 4 for details as to how to wash a precipitate.

[3] See Note 6 on page 37.

nitric acid; this will require 5 ml. or more of the 6 *M* acid. Shake or stir to mix well. A white precipitate indicates the presence of silver ion.[1] (*Micro: centrifuge to estimate the quantity.*)

NOTES

1. The quantity of hydrochloric acid added, 2 ml. of 6 *M* HCl, should be sufficient to precipitate all of the hydrochloric acid group, provided that the quantity of the unknown material in the sample did not exceed that specified above. If it is suspected that the group may not be completely precipitated, the filtrate may be tested by the addition of more hydrochloric acid. It is very essential that the group separations be made complete.

2. The filtrate from the hydrochloric acid group may contain the other four groups. If a solution like this is to stand for any length of time before it is used, for instance until the next laboratory period, the flask containing it should be carefully stoppered and labeled. This filtrate can be labeled (2). Number (2) can be found from Outline 2 to mean the filtrate from the hydrochloric acid group.

3. Acid of 1 *M* concentration can be made from 6 *M* acid by diluting 2 ml. to 12 ml., or from 3 *M* acid by diluting with twice its volume of water. The diluted solution should be mixed well.

4. Some information about washing a precipitate is given in Exercise 3. For ordinary-scale work when the precipitate is filtered from the solution from which it was precipitated, washing should be accomplished in the following manner. Direct a stream from the wash bottle that contains the wash solution on the edge of the filter paper. When all of the precipitate has been wet by the wash solution, allow all the solution to run through. If a precipitate is to be washed more than once, all of the previous wash solution should be allowed to pass through the filter before more is added.

The reason for washing precipitates after filtration is to free them from the liquid in which they were formed, often called the "mother-liquor." The mother-liquor may contain substances that would interfere with the tests for the cations in the precipitate. Hence, washing the precipitate should not be omitted. Wash solutions after use may generally be thrown

---

[1] Since silver is expensive, residues containing it are sometimes saved for recovery of the silver. If a bottle for this purpose is provided in the laboratory, put all waste silver residues in it rather than in the waste jar or the sink. Solutions containing silver salts may be treated with hydrochloric acid to precipitate silver chloride before putting into the silver-residues bottle to avoid the storage of a large volume of liquid.

away, although ordinarily no harm is done if they are added to the filtrate.

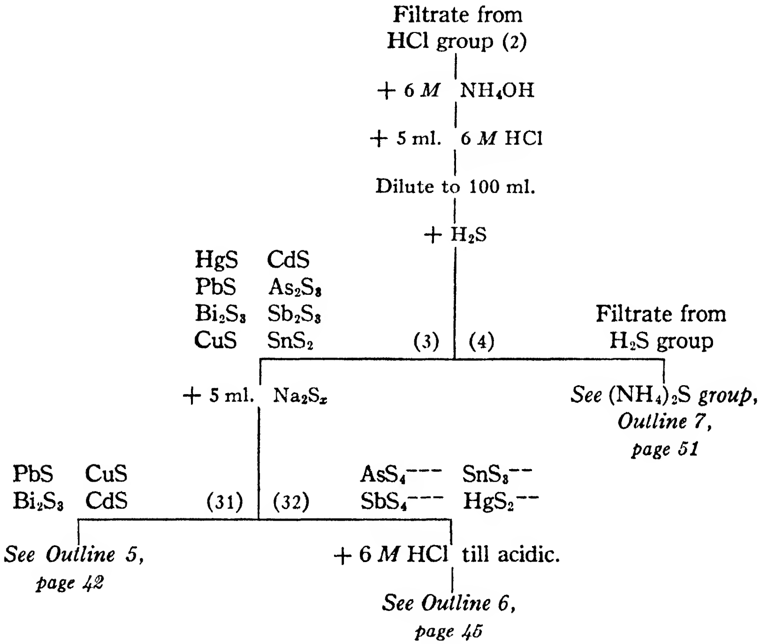
5. A solution of hydrochloric acid is used for washing the hydrochloric acid group precipitate instead of pure water, because lead chloride is much less soluble in a solution containing considerable chloride ion than in water or a solution containing no chloride ion. The solubilities of the other chlorides are affected similarly, but they are very small even in pure water. Water could be used for washing silver and mercurous chlorides without appreciable loss except that these chlorides might go into the colloidal state and become suspended in the wash-water in the absence of electrolytes.

6. Heating a liquid in a narrow tube such as a 3-ml. test tube or centrifuge tube is conveniently accomplished by immersing the lower half or more of the tube in hot water. If the attempt is made to heat a liquid in such a small tube over a flame, there is considerable danger of the liquid being driven from the tube by sudden violent boiling. It is advisable to heat by immersing the container in hot water whenever it is necessary to heat a liquid in a small tube. When it is necessary in semi-micro analysis to evaporate a liquid, this can be accomplished by transferring the liquid to a porcelain crucible or small beaker and heating by means of a flame or a hot plate.

THE HYDROGEN SULFIDE GROUP

The hydrogen sulfide group consists of the ions in the filtrate from the hydrochloric acid group that can unite with sulfide ion in an acid solution to form sulfide precipitates. The group is precipitated (after careful regulation of the hydrogen ion concentration of the solution) by saturating the solution with hydrogen sulfide gas. The hydrogen sulfide group is divided into two sub-groups. By treatment of the precipitated sulfides with sodium sulfide and sodium disulfide, the sulfides of mercury, arsenic, antimony and tin are dissolved and can be separated from the others by filtration. These are the tin sub-group. The others constitute the copper sub-group. Outline 4 shows the precipitation of the group and the separation of the copper and tin groups, and Outlines 5 and 6 show the analyses of these sub-groups. The procedure is given in detail in Sections 14 to 24.

14. Precipitation of the Group. The hydrogen sulfide group is to be precipitated from the filtrate from the hydrochloric acid group. To the filtrate from the hydrochloric acid group add 6 *M* NH_4OH a few drops at a time (*micro: one small drop of 3 M* NH_4OH *at a time*), shaking or stirring after each addition, and testing with methyl orange (see Exercise 5) until the solution turns yellow methyl orange to a very pale pink or orange color. The addition of ammonium hydroxide may cause a precipitate to form, but this will not interfere. Then add just 5 ml. of 6 *M* HCl. (*Micro: 0.5 ml. of 3 M HCl.*) If there should be a colored precipitate left after the addition of the acid, heat until it dissolves. A white precipitate will do no harm. Dilute the solution to 100 ml. (*micro: dilute to 5 ml. in a 30-ml. test tube*) with distilled water, disregarding any precipitate that is formed, and pour the solution into the precipitation flask. (*Micro: a 30-ml. test tube will serve in place of a flask.*) Pass in hydrogen sulfide gas, shaking the flask continuously, until the solution is saturated with the gas. Then heat the solution containing the precipitate to the boiling point.



OUTLINE 4. Precipitation of the hydrogen sulfide group and separation into sub-groups.

Filter by suction (*micro: filter by suction unless the quantity of precipitate is small, in which case centrifuge*) and save the filtrate. Wash the precipitate at least twice with a solution made by passing hydrogen sulfide into 50 ml. of water and adding about 1 ml. of 6 *M* HCl. The wash solution can be rejected.

Before proceeding, the filtrate should be tested to see if the precipitation was complete. Heat the filtrate to the boiling point and pass in more hydrogen sulfide. Allow the solution to cool considerably before disconnecting the flask from the source of hydrogen sulfide. Absence of a colored precipitate shows that precipitation was complete the first time. In this case the solution can be set away until the ammonium sulfide group is to be precipitated.

If there is a precipitate on second addition of hydrogen sulfide, the mixture must be filtered and the precipitate washed and united with the first one for the treatment below. The filtrate must be tested again for completeness of precipitation, and the treatment must be repeated until precipitation is complete.

If on the second treatment with hydrogen sulfide a finely divided yellow precipitate is formed slowly, arsenate ion, $AsO_4^{\equiv}$, is probably present. This reacts slowly with hydrogen sulfide. The reaction can be hastened by evaporating to small volume, adding more hydrochloric acid and a small crystal of iodine or ammonium iodide, heating and then passing in hydrogen sulfide.

15. Separation into Sub-Groups. Transfer the hydrogen sulfide group precipitate to a casserole (*micro: crucible*) without the addition of water, if possible. This may be done by first washing the stem of the funnel, then inverting the funnel over the casserole and blowing sharply through the stem. The filter paper can then be removed with the help of a glass rod. If the quantity of precipitate is very small, it may be necessary to wash it from the paper by water. In this case pour off as much of the water as possible. Add to the precipitate 5 ml. of 2.5 *M* sodium polysulfide solution.[1] (*Micro: after the addition of the sodium polysulfide, transfer the mixture to a centrifuge tube.*)

Thoroughly mix the precipitate and the sodium polysulfide solution in the casserole and then heat the casserole on a steam bath or over a beaker of boiling water, stirring continuously,

---

[1] Sodium polysulfide solution contains sodium sulfide, Na_2S, and sodium disulfide, Na_2S_2.

for four minutes, unless the precipitate is completely dissolved in less time. Mercuric, arsenic, antimony and tin sulfides react to form the ions $HgS_2^{=}$, $AsS_4^{=}$, $SbS_4^{\equiv}$, and $SnS_3^{\equiv}$ which pass into the solution. The other sulfides are not appreciably affected. Filter and wash the precipitate remaining on the filter (presumably the copper group) twice with water, rejecting the washings.

Test the filtrate containing the sodium polysulfide to see whether or not any of the tin group is present, by adding 4 ml. of 6 *M* HCl, testing with litmus, and if necessary adding more acid 1 ml. at a time until the solution is acid to litmus. A nearly white, finely divided precipitate is sulfur, which indicates that the tin group is absent. Sometimes traces of the copper group color the sulfur brown. A black, yellow or orange precipitate shows that the tin group is present. If in doubt as to the color of the precipitate, acidify 5 ml. of the original sodium polysulfide solution and compare with the unknown precipitate. If the unknown precipitate is brown, add a drop of copper nitrate solution to some sodium polysulfide solution, filter, and then acidify and compare with the unknown precipitate.

If the tin group is shown to be absent, the next four paragraphs after this one may be omitted. In this case proceed directly to the analysis (according to Sections 16 to 19) of the yellow or black precipitate that did not dissolve in the sodium polysulfide solution.

If the tin group is present, and if in addition there is no precipitate left on the filter (*micro: in the centrifuge tube*), the separation is complete and the copper group is absent. The tin-group precipitate can then be analyzed as directed in Sections 20 to 24.

If the tin group is present, and if in addition a precipitate remains on the filter (*or in the centrifuge tube*) the copper group *may* also be present, but this has not been proved, because it has not been shown that enough sodium polysulfide has been added to dissolve all of the tin group. Therefore, treat the precipitate that was not dissolved with another 5-ml. portion of the sodium polysulfide solution in the same manner as before, and filter. Acidify the new sodium polysulfide filtrate to see if any more of the tin group is present in it. If a precipitate of nothing but sulfur is obtained (possibly slightly colored by traces of the copper group), the separation was complete the first time. In this case reject this solution and the sulfur. The precipitate that remained undissolved is the copper group precipitate.

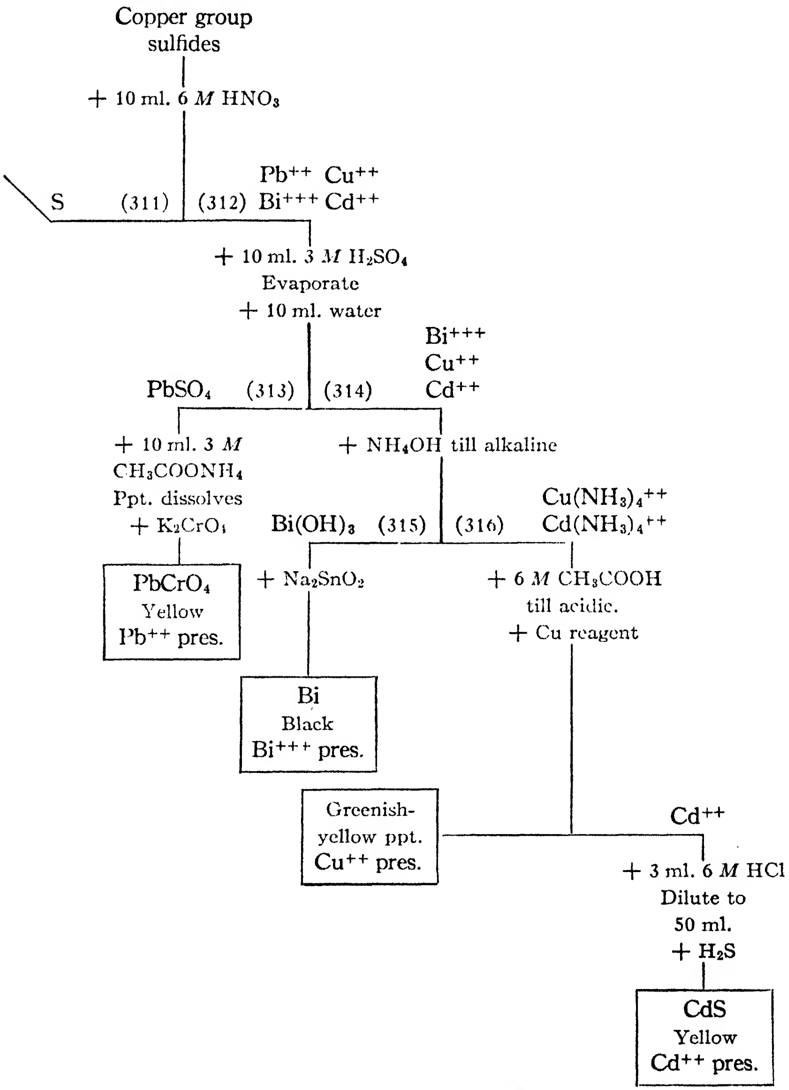
If a yellow, orange or black precipitate is obtained on acidifying the second sodium polysulfide filtrate, add this precipitate together with the solution from which it was precipitated to the similar one obtained in the first treatment with sodium polysulfide. If any precipitate remained undissolved in the second treatment with sodium polysulfide, treat it with a third 5-ml. portion of sodium polysulfide solution. The residue undissolved by the third portion of sodium polysulfide may be taken as the copper group precipitate. Combine all of the various portions of the tin group precipitate without filtering and set the mixture aside until the tin group is to be analyzed.

If both copper and tin groups are present, analyze the copper group first, as directed in Sections 16 to 19, and save the tin group, without filtering, until it can be analyzed as directed in Sections 20–24.

16. Dissolving the Copper-Group Precipitate. Wash the copper-group precipitate into a beaker by making a hole in the filter paper and directing on the precipitate a stream of water from the wash bottle. (*Micro: leave in the centrifuge tube.*) Pour off as much of the water as possible without loss of precipitate. Add 10 ml. of 6 *M* HNO_3, mix, and heat until a reaction takes place, and as long as the reaction continues. Filter, if necessary, and reject the residue, which is largely or entirely sulfur. The filtrate may contain lead, bismuth, copper and cadmium nitrates.

17. Lead Ion. To the solution containing lead, bismuth, copper and cadmium ions add 10 ml. of 3 *M* sulfuric acid. Put the solution into a porcelain casserole or pyrex beaker (*micro: porcelain crucible*) and evaporate carefully (under a hood or near a hole in the fume duct) until white fumes of sulfur trioxide appear. These fumes do not disappear as soon after they leave the dish as the steam and nitric acid vapors that come off first. Cool the mixture by immersing the lower part of the vessel in cold water, and pour the mixture a little at a time into 10 ml. of cold water in a test tube, keeping the solution cool all the time.

Rinse the casserole with a little of the solution from the test tube and pour the rinsings back into the test tube. Let the mixture stand for about 5 minutes *but not longer.* Absence of a precipitate shows the absence of lead ion. In this case the solution need not be filtered, but can be treated as described



OUTLINE 5. Analysis of the copper group.

below for the detection of bismuth, copper and cadmium ions. If there is a precipitate it is probably lead sulfate. Filter and save the filtrate to test for bismuth, copper and cadmium ions. If lead ion was found in the hydrochloric acid group, it is unnecessary to test the precipitate; it can be rejected and the next paragraph omitted. If lead ion was not found in the hydrochloric acid group, the precipitate must be tested as described in the next paragraph.

Wash the lead sulfate precipitate with a little water, rejecting the washings, then pour on it 10 ml. of 3 *M* CH_3COONH_4 (ammonium acetate), catching the solution in a test tube as it runs through the filter. (*Micro: stir the precipitate with the ammonium acetate solution in a centrifuge tube, and centrifuge if any residue remains undissolved.*) Add to the filtrate a few drops of potassium chromate solution. A yellow precipitate shows the presence of lead ion.

18. Bismuth and Copper Ions. To the solution that may contain bismuth, copper and cadmium ions add 15 ml. of 6 *M* NH_4OH (*micro: 1.5 ml. of 3 M* NH_4OH) and mix well, and if necessary add more, 5 ml. at a time until the solution is distinctly alkaline to litmus or turns to a darker blue color than it was originally. If the solution turns to the darker blue color of the tetrammine cupric ion, $Cu(NH_3)_4^{++}$, when it becomes alkaline, the presence of copper ion is shown. Entire absence of this color change would show the absence of copper ion, but if no change is observed it is wise to test for copper ion as described in Section 19. Absence of a precipitate (observe carefully) shows the absence of bismuth ion. In the latter case filtration is unnecessary and the solution, as it is, can be treated for the detection of cadmium ion as directed below. If a precipitate is formed, it is probably bismuth hydroxide. Filter and save the filtrate for the detection of cadmium ion.

Wash the bismuth hydroxide precipitate twice with water, rejecting the washings. Prepare a solution of sodium stannite by taking 1 ml. of 0.2 *M* $SnCl_2$ (stann*ous* chloride) solution (do not use stann*ic* chloride, $SnCl_4$) and adding 6 *M* NaOH (do not use ammonium hydroxide) and mixing until the solution is clear after shaking and the addition of more sodium hydroxide does not cause a precipitate to form. Pour some of the sodium stannite solution on the bismuth hydroxide precipitate. If the precipitate turns black *immediately* (because of the formation of free bismuth in a finely divided state) the presence of bismuth ion is confirmed. Darkening after a lapse of time should not be interpreted as showing the presence of bismuth ion.

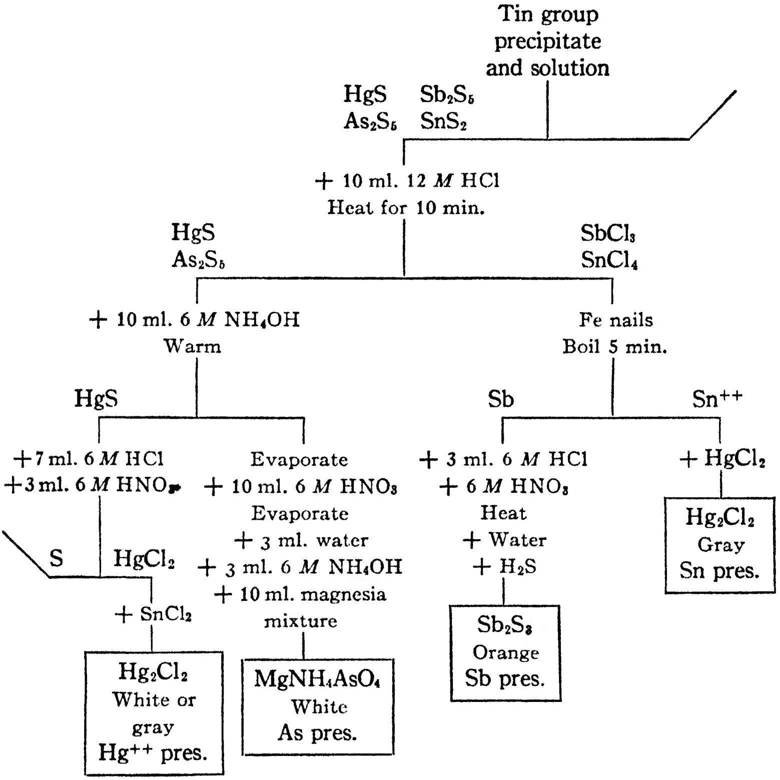
19. Separation of Copper and Cadmium Ions. Acidify the solution containing the copper and cadmium complex ions with 6 M acetic acid, adding acid and mixing until the dark blue color changes to a much lighter blue, or in the absence of enough copper ion to make an observable change, add the acetic acid until the solution is acid to litmus.

If the depth of the blue color of the acidified solution indicates considerable copper ion,[1] take one quarter to one half of the solution for the copper and cadmium ion tests. If only a moderate or small amount of copper ion is indicated by the color, or if the solution appears colorless, use the whole solution. Add 5 to 10 ml. of a 0.2 M solution of the sodium salt of salicyl-aldoxime ("copper reagent"). The amount of reagent should depend on the estimated quantity of copper ion, and should be more than enough to discharge all the blue color of the solution. A voluminous, pale greenish-yellow precipitate shows the presence of copper ion. Allow the mixture to stand for at least 30 minutes to insure completeness of precipitation. When the precipitate has settled sufficiently, test the solution to see if enough reagent was used by adding a few drops more to the clear solution. If more precipitate is formed, add 5 ml. more of the copper reagent and mix well. When the precipitation has been shown to be complete, and the mixture has stood for 30 minutes, heat to make the precipitate more easily filtrable and filter, rejecting the precipitate. (*Micro: filter by suction. If the solution after filtration is cloudy, it can be refiltered conveniently by placing a small pad of cotton over and around the end of a dropper, squeezing the bulb and with the end*

---

[1] The quantity of copper ion added in Exercise 7 (2 ml. of 0.5 M $Cu(NO_3)_2$) should not be taken as "considerable." If the quantity of copper ion is appreciably larger than this, however, the solution should be divided as described above. It can be determined whether or not division is necessary by diluting 2 ml. of 0.5 M $Cu(NO_3)_2$ to the volume of the solution to be tested and comparing the colors. If the color of the solution to be tested is darker blue than the other, it contains too much copper ion for the test, and only a part of it should be taken.

of the dropper and the cotton pressed against the bottom of the test tube drawing the solution through the cotton.) Acidify the filtrate with 3 ml. of 6 *M* HCl (*micro: 6 drops of 3 M HCl*), dilute to 50 ml. (*micro: dilute to 2 or 3 ml.*) and pass in hydrogen sulfide. A yellow precipitate shows the presence of cadmium ion.



OUTLINE 6. Analysis of the tin group.

20. The Tin Group. Separation of Arsenic and Mercury from Antimony and Tin. Filter the tin group precipitate by suction from the solution under which it has been standing, (*micro: filter by suction*) and suck as nearly dry as possible. Transfer the precipitate to a test tube (*micro: centrifuge tube*). Add exactly 10 ml. of 12 *M* HCl (*micro: 0.5 ml.*) and stir well. Heat the test tube by immersing it at least up to the level of the top of the hydrochloric acid solution in warm water in a small beaker[1] and heating the water in the beaker until bubbles of gas are liberated from the mixture in the test tube. Keep the mixture just hot enough to cause a slight bubbling in the tube for ten minutes and stir the mixture occasionally. Then remove the flame but keep the tube in the hot water, and by means of a delivery tube with a drawn-out tip pass a slow stream of small bubbles of hydrogen sulfide through the solution for about a minute. Finally add, a little at a time, 3 ml. of hot water, mixing well after each addition (*micro: it is unnecessary to add the water*) and filter by suction immediately (*micro: centrifuge immediately and remove the solution from the residue before it cools appreciably*). If an orange precipitate forms as the solution cools it is probably antimony sulfide and belongs with the filtrate and not with the other precipitate. Wash the precipitate first with 6 *M* HCl and then with water, and reject the wash solution. (*Micro: wash once with 12 M HCl and twice with water.*) The residue undissolved by 12 *M* HCl contains arsenic and mercuric sulfides, while the solution contains antimony and tin chlorides, $SbCl_3$ and $SnCl_4$.

21. Mercuric Ion. Transfer the residue containing arsenic and mercuric sulfides to a beaker (*micro: leave in the centrifuge tube*) add 10 ml. of 6 *M* NH_4OH (*micro: 1 ml. of 3 M* NH_4OH) and warm for two or three minutes, stirring frequently. Arsenic sulfide dissolves, leaving mercuric sulfide undissolved. Filter and wash the residue with water, rejecting the washings. If the residue is light-colored, mercury is probably absent, mercuric sulfide being black. The solution is to be tested for arsenic, and the residue for mercury.

Transfer the residue presumed to contain mercuric sulfide to a beaker (*micro: leave in the centrifuge tube*) and add 7 ml. of 6 *M* HCl (*micro: add 4 drops of 12 M HCl*) and 3 ml. of 6 *M* HNO_3 and heat, with constant stirring, until the black color disappears. Some sulfur will probably remain. Filter if necessary. Add 0.05 *M* $SnCl_2$, first a drop or two and then 2 ml. or more. A white precipitate that turns gray as more stannous chloride is added shows the presence of mercuric ion.

22. Arsenic. Evaporate the ammonium hydroxide solution, which presumably contains the arsenic, to small volume. (*Micro: evaporate in a crucible.*) Add 5 ml. of 6 *M* HNO_3 and

---

[1] To save time in heating avoid using more water than necessary.

heat nearly to boiling until the residue dissolves or only sulfur is left. The arsenic compound is oxidized to arsenic acid, H_3AsO_4. Evaporate nearly to dryness and add 3 ml. of water and 3 ml. of 6 M NH_4OH, filter to remove any residue and receive the filtrate in a test tube. Add 10 ml. of magnesia mixture[1] and if no precipitate is formed immediately, allow the solution to stand for 10 minutes before concluding that the test is negative. A white precipitate is probably magnesium ammonium arsenate, $MgNH_4AsO_4$.

Filter, wash the white precipitate with a little water and pour over it on the filter 1 ml. of 0.2 M $AgNO_3$ to which 0.25 to 0.5 ml. of 6 M acetic acid has been added. (*Micro: add to the precipitate in the centrifuge tube 2 drops of 6 M acetic acid and 1 drop of 0.2 M* $AgNO_3$.) If a dark red precipitate of silver arsenate is formed, the presence of arsenate ion is shown, and this indicates the presence of arsenic in some form in the material analyzed.

23. Antimony. The concentrated hydrochloric acid solution separated from the arsenic and mercuric sulfides is to be tested for antimony and tin. To separate antimony from tin add two small iron nails to the filtrate containing the antimony and tin ions. Hydrogen should be evolved. Keep the solution at or near boiling for 5 minutes. A dark colored precipitate is probably metallic antimony. Absence of an appreciable precipitate shows absence of antimony. A few black specks may come from the nails. If a precipitate is formed, filter. If a loose crust adheres to the nails, wash it into the filter with a stream of water. Save the filtrate for the test for stannous ion. To confirm the presence of antimony in the precipitate on the filter, perforate the filter and wash the precipitate into a test tube by a small amount of water from the wash bottle. (*Micro: leave in the centrifuge tube.*) Add 3 ml. of 6 M HCl, heat to boiling, then add a few drops of 6 M HNO_3 and continue heating. This will dissolve the precipitate. Finally, place this solution in the precipitation flask, add an equal volume of water, and saturate the solution with hydrogen sulfide. An orange-colored precipitate confirms the presence of antimony.

---

[1] Magnesia mixture is a solution containing magnesium nitrate, ammonium hydroxide and enough ammonium nitrate to prevent the precipitation of magnesium hydroxide.

24. Tin. To the filtrate from the nail treatment add about 1 ml. of 0.1 *M* $HgCl_2$. The formation of a gray or white precipitate indicates the presence of stannous ion and of tin in some form in the original sample.

NOTES

1. If the acid concentration during the precipitation of the hydrogen sulfide group is much larger than 0.3 *M* HCl, some of the ions of the hydrogen sulfide group are not completely precipitated. On the other hand, if the acidity is much smaller than 0.3 *M*, some of the ammonium sulfide group ions may be precipitated in the hydrogen sulfide group where they are not wanted. To adjust the acidity, the acid present in the filtrate from the hydrochloric acid group is neutralized, since its concentration is unknown, and just enough more acid added to give the required hydrogen ion concentration when the solution is diluted.

2. When a solution containing a chloride of antimony, bismuth or tin is neutralized or the acid concentration decreased by dilution, a precipitate of oxychloride is likely to be formed.

$$Sb^{+++} + 3\,H_2O + Cl^- \rightleftarrows SbOCl + 2\,H_3O^+$$

$$Bi^{+++} + 3\,H_2O + Cl^- \rightleftarrows BiOCl + 2\,H_3O^+$$

$$2\,Sn^{++} + 3\,H_2O + 2\,Cl^- \rightleftarrows SnO.SnCl_2 + 2\,H_3O^+$$

The reactions are reversible, and either an increase of hydronium ion concentration or a decrease in the free cation concentration (on the left-hand side of the equation) causes the precipitate to dissolve. The oxychloride precipitates dissolve when hydrogen sulfide is added and are converted completely to sulfides, because hydrogen sulfide precipitates the antimony, bismuth and tin ions from solution as fast as they enter.

3. Large quantities of oxidizing ions make trouble when the hydrogen sulfide group is precipitated, because these ions oxidize sulfide ion to sulfur. Two oxidizing ions that might act in this way are ferric ion, Fe^{+++}, and dichromate ion, $Cr_2O_7^{=}$.

$$2\,Fe^{+++} + S^{=} \longrightarrow 2\,Fe^{++} + S$$

$$Cr_2O_7^{=} + 14\,H_3O^+ + 3\,S^{=} \longrightarrow 2\,Cr^{+++} + 21\,H_2O + 3\,S$$

In the absence of the hydrogen sulfide group, a precipitate of sulfur is obtained. This may be removed by boiling the solution and then filtering. When oxidizing ions like dichromate ion are reduced, hydronium ion is removed from the solution, as can be seen from the equation. A large quantity of the oxidizing ion might remove so much acid that some of the ammonium sulfide group ions would be precipitated with the hydrogen sulfide group. When large amounts of such oxidizing ions are present, it is well to reduce the oxidizing ion by the addition of formaldehyde, HCHO, and heating (finally boiling out all of the formaldehyde) before preparing the solution for the precipitation of the hydrogen sulfide group.

4. If arsenate ion is present in the filtrate from the hydrochloric acid group, it reacts slowly with hydrogen sulfide. It is not likely to react completely even in two treatments with hydrogen sulfide. If a fine, yellow precipitate is formed slowly when hydrogen sulfide is added, arsenate ion is probably present. Time will then be saved by evaporating to small volume, in order to concentrate the acid, adding more acid and some iodine or ammonium iodide to act as a catalyst, then passing in hydrogen sulfide. Under these conditions the reaction is more rapid.

5. The tin group is separated from the copper group by conversion of the mercuric, arsenic, antimony and tin sulfides to the soluble thio-salts, Na_2HgS_2, Na_3AsS_4, Na_3SbS_4 and Na_2SnS_3. For example, in the case of arsenic,

$$,As_2S_5 + 3\,S^{=} \longrightarrow 2\,AsS_4^{\equiv}$$

If arsenic, antimony and tin are present in the group precipitate as the lower sulfides, As_2S_3, Sb_2S_3 and SnS, they must be oxidized to the state of higher valence before conversion to the higher salt. For this reason some sodium disulfide, Na_2S_2, is included in the sodium sulfide reagent and the reagent is called sodium polysulfide to distinguish it from either of the pure sulfides.

Mercuric sulfide reacts with sodium sulfide with a little difficulty, and if sufficient care is not taken, it may not be converted entirely to the thio-salt.

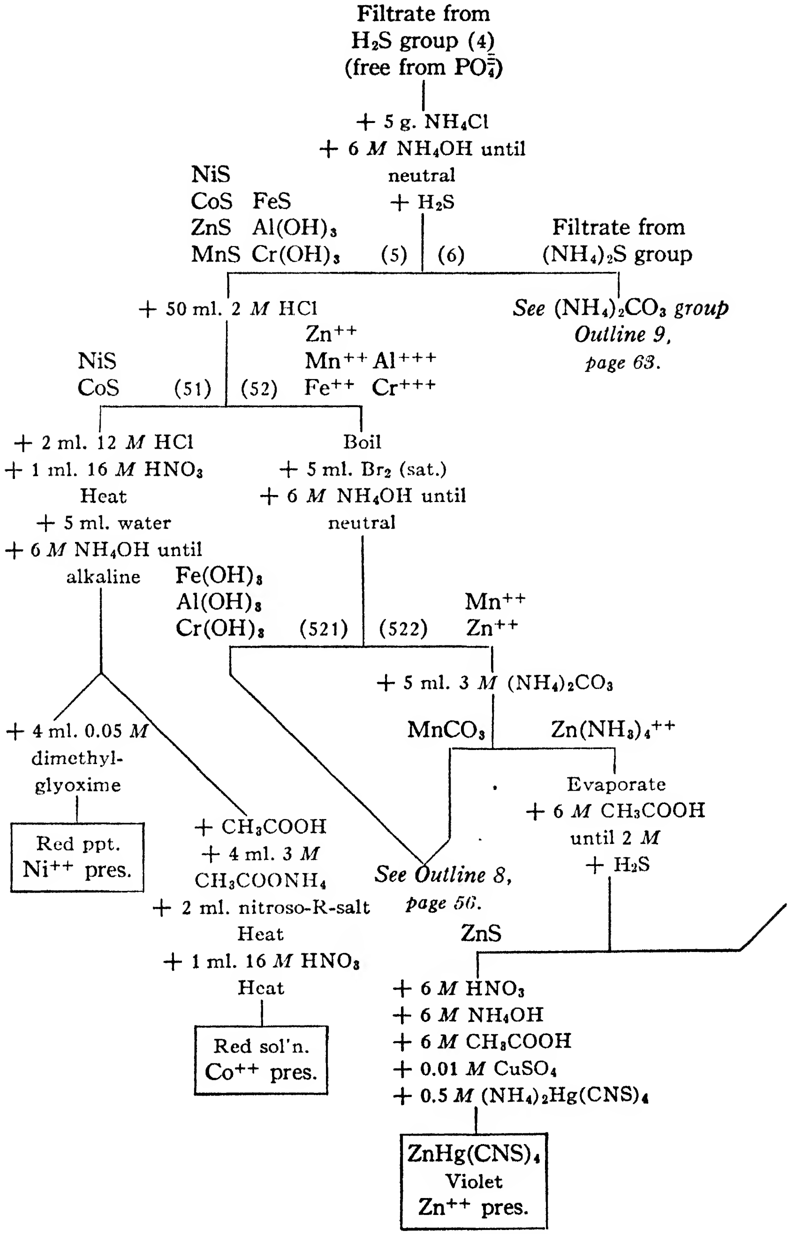
6. If lead ion was found in the hydrochloric acid group it must necessarily be present in the hydrogen sulfide group, because lead chloride is appreciably soluble. The quantity found in the hydrogen sulfide group should never be large, however. A large precipitate at that point might be largely or entirely basic bismuth sulfate resulting from faulty procedure. It is necessary to separate the lead ion by precipitation as the sulfate even though it is known to be present, because if left in the solution it would interfere with the tests for the other ions.

THE AMMONIUM SULFIDE GROUP

The ammonium sulfide group consists of ions that do not react with chloride ion or with sulfide ion in an acid solution to form precipitates, but that react with either hydroxide ion or sulfide ion in a very slightly acidic or alkaline solution to form hydroxide or sulfide precipitates. Accordingly, the ammonium sulfide group is precipitated from the filtrate from the hydrogen sulfide group by the addition of ammonium hydroxide and hydrogen sulfide. Outlines 7 and 8 show the method of precipitating and analyzing the group, and the procedure is described in detail in Sections 25 to 32.

25. Removal of Phosphate Ion. Phosphate ion, if present, interferes with the analysis of the ammonium sulfide and ammonium carbonate groups and must be removed from the filtrate from the hydrogen sulfide group before the ammonium sulfide group is precipitated. If phosphate ion is known to be absent, the remainder of this section may be omitted. If not, test for the presence of phosphate ion in the following manner. Boil a 5-ml. portion of the filtrate from the hydrogen sulfide group (or a smaller portion if the solution was evaporated to small volume in the precipitation of arsenic sulfide) until the hydrogen sulfide is expelled. Pour this test portion into a mixture of 5 ml. of 16 M HNO_3 and 5 ml. of 0.5 M $(NH_4)_2MoO_4$, and heat to about 70°. A yellow precipitate which may form rather slowly shows the presence of phosphate ion. If no precipitate forms immediately, wait 5 to 10 minutes before concluding that phosphate ion is absent. If phosphate ion is absent, the remainder of this section may be omitted and the ammonium sulfide group precipitated without further treatment of the filtrate from the hydrogen sulfide group.

If phosphate ion is present, transfer the remainder of the filtrate from the hydrogen sulfide group to a pyrex beaker or a porcelain casserole (*micro: porcelain crucible*) and evaporate it to about 1 ml. by gently heating. Add 10 ml. of 16 M HNO_3 and evaporate to dryness, taking care to heat very gently as the mixture approaches dryness to avoid breaking the dish and also to avoid making the residue difficult to dissolve. Add another 10-ml. portion of 16 M HNO_3 and again evaporate to dryness. This procedure removes all of the chloride ion as hydrogen chloride. Then add 10 ml. of 16 M HNO_3 and stir the mixture. Add about 1 g. (*micro: 0.05 g.*) of metallic tin (preferably in the form of foil) a little at a time with continuous stirring. A white precipitate of metastannic acid is formed. Heat to boiling and evaporate slowly to about 0.5 ml. Add



Outline 7. Precipitation of the ammonium sulfide group and separation and detection of nickel, cobalt and zinc ions.

25 ml. of water, stir, allow to stand until the precipitate settles and filter. Reject the residue of metastannic acid, which carries along with it the phosphate ion.

Neutralize the filtrate from the metastannic acid by adding 6 M NH_4OH a little at a time until the solution is no longer acid to methyl orange, then add 3 ml. of 6 M HCl and dilute to 50 ml. (*Micro: add 0.3 ml. of 3 M HCl and dilute to 2.5 to 3 ml.*) Saturate the solution with hydrogen sulfide to precipitate lead and copper ions. These may have been introduced along with the tin, since lead and copper may be present as impurities in tin. Filter, reject the precipitate, and use the filtrate as the filtrate from the hydrogen sulfide group in the precipitation of the ammonium sulfide group.

26. Precipitation of the Ammonium Sulfide Group. To the filtrate from the hydrogen sulfide group, which is known to be free from phosphate ion, add 5 g. (*micro: 250 mg.*) of ammonium chloride and shake or stir well to dissolve it. With the solution in a precipitation flask add 2 to 4 ml. of 6 M NH_4OH (*micro: 0.2 to 0.4 ml. of* 3 *M* NH_4OH), depending on how much acid is known to be present; the ammonium hydroxide added should be *insufficient* to neutralize the acid present. Now add more ammonium hydroxide solution drop by drop (*micro: use a dropper with a small tip*) with continuous shaking or stirring until the solution turns red litmus paper to a violet color.

Aluminum and chromium hydroxides precipitate when the acid concentration becomes very small, and if some hydrogen sulfide remains in the solution some of the sulfides of the ammonium sulfide group may precipitate when the concentration of acid becomes small. It is necessary that aluminum and chromium hydroxides be precipitated in a slightly acidic solution rather than in an alkaline solution to minimize the carrying down of the ions of the ammonium carbonate group with the precipitate.

The solution is now ready for the addition of hydrogen sulfide. Pass in hydrogen sulfide gas as in the precipitation of the hydrogen sulfide group, until the solution is saturated with the gas.

If there is no precipitate, add 2 ml. of 6 M NH_4OH and if there is still no precipitate pass to the ammonium carbonate group, Section 33, treating the solution as if it were the filtrate from the ammonium sulfide group.

If there is a precipitate, filter and test the filtrate by again adding 6 *M* NH_4OH drop by drop, this time until the solution is slightly basic to litmus, and saturating with hydrogen sulfide. If any more precipitate is formed, filter on a new paper (*micro: centrifuge in clean tubes*) and again test the filtrate for completeness of precipitation in the same way as before. Repeat until precipitation is complete. Wash each of the precipitates with a solution made by diluting 1 ml. of 6 *M* NH_4OH to 100 ml. and passing in some hydrogen sulfide. Reject the washings. Set aside the filtrate until the ammonium carbonate group is to be precipitated. Do not allow the precipitate to stand long before the next step.

27. Nickel and Cobalt Ions. Transfer the precipitates to a beaker, including the filter papers if necessary, and add 50 ml. of 2 *M* HCl. (*Micro: add to the combined precipitates 1 ml. of water, transfer to a large test tube and add 2 ml. of 3 M HCl.*) Stir until no further change is observed (a black precipitate may remain undissolved) and then filter. (*Micro: transfer the solution removed from the black precipitate to a crucible.*) Do not leave the black precipitate, if present, in contact with the acid longer than necessary.

A black precipitate may be either cobalt sulfide, nickel sulfide or a mixture of the two. The other sulfides and a little of the cobalt and nickel sulfides are dissolved by the acid. Set the filtrate aside temporarily. Wash the precipitate with water, rejecting the washings.

Wash the black precipitate into a beaker and decant as much as possible of the water. (*Micro: leave the precipitate in the centrifuge tube.*) Add 2 ml. of 12 *M* HCl and 1 ml. of 16 *M* HNO_3 and heat until most of the black color disappears, showing that the sulfides have been dissolved. More acid may be added if necessary. Boil the solution until the precipitated sulfur collects into a globule. Add 5 ml. of water and enough 6 *M* NH_4OH to make the solution slightly alkaline.

To about one-quarter of the solution add 4 ml. of 0.05 *M* dimethyl glyoxime solution. A bright red precipitate shows the presence of nickel ion.

Acidify another quarter of the solution with acetic acid, then add 4 ml. of 3 *M* CH_3COONH_4 (ammonium acetate) and 2 ml. of a 0.5% solution of nitroso-R-salt and heat to boiling. Add

1 ml. of 16 M HNO_3, a little at a time, and keep near the boiling temperature for about a minute. If the solution is red at the end of this treatment, the presence of cobalt is shown. If the tests for nickel and cobalt ions were satisfactory, the remainder of the solution containing these ions may be rejected.

28. Zinc Ion. The solution filtered from the nickel and cobalt sulfides may contain zinc, manganous, ferrous, aluminum and chromic ions.[1] Boil the solution (*micro: in a crucible*) for about half a minute to expel hydrogen sulfide, then add 5 ml. of saturated bromine water.[2] This oxidizes the iron from the ferrous to the ferric state.

Prepare two portions of a test solution by mixing in each of two test tubes 2 ml. of 0.3 M Na_2HPO_4, 2 ml. of starch solution and 2 ml. of 0.2 M KI. To one portion add 1 ml. of the solution to which the bromine water was added. A blue color shows that excess bromine is present. If no blue color is developed, add 5 ml. more bromine water and test again, using the same test solution. When it is shown that excess bromine is present, boil the solution containing the zinc, ferric, manganous, aluminum and chromic ions for one minute and test again by the addition of 1 ml. to the second portion of starch-iodide-phosphate test solution; free bromine should now be absent. If the test is positive (blue color, showing bromine present) continue the boiling and test again, repeating until the test is negative. Carefully add 6 M NH_4OH, with stirring, stopping when the first permanent precipitate is formed or when the solution becomes slightly alkaline; about 16 ml. should be required (*micro: 2 ml. of 3 M* NH_4OH). If a precipitate is formed (aluminum, chromium and ferric hydroxides) continue the addition of the 6 M NH_4OH drop by drop (*micro: from a dropper with a small tip*) with continuous shaking or stirring, as long as the precipitate continues to form, or until the solution becomes neutral or slightly alkaline to litmus. Then filter and wash once or twice with water, adding the washings to the filtrate, and add to the filtrate 5 ml. of 3 M $(NH_4)_2CO_3$. If a precipitate is formed (probably manganese carbonate) filter

---

[1] The solution may also contain traces of nickel and cobalt ions.

[2] Saturated bromine water is reddish-brown in color. If a solution is yellow or colorless, much or all of the bromine must have escaped. Be sure that the solution is good.

through a new paper. Save this and the previous precipitate of aluminum, chromium and ferric hydroxides for later analysis, and test the filtrate for zinc ion as described in the next paragraph.

Evaporate the filtrate containing zinc ion to a volume of 10 to 20 ml., acidify with 6 *M* CH_3COOH and add a volume of 6 *M* CH_3COOH equal to approximately half the volume of the filtrate, thus making the solution 2 *M* with respect to acetic acid. Add some hydrogen sulfide, but do not leave connected to the source of hydrogen sulfide very long. A white precipitate may be zinc sulfide. Filter soon after the white precipitate is formed, rejecting the filtrate. Dissolve some of the precipitate by a few drops of hot 6 *M* HNO_3 (*micro: add one or more drops of* 6 *M* HNO_3 *depending on the quantity of precipitate, heat, and then centrifuge and remove the solution to another centrifuge tube*). Neutralize the solution thus formed (which presumably contains zinc ion) with 6 *M* NH_4OH and add a few drops in excess. Acidify with 6 *M* CH_3COOH and add a few drops (*micro: one drop*) of 0.01 *M* $CuSO_4$ and a few drops (*micro: one drop*) of 0.5 *M* $(NH_4)_2Hg(CNS)_4$ (or $K_2Hg(CNS)_4$). A violet precipitate which may form slowly shows the presence of zinc ion. The shade of violet varies with the quantity of zinc ion present, from light violet when there is much zinc ion to very dark, almost black, when there is only a little zinc ion.

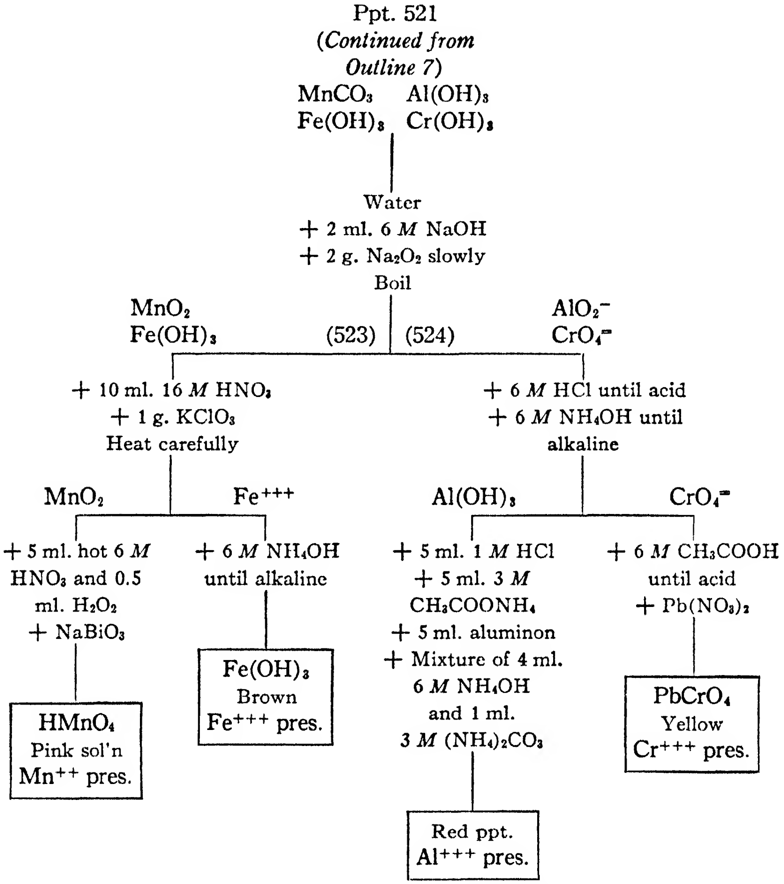
If there is doubt as to the presence of zinc ion, place a drop of the solution supposed to contain zinc ion on a potassium cobalticyanide test paper, dry by careful heating and burn the paper. A spot of green color, Rinman's green, $CoZnO_2$, on the black ash of the paper shows the presence of zinc ion.

29. Separation of Aluminum and Chromium from Manganese and Iron. Combine the precipitate of aluminum, chromium and ferric hydroxides with the precipitate of manganese carbonate in a flask, by perforating the filter papers and washing the precipitates from the papers by means of a stream of water from a wash bottle. (*Micro: combine the precipitates in a 30-ml. test tube using a little water to aid in transferring them from the centrifuge tubes.*) Add 2 ml. of 6 *M* NaOH. Weigh 2 g. (*micro: 0.1 g.*) of Na_2O_2 and put it into a dry test tube.[1]

---

[1] Sodium peroxide can be weighed on a piece of dry paper, but should not be handled on paper when there is any danger of water splashing on it. A

Cool the solution by holding it under running water and shaking. Then add the sodium peroxide a little at a time. Shake or stir well after each addition and keep the solution cool. When all the sodium peroxide has been added, boil the solution for one minute. This is important, as the excess sodium peroxide, which is destroyed by boiling, would make trouble later if left



OUTLINE 8. Separation and detection of manganese, iron, aluminum and chromium ions.

---

little water on the sodium peroxide may set the paper on fire. This might happen without warning and cause a burn. Unused sodium peroxide should not be thrown into waste jars, but should be dissolved in water and thrown into the sink.

in the solution. Dilute the solution to about 60 ml. (*micro: about 3 ml.*). If there is no appreciable residue left after the sodium peroxide treatment, manganese and iron ions are absent. If there is a residue, the presence of either manganese ion or ferric ion or both is indicated.

If there is no residue, or if the residue is too small to test, filter (*micro: filter by suction*), reject the paper, and proceed to test the filtrate for aluminum and chromium ions as directed below. Filtering at this point is desirable because otherwise a small amount of ferric ion might give a test for aluminum ion.

If an appreciable residue is formed by the sodium peroxide treatment, filter on a hardened filter paper[1] by suction. (*Micro: centrifuge and pass the solution removed from the precipitate through a plug of cotton or a suction filter to remove all traces of ferric hydroxide.*) Wash the residue with a little water and reject the wash solution. The residue may be a mixture of manganese dioxide and ferric hydroxide, while the filtrate may contain aluminum and chromium in the negative ions AlO_2^- and $CrO_4^=$, respectively. Set the filtrate aside for later analysis.

30. Manganese. The next step is to separate the manganese dioxide from the ferric hydroxide and test for the manganese ion. Put the residue and filter paper into a casserole (*micro: leave in the centrifuge tube*) and pour over it 10 ml. of 16 M HNO_3. Remove the paper by means of a glass rod and throw it away. Pour the solution, with any undissolved residue, into a test tube (*micro: leave in the centrifuge tube*) and put the test tube into a beaker partly full of boiling water. If necessary, use some of the solution in the test tube to rinse the residue from the casserole. When the mixture in the test tube is hot, add about 0.3 g. (*micro: 15 mg.*) of solid $KClO_3$. (Weigh out 1 g. — *micro: 50 mg.* — of $KClO_3$ and add a third of it, saving the remainder to be added later if necessary.) Stir with a stirring rod and heat for a minute or two. If there is no brown or black residue of manganese dioxide at this point, manganese ion is absent. In this case test the solution for ferric ion as

---

[1] Hardened filter paper is a specially prepared filter paper which will withstand contact with strongly acid and alkaline solutions better than ordinary filter paper. It is necessary to use hardened filter paper here, because the solution to be filtered is strongly alkaline and because the next step requires that the paper come in contact with 16 M nitric acid.

described below, treating it as if it were the filtrate from the manganese dioxide residue.

If there is a brown or black residue after the addition of the potassium chlorate, add in small portions 0.7 g. (*micro: 35 mg.*) more potassium chlorate and shake frequently. Then filter the mixture through an asbestos filter. (*Micro: centrifuge.*) To make an asbestos filter, set up the suction filter in the usual way, but without a filter paper. Put some asbestos fibers into a beaker, add considerable water, stir the mixture and filter through the funnel of the suction filter. If enough asbestos has been used, it will clog the holes of the funnel and make a pad which will serve in place of a filter paper.

Remove the filtrate and set it aside to be tested for iron. Wash the manganese dioxide once with water and reject the wash solution. Heat 5 ml. of 6 M HNO_3 in a test tube and slowly mix with it either 0.5 ml. of hydrogen peroxide solution or, with stirring, about 0.05 g. (*micro: 2 to 5 mg.*) of sodium peroxide. Pour this solution over the precipitate on the asbestos filter and apply the suction. The solution should dissolve some of the precipitate.

To the solution which has dissolved some of the manganese dioxide precipitate add solid sodium bismuthate, $NaBiO_3$, about 0.1 g. (*micro: 5 mg.*) at a time, shaking well, until some of the solid bismuthate remains undissolved. Let the solid settle (*micro: centrifuge*). A pink or purple color in the clear solution shows the presence of permanganate ion, MnO_4^-, which is evidence of the presence of an ion of manganese in the original sample.

31. Iron. To the filtrate from the manganese dioxide add 30 ml. of 6 M NH_4OH, and if necessary, enough more to make the solution alkaline. A reddish-brown precipitate shows that ferric ion is present, and absence of any traces of such a precipitate may be taken as conclusive evidence of the absence of iron.

Iron compounds in small quantities are very frequent impurities in reagents as well as in other materials. If only a small quantity of ferric ion is present, it is of interest to determine whether or not the quantity is to be considered appreciable.

For this purpose the precipitate obtained may be compared with a similar precipitate obtained from a known amount of ferric ion. Take 1 ml. of 0.5 *M* $Fe(NO_3)_3$, or an equivalent amount of a ferric solution of any other concentration, and dilute it to 10 ml. Pour the solution into a beaker or flask and mix well. To 1 ml. of the solution add 35 ml. of water and 5 ml. of 6 *M* nitric acid. Then add 7 ml. of 6 *M* ammonium hydroxide and more if necessary to make the solution alkaline. Allow the solution to stand until a precipitate forms, and compare the amount of ferric hydroxide with the amount obtained from the sample being analyzed. The ferric hydroxide in the known solution represents about 3 mg. of iron. If the amount of precipitate obtained from the sample is appreciably less than this, it can be considered that only a very small amount of iron is present.

If it is desired to confirm the presence of iron by testing the precipitate that is presumed to be ferric hydroxide, this can be done as follows. Dissolve a little of the precipitate in a small quantity of 6 *M* HCl, dilute with five times its volume of water and add a few drops of a solution of potassium ferrocyanide, $K_4Fe(CN)_6$.[1] A blue sol of $KFe[Fe(CN)_6]$ or a blue precipitate of ferric ferrocyanide, $Fe_4[Fe(CN)_6]_3$, is evidence of the presence of ferric ion. If the quantity of the ferric ion is very small, only a blue or green color in the solution may be produced and no precipitate. The green color is the result of the combination of the blue color of potassium ferric ferrocyanide and the yellow color of the excess ferrocyanide ion. If there is doubt as to the interpretation of the results, make a test on a dilute hydrochloric acid solution similar to the unknown solution tested, but with no ferric hydroxide added. Test also a solution made by diluting a drop or two of 0.5 *M* $FeCl_3$ with considerable water. Another well-known test for ferric ion consists in adding a potassium or ammonium thiocyanate solution to the solution to be tested. If ferric ion is present, un-ionized ferric thiocyanate, $Fe(CNS)_3$, which has an intense red color, is formed.

32. Aluminum. The filtrate resulting from the sodium peroxide treatment may contain aluminate and chromate ions. Add to it 6 *M* hydrochloric acid 5 ml. at a time until the solu-

---

[1] Be careful to use potassium ferrocyanide, $K_4Fe(CN)_6$, and not potassium ferricyanide, $K_3Fe(CN)_6$, as the ferricyanide does not give a precipitate with ferric ion.

tion is acid, then 6 *M* NH_4OH 2 ml. at a time until it is basic, and finally 2 ml. of NH_4OH in excess. A white gelatinous precipitate may be aluminum hydroxide. It may also be silicic acid dissolved from the glass vessels by the strongly alkaline solution, or some other hydroxide present as the result of an incomplete separation. Filter off the precipitate and save the filtrate to test for chromate ion.

Pour over the precipitate on the paper 5 ml. of 1 *M* hydrochloric acid (made by mixing 1 ml. of 6 *M* acid and 5 ml. of water) and let the solution run into a flask. The precipitate is dissolved by the acid solution and the filtrate contains aluminum ion, if it is present. Add to the solution in the flask 5 ml. of 3 *M* CH_3COONH_4, mix well, then add 5 ml. of a 0.1% solution of aluminon (the ammonium salt of aurin tricarboxylic acid). Finally add enough of a mixture of 4 ml. of 6 *M* ammonium hydroxide and 1 ml. of 3 *M* $(NH_4)_2CO_3$ either to form a red precipitate or (in the absence of a precipitate) to turn the color of the solution orange or yellow. A red precipitate shows the presence of aluminum ion.

33. Chromium. To the filtrate containing chromate ion add 4 ml. of 6 *M* acetic acid and enough more, 1 ml. at a time, to make the solution acid. If the solution is yellow, the presence of the chromate ion is indicated. This, of course, indicates that chromic ion, Cr^{+++}, was present in the filtrate from the hydrogen sulfide group, and that some chromium compound was present in the original sample. Add to the solution a drop or two of lead nitrate solution. A yellow precipitate confirms the presence of chromate ion.

NOTES

1. Certain ions, such as ferric ion, dichromate ion and permanganate ion, react with sulfide ion to precipitate sulfur. In such reactions the sulfide ion is oxidized to sulfur and the other ions are reduced. Consequently, after the precipitation of the hydrogen sulfide group the elements iron, chromium and manganese, if present, will be present as ferrous, chromic and manganous ions, Fe^{++}, Cr^{+++} and Mn^{++}, respectively, regardless of which particular ions of these elements were present at the beginning.

2. If aluminum and chromium hydroxides are precipitated in the presence of magnesium ion they carry down with them

more or less of the magnesium ion, even though conditions are such that magnesium hydroxide if present alone could not precipitate. The same is true to some extent of the other ions of the ammonium carbonate group. It has been found that when the aluminum and chromium hydroxides are precipitated in very slightly acid solutions they carry down less of the carbonate-group ions than when precipitated in alkaline solutions. Consequently, in precipitating the ammonium sulfide group the ammonium hydroxide should be added slowly with constant stirring to prevent local excesses of hydroxide ion, and the addition should be stopped while the solution is still slightly acidic.

3. Since nickel and cobalt sulfides are not precipitated from acidic solutions, one would expect them to be dissolved by acids. However, the rate at which they react with acids is very slow and in the time required for the other sulfides to dissolve, only a little of the nickel and cobalt sulfides react. This makes possible a separation of nickel and cobalt sulfides from the ions of the other metals, but it should be noticed that the separation is not a perfect one, and both nickel and cobalt ions will be present in small quantity in the solution along with the remaining ions of the group.

4. Zinc ion as well as magnesium ion is carried down by precipitates of aluminum, chromium and ferric hydroxides. Consequently, in the precipitation of these hydroxides when it is desired that zinc ion remain in solution it is necessary that the ammonium hydroxide be added very slowly.

5. The white precipitate of zinc sulfide in the test for zinc ion may turn greenish or gray on standing, if the solution from which it was precipitated contained nickel or cobalt ion. Nickel and cobalt ions, if present in the ammonium sulfide group precipitate, will be present in traces in the solution tested for zinc ion. This is because small amounts of nickel and cobalt sulfides dissolve in the 1 *M* hydrochloric acid when they are being separated from the other ions of the group as explained in Note 3. If it is desired to test for traces of nickel and cobalt ions at this point, the zinc sulfide can be filtered out and the solution can be made alkaline with ammonium hydroxide and saturated with hydrogen sulfide. The black precipitate of nickel and cobalt sulfides can then be tested in a manner described above for nickel and cobalt tests.

6. When ferric hydroxide and manganese dioxide are treated with nitric acid, only the ferric hydroxide is dissolved. Manganese dioxide can be dissolved by nitric acid with the aid of a reducing agent to reduce the manganese to the manganous state. Particles of filter paper and impurities in the nitric acid reduce manganese dioxide to some extent. The part that is reduced and dissolved must be reoxidized and reprecipitated.

For this purpose the potassium chlorate is added to the hot solution.

$$KClO_3 + HNO_3 \longrightarrow HClO_3 + KNO_3$$

$$2\,HClO_3 + Mn(NO_3)_2 \longrightarrow MnO_2 + 2\,HNO_3 + 2\,ClO_2$$

The potassium chlorate should be added a little at a time to avoid too rapid formation of chlorine dioxide. Chlorine dioxide is explosive and is unpleasant to breathe. The mixture should be heated on a water bath so that the temperature will not become high enough to cause the chlorine dioxide to explode.

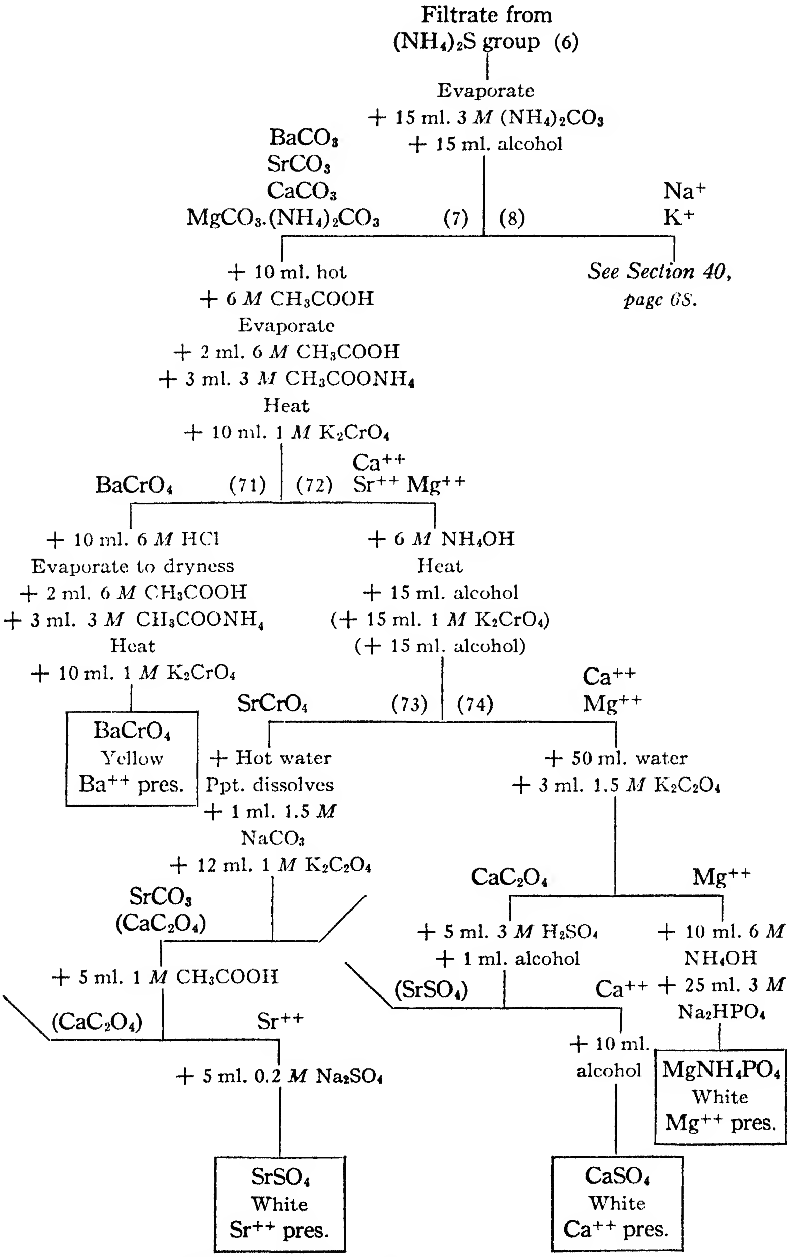
THE AMMONIUM CARBONATE GROUP

The ammonium carbonate group consists of cations present in the filtrate from the ammonium sulfide group that are precipitated by ammonium carbonate in a solution containing a large proportion of alcohol. These ions are barium, strontium, calcium and magnesium ions. The method of precipitation and analysis is shown in Outline 9 and described in detail in Sections 34 to 39.

34. Preliminary Treatment. Evaporate the filtrate from the ammonium sulfide group by gentle heating in a porcelain casserole or a pyrex beaker (*micro: porcelain crucible*) to a volume of less than 10 ml. (*micro: less than 0.5 ml.*). Dilute to 10 ml. (*micro: 0.5 ml.*) and filter if there is any undissolved residue.

35. Precipitation of the Ammonium Carbonate Group. To the 10 ml. of solution obtained as described in the last paragraph (*micro: in a centrifuge tube*) add 15 ml. of 3 M $(NH_4)_2CO_3$ and 15 ml. of denatured alcohol (*micro: 1 ml. of each*) and mix well by shaking or stirring. Allow to stand for 30 minutes, or if convenient until the next laboratory period. In the latter case see that the container is tightly stoppered to prevent evaporation.

Filter, using suction if the precipitate is large. Wash once with a mixture of equal parts of 3 M $(NH_4)_2CO_3$ and alcohol. The precipitate may contain the carbonates of any or all of the metals of the ammonium carbonate group, while the filtrate may contain sodium and potassium ions. Reserve the filtrate for the analysis of the alkali group. On pouring the solution and precipitate into the filter, it may be found that some of the



Outline 9. Precipitation and analysis of the ammonium carbonate group.

precipitate adheres to the inside of the flask in which the precipitation was carried out. (*This trouble is not experienced in work on the semi-micro scale if the mixture is centrifuged in the tube in which the precipitation was made.*) In such a case, this portion of the precipitate may be left in the flask until the precipitate is to be analyzed. Then it can be dissolved by 6 M CH_3COOH and the same solution used for dissolving the main portion of the precipitate. If the precipitate is to be preserved for any length of time, it can be conveniently preserved on the paper in the flask in which the precipitation was made.

36. Barium Ion. Pour through the filter 10 ml. of hot 6 M CH_3COOH and if the acid does not dissolve all of the precipitate pour it through again and repeat until all of the precipitate is dissolved. (*Micro: add 6 M CH_3COOH drop by drop with efficient stirring until the precipitate is entirely dissolved.*) Carefully evaporate the solution nearly to dryness in a porcelain casserole or pyrex beaker (*micro: crucible*) under the hood or near a fume duct, taking special care not to heat the residue much near the end of the evaporation; acetates are easily decomposed by heat.

Add to the residue from the evaporation 2 ml. of 6 M CH_3COOH, 3 ml. of 3 M CH_3COONH_4 and 10 ml. of water. Transfer the mixture to a flask (*micro: centrifuge tube*) heat nearly to boiling and add, 1 ml. at a time with shaking or stirring, 10 ml. of 1 M K_2CrO_4. Keep the mixture hot for about 5 minutes and shake or stir frequently. If no precipitate is formed, barium ion is absent, in which case treat the solution as if it were the filtrate from the barium chromate precipitate and pass on to the test for strontium ion. A yellow precipitate is probably barium chromate, but this may need to be confirmed. If the precipitate settles, leaving a clear solution above, observe whether or not the solution is yellow in color. If not, add 10 ml. more of the 1 M K_2CrO_4.

Filter and if the filtrate is not yellow in color add 10 ml. more 1 M K_2CrO_4 and if any further precipitate is formed, filter again. If the filtrate is yellow, the precipitation of the barium chromate can be considered complete. Set aside the barium chromate precipitate, which need not be washed, and, skipping the next paragraph, test the filtrate for strontium ion. If much strontium ion is found present, test the barium chromate precipitate as described in the next paragraph. Otherwise the yellow precipitate of barium chromate can be taken as conclusive evidence of the presence of barium ion.

If much strontium ion is present, dissolve the yellow precipitate that is presumed to be barium chromate by means of 5 to 10 ml. of hot 6 *M* HCl and carefully evaporate the solution just to dryness. Repeat the procedure for the precipitation of barium chromate. If a yellow precipitate is again obtained on the addition of acetic acid, ammonium acetate and potassium chromate, it is definite evidence of the presence of barium ion. Absence of a yellow precipitate this time is evidence that the first yellow precipitate was strontium chromate obtained in place of barium chromate through faulty procedure.

37. Strontium Ion. To the filtrate from the barium chromate precipitate add 6 *M* NH_4OH a little at a time until the color of the solution changes from orange to yellow, indicating that the solution is about neutral. Then add 5 ml. of 6 *M* NH_4OH in excess. Heat the solution to about 60° and add three 5 ml. portions of denatured alcohol, shaking (or stirring) after each addition if a precipitate appears. Cool the mixture and allow it to stand at least 5 minutes. Absence of a precipitate indicates absence of strontium ion, in which case pass on to the test for calcium ion. A yellow precipitate is probably strontium chromate, but this needs confirmation. If a precipitate is formed, add 15 ml. of 1 *M* K_2CrO_4 and 15 cc. of alcohol and allow to stand at least 5 minutes. Filter with suction, but do not wash the precipitate. Save the filtrate to be tested for calcium and magnesium ions.

Pour a 10-ml. portion of hot water repeatedly through the filter to dissolve as much of the precipitate as possible. (*Micro: add 0.5 ml. of water, stir and heat by immersion in boiling water, stirring frequently. If any precipitate remains, centrifuge while still hot and transfer the solution to another centrifuge tube.*) Add to the hot solution 1 ml. of 1.5 *M* Na_2CO_3 and 12 ml. of 1.5 *M* $K_2C_2O_4$ (potassium oxalate). Keep the mixture at or near boiling temperature for 5 minutes. (*Micro: immerse the centrifuge tube in boiling water for 5 minutes and stir frequently.*) This treatment, provided the solution is hot, precipitates strontium ion as strontium carbonate, $SrCO_3$, and any calcium ion present as calcium oxalate, CaC_2O_4. Barium ion is not likely to be present because barium chromate could not have been dissolved by hot water. Filter while still hot and wash the precipitate thoroughly with water. Pour repeatedly through the filter 5 ml. of cold 1 *M* CH_3COOH. (Dilute 1 ml. of 6 *M* CH_3COOH to 6 ml.) (*Micro: add to the precipitate 5 drops of water and one drop of 6 M CH_3COOH, stir and centrifuge.*) This dissolves the strontium carbonate but not the calcium oxalate. To the solution, which should contain the strontium ion, if any is present, add 5 ml. of 0.2 *M* Na_2SO_4 and allow to stand 10 minutes. Absence of a precipitate shows the absence of strontium ion, while a white precipitate of strontium sulfate, $SrSO_4$, indicates the presence of strontium ion.

38. Calcium Ion. Dilute the filtrate from the strontium chromate with 50 ml. of water and add 3 ml. of 1.5 *M* $K_2C_2O_4$ to precipitate calcium oxalate. If no precipitate appears, allow the solution to stand 15 minutes before concluding that calcium ion is absent. If no precipitate is present at the end of that time, test the solution for magnesium ion, skipping the next paragraph.

A precipitate is probably calcium oxalate, but its identity should be confirmed. Filter and save the filtrate for testing for magnesium ion. Wash the precipitate with water and reject the washings. Pour repeatedly over the precipitate 5 ml. of 3 *M* H_2SO_4 to which 1 ml. of denatured alcohol has been added. (*Micro: add to the precipitate 5 drops of 3 M H_2SO_4 and 1 drop of alcohol, stir well and centrifuge.*) This dissolves at least part of the calcium oxalate but converts strontium oxalate into the insoluble sulfate. To the filtrate add 10 ml. of alcohol (*micro: 0.5 ml.*) and let the mixture stand for several minutes. A white precipitate shows the presence of calcium ion.

39. Magnesium Ion. To the filtrate from the calcium oxalate add 10 ml. of 6 *M* NH_4OH and 25 ml. of 0.3 *M* Na_2HPO_4 (*micro: 1 ml. of 3 M NH_4OH and 1 ml. of 0.3 M Na_2HPO_4*) and shake or stir. If no precipitate forms, allow the solution to stand about 30 minutes with frequent shaking or stirring before concluding that magnesium ion is absent. A precipitate of magnesium ammonium phosphate, $MgNH_4PO_4$, may be taken as evidence of the presence of magnesium ion if there is a fair quantity of it, but if small or if there is doubt as to its identity a confirmatory test should be made. The phosphates of many of the metals can be precipitated from alkaline solutions by the addition of a soluble phosphate.

To confirm the presence of magnesium ion, filter, wash the supposed magnesium ammonium phosphate precipitate once with alcohol, and dissolve some or all of it by means of 5 ml. of 1 *M* H_2SO_4 (dilute 2 ml. of 3 *M* H_2SO_4 to 6 ml.), add 10 ml. of alcohol and shake or stir for 2 or 3 minutes. A precipitate formed at this point is probably calcium sulfate. If a precipitate is formed, filter and reject it and add to the filtrate 10 ml. of water, 20 ml. of 6 *M* NH_4OH and 5 ml. of 0.3 *M* Na_2HPO_4. If no precipitate is formed, allow the mixture to stand for 30 minutes with frequent shaking or stirring before concluding that magnesium ion is absent. A white precipitate is magnesium ammonium phosphate and shows the presence of magnesium ion.

NOTES

1. In the precipitation of the ammonium carbonate group the volume of solution is kept small and a large excess of the reagent is added in order to make the precipitation nearly enough complete. The carbonates of the alkaline earth metals and magnesium are a little too soluble for best results unless these conditions are maintained. Magnesium ion is precipitated as a double salt, $MgCO_3 \cdot (NH_4)_2CO_3 \cdot 4H_2O$, which is fairly soluble in water, but not in a solution containing considerable ammonium carbonate. The alcohol is added to make the precipitation more rapid than it would otherwise be, but at best it is somewhat slow.

2. The chromates of barium, strontium, calcium and magnesium differ in their solubility, barium chromate being the least soluble and magnesium chromate the most. Barium chromate is precipitated in a solution containing acetic acid while the others are not. Strontium chromate is precipitated practically completely from an alkaline solution containing alcohol, while calcium and magnesium chromates are not. Salts are generally less soluble in a mixture of alcohols and water than in water alone.

THE ALKALI GROUP

The alkali group consists of the ions that are left after the precipitation of the other groups, namely potassium, sodium and ammonium ions. These are not precipitated as a group.

Appropriate tests are made for sodium and potassium ions in the filtrate from the ammonium carbonate group, but the test for ammonium must be made on the original unknown material because ammonium salts are added in the course of the analysis.

40. Preparation of the Solution. Evaporate the filtrate from the carbonate group to dryness in a casserole (*micro: in a crucible*). During the evaporation the vapors given off may contain enough alcohol to catch fire. So long as the flame is only a few centimeters high no particular harm is done, but it is well to remove the burner while the vapors burn. If the flame of the burning vapor becomes too large, both the fire hazard and the danger of breaking the dish are much increased. The flame can be extinguished by placing a watch glass or some other non-inflammable object over the casserole. When the evaporation is completed, heat (under a hood or near an opening in the fume duct) until the white ammonium salts stop coming off. It is very important that all traces of ammonium salts be expelled, because ammonium ion if present will give a test for potassium ion. Complete absence of a residue at this point shows the absence of sodium and potassium ions, but it should be remembered that a white solid cannot be seen easily against a white background, and even a large quantity of sodium and potassium salts looks surprisingly small when dry.

After the removal of the ammonium salts, allow the dish to cool, add 5 ml. of water and by warming the water and rubbing the residue into small pieces with a stirring rod get a maximum portion dissolved. Add 10 ml. of 0.2 M $Ba(OH)_2$, stir and filter if any precipitate is formed, rejecting the precipitate. To the filtrate add 5 ml. of 3 M $(NH_4)_2CO_3$, or enough to precipitate all of the barium ion, and heat the solution to boiling, after which let it stand for about 5 minutes. Then filter again and reject the precipitate.

Evaporate the filtrate to dryness, heating carefully when the water is nearly gone to avoid breaking the dish. Moisten the residue with 6 M HCl, evaporate to dryness again and bake to remove all ammonium salts. Absence of any residue shows that sodium and potassium ions are absent, but the observation should be made with care. If a residue remains, add 5 ml. of water, stir well and filter, if necessary, to remove any undissolved residue. Reject the residue. The filtrate should contain the sodium and potassium ions and should be free from ammonium ion. Do not allow the filtrate to be exposed to air containing ammonia. Divide the solution into two approximately equal portions.

41. **Potassium Ion.** To one portion of the solution add 1 ml. of 3 *M* NaOH and then 2 ml. of 3 *M* CH_3COOH. Test with blue litmus. If the solution is not acid to litmus, add more acetic acid and test again. Prepare a solution of sodium cobaltinitrite, $Na_3Co(NO_2)_6$, by adding 2 ml. of water to 0.5 to 1 g. (*micro: 25 to 50 mg.*) of solid sodium cobaltinitrite in a test tube and stirring. Add this solution to the acidified solution to be tested. If a precipitate is not formed immediately, stir vigorously and allow to stand for 15 minutes. A yellow precipitate, $K_2NaCo(NO_2)_6$, shows the presence of potassium ion.

42. **Sodium Ion.** If much potassium ion is present, it must be removed previous to the test for sodium ion. If not, the solution can be tested for sodium ion immediately. To separate potassium ion add 1 ml. of 6 *M* $HClO_4$ to the solution to be tested for sodium ion. All but a little potassium ion is precipitated as potassium perchlorate. Filter and remove 1 ml. of the clear solution containing the sodium ion to a test tube. Add 10 ml. of zinc uranyl acetate solution. A light-colored precipitate of sodium zinc uranyl acetate that settles quickly to the bottom of the tube shows the presence of sodium ion.

43. **Ammonium Ion.** Since ammonium salts are added in the course of an analysis, the test for ammonium ion must be made on the original sample. Place some of the solid (or solution) to be tested in a beaker and add enough 6 *M* NaOH to make the mixture strongly alkaline. See if the odor of ammonia can be recognized. If not, try the following test. Wet a piece of red litmus paper and stick it to the convex side of a watch glass. Place the watch glass over the beaker containing the sample with the convex side down and the litmus paper inside the beaker. Warm the mixture in the beaker to about 60°, but be careful not to boil the solution, because boiling would cause small drops of the sodium hydroxide solution to spatter on the litmus paper and turn it blue. If the litmus turns blue without any sodium hydroxide spattering on it, ammonium ion is present.

For work on the semi-micro scale or when the above test is uncertain, the following procedure is recommended.

Set up an apparatus like that of Fig. 6, using a 30-ml. test tube and a 3-ml. centrifuge tube or test tube. The 30-ml. test tube is fitted with a two-hole rubber stopper and the centrifuge tube with a one-hole cork stopper. The cork should fit fairly loosely in the centrifuge tube or have a notch cut (or filed) in it so that air may be drawn past it. Place 2 ml. of water and 2 drops of 3 *M* HCl in the larger test tube. Place about 10 mg. of the sample to be tested (or 2 or 3 drops if the sample is a solution) in the centrifuge tube, add 2 or 3 drops of 3 *M* NaOH (or enough to make the mixture strongly alkaline) and quickly put the tube in place. Connect the outlet tube of the 30-ml. test tube to a vacuum outlet or filter pump and draw a *slow* stream of air through the apparatus. The velocity of the air stream may be judged by the frequency of the bubbles in the large test tube; 2 to 4 bubbles a second is about right. Now carefully heat the mixture in the centrifuge tube to the boiling point, but avoid violent boiling. Keep hot for at least 2 minutes with the air stream passing continuously. Finally add to the solution in the larger test tube 2 drops of 3 *M* NaOH and one drop of Nessler's reagent, which is a solution 0.5 *M* with respect to potassium mercuric iodide, K_2HgI_4, and 3 *M* with respect to sodium hydroxide. A brown precipitate or brown coloration in the solution shows the presence of ammonia, indicating that ammonium ion was present in the original unknown material.

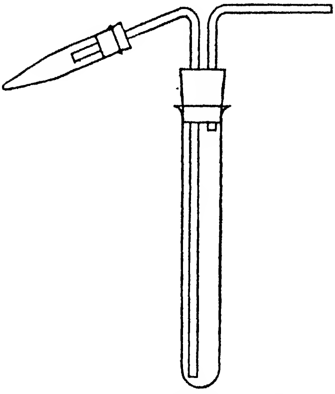


FIG. 6. Apparatus for the ammonia test.

This test is very delicate and it is quite possible to take in enough ammonia from the laboratory air to give a positive test. To avoid erroneous conclusions, see that no odor of ammonia can be detected in the air drawn through the system, and in addition make a blank test to determine how much ammonia is taken from the air. For a blank test, make a test just as described above, using all of the regular reagents, but without any sample. If the color produced by Nessler's reagent in the test on the sample is no darker than that produced in the blank test, ammonium ion is absent from the sample.

NOTES

1. Relatively few sodium and potassium salts have such small solubilities that they can be used in testing for sodium and potassium ions. Even the few salts available are sufficiently soluble so that in testing small quantities, the volume of the solution must be kept small and a large excess of the reagent added.

2. Potassium zinc uranyl acetate, $KZn(UO_2)_3(OOCCH_3)_9$, is much more soluble than the sodium salt, and potassium ion is not likely to interfere with the sodium ion test unless it should be present in large quantity. In such a case most of the potassium ion can be precipitated by perchloric acid because potassium perchlorate has only a small solubility. The quantity of potassium ion remaining in solution after the precipitation of the potassium perchlorate is too small to interfere with the sodium ion test.

3. The reactions taking place in the ammonium ion test are the following:

Ammonia is liberated from the ammonium compound in the sample by sodium hydroxide.

$$NH_4^+ + OH^- \rightleftarrows NH_3 + H_2O$$

The liberated ammonia escapes from the solution and if present in sufficient quantity it can be detected by its odor. When this reaction is carried out in the centrifuge tube in the semimicro test for ammonium ion, the ammonia is driven from the solution when the temperature is raised and is carried into the acid solution by the air stream. In the acid solution the ammonia is converted to ammonium ion which is held in solution.

$$NH_3 + H^+ \longrightarrow NH_4^+$$

On the addition of sodium hydroxide, the ammonia is liberated again and reacts with the potassium mercuric iodide (potassium iodo-mercuriate), K_2HgI_4, to give a brown solution or a brown precipitate of $HgO \cdot Hg(NH_2)I$.

Chapter IV

THE DETECTION OF THE ANIONS

For the complete identification of salts, tests for both cations and anions are required. Tests involving reactions in solution show what cations and anions are present, but cannot show what salts were present in the original mixture. In this book, only the identification of ions is considered, and it is the purpose of this chapter to show how the anions may be separated and identified.

The detection of the following anions will be considered:

Arsenate	$AsO_4^{\equiv}$	Iodide	I^-
Arsenite	$AsO_3^{\equiv}$	Nitrate	NO_3^-
Bromide	Br^-	Nitrite	NO_2^-
Carbonate	$CO_3^{=}$	Phosphate	$PO_4^{\equiv}$
Chloride	Cl^-	Silicate	$SiO_3^{=}$
Chromate	$CrO_4^{=}$	Sulfate	$SO_4^{=}$
Ferricyanide	$Fe(CN)_6^{\equiv}$	Sulfide	$S^{=}$
Ferrocyanide	$Fe(CN)_6^{==}$	Sulfite	$SO_3^{=}$
Fluoride	F^-	Thiocyanate	CNS^-

Certain limitations are set by the procedure to be given, and advantage should be taken of them in interpreting the results. It is assumed that, in general, anions that are oxidizing agents in an acid solution will not be present along with ions that are reducing agents. The reason is that an oxidizing ion would react with a reducing ion, either in the original mixture or when the material was dissolved, and one or the other would disappear, depending on which was present in the larger proportion. The oxidizing ions of the above list are the following:

Arsenate
Chromate
Ferricyanide
Nitrate
Nitrite

The reducing ions are

Arsenite
Ferrocyanide
Nitrite
Sulfide
Sulfite
Iodide

There are some exceptions to this restriction, however, and it will be assumed that such combinations as arsenate and arsenite, and ferricyanide and ferrocyanide ions may be present. Sulfide and sulfite ions should not be present together, as these react to give sulfur. Nitrate and nitrite ions should not both be present because no provision has been made for detecting nitrate ion in the presence of nitrite ion. It will be assumed that no silicates that are soluble in water will be present, and if silver ion is present there will be no halide ions.

44. Preliminary Observations. The results of the cation analysis may be helpful in the anion analysis, and it is assumed that the cation analysis will be carried out first.

(1) In the precipitation of the hydrogen sulfide group of cations, arsenate and arsenite ions are converted to sulfides of arsenic, and consequently arsenic is found in the tin group. Absence of arsenic is proof of the absence of arsenate and arsenite ions.

(2) Hydrogen sulfide reduces chromate ion (or dichromate ion) to chromic ion, Cr^{+++}, and this is then detected in the ammonium sulfide group. Absence of chromic ion among the cations is proof of the absence of chromate or dichromate ion. The presence of chromic ion, however, is not a proof of the presence of chromate ion, because it could have been furnished by a chromic salt such as chromic chloride, $CrCl_3$.

(3) The presence or absence of the silicate ion becomes evident when the unknown material is brought into solution for the cation analysis and no other tests need be made.

(4) In the cation analysis it is necessary to know whether or not phosphate ion is present, and unless it is known to be absent a test is made for it previous to the precipitation of the ammonium sulfide group.

(5) A knowledge of the cations present, together with a knowledge of the behavior of the mixture when treated with water or acids, usually reveals something concerning the anions present. To take advantage of these facts one must have in mind some data as to the solubilities of various compounds; such data as is given on page 96. If a material is completely soluble in water and no cations other than sodium, potassium and ammonium are present, any of the anions might be present. However, if other cations are present, the behavior

of the material when the attempt is made to dissolve it often shows that one or more of the anions must be absent, and may give some hints as to the ions present. For example, if an unknown material not soluble in water is completely dissolved by 6 *M* HCl and contains barium ion, it cannot contain sulfate ion. Barium sulfate is not dissolved by 6 *M* HCl. If in addition a gas is evolved on treatment with the acid, the unknown material must contain an ion of one of a limited number of acids that decompose to give gases, possibly carbonate ion.

Before starting the anion analysis, one should consider carefully what conclusions may be drawn from the results of the cation analysis.

45. Preparation of a Solution for Systematic Analysis. It is first necessary to dissolve the unknown material. If no cations other than the alkali metal and ammonium ions are present, a solution can be prepared by dissolving about 3 g. in 45 ml. of water (*micro: 0.2 g. in 3 ml.*) heating gently, if necessary, and stirring.

If other cations are present, the sample must be treated to remove them before proceeding with the analysis. To about 3 g. of the finely powdered material (*micro: 0.2 g. in a large test tube*) add 45 ml. of 1.5 *M* Na_2CO_3 (*micro: 3 ml.*) and boil gently for 5 minutes, shaking or stirring frequently to mix the solid material with the solution. Replace the water lost by evaporation. Filter and reject the solid portion.

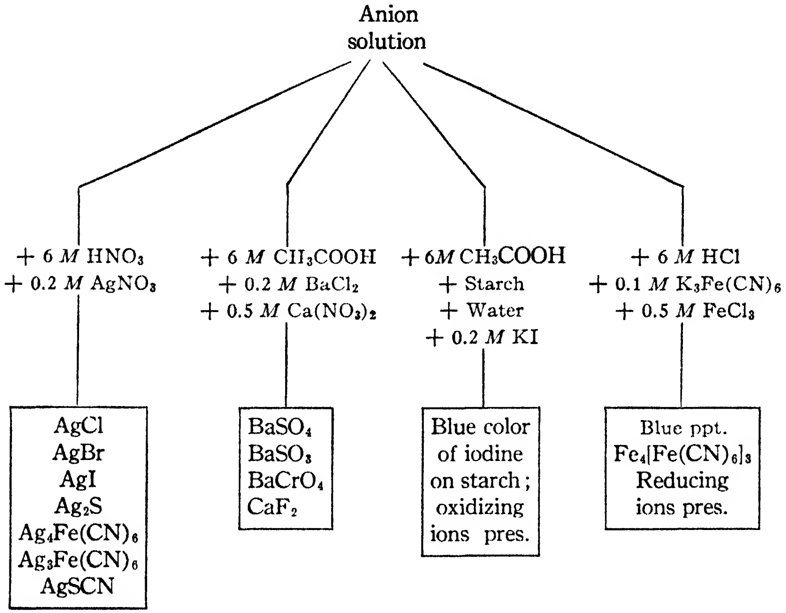
The solution containing the anions, whether prepared by dissolving the alkali metal or ammonium salts or by the sodium carbonate treatment, will be called the "anion solution" in the directions that follow.

Even if the unknown material is insoluble in water, the treatment with sodium carbonate ordinarily results in getting at least a part of each anion species into solution. For example, when lead sulfate is treated in this way, insoluble lead carbonate and soluble sodium sulfate are formed.

$$\underline{PbSO_4} + Na_2CO_3 \longrightarrow \underline{PbCO_3} + Na_2SO_4$$

If silver halides are present in the unknown, however, treatment with sodium carbonate fails to bring the halide ion into solution. Also, some of the sulfides and phosphates are not decomposed in this way.

The first step in the systematic analysis is to test for the presence of four different groups of anions. The procedure is shown briefly in Outline 10 and described in detail below. A fifth group of anions consists of ions not included in or not satisfactorily detected in the other four groups, but there is no group test for them.



OUTLINE 10. Tests for the anion groups.

46. Group 1. The Halogen Group. The first group of anions consists of the following ions which are precipitated from an acid solution by silver nitrate.

Ion		*Color of Ag Salt*
Chloride	Cl^-	white
Bromide	Br^-	light yellow
Iodide	I^-	light yellow
Sulfide	$S^=$	black
Ferrocyanide	$Fe(CN)_6^{----}$	white[1]
Ferricyanide	$Fe(CN)_6^{\equiv}$	orange
Thiocyanate	SCN^-	white

[1] Accompanied by a small quantity of blue ferric ferrocyanide.

To test for the presence of the halogen group, acidify 1 ml. of the anion solution with 6 M HNO_3 and add 1 ml. in excess. Add 1 ml. of 0.2 M silver nitrate. Absence of a precipitate shows the absence of all of the halogen group. Formation of a precipitate shows the presence of one or more of the above ions.

Observe the color of the precipitate. Some idea of the composition of the precipitate can be obtained from its color. If the color is pure white, only silver chloride or silver thiocyanate, or possibly silver ferrocyanide, or a mixture of these can be present. If the precipitate is black, on the other hand, it is not safe to assume the absence of any of the anions. Likewise, an orange precipitate of silver ferricyanide can mask either a yellow or a white precipitate mixed with it.

In observing the color of a precipitate there is danger of an incorrect conclusion if the precipitate was formed in a colored solution, with the colored substance remaining in solution. A white precipitate may be colored yellow by a yellow solution, and the yellow color may remain, for example, even after filtering, or centrifuging, and washing. When the color of a silver salt is thus in doubt, it is well to centrifuge, wash the precipitate, dissolve by means of ammonium hydroxide if possible (silver iodide, ferrocyanide and sulfide are not dissolved by ammonia) and reprecipitate by adding nitric acid. This second precipitate should have its true color.

47. Group 2. The Sulfate Group. The sulfate group consists of the ions that are precipitated by either barium ion or calcium ion in a slightly acid solution, namely the following:

Ion		*Color of Ba or Ca Salt*
Sulfate	$SO_4^{=}$	white
Sulfite	$SO_3^{=}$	white
Chromate	$CrO_4^{=}$	yellow
Fluoride	F^-	white

To 2 ml. of the anion solution add enough 6 M acetic acid, 0.5 ml. at a time, to make the solution acid to methyl orange paper. If any precipitate forms, remove it by centrifuging and reject it. Add 1 ml. each of 0.2 M $BaCl_2$ and 0.5 M $Ca(NO_3)_2$, heat the mixture nearly to boiling and if no precipitate appears immediately, let it stand for at least 10 minutes. A precipitate shows the presence of the sulfate group.

48. Group 3. The Oxidizing Group. This group is composed of anions that can oxidize iodide ion to iodine in an acid solution.

The Oxidizing Group of Anions

Dichromate [1]	$Cr_2O_7^{-}$
Ferricyanide	$Fe(CN)_6^{\equiv}$
Nitrite	NO_2^-

To 2 ml. of the anion solution add 2 ml. of 6 *M* CH_3COOH. Add 1 ml. of starch solution and 5 ml. of water. Finally add 1 ml. of 0.2 *M* KI. A blue color shows the presence of one or more ions that can oxidize iodide ion to iodine. The color is caused by adsorption of the iodine by the starch. Nitrate ion does not give a blue color unless more acid is added than is specified above.

49. Group 4. The Reducing Group. Four of the anions can reduce ferricyanide ion to ferrocyanide ion, and these belong to the reducing group. Ferrocyanide ion also belongs to this group, because the group is detected by a test for ferrocyanide ion after adding ferricyanide ion, which is reduced.

The Reducing Group of Anions

Ferrocyanide	$Fe(CN)_6^{--}$
Iodide	I^-
Nitrite	NO_2^-
Sulfide	S^-
Sulfite	SO_3^-

Acidify 2 ml. of the anion solution and add 1 ml. of 6 *M* HCl, dilute with 20 ml. of water and add a few drops of 0.1 *M* potassium ferricyanide, $K_3Fe(CN)_6$, (*not* $K_4Fe(CN)_6$) and 1 ml. of 0.5 *M* $FeCl_3$. If reducing ions are present, the ferricyanide ion is reduced to ferrocyanide ion and a blue or green sol (colloidal solution) or a blue precipitate of ferric ferrocyanide results. This solution or precipitate should be compared with the results of a blank test as described in the next paragraph.

It is not safe to draw conclusions from the test for reducing ions unless a blank test is made to test the reagents. Repeat the test using water as the sample and compare the color with the color resulting from the test on the anion solution. If the blue (or green) color of the latter test is much more pronounced

---

[1] Dichromate ion is formed when hydrogen ion is added to a chromate.

$$2\,CrO_4^- + 2\,H^+ \longrightarrow Cr_2O_7^- + H_2O$$

than that of the blank, reducing ions may be considered present. If both are the same color, reducing ions are absent.

Group 5. Ions for which adequate provision has not been made in other groups are included in Group 5.

Group 5 of the Anions

Arsenite	$AsO_3^{\equiv}$
Carbonate	$CO_3^{=}$
Phosphate	$PO_4^{\equiv}$
Silicate	$SiO_3^{=}$
Sulfide	$S^{=}$

These ions are not detected by a group reagent, but separate tests are made at the appropriate times and on appropriate samples. Sulfide ion is included here even though it appears in Group 1, because the carbonate treatment of the original sample may not bring sulfide ion into solution. Therefore the original sample must be tested for this ion if it is not found in Group 1.

50. Results of Group Tests. Several of the anions appear in more than one group. With the exception of the sulfide ion, absence of an ion in any one group is proof of its absence in any other group in which it appears. For example, if Group 3 is found absent, the ferricyanide ion can be considered absent when Group 1 is analyzed, and no test need be made for it. Therefore, tests for all of the groups should be made before any of the groups are analyzed.

51. Analysis of the Halogen Group. (*a*) *Sulfide Ion.* If the halogen group is present, take a new sample consisting of 5 ml. of the anion solution and add 5 ml. of water. If the anion solution was prepared without the addition of sodium carbonate, add 2 ml. of 1.5 M Na_2CO_3 at this point. Add 1 ml. of 0.1 M $Pb(NO_3)_2$; this will give either a black or a white precipitate or a mixture of the two. A black precipitate is lead sulfide, which shows the presence of sulfide ion. A pure white precipitate is lead carbonate caused by the sodium carbonate present, and indicates the absence of sulfide ion *in the solution tested.*[1]

---

[1] It should be remembered that when the unknown material is treated with sodium carbonate, sulfide ion may not be brought into solution with the other anions. Therefore, if sulfide ion is found absent here, another test is made in Group 5.

If sulfide ion is absent (in this solution) filter, wash the precipitate twice, adding the washings to the main part of the solution, and reject the precipitate.

If sulfide ion is present, continue the addition of 0.1 *M* $Pb(NO_3)_2$ until a white precipitate is formed on further addition instead of a black one. This indicates complete precipitation of the sulfide ion. If the color of the newly formed precipitate on the addition of a drop of reagent cannot be seen because of too much black lead sulfide, filter a portion and test the filtrate. After the test, return the filtered portion to the main body of the solution. (*Micro: centrifuge and without separating the solution add a drop of reagent to the clear solution above the precipitate.*) If the result of this test is more black precipitate, repeat the addition of lead nitrate solution and the testing until a white precipitate is formed. Then filter and reject the precipitate.

(*b*) *Ferricyanide and Ferrocyanide Ions.* Acidify the filtrate from the lead sulfide or lead carbonate by the addition of 6 *M* CH_3COOH drop by drop, stirring well and testing with litmus. Add in excess approximately one-third as much of the acetic acid as was required to acidify the solution and stir well. Add 5 to 10 ml. of 0.5 *M* $Ni(NO_3)_2$. A precipitate shows the presence of ferricyanide ion or ferrocyanide ion, or both. Filter and wash the precipitate twice, adding the washings to the filtrate, and reject the precipitate.

If a precipitate is obtained when nickel nitrate is added, a portion of the original anion solution must be tested for both ferricyanide and ferrocyanide ions, in the following manner. To 1 ml. of the solution to be tested, add 1 ml. of 6 *M* HNO_3 (or more if necessary) to acidify the solution, and then add a few drops of 0.5 *M* $FeCl_3$. A dark blue finely divided precipitate (ferric ferrocyanide, often called Prussian blue) shows the presence of ferrocyanide ion. Filter and test for completeness of precipitation by adding another drop of 0.5 *M* $FeCl_3$. If precipitation is complete, add a few drops of 0.5 *M* $FeSO_4$ (ferr*ous* sulfate). A dark blue precipitate shows the presence of ferricyanide ion.

(*c*) *Thiocyanate and the Halide Ions.* To the solution from which the nickel salts were precipitated (or the solution to which the nickel nitrate was added, if no precipitate was obtained) add 5 ml. of 6 *M* HNO_3 and 1 to 2 ml. of 0.2 *M* $AgNO_3$. A precipitate shows the presence of either chloride, bromide, iodide or thiocyanate ion or any combination of these. Absence of a precipitate shows the absence of these ions. If a precipitate is formed, add enough more 0.2 *M* $AgNO_3$ to complete the precipitation; this may require as much as 5 to 10 ml. Filter, test for completeness of precipitation and reject the filtrate.

Transfer the filter paper containing the silver salts to a beaker, add 5 ml. of 15 *M* NH_4OH (**caution:** *avoid inhaling the fumes from concentrated ammonia solutions*), stir well and remove the paper. Ammonia dissolves all of the silver chloride present and part of the bromide and thiocyanate, but practically none of the iodide. Transfer the mixture to a precipitation flask and saturate the solution with hydrogen sulfide.[1] Filter, receiving the solution in a porcelain casserole (*micro: crucible*) and reject the silver sulfide precipitate.[2] The solution may contain thiocyanate, iodide, bromide and chloride ions.

(*d*) *Iodide and Thiocyanate Ions.* Boil the solution in the casserole to remove ammonia and hydrogen sulfide,[3] then add 5 ml. of water and filter if there is any precipitate, rejecting the precipitate. Transfer the solution to a flask (*micro: centrifuge tube*), acidify with 6 *M* HNO_3 and add 10 ml. of 0.2 *M* $Fe(NO_3)_3$ and 1 or 2 ml. of carbon tetrachloride, CCl_4.[4] Shake the flask

---

[1] Silver sulfide is precipitated.

$$Ag^+ + S^= \longrightarrow \underline{Ag_2S}$$

Silver iodide gives enough silver ion to take part in this reaction also.

$$\underline{AgI} \longrightarrow Ag^+ + I^-$$

Because of the extremely small solubility of silver sulfide, silver iodide reacts practically completely to form silver sulfide and iodide ion.

$$2\,\underline{AgI} + S^= \longrightarrow \underline{Ag_2S} + I^-$$

However, silver iodide particles that become surrounded by silver sulfide and cut off from contact with the solution will fail to react.

[2] See footnote on page 36 about saving silver residues.

[3] The ammonium sulfide decomposes.

$$2\,NH_4^+ + S^= \longrightarrow NH_3\uparrow + NH_4^+ + HS^-$$

$$NH_4^+ + HS^- \longrightarrow NH_3\uparrow + H_2S\uparrow$$

Removal of ammonia and hydrogen sulfide by boiling causes both reactions to proceed toward the right, and eventually results in complete decomposition of the ammonium sulfide.

[4] Ferric ion oxidizes iodide ion to iodine and also unites with thiocyanate ion to form un-ionized ferric thiocyanate, $Fe(CNS)_3$, which is intensely red

to mix thoroughly. (*Micro: stopper the tube and shake.*) If the carbon tetrachloride is colored pink or purple by dissolved iodine, the presence of iodide ion is shown.

If much iodide ion is present (purple color) transfer the water solution to another flask (a medicine dropper will help) and reject the colored carbon tetrachloride; then add more carbon tetrachloride, shake, and separate to remove more iodine from the solution. Repeat until the carbon tetrachloride layer no longer becomes a dark purple. A pink color signifies satisfactory separation for the present. If after this treatment the water solution is red in color, the presence of thiocyanate ion is shown.

(*e*) *Bromide Ion.* Any iodine remaining and also the ferric and ferrous ions must be removed and the thiocyanate ion destroyed before a test is made for bromide ion. If iodide ion has been found present, boil the water solution in a casserole gently for one minute. (*Micro: heat in a crucible without boiling.*) If iodide ion is absent, the boiling may be omitted, as its purpose is to expel the remainder of the iodine. Make the solution alkaline by addition of 6 M NaOH and filter. This removes the iron in the form of ferric and ferrous hydroxides. The remainder of this paragraph may be skipped if thiocyanate ion is absent. Transfer the filtrate from the iron hydroxides to a casserole, add 10 ml. of 1.5 M Na_2CO_3 and 0.5 g. (*micro: 25 mg.*) of potassium persulfate ($K_2S_2O_8$) and evaporate to dryness. Dissolve the residue in 10 ml. of water.

To the solution from which iron and thiocyanate ions have been removed, which should have a volume of 10 ml. (evaporate if necessary), add 1 or 2 ml. of CCl_4, acidify with 6 M HNO_3, add a few small crystals of potassium persulfate, warm gently and shake or stir. If any iodine is liberated, remove the water solution from the carbon tetrachloride and repeat the treatment. If no iodine is liberated, proceed with the next step without separating the carbon tetrachloride.

Cool the mixture in a porcelain casserole, add 4 ml. of 16 M HNO_3 and stir vigorously. If thiocyanate ion was present, an orange color will appear, caused by the oxidation products of

in color. The carbon tetrachloride is added to extract the iodine from the water solution. Iodine dissolved in carbon tetrachloride is pink or purple in color.

the thiocyanate ion. This color should disappear in the course of a minute if the solution is stirred occasionally. If after standing a minute the carbon tetrachloride remains yellow or brown, the presence of bromide ion is shown. The nitric acid oxidizes bromide ion to bromine, which is extracted by the carbon tetrachloride.

(*f*) *Chloride Ion.* Separate the water solution from the carbon tetrachloride, rejecting the latter, and dilute the water solution to 25 or 30 ml. (*micro: 1 to 1.5 ml.*). If bromide ion is absent, the remainder of this paragraph may be skipped and the solution tested immediately for chloride ion. If bromide ion is present, add 0.02 M $KMnO_4$ a drop or two at a time with continuous shaking or stirring until the solution remains pink for at least one minute. This oxidizes any remaining bromide ion to bromine. Then dilute to 100 ml. (*micro: 5 ml.*) and boil gently for 5 minutes. Disappearance of the pink color is to be expected. If a precipitate is formed, filter and reject it.

To the solution from which bromide ion has been removed (or in which it has been found absent) add 2 ml. of 0.2 M $AgNO_3$. A white precipitate shows the presence of chloride ion.[1]

If the white precipitate is small in quantity, the chloride ion may have come from the reagents rather than from the sample. If this is suspected, make a solution for a blank test by mixing the following:

15 ml. of 1.5 M Na_2CO_3
10 ml. of 0.5 M $Ni(NO_3)_2$
10 ml. of 0.2 M $Fe(NO_3)_3$
5 ml. of 15 M NH_4OH

Filter, reject the precipitate, acidify the filtrate with 6 M HNO_3 and add 2 ml. of 0.2 M $AgNO_3$. Compare the result of this test with the result of the test on the unknown material. If the quantities of precipitate in the two tests are practically equal, chloride ion was probably absent or present to the extent of only a trace in the sample.

52. Analysis of the Sulfate Group. (*a*) *Sulfate Ion.* If the sulfate group has been found present, take for analysis a new sample of 5 ml. of the anion solution. Sulfide and thiocyanate

---

[1] See footnote on page 36 about saving silver residues. Add enough hydrochloric acid to precipitate all of the silver as silver chloride.

ions, if present, must be removed. If they are absent, omit the next paragraph.

If the anion solution was made without adding sodium carbonate, add to the sample 2 ml. of 1.5 M Na_2CO_3. Then add 5 ml. of 0.2 M $AgNO_3$, filter and reject the precipitate.[1] If sulfide ion was present, test the filtrate with another drop of 0.2 M $AgNO_3$; a *black* precipitate indicates that still more silver nitrate must be added. In this case filter again. When all of the sulfide ion has been precipitated, or if sulfide ion was absent, remove a few drops of the solution, acidify with 6 M HCl, and test for thiocyanate ion by adding a drop or two of 0.5 M $FeCl_3$ solution. If thiocyanate ion is still present, add more silver nitrate to precipitate it, filter again and reject the precipitate. Test for thiocyanate ion again. When the solution has been freed from both sulfide and thiocyanate ions, proceed with the following paragraph.

Acidify the sample (which must be free from sulfide and thiocyanate ions) with 6 M HCl, adding 0.5 ml. at a time and testing with litmus, and add 1 ml. in excess. If any silver chloride is precipitated, heat nearly to boiling and filter to remove it. Then add 5 ml. of 0.2 M $BaCl_2$. A white precipitate of barium sulfate shows the presence of sulfate ion. Filter, rejecting the precipitate, and add 3 ml. more of the 0.2 M $BaCl_2$ to the filtrate. If a precipitate is formed, filter again and repeat.

(*b*) *Sulfite Ion.* When no more precipitate is formed on the addition of barium chloride in the test for sulfate ion, add saturated bromine solution (bromine water) 1 ml. at a time until a small portion of the solution removed on the end of a glass rod turns starch-iodide paper dark blue. Heat the mixture nearly to boiling. A white precipitate of barium sulfate shows the presence of sulfite ion. Filter and reject the precipitate.

(*c*) *Chromate and Fluoride Ions.* To the filtrate from the barium sulfate precipitate in the test for sulfite ion add 10 ml. of 3 M CH_3COONH_4. A yellow precipitate is barium chromate, which shows the presence of chromate ion. If no precipitate is formed, add a few drops of 0.2 M $BaCl_2$ to insure the presence of barium ion. If a precipitate is formed, filter and

---

[1] See footnote on page 36 about saving silver residues.

test for completeness of precipitation by adding a few drops more of 0.2 *M* $BaCl_2$. If necessary add more reagent and filter again. Save the filtrate for the test for fluoride ion.

If there is any doubt as to the identity of the supposed barium chromate precipitate, test it in the following manner. Add enough 6 *M* HNO_3 to dissolve it, and then add 5 ml. of water and several drops of hydrogen peroxide solution, which can be prepared, if necessary, by adding about 0.1 g. of sodium peroxide, Na_2O_2, to 1 ml. of cold 6 *M* HNO_3 (*micro: 20 mg. to 4 drops of 6 M* HNO_3*, approximately*). A blue coloration that disappears fairly rapidly is evidence of the presence of dichromic acid, $H_2Cr_2O_7$, which indicates that the original sample contained either chromate or dichromate ion.

To the solution separated from the barium chromate, which is to be tested for fluoride ion, add 0.5 *M* $Ca(NO_3)_2$ a few drops at a time as long as a precipitate is formed. A white gelatinous precipitate is calcium fluoride, CaF_2. Filter and reject the filtrate. (*Micro: if the precipitate does not settle well on centrifuging, try adding some sodium chloride to flocculate it.*) Wash the precipitate once with about 10 ml. of water, and transfer it to a test tube. (*Micro: leave in the centrifuge tube.*) Add to the precipitate 1 ml. at a time some 1 *M* $Al(NO_3)_3$ with stirring or shaking. If the precipitate is calcium fluoride, it is dissolved by the addition of an aluminum salt.

53. Oxidizing and Reducing Anions. Some of the oxidizing and reducing ions were included in Groups 1 and 2 and it is assumed that tests for them have already been made.

(*a*) *Arsenate and Arsenite Ions.* While arsenate ion does not belong in the two groups, it is convenient to test for it along with arsenite ion. To 5 ml. of the anion solution, add 10 ml. of water and enough 6 *M* HNO_3, 1 ml. at a time, to make the solution slightly acid to litmus. Then add 6 *M* NH_4OH, 0.5 ml. at a time, until the solution is just alkaline to litmus. If there is a precipitate, filter and reject it. Add 10 ml. of magnesia mixture, and allow to stand for 10 minutes, stirring frequently. A white precipitate is either magnesium ammonium arsenate, $MgNH_4AsO_4$, or magnesium ammonium phosphate, $MgNH_4PO_4$, or a mixture of the two, and shows the presence of arsenate ion or phosphate ion, or both. Filter and set the filtrate aside for the arsenite test. Pour on the precipitate on the filter a mixture of 1 ml. of 0.2 *M* $AgNO_3$ and a few drops of 6 *M* CH_3COOH. (*Micro: to the precipitate add a few drops of 6 M* CH_3COOH *and a drop of 0.2 M* $AgNO_3$ *and stir.*) If the precipitate turns dark red, the presence of arsenate ion is shown; silver arsenate, Ag_3AsO_4, is formed as a dark red precipitate. If the result is doubtful, dissolve some of the precipitate in 5 ml. of 6 *M* HCl, add 1 ml. of 0.2 *M* KI and a few milliliters of carbon tetrachloride and shake. If the carbon tetrachloride extracts iodine from the mixture immediately, becoming pink or purple in color, arsenate ion must have been present, because neither phosphate ion nor arsenite ion can oxidize iodide ion to iodine. Oxygen from the air oxidizes iodide ion slowly. No definite test for phosphate ion is made at this point.

Test the solution separated from the magnesium ammonium arsenate (or phosphate) precipitate for arsenite ion. Add 6 *M* HCl, 1 ml. at a time, until the solution is acid to litmus and pass in hydrogen sulfide. An immediate yellow precipitate shows the presence of arsenite ion. Some arsen*ate* ion might be present in this solution because of incomplete precipitation by the magnesia mixture, but its reaction with hydrogen sulfide in a weakly acid solution is so slow that it is not likely to be confused with arsen*ite* ion.

(*b*) *Nitrate and Nitrite Ions.* A test for nitrate and nitrite ions together is made by reducing these ions to ammonia and testing for the ammonia by means of Nessler's reagent, as in the test for ammonium ion. This test is best carried out on a semi-micro scale in the apparatus shown in Fig. 6, page 70. The material so tested must be free from ammonium ion. If the unknown material has not already been tested for ammonium ion, a portion of the anion solution must be tested for it at this point. If ammonium ion is present, it must be removed from the solution to be tested for nitrate and nitrite ions as described in the next paragraph; if absent, the steps necessary for its removal may be omitted.

To remove ammonium ion from a sample of the anion solution, place 5 drops of the solution in a porcelain crucible, add about 10 drops of water and 5 drops of 6 *M* NaOH and boil carefully until about three quarters of the liquid has been boiled away. Transfer the remainder of the liquid to the sample tube of the apparatus used for the ammonium ion test, and test to see whether or not more ammonia is given off when the solution is heated and a *slow* stream of ammonia-free air drawn through it. Keep the solution resulting from the ammonia test for comparison with the results of the nitrate-nitrite test.

If ammonium ion is known to be absent from the solution to be tested, place the sample in the smaller tube of the apparatus shown in Fig. 6, page 70, and place 2 ml. of water and one drop of 6 *M* HCl in the large test tube as if an ammonia test were to be made. If ammonium ion was present, use the sample on which the ammonium ion test has just been made. Add 5 drops of 6 *M* NaOH and a few small pieces of aluminum metal to the sample to be tested for nitrate and nitrite ions, attach the sample tube to the apparatus for the ammonium ion test, draw a slow current of ammonia-free air through it, and heat carefully until hydrogen is being evolved rapidly, and for about a minute thereafter. Then remove the large test tube from the apparatus (before disconnecting from the suction) and test the solution in it for ammonia.[1] If an ammonium ion test has been made, compare the results of the two tests. A positive test for ammonia in the nitrate-nitrite test shows the presence of nitrate or nitrite ion or both in the solution tested.

(*c*) *Nitrite Ion.* If the presence of nitrite or nitrate ion has been shown in the previous test, a separate test on the original anion solution should be made for the presence of nitrite ion. This is done by the reaction of nitrite ion with thio-urea, $H_2S \cdot CS \cdot NH_2$, to give thiocyanate ion.

$$H_2N \cdot CS \cdot NH_2 + NO_2^- \longrightarrow N_2 + SCN^- + 2\,H_2O$$

If thiocyanate ion has been shown to be present in the anion solution, it must be removed before testing for nitrite ion. This can be done by shaking 2 ml. of the anion solution with 0.1 to 0.2 g. (*micro: 10 to 20 mg.*) of Ag_2CO_3. The mixture should then be filtered,[2] and a few drops of the filtrate tested for thiocyanate ion by acidifying with 6 *M* HCl and adding a drop of 0.5 *M* $FeCl_3$. If thiocyanate ion is still present, repeat

---

[1] In the strongly alkaline solution, aluminum reduces nitrate and nitrite ions to ammonia and also reacts with the hydroxide ion to liberate hydrogen.

[2] The solid silver salts are rejected. See footnote on page 36 about saving silver residues.

the treatment with silver carbonate. When the solution is entirely free from thiocyanate ion, test for nitrite ion as follows.

To 1 ml. of the solution to be tested for nitrite ion add 1 ml. of 6 M CH_3COOH (this should be enough to make the solution acid) and then add 1 ml. of 1 M thio-urea solution and let the mixture stand for 5 minutes. Add 1 ml. of 6 M HCl and a few drops of 0.5 M $FeCl_3$. The red color of ferric thiocyanate shows the presence of nitrite ion.

54. Carbonate, Sulfide and Phosphate Ions. When the anion solution used for the above tests is prepared with the use of a sodium carbonate solution, the test for carbonate ion must be made on a separate portion of the original unknown material. Even when the unknown material is soluble and contains no cations other than the alkali metals, it is convenient to make the carbonate test on the original solid material.

A test for sulfide ion has presumably been made in the analysis of Group 1, but if this test was negative, and if the unknown material was treated with sodium carbonate solution to prepare the anion solution, a test should be made for sulfide ion in the original unknown material. The reason for this is that a number of the sulfides are not decomposed by sodium carbonate. If sulfite ion was found present, however, it is to be assumed that sulfide ion is absent and no further test for it need be made. If a test for sulfide ion is to be made, it can be made conveniently along with the test for carbonate ion. The tests for carbonate and sulfide ions may be made conveniently on the semi-micro scale, even though the other tests are made on the ordinary scale.

Set up the apparatus used in the ammonium ion test, but with a stopper in the smaller tube that fits tightly. Do not connect with the suction; carbon dioxide from the air must not be allowed to enter. In the larger test tube place 2 ml. of 0.2 M $Ba(OH)_2$. In the smaller tube place a *mixture* of 30 mg. of the finely powdered unknown material and 50 mg. of granulated zinc. To this add about 0.5 ml. of water. The next thing to be added depends on whether sulfite ion ($SO_3^{=}$) is present or not; do either *a* or *b* following. (*a*) If sulfite ion is present, measure 1 ml. of 6 M HCl and add to it in very small portions, with cooling if necessary, 50 mg. of sodium peroxide. This reacts with some of the acid to give hydrogen peroxide, which will oxidize sulfite ion to sulfate ion. Add the acid solution containing the hydrogen peroxide to the sample in the small tube of the apparatus and quickly put the stopper in the tube. (*b*) If sulfite ion is absent, omit the sodium peroxide and add to the sample 0.5 ml. of 6 *M* HCl and stopper the tube immediately.

If bubbles of gas are not evolved rapidly, heat by immersing the small tube in hot water. In any case heat in this manner when the evolution of gas becomes slow or ceases. This helps to drive the gases evolved into the barium hydroxide solution. A white precipitate after time has been allowed for the carbon dioxide to get into the barium hydroxide solution shows the presence of carbonate ion in the unknown material. Acidify the mixture of barium carbonate and barium hydroxide solution with 6 *M* CH_3COOH; the precipitate should dissolve.

If sulfite ion is absent from the unknown material, and only 0.5 ml. of 6 *M* HCl has been added instead of the mixture of acid and hydrogen peroxide, a test for sulfide ion may be made. When the solution in the larger tube has been acidified with acetic acid, add a drop or two of lead nitrate solution. A black precipitate shows the presence of sulfide ion.

If an analysis for the cations has been made, it should be unnecessary to test for phosphate ion. Previous to the precipitation of the ammonium sulfide group in the cation analysis a test for phosphate ion must be made, unless this ion is known to be absent. However, if no analysis for the cations has been made, it may be necessary to test for phosphate ion.

If arsenate and arsenite ions are known to be absent, acidify 2 ml. of the solution containing the anions with 16 *M* nitric acid and add 5 ml. in excess, then add 5 ml. of 0.5 *M* $(NH_4)_2MoO_4$ (ammonium molybdate) and heat gently. If no precipitate appears, allow to stand 5 or 10 minutes before drawing final conclusions. A fine yellow precipitate of ammonium phospho-molybdate shows the presence of phosphate ion.

If either arsenate or arsenite is present, it must be removed before testing for phosphate ion, because these ions interfere with the test for phosphate ion. To 2 ml. of the anion solution (*micro: in a centrifuge tube*) add 2 ml. of 12 *M* HCl and a few drops of 0.2 *M* KI. Saturate the solution with hydrogen sulfide to precipitate arsenic sulfide. (*Micro: connect the centrifuge tube with the source of hydrogen sulfide by means of a glass tube and a tight-fitting one-hole stopper.*) Filter and test for completeness of precipitation. (*Micro: to test for completeness of precipitation, centrifuge and without removing the solution, pass more hydrogen sulfide into the tube and observe whether or not more precipitate is formed.*) When precipitation is complete, filter and reject the precipitate. Boil the filtrate to expel hydrogen sulfide and some of the acid, and then add 3 ml. of water, 5 ml. of 16 M HNO_3 and 5 ml. of 0.5 M $(NH_4)_2MoO_4$ to test for phosphate ion, as above.

EXERCISES

1. Suppose that a white unknown material was found to be completely soluble in water giving a neutral solution and to contain the following metallic ions. Ag^+, Cd^{++}, Zn^{++}, Ca^{++} and Ba^{++} and no others. Which anions could be assumed absent and which might be present? Give reasons for your conclusions.

2. Draw what conclusions you can as to the anions present from the following facts about an unknown mixture, giving the reasons by which you arrived at the conclusions:

(*a*) The material was a white powder.

(*b*) It was dissolved easily by very dilute hydrochloric acid with evolution of a gas. It was not soluble in water, or at least not entirely.

(*c*) Analysis for the cations showed the presence of Al^{+++}, Ba^{++}, Ca^{++} and Mg^{++}. Phosphate ion was absent.

(*d*) The solid was treated with sodium carbonate solution and filtered. The filtrate on being acidified with nitric acid gave a white precipitate with silver nitrate.

(*e*) The filtrate from the sodium carbonate treatment gave no test for the reducing group of anions.

Chapter V

THE ANALYSIS OF SOLID MATERIALS

PREVIOUS to the qualitative analysis of an unknown solid material by the methods of Chapters III and IV the material must be brought into solution. In many cases this presents no great difficulty. Many salts are soluble in water and many others are easily brought into solution by the action of acids. Sometimes, however, these relatively simple methods of treatment are not sufficient for getting an unknown material into solution completely. It has been stated in Chapter IV that, for most materials, treatment with sodium carbonate solution brings at least some of each of the anions into solution and at the same time precipitates most of the cations. This gives a solution well adapted to the detection of the anions. This chapter will be mainly concerned with the bringing of unknown materials into solution in preparation for cation analysis.

55. Preparation of the Sample. The first step to be taken in the analysis of a solid material is a careful examination of the sample, to gain any possible information of use in connection with the analysis. Observe the color and the odor, if any, and try to determine whether the material is composed of a single substance or more than one substance. Next, finely powder one or two grams (*micro: 0.1 g.*) of the solid, if this has not already been done. If the material is a brittle metal it may often be powdered in a mortar. A tough metal may be filed with a clean file and the filings caught on clean paper, or some small pieces may be cut from the metal in a lathe. The sample should be reduced to pieces as small as circumstances will allow, before any attempt is made to dissolve it.

56. Methods for Dissolving Solids. Two general methods are described below for attempting to dissolve solid materials. The first and simpler of these is called the "trial method," and the second and more time-consuming is the "fusion method." The more laborious fusion method brings about the dissolving of many solids not affected by the trial method. But the quickly applied trial method is sufficient for dissolving most solids met in elementary courses in qualitative analysis and should always be tried before resorting to the fusion method.

If the material to be analyzed is not a metal or alloy, the first step in the trial method is to try to dissolve a small portion of the powdered material in water, following the procedure in Section 57. Metals and alloys generally do not react with water, and acids must be used to dissolve them. Specific directions for dissolving metals and alloys are given in Section 58.

If water does not dissolve the trial sample, an attempt is made to dissolve a second small portion by means of some chemical reagent. If the first reagent tried does not work, others are tried with other small portions of the sample until a reagent is found that dissolves the trial portion completely. The reagent that dissolved the small trial portion is then used to dissolve a sample of a size suitable for analysis.

The tests to find a reagent for dissolving the sample should not be hurried, as the process of dissolving is usually much slower than the reverse process of precipitation. Continued agitation and heating often help considerably. Whenever a choice of dissolving reagents is possible, the preference is in the following order: water, hydrochloric acid, nitric acid, sodium or potassium hydroxide, and aqua regia. When all of these fail, the fusion method should be tried.

Sometimes a reagent will dissolve a sample completely except for a slight cloudiness or a few minute particles. Often no kind of ion is lost if these particles are removed by filtration and rejected. The cloudiness may be caused by impurities in the reagents. The solid particles may sometimes fail to be dissolved because the sample was not sufficiently pulverized before beginning the analysis; coarse particles dissolve more slowly than fine ones. Consult the instructor before rejecting any part of the sample that does not dissolve.

57. The Trial Method for Solids Other than Metals and Alloys. For the first trial, place in a test tube 0.05 to 0.1 g. (*micro: 5 to 10 mg.*) of the finely powdered unknown material and 5 ml. of water. Thoroughly agitate (or stir) the contents of the tube. If solid matter remains, heat the liquid. Continue the agitation and heating as long as any solid seems to be dissolving. If the trial sample is dissolved by water, dissolve a 0.5 g. (*micro: 50 mg.*) portion of the powdered sample in water and proceed with the separation and detection of the cations as directed in Chapter III.

If the first trial sample is not dissolved by water, try in the same manner to dissolve other portions, one at a time, in 5-ml. portions of the following reagents, trying the reagents in the order given: 2 or 3 M HCl, 2 M HNO_3, 6 M HNO_3, 6 M NaOH or KOH, and a mixture of four volumes of 12 M HCl with one volume of 16 M HNO_3.[1]

If none of the reagents dissolves the sample satisfactorily, skip the remainder of this section and treat the sample by means of the carbonate fusion method, directions for which are given in Section 59.

If a reagent is found that dissolves the trial portion completely, dissolve a 0.5 g. (*micro: 50 mg.*) sample of the powdered unknown material in as little as possible of the reagent. When the sample is completely dissolved, proceed according to the appropriate one of the following alternatives and analyze the solution for the cations.

1. If the sample was dissolved by water or 2 M HNO_3, begin with the precipitation of the hydrochloric acid group, Section 11, Chapter III.
2. If the sample was dissolved by 2 or 3 M HCl, the hydrochloric acid group must be absent. Treat the solution as the filtrate from the hydrochloric acid group and begin with the precipitation of the hydrogen sulfide group, Section 14.
3. If the sample was dissolved by 6 M NaOH or KOH, add 6 M HCl until the solution is acid to litmus, then 10 ml. in excess. Shake well and start the analysis with the precipitation of the hydrogen sulfide group, Section 14.
4. If the sample was dissolved by 6 M HNO_3 or by the mixture of hydrochloric and nitric acids (aqua regia) evaporate the solution (*micro: in a crucible*) under a hood or near an opening in the fume duct to a volume of about 2 to 3 ml. Add 25 ml. of water and begin the analysis with the precipitation of the hydrochloric acid group, Section 11, if nitric acid dissolved the sample, or with Section 14 if aqua regia was used.

---

[1] Mixtures of hydrochloric and nitric acids are often called "aqua regia," Latin for "royal water."

58. The Trial Method for Metals and Alloys. Treat 30 to 50 mg. (*micro: 3 to 5 mg.*) of the finely divided metal or alloy with one or two milliliters of $6\,M$ HNO_3 and heat. If the sample is not attacked, try $16\,M$ HNO_3 in the same way. If nitric acid is unsatisfactory, try some $12\,M$ HCl, using a new sample. Heat as long as any reaction seems to be taking place. If $12\,M$ HCl does not react with the sample, add just enough $16\,M$ HNO_3 to start a reaction and heat. Add more $16\,M$ HNO_3 in small portions if necessary to keep the reaction going, but avoid adding more than necessary.

It may be found that both nitric acid and the mixture of hydrochloric and nitric acids attack the sample, but leave a white residue undissolved. One way to proceed in such a case is to use hydrochloric and nitric acids and treat the residue as the hydrochloric acid group precipitate.[1] Another way is to treat the sample with nitric acid, then filter, wash the white residue and treat it with $12\,M$ HCl. A third possibility is to fuse the residue with sodium carbonate, as described in Section 59. It will be assumed that samples of metals and alloys not attacked by one of the acid treatments will not be given in an elementary course in qualitative analysis.

When a satisfactory acid treatment has been found, dissolve a sample of 0.2 to 0.3 g. (*micro: 20 to 30 mg.*) and evaporate the solution nearly to dryness to remove the excess acid. Dissolve the residue in a small quantity of water, adding more acid if necessary. If nitric acid alone was used to dissolve the sample, start the analysis with the hydrochloric acid group, Section 11. If hydrochloric acid was used and no white residue was left behind, or if a white residue was separated and analyzed as the hydrochloric acid group precipitate, start the analysis with the hydrogen sulfide group, Section 14.

59. The Fusion Method. Materials that are not dissolved by acid treatment may be brought into solution by the fusion method. The sample is first treated with an acid to dissolve as much of it as possible. The undissolved residue is dried, mixed with sodium and potassium carbonates and heated until the whole mass melts, or "fuses." The molten material or "melt" is allowed to cool and is then treated with water. This gives a soluble portion and a residue consisting at least partly

---

[1] Mercury, if present, will probably be oxidized to the mercuric state.

of carbonates, which react readily with acids to give soluble compounds. The sample is thus separated into three parts, the first part going into the acid solution before the fusion, the second part dissolving in water after fusion and the third remaining undissolved by the water after fusion. The third part is brought into solution by nitric acid. These three solutions may sometimes be combined for analysis. Tests for sodium and potassium ions cannot be made in the second and third parts of the sample, or in a combined solution, since these ions have been added. It is preferable to analyze each of the three solutions separately.

Procedure. As a result of the trial method something should be known about the behavior of the sample with acids. Treat 0.5 g. (*micro: 50 mg.*) of the finely powdered unknown material with 5 ml. (*micro: 10 drops*) of the particular reagent found to have the most dissolving effect, or if no difference was apparent use 5 ml. of 12 M HCl. Filter and reserve the filtrate for analysis. Transfer the residue to a casserole (*micro: porcelain crucible*). This may be accomplished by unfolding the filter paper, holding it over the casserole, and washing the residue from it into the casserole by means of a stream of water. An alternative procedure is to burn the paper with the residue on it, allowing the ash to fall into the casserole. If water was used to transfer the residue, add 10 ml. of 1.5 M Na_2CO_3 and evaporate just to dryness, heating very carefully when the volume becomes small to avoid breaking the casserole. Loosen and pulverize the solid material by means of a glass rod. Add 2 g. (*micro: 0.2 g.*) each of anhydrous sodium and potassium carbonates and mix thoroughly. Transfer the mixture to a 10-ml. nickel crucible and heat with a Bunsen or Meker burner until the mixture is completely melted. If the mixture does not melt when the crucible has been brought to a red heat, it is probable that the preparation of the mixture was faulty. When the mixture has been melted (fused) allow it to cool, place the crucible on its side in a beaker and add enough water to cover the crucible. Allow to stand until the melt has crumbled, then scrape the solid material from the crucible, and heat and stir to dissolve as much as possible.

While the fused mass is dissolving, analyze the first (acid-soluble) portion of the unknown. First evaporate the solution to small volume to eliminate the excess acid, then dilute and analyze. The starting point for the analysis will depend on the acid used, as explained in connection with the trial method, Section 57.

On returning to the analysis of the fused portion, filter to separate the part that is soluble in water (second portion of the sample) from the part that does not dissolve in water (third portion) and set the filtrate aside for later examination. Transfer the residue (third portion) to a casserole, add 6 *M* HNO_3 with stirring until effervescence ceases and then 5 ml. in excess. Heat to boiling and, if any reaction seems to be taking place, continue to heat as long as the reaction continues. Filter, if necessary, and reject the residue.[1] Analyze the solution containing the third portion of the sample, omitting the analysis of the alkali group.

Acidify the filtrate containing the second portion of the sample with 12 *M* HCl, add 1 ml. in excess, and evaporate to dryness, heating carefully near the end of the evaporation to avoid breaking the casserole. The residue will contain a considerable amount of sodium and potassium chlorides. When the residue is entirely dry, heat for 5 or 10 minutes with a low flame and allow to cool. This renders any silica (SiO_2) present insoluble. Powder the residue with a glass rod and add 5 ml. of 6 *M* HCl and 15 ml. of water and heat to dissolve as much of the residue as possible. A white residue at this point is silica and shows the presence of silicate ion.[2] Filter, if necessary, and reject the residue. Analyze the solution, treating it as the filtrate from the hydrochloric acid group, and omitting the analysis of the alkali group.

REACTIONS INVOLVED IN DISSOLVING SOLIDS

In dissolving solid materials, observations of value in connection with the analysis can be made if one knows something

---

[1] The residue may consist of scale from the crucible or portions of the unknown material not attacked in the fusion because of large particle size or for other reasons. It is assumed that no appreciable part of the unknown material is lost in this way. If the residue to be rejected seems unreasonably large, consult the instructor. A few substances, such as stannic oxide, SnO_2, and silver chloride, are not attacked in a carbonate fusion.

[2] This is the only test given in this book for silicate ion. It is assumed that silicates given for analysis will not be dissolved by water or acids and must be treated by the fusion method.

of the solubility of various compounds and is familiar with the reactions that may take place. It is the purpose of the following sections to give some generalizations with respect to solubility and to describe briefly the types of reactions involved in dissolving the solid materials ordinarily met in qualitative analysis.

60. The Solubility of Salts in Water. Many salts dissolve freely in water, and many others do not. If we consider only the cations for which tests are given in the qualitative analysis scheme in this book and a few of the more common anions, it is possible to make some generalizations that are very useful in helping to keep solubility information in mind. The following generalized statements, while usually true, may not always be so. The term soluble, as here used, implies solubility to a degree useful in dissolving unknowns preparatory to analysis.

1. The following classes of substances are soluble in water:

(*a*) All nitrates.

(*b*) All salts of the alkali group metals.

(*c*) All chlorides, bromides and iodides except those of lead, silver and mercurous mercury.

(*d*) All sulfates except those of lead, silver, mercurous mercury, barium, strontium and calcium.

2. The following classes of substances are not soluble in water:

(*a*) All metallic oxides and hydroxides except those of barium, strontium, calcium and the alkali metals.

(*b*) All metallic sulfides, except those of the alkali and alkaline earth group metals.

(*c*) All carbonates except those of potassium, sodium and ammonium.

(*d*) All phosphates except those of potassium, sodium and ammonium.

(*e*) Most silicates.

Further information about the solubility of chemical compounds can be obtained from a chemical handbook or from other reference books.

61. Reaction of Salts with Acids. In general, a strong acid reacts with a salt of a weak acid to form the free weak acid and a salt of the strong acid. For example, sodium acetate, a salt of the weak acetic acid, reacts with hydrochloric acid to give acetic acid and sodium chloride.

$$CH_3COONa + HCl \longrightarrow CH_3COOH + NaCl$$

Written in the ionic form and representing hydrochloric acid in water solution as hydronium chloride, $H_3O^+ + Cl^-$, this reaction is:

$$CH_3COO^- + Na^+ + H_3O^+ + Cl^- \longrightarrow CH_3COOH + H_2O + Na^+ + Cl^-$$

or, more simply, omitting the sodium and chloride ions:

$$CH_3COO^- + H_3O^+ \rightleftarrows CH_3COOH + H_2O$$

The hydronium ion, H_3O^+, which is a strong acid, gives a proton (H^+) to the acetate ion. The acetate ion, being a stronger base than water, holds the proton more tightly than does the water. This reaction is reversible to a small extent (in other words, acetic acid ionizes in water) but in the presence of an excess of strong acid (H_3O^+) the reversibility is small.

If the salt of the weak acid is only slightly soluble in water, and the corresponding salt of the strong acid is soluble, the reaction results in the dissolving of the salt of the weak acid. When the strong acid is added to a solution in contact with the salt, the hydronium ion reacts first with the anion of the small dissolved portion of the salt. The result is to make the solution unsaturated with respect to the salt, and more salt dissolves. The newly dissolved portion reacts with the hydronium ion as soon as it comes into solution, and the solution is kept unsaturated. The passage of the salt into solution continues as long as any solid salt is left or until the supply of the strong acid is exhausted. For example, zinc sulfide, a salt of the weak acid hydrogen sulfide, is very little soluble in water but is dissolved readily by 1 *M* HCl solution. The reaction may be represented as follows:

$$ZnS \text{ (solid)} \rightleftarrows Zn^{++} + S^{=} \text{ (in solution)}$$

$$S^{=} + 2\,H_3O^+ \longrightarrow H_2S + 2\,H_2O$$

If the volume of the acid solution is small, hydrogen sulfide escapes as a gas, which favors the second reaction. The main reason why the reaction goes to completion, however, is that the sulfide ion is a fairly strong base and the protons from two hydronium ions unite with it to form un-ionized hydrogen sulfide. The removal of the sulfide ions upsets the equilibrium expressed in the first equation, causing more zinc sulfide to dissolve. The case of zinc sulfide is typical for salts of weak acids not soluble in water, most of which can be dissolved by strong acids.

The following classes of salts can be dissolved by dilute solutions of strong acids.

(*a*) Most oxides and hydroxides.
(*b*) All carbonates and phosphates.
(*c*) Most sulfides.
(*d*) Chromates.

Sometimes the physical state is of importance in determining whether or not a salt can be dissolved by an acid. Freshly precipitated salts are usually dissolved easily, while salts that have been heated to high temperatures sometimes react slowly.

Salts of *strong* acids that are not soluble in water are not dissolved to any practical extent by other strong acids. Barium sulfate and silver chloride are examples of this class of salts. The anions of such salts are very weak bases and do not take protons from hydronium ions. Therefore, the addition of a strong acid to a saturated solution of such a salt has practically no dissolving effect.

Another class of salts not dissolved by strong acids consists of salts of weak acids of very small solubility. Arsenious and mercuric sulfides, for example, are not dissolved even by 12 M HCl, because their solubility in water is extremely small.

62. Reaction of Metals with Acids. Metals above hydrogen in the electromotive series displace hydrogen from solutions of hydrochloric acid. These metals can therefore be dissolved by hydrochloric acid, with the practical exception of lead and tin, which react slowly. Most of the metals react more readily with nitric acid, which has an oxidizing action. Nitric acid reacts with some of the metals below hydrogen in the electromotive series as well as with nearly all of the metals above. Aluminum is exceptional in not reacting with nitric acid. A typical equation for the reaction of nitric acid with a metal is the following, in which it is assumed that the acid is dilute:

$$3\,Cu + 2\,NO_3^- + 8\,H_3O^+ \longrightarrow 3\,Cu^{++} + 2\,NO + 12\,H_2O$$

If the nitric acid is concentrated, nitrogen dioxide is formed instead of nitric oxide:

$$Cu + 2\,NO_3^- + 4\,H_3O^+ \longrightarrow Cu^{++} + 2\,NO_2 + 6\,H_2O$$

Antimony and tin react with nitric acid to form an oxide of antimony and metastannic acid ($H_{10}Sn_5O_{15}$), respectively, neither of which dissolves in the nitric acid solution or in water. Since antimony is below hydrogen in the electromotive series and tin just above, hydrochloric acid does not react well enough for practical purposes with either. Hydrochloric acid to which a little nitric acid is added, however, dissolves both antimony and tin. The function of the nitric acid is to oxidize the metals to ions, which then unite with chloride ions to form un-ionized molecules or complex ions.

An alloy containing antimony or tin and a metal of the hydrochloric acid group gives a white precipitate when treated with either nitric acid alone or nitric acid mixed with hydrochloric acid. In the first case the insoluble antimony oxide or metastannic acid is formed, and in the second case the chloride of the hydrochloric acid group metal is formed. For such an alloy the treatment with hydrochloric and nitric acids can be used and the precipitate treated as a hydrochloric acid group precipitate.

63. Dissolving Solids by Means of Sodium or Potassium Hydroxide. Some substances not dissolved by acids can be dissolved by solutions of soluble hydroxides. To this class of substances belong oxides or other compounds of elements having non-metallic properties. For example, arsenious oxide is dissolved by sodium hydroxide solution more easily than by either water or acids.

$$As_2O_3 + 6\,NaOH \longrightarrow 2\,Na_3AsO_3 + 3\,H_2O$$

When sodium arsenite ionizes, the negative ion is $AsO_3^{\equiv}$. The elements lead, arsenic, antimony, tin, zinc and aluminum are often found in negative ions. As a general, though not universal, rule the higher the valence of an element the greater is its tendency to become part of a negative ion.

64. Carbonate Fusion. The carbonate fusion is effective in dissolving most substances that are not volatilized below about 1000°. Its use in the laboratory is probably most often required for dissolving substances containing silicon compounds. Many of these have been exposed to high temperatures either in nature or in a manufacturing process and hence are sometimes termed "igneous" substances. Examples of igneous substances are blast furnace slags, smelter mattes, glass, cement, porcelain, chinaware, bricks, tiles and nearly all soils, clays and rocks.

As an example of a non-igneous substance that often requires fusion to dissolve it may be mentioned barium sulfate.

The carbonate fusion represents a type of reaction different from most of those met in qualitative analysis, a reaction not in water solution, but in molten sodium carbonate solution. To afford an idea of what happens during the process of fusion, the reactions used in dissolving asbestos (magnesium calcium silicate) will be described. The reaction during fusion may be represented by the following equation.

$$\underset{\substack{\text{Insol. in water.}\\ \text{Not dissolved by acids.}}}{Mg_3Ca(SiO_3)_4}+4\,Na_2CO_3\longrightarrow\underbrace{3\,MgCO_3+CaCO_3}_{\substack{\text{Insol in water.}\\ \text{Dissolved by acids.}}}+\underset{\text{Sol. in water.}}{4\,Na_2SiO_3}$$

When the melt is treated with water, the part that dissolves may be called the "soluble portion" and the part that does not dissolve, the "insoluble portion." Here the soluble portion contains sodium silicate and also the excess sodium carbonate. The insoluble portion is composed of a mixture of calcium and magnesium carbonates. After fusion the metallic elements of the asbestos are found in the insoluble portion, and the acid radical is found in the soluble portion. Fusion, besides providing a method for dissolving refractory materials, provides also a method for separating the cations from the anions of a material. At this point it may be well to recall that a number of anions contain metallic elements, and that if substances containing certain of the metallic elements are fused, anions of these metallic elements will be found in the soluble portion. Arsenate, antimonate, chromate, and permanganate ions are examples. For this reason the soluble portion is also analyzed for cations.

When the soluble and insoluble portions of the melt have been digested in water and separated by filtration, each portion receives a different treatment. The insoluble portion is dissolved by nitric acid and analyzed. The soluble portion is first made acid with 12 *M* HCl.

$$Na_2CO_3 + 2\,HCl \longrightarrow H_2O + CO_2 \uparrow + 2\,NaCl$$

$$Na_2SiO_3 + 2\,HCl \rightleftarrows H_2SiO_3 + 2\,NaCl$$

In the second reaction both of the products remain in solution. The next process, which consists of evaporating to dryness and baking the residue, affects only the silicic acid.

$$H_2SiO_3 \longrightarrow H_2O \uparrow + SiO_2$$

As the silicon dioxide is not soluble in water, the reaction is not reversible. This procedure is often spoken of as dehydrating the silica. Since the presence of soluble silicate ions interferes with many reactions in the scheme of analysis, it is important that this ion be removed. The "dehydration of the silica" provides a rather simple method for its removal.

Since a carbonate fusion is rather easily made, and since by it practically everything can be dissolved, the question may arise: "Why not make a fusion in the first place and omit the work of the acid treatment?" A temperature of from 800° to 900° is necessary to cause fusion. Any compounds that vaporize at or below these temperatures might be lost if they were not removed before the fusion. Compounds of mercury, arsenic, antimony and ammonium would thus be vaporized. By the acid treatment such volatile compounds may be removed from the sample before fusion.

The process of fusion usually dissolves enough of the crucible to give a test for the metal or metals of which it is composed. If this metal is found in the analysis of the fused portion, it may not be concluded with assurance that it was present in the sample. Similar reasoning applies to the sodium and potassium ions introduced as fluxing materials. (A flux is a substance mixed with another substance to promote fusion.)

On account of the foregoing considerations the procedure is planned so that the solution resulting from the acid treatment is analyzed by itself.

PART II

THEORY

Chapter VI

SOLUTIONS

A SOLUTION is a homogeneous mixture in which every part is just like every other part as far as can be observed. When blue copper sulfate is well mixed with sufficient water, the mixture is blue in color, and each drop of the mixture is the same shade of blue as every other drop. No solid particles are to be seen, even with the aid of a microscope, and there is no part of the mixture that differs in composition from any other part. Such a mixture is a solution.

Solutions are not necessarily liquids. Mixtures of gases are solutions, although it is not customary to call them so. Some mixtures of solids are solutions, and some are not. The discussion below will be limited to liquid solutions, and in particular to solutions in which water is the main component. Such solutions are the most common in nature, and they are the most important from the standpoint of analytical chemistry.

65. Solvent and Solute. In most solutions one of the components is present in much larger proportion than the other, or others. In a solution composed of a liquid and one or more solids, it is usually the liquid that is present in the largest proportion. If the solution is a mixture of liquids, one liquid often predominates. When such is the case, it is customary to call the component present in largest proportion the *solvent*, and to call the other components the *solutes*. If one gram of sugar is dissolved in 100 ml. of water, a solution is obtained in which sugar is the solute and water is the solvent. If to this sugar solution were added a small quantity of salt, there would be two solutes, sugar and salt dissolved in the solvent water.

Occasionally it is difficult or impossible to make a distinction between the solute and solvent. This is true, for example, in a solution composed of equal parts of alcohol and water.

It is usually important in dealing with a solution to know how much of the solute is present in a given quantity of solution. Sometimes it is sufficient to know whether the quantity of solute is large or small. In this case, the terms concentrated and dilute are often used. A concentrated solution contains a large quantity of solute and a dilute solution a small quantity of solute in a given quantity of solution.

However, the terms concentrated and dilute are often too indefinite. It is better when possible to have a numerical measure of the composition. One method of expressing the composition numerically is to state the number of grams of solute in either 100 ml. or in one liter of solution. Another method, which is often preferable, involves the use of the *mole,* or gram-molecular-weight, as a unit in stating the quantity of solute.

66. The Mole as a Chemical Unit. A mole of any pure substance is 6.06×10^{23} or 606,000,000,000,000,000,000,000 molecules of that substance. This very large number is called Avogadro's number and is denoted by the letter N.[1]

While the number of molecules in a mole is the same for all substances, the weight of a mole in grams varies widely. An analogy may illustrate this point. The number of eggs in a dozen eggs is equal to the number of bricks in a dozen bricks, but the weight in grams of a dozen eggs is much less than the weight in grams of a dozen bricks. The method of learning the weight of a dozen eggs or bricks is to weigh them. Similarly the weight of N molecules of a substance can be learned by weighing. This has been done for thousands of substances and the results have been summarized by means of chemical formulas and the atomic weight table. As a result, the weight in grams of a mole of any pure substance for which the formula is known can easily be calculated, since it is always numerically equal to the molecular weight of that substance. For example, N molecules (one mole) of water, H_2O (which has a molecular weight of 18), weigh 18 grams, while N molecules of hydrochloric acid, HCl, weigh 36.45 grams. Hence one molecule of hydrochloric acid is about twice as heavy as one of water. Also, if one mole (N molecules) of water weighs 18 grams, the weight of one molecule of water is obtained by dividing 18 by N.

---

[1] The letter N is used to stand for Avogadro's number and the letter *N* for the word "normal" in one method of expressing the concentration of a solution. The two should not be confused.

A solution of such concentration that one mole of solute is present in one liter of solution is called a 1 molar solution. A solution half as concentrated as a molar solution (0.5 mole per liter) is a half molar solution, or 0.5 *M*, the letter *M* standing for molar. A solution containing 0.0362 mole per liter is a 0.0362 molar or 0.0362 *M* solution.

When chemical thinking involves only the weights of substances taking part in a chemical reaction, the measurement of concentration in moles per liter offers no advantage over grams per liter. But when the numbers of molecules taking part in a chemical reaction are of importance, the usefulness of the mole becomes apparent. For example, the molecular weight of alcohol is 46 and that of sugar is 342. Hence a liter of 1 *M* alcohol solution contains 46 grams of alcohol while a liter of 1 *M* sugar solution contains 342 grams of sugar. A liter of the sugar solution contains more than seven times as much solute by weight as the alcohol solution, yet equal volumes of these solutions contain the same number of solute molecules. The two solutions have the same freezing point, because the freezing point depends on the numbers of dissolved molecules per unit volume of solution. Similarly certain other properties of the two solutions are the same.

Thus far it has been assumed that when a solid is dissolved in water it becomes separated into a very large number of very small pieces called molecules, and that the composition of each molecule is correctly represented by the formula assigned to the solid. Cane sugar has the formula $C_{12}H_{22}O_{11}$ and the presumption is that each of the molecules of sugar in a sugar solution is composed of 12 carbon atoms, 22 hydrogen atoms and 11 oxygen atoms. This presumption that the usual formula represents the composition of the dissolved molecules of a solute is generally in harmony with experience, unless the substances in question are salts.

According to the theory of ionization, salts are dissociated into *ions* in solution. The formula NaCl does not express the composition of the particles of solute in a sodium chloride solution. The particles are sodium ions, Na^+, and chloride ions, Cl^-. Nevertheless, a molecular weight may be calculated for sodium chloride from the formula NaCl and used in calculating molar concentrations without taking account of the dissociated state of sodium chloride in solution.[1] Thus a 1 *M* solution of sodium chloride contains 23 + 35.5 = 58.5 g. of NaCl per liter.

Even though there are no actual molecules having the formula NaCl in a crystal of sodium chloride, and few or none in a solution, the formula NaCl may be taken to stand for a unit quantity of sodium chloride. This unit quantity consists of one sodium ion, Na^+, and one chloride ion, Cl^-. A mole of sodium chloride on this basis consists of N sodium ions and N chloride ions.

This method of expressing the concentrations of salt solutions is often convenient and has been used frequently in this book.

When a concentration is given in grams per liter, it may be converted to molar concentration by dividing by the molecular weight. A sodium chloride solution containing 15.7 g. NaCl per liter has a molar concentration of

$$\frac{15.7}{58.5} = 0.268$$

the molecular weight of sodium chloride being 58.5.

67. Saturated Solutions. Solubility. The quantity of a solid that can dissolve in a given quantity of a liquid is limited. This quantity varies greatly for different solids in any one liquid and also for any one solid in different liquids. If more solid is added to a liquid than can be dissolved, and the two well mixed so that as much as possible of the solid dissolves, the solution is said to be a *saturated solution.* For example, if about 50 g. of sodium chloride should be added to 100 ml. of water, and the two mixed well at room temperature, 36 g. of the salt would dissolve and 14 g. would be left undissolved. The solution would be a saturated solution of sodium chloride in water. If a similar experiment should be carried out with silver chloride, only 0.0002 g. (or 0.2 mg.) would dissolve in 100 ml. of water, giving a saturated solution of silver chloride.

The concentration of a saturated solution is a measure of the ability of the solute to dissolve, and is called the *solubility* of the solute. The solubility can be expressed in several ways, the most important of these being (*1*) in grams of solute per

---

[1] The molecular weight so calculated is sometimes called a "formula weight" to distinguish it from a true molecular weight.

100 grams of water (which is practically 100 ml.); (*2*) in grams of solute per 100 g. of solution; (*3*) in grams of solute per liter of solution; and (*4*) in moles of solute per liter of solution. The fourth is the molar concentration of a saturated solution, and is sometimes called the molar solubility. When the solubility of a substance is given without mention of the solvent, it is usually understood that the solvent is water.

Different substances have different solubilities in water. Some are so little soluble that for most purposes they can be considered insoluble. It is probably wrong to consider anything to be absolutely insoluble, and the term insoluble should be understood to mean insoluble for practical purposes.

68. Supersaturated Solutions. It is often possible to prepare solutions that are more concentrated than saturated solutions. Such solutions are said to be *supersaturated.* One method of preparing a supersaturated solution is to prepare a saturated or nearly saturated solution at a high temperature, then to separate the solution carefully from any excess of solute and allow it to cool. Solubility usually increases with temperature, and a solution saturated at a high temperature becomes supersaturated when it cools. In time, solid solute usually separates from a supersaturated solution, and the concentration falls to the saturation value. The separation of the excess solid is favored by the addition of a crystal of the solid or sometimes by particles of dust, by crystals of other solids, or even by the rubbing of the inner wall of the container below the level of the solution with a glass rod.

When two substances react in solution to form a product of very small solubility, the first step in the reaction is undoubtedly the production of a supersaturated solution. In such a case the so-called "degree of supersaturation" is usually very large (that is, the concentration is many times as large as the solubility) and precipitation of the excess solute follows immediately. Such reactions are the foundation of qualitative analysis.

69. Equilibrium between Solute and Saturated Solution. According to the kinetic theory, when a solid substance is in contact with its saturated solution, there is a continuous interchange of molecules between the solid and the solution. When a solid dissolves, molecules pass from the solid into the solution.

The passage of molecules from solid to solution is partially compensated by the deposition of molecules from the solution on the solid. When the solution becomes saturated, the dissolving process (passage of molecules from solid to solution) goes on as before, but it is now exactly compensated by the precipitation (or crystallization) process, which consists in the passage of molecules from the solution to the solid. Exactly as many molecules pass from solid to solution in a given time as from solution to solid. The result is that there appears to be no further change. When the system has come to this state, it is said that the solid and solution are in *equilibrium* with each other. The term saturated solution is often defined as meaning a solution of such composition that it can exist in equilibrium with the pure solid solute.

70. Freezing Points of Solutions. Much light has been thrown on the condition of solutes in solution by studies of certain of the properties of solutions. Among the important properties studied is the property of beginning to solidify or freeze at a definite temperature.

The freezing point of either a pure solvent or a dilute solution is the temperature at which the liquid (solvent or solution) is in equilibrium with the frozen (or solid) *solvent*. When a dilute solution starts to freeze, the solid material formed consists of crystals of the pure solvent, and does not contain the solute at all. When salt water starts to freeze, the ice formed is pure ice, not ice containing salt. A salt solution, consequently, can be in equilibrium with pure ice.

A particular solution can exist in equilibrium with ice only at a single definite temperature. The temperature at which a water solution can exist in equilibrium with ice is called the *freezing point* of the solution.

The freezing point of a pure liquid is a very definite temperature characteristic of the liquid. The freezing point of pure water is 0° C., and at no other temperature can pure water be in equilibrium with ice, under atmospheric pressure. The freezing points of several pure liquids are given in Table 2.

The freezing point of a dilute solution is lower than the freezing point of the pure solvent. When a small quantity of a solute is added to water in equilibrium with ice, some of the ice melts and the temperature decreases. The temperature of a mixture of water and ice is 0°, and when salt is added the temperature drops below zero. The amount of decrease of the temperature depends on the quantity of salt added, provided the ice does not all melt before equilibrium is attained.

TABLE 2

FREEZING POINTS OF PURE LIQUIDS

Name	*Formula*	*Freezing Point* ° C
Water	H_2O	0
Ammonia	NH_3	− 78
Mercury	Hg	− 39
Sodium Chloride	$NaCl$	804
Carbon Tetrachloride	CCl_4	− 23
Acetic Acid	CH_3COOH	17
Sulfuric Acid	H_2SO_4	10
Ethyl Alcohol	C_2H_5OH	− 117

There is a simple law that gives the approximate relationship between the composition of a solution and its freezing point. The law is expressed by the equation

$$T_0 - T = k\frac{x}{M}$$

in which T_0 is the freezing point of the pure solvent, T the freezing point of the solution, x the quantity of solute in grams added to 1000 g. of solvent and M the molecular weight of the solute. The letter k stands for a fixed number, or constant, which is characteristic of the particular solvent. The quantity x/M is the quantity of solute in moles dissolved in 1000 g. of solvent. This equation states that the depression of the freezing point $(T_0 - T)$ is proportional to the quantity of solute (expressed in moles) dissolved in 1000 g. of solvent. Another way of reading it is that the depression of the freezing point can be calculated by multiplying the number of moles of solute dissolved in 1000 g. of solvent by k. In view of the fact that a mole represents a definite number of molecules, the law implies that the freezing point depends on the number of foreign molecules present, regardless of their chemical nature.

The value of k when water is the solvent is 1.86. Let us calculate the freezing point of a sugar solution containing 1 g.

of sugar in 1000 g. of water. Besides k we have x and T_0 given; the former is 1 g. and the latter is 0°, the freezing point of water. The molecular weight of sugar is 342. We desire to find the value of T.

$$0 - T = 1.86 \times \tfrac{1}{342}$$
$$T = -\ 0.0054^\circ$$

The law of freezing-point depression has been tested by numerous experiments, and though it is not exact as stated, it holds sufficiently well to be of importance. In Table 3 is given some experimental data by which the applicability of the law is illustrated. For the purpose of the test the equation can be put into the form

$$k = (T_0 - T)\frac{M}{x}$$

The freezing points of certain solutions of known concentration were determined experimentally. The difference between the freezing point of water and the observed freezing point gave $T_0 - T$. The value M/x was calculated from the concentration, and then by means of the equation the values of k were calculated. All values of k should be the same, according to the law as stated above.

TABLE 3

VALUES OF k FOR FOUR DIFFERENT SOLUTES IN WATER

Solute	*Formula*	M/x	$T_0 - T$	k
Sugar	$C_{12}H_{22}O_{11}$	20	0.094	1.88
Alcohol	C_2H_5OH	10	.183	1.83
Glycerine . . .	$C_3H_8O_3$	5	.374	1.87
Sodium Chloride	NaCl	100	.036	3.60

One important limitation of the law is illustrated in the table; it does not hold for salts. Another limitation of lesser importance is that even when salts are excluded, k is not always exactly the same, but is somewhat dependent on the nature of the substance. Also, if results for the same substance at different concentrations were given, it could be shown that k is not quite the same for all concentrations.

The law as given is only an approximation. It becomes more and more nearly exact the more dilute the solutions. A much more exact law has been formulated, but it is more complicated. A better, but more complicated law would not serve the present purpose any better than the one given, so it need not be considered.

The behavior of sodium chloride illustrated in Table 3 is typical of salts. The actual lowering of the freezing point by a salt is much larger than the calculated value.

71. Molecular Weights. As implied above, the lowering of the freezing point of a liquid by a solute and the concentration of the solute can be measured without much trouble. If k is also known, the equation can be solved to give the molecular weight. This gives a method for the determination of molecular weights in solution. The method is applicable to the extent to which the equation holds good. Obviously the molecular weights of salts cannot be determined in this way.

Let us illustrate the determination of a molecular weight by the freezing point method. A quantity of dextrose (corn sugar) weighing 3.5 g. was dissolved in 100 g. of water and the freezing point of the solution was found to be $-0.37°$. What is the molecular weight of dextrose?

A solution containing 3.5 g. per 100 g. of water contains 35 g. per 1000 g. If $T = -0.37°$, and $T_0 = 0°$,

$$T_0 - T = 0.37$$

$$0.37 = 1.86 \frac{35}{M}$$

$$M = 176$$

The true molecular weight is 180 corresponding to the formula $C_6H_{12}O_6$. The difference between 176 and 180 can be ascribed to experimental error.

72. Limitations of the Freezing Point Law. Besides being limited to substances other than salts, the freezing point law is not an exact law as given. This has been mentioned above, and is illustrated by the figures in Table 3.

The depression of the freezing point by a solute is not exactly proportional to the number of solute molecules present. The reason for this is connected with the attraction of the solute molecules for each other. The more concentrated the solution, the greater is this attraction, because the solute molecules are nearer together. Other unknown effects may have their influence also.

The behavior of solutes is somewhat similar to that of gases. Gas molecules attract each other and so do not obey the gas laws exactly. When gases are under high pressures, the attractive forces are quite large, and the gas laws are quite far from expressing the actual conditions.

73. Boiling Points. When a solute is dissolved in a solvent, the boiling point is raised. Just as in the lowering of the freezing point, the amount by which the boiling point is raised is proportional to the quantity of solute (in moles) regardless of what the solute is, and solutions of salts are exceptional. The molecular weight of a solute can be determined by the measurement of the elevation of the boiling point for a solution of known concentration. This is usually more difficult experimentally than the measurement of the depression of a freezing point.

74. Problems Involving Substances in Solution. While calculations are not particularly necessary in practical qualitative analysis, the understanding of certain calculations is necessary if the procedure is to be thoroughly understood. For example, let us assume that a piece of metal is being analyzed and that it contains silver, but no lead or mercury, and let us inquire as to how much 3 *M* HCl must be added in the hydrochloric acid group in order to be sure of precipitating all of the silver ion as silver chloride. If the sample of metal, weighing 25 mg., or 0.025 g. (semi-micro procedure) should be entirely composed of silver, the quantity of acid required would be the largest ever needed for the hydrochloric acid group with a 25 mg. sample. Let us calculate this quantity. We can assume that the sample has been dissolved by nitric acid, giving silver nitrate.

$$AgNO_3 + HCl \longrightarrow AgCl + HNO_3$$

One gram-atom of silver requires one mole of hydrochloric acid. The quantity of silver in the sample is

$$\frac{0.025}{108} = 0.00023 \text{ gram-atom of silver.}$$

This requires 0.00023 mole of acid. Now 1000 ml. of 3 *M* acid solution contains 3 moles of acid. Let x equal the volume of 3 *M* HCl that contain 0.00023 mole of acid.

$$\begin{aligned} 1000:3 &= x:0.00023 \\ 3\,x &= 1000 \times 0.00023 \\ x &= 0.08 \text{ ml. (approximately)} \end{aligned}$$

Therefore, to be sure of precipitating the maximum quantity of silver that could be present, at least 0.08 ml. of 3 *M* HCl must be added.

Another useful calculation is illustrated by the following problem. Suppose that some 1 *M* HCl is needed, and a supply of 3 *M* HCl is available. How much of the 3 *M* solution must be diluted to 10 ml. to make a 1 *M* solution? The following equation may be used:

$$V_1C_1 = V_2C_2$$

in which V_1 and C_1 are the volume and concentration, respectively, of the solution before dilution, and V_2 and C_2 are the volume and concentration of the diluted solution. By multiplying the volume of a solution by its concentration, the quantity of solute contained in the solution is calculated. Thus, V_1C_1 is the quantity of solute before dilution and V_2C_2 is the quantity of solute after dilution. The equation states that the quantity of solute before dilution is equal to the quantity after dilution, which obviously must be true, since no solute is added or subtracted. Applying this equation to the present problem, we have: $V_1 = x$, $C_1 = 3$, $V_2 = 10$, and $C_2 = 1$.

$$\begin{aligned} 3\,x &= 10 \\ x &= 3.3 \text{ ml.} \end{aligned}$$

Another way in which a solution may be diluted to a definite concentration is to add a calculated volume of water to a measured volume of the solution. To make this calculation in a simple manner involves the assumption that there is no contraction or expansion in volume on dilution; that is, that the volume of the diluted solution is equal to the volume of the more concentrated solution plus the volume of the water added. This is seldom, if ever, exactly true, but is a close enough approximation for purposes of qualitative analysis. Let us calculate how much water must be added to 2 ml. of

3 *M* HCl to make a 0.5 *M* solution. Let x be the final volume of 0.5 *M* HCl after dilution.

$$2 \times 3 = 0.5\,x$$
$$x = 12 \text{ ml.}$$

Since the final volume must be 12 ml. and the original volume was 2 ml., it is evident that 10 ml. of water must be added.

Another type of problem is illustrated by the following. What volume of 3 *M* H_2SO_4 must be added to react with the barium chloride in 5 ml. of 0.5 *M* $BaCl_2$?

$$H_2SO_4 + BaCl_2 \longrightarrow 2\,HCl + BaSO_4$$

This problem can be made very similar to the problem of the dilution of a solution. Since one mole of sulfuric acid is required for one mole of barium chloride, 5 ml. of 0.5 *M* $BaCl_2$ requires 5 ml. of 0.5 *M* H_2SO_4. We have only to calculate how much 3 *M* H_2SO_4 is required for the preparation of 5 ml. of 0.5 *M* H_2SO_4; this will be the quantity required for reaction with the barium chloride. Let x equal the required quantity of 3 *M* H_2SO_4.

$$3\,x = 5 \times 0.5$$
$$x = 0.83 \text{ ml.}$$

EXERCISES

1. How many grams are there in 1 mole each of NaCl, NaOH, $FeSO_4$, and $Cu(NH_3)_4SO_4$? *Ans.* 58.46, 40, 151.85, 227.71.

2. What weight of NaOH in grams is present in 250 ml. of 0.5 *M* NaOH solution? *Ans.* 5 g.

3. How many ml. of 1 *M* HCl will react with one mole of each of the following: NaOH, $Ca(OH)_2$, $Al(OH)_3$? How many ml. of 1 *M* H_2SO_4 will react with one mole of each of these substances?

4. How many moles of solute are there in the indicated quantities of each of the following solutions: 500 ml. of 6 *M* H_2SO_4, 6 ml. of 2 *M* $AlCl_3$, 15 ml. of 0.0003 *M* $AgNO_3$?

5. Assuming that the volumes are perfectly additive when solutions are mixed, compute the molar concentration that would result from mixing a liter of water and a liter of 2 *M* H_2SO_4. One liter of water and 500 ml. of 1 *M* HCl. How many ml. of water must be mixed with 20 ml. of 3 *M* H_2SO_4 to get a 2 *M* H_2SO_4 solution?

6. Compute the molar concentration of a nitric acid solution containing 378 grams of solute per liter of solution. *Ans.* 6 *M*.

7. Compute the molar concentration of a nitric acid solution containing 0.0043 grams of solute in 15 ml. of solution. *Ans.* 0.0043 *M*.

8. How many hydrogen atoms are there in 1 mole of H_2SO_4?

9. Which contains more molecules, 1 pound of alcohol (mol. wt. 46) or 1 pound of sugar (mol. wt. 342)?

10. If 1 ml. of water weighs 1 g., compute the number of moles and the number of molecules in 1 liter of water. *Ans.* 55.5, 55.5 N.

11. What is the molar solubility of potassium chloride (mol. wt. 74.6) if a liter of saturated solution contains 285 grams of solute? *Ans.* 3.83 *M*.

12. What is the molar solubility of mercurous chloride (mol. wt. 236) if a liter of saturated solution contains 0.00000045 (4.5×10^{-7}) grams of solute? *Ans.* 1.9×10^{-9} *M*.

13. If the molar solubility of potassium chlorate is 0.52, compute the number of grams in 100 ml. of saturated solution. *Ans.* 3.9 g.

14. Calculate the freezing point of a water solution of ethyl alcohol (mol. wt. 46) containing 10 g. of alcohol per 1000 g. of water. *Ans.* − 0.404°.

15. Calculate the freezing point that a solution of barium chloride containing 0.01 mole per 1000 g. of water would have if it were a normal electrolyte with a molecular weight corresponding to the formula $BaCl_2$. The actual freezing point is − 0.0503°. *Ans.* − 0.0186°.

16. The freezing point of a solution of glycerol, $C_3H_8O_3$, containing 0.460 g. of glycerol in 10 g. of water is − 0.945°. Calculate the molecular weight of glycerol. *Ans.* 90.5.

17. Given sufficient 16 *M* HNO_3 show how to prepare one liter of 3 *M* HNO_3. *Ans.* Dilute 188 ml. of 16 *M* acid to one liter.

18. How much 5 *M* H_2SO_4 is required to neutralize 20 ml. of 0.4 *M* NH_4OH? *Ans.* 0.8 ml.

19. How would the freezing point of a 0.1 *M* sugar solution compare with that of 0.1 *M* salt (NaCl) solution? Give reason.

20. How many grams of dextrose, $C_6H_{12}O_6$, must be dissolved in 200 g. of water in order to make a solution with a freezing point of − 0.1°? *Ans.* 1.94 g.

21. Calculate the freezing point of a solution of sugar (mol. wt. 342) containing 2.00 g. of sugar in 50 ml. of water. *Ans.* − 0.218°.

22. What volume of 18 *M* H_2SO_4 must be added to water and diluted to one liter to make a 3 *M* solution? *Ans.* 167 ml.

23. If 25 ml. of 0.1 *M* HCl is diluted to 150 ml., what is the concentration of the resulting solution? *Ans.* 0.0167 *M*.

24. Calculate the molar concentration of a solution made by the dilution of (*a*) 5 ml. of 6 *M* HCl to 100 ml., (*b*) 0.5 ml. of 3 *M* HCl to 5 ml. *Ans.* Both 0.3 *M*.

Chapter VII

ELECTROLYTIC DISSOCIATION (PART I)

SALTS are an important group of chemical compounds, and a knowledge of their behavior in water solution is necessary for a proper understanding of inorganic analytical chemistry. Some of the properties of salts in solution are discussed in this chapter.

75. Salts. It will be recalled that salts are compounds in which oppositely charged atoms or groups of atoms are held together by electrovalent bonds.[1] In the pure state and at ordinary temperatures, salts are crystalline solids. Investigation of salt crystals by means of X-rays has shown that the oppositely charged particles, usually called *ions*, are arranged in an orderly manner in the crystal, but in such a way that no molecules of the salt can be distinguished. Thus, a crystal of sodium chloride consists of sodium ions (positively charged sodium atoms, Na^+) and chloride ions (negatively charged chlorine atoms, $[:\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}:]^-$) arranged according to an orderly pattern. The ions hold each other in place in the crystal by means of their electrostatic charges. The ions should not be imagined as occupying fixed positions, but rather as vibrating within the crystal; never at rest, but never getting very far away from their average positions. The motion varies from ion to ion; some move slowly and some move rapidly. The motion is the more rapid the higher the temperature.

76. Salts in Solution. Keeping in mind this picture of a crystal of a salt, let us imagine it dropped into a vessel of water. Opposite electric charges have much less attraction for each other in water than in air (or various other media), and similar charges have correspondingly less repulsion. When the crystal is put into water, the effect is to lessen the attraction of the surface atoms for each other. Since the ions are vibrating as

---

[1] It is assumed that the reader is familiar with the modern theory of the structure of atoms and molecules. If not, it is recommended that the subject be reviewed in a modern textbook of general chemistry.

usual, some of the fast ones on the surface travel into the water a short distance. The electrical forces tending to draw them back are much weaker than when the crystal was surrounded by air, and the fastest of these ions escape entirely. The escape of some of the ions from the surface exposes others, which also escape. Since the violence of the vibratory motion of any one ion varies from time to time, all of the exposed ions have a chance to escape if they remain exposed long enough. Occasionally an ion from the solution comes back and is drawn into the crystal lattice again. Sometimes, however, the amount of solvent is large, and the crystal or crystals relatively small in amount, and the rate at which ions come back to the crystal remains smaller than the rate at which they leave the surface. In such a case, all of the crystalline material eventually dissolves.

If this mechanism for the dissolving of a salt is correct, one of two possible assumptions may be made as to the state of the salt in the solution. The first is that the ions remain more or less independent of each other in the solution and behave as separate particles. Doubtless they must attract each other somewhat because of their charges, but the attraction must be weaker than in the crystal, because of larger distances between ions, and because the water is a good dielectric. The second assumption is that the oppositely charged ions, on dissolving, unite to form molecules. We shall see that the second assumption is not in accordance with experimental evidence, and the first is the more probable. The possibility of a very small part of a dissolved salt being in the form of molecules is not excluded, however, especially in the more concentrated solutions.

77. Freezing Points of Salt Solutions. It has been mentioned in Chapter VI that sodium chloride solutions do not obey the law of freezing-point depression as substances like sugar and alcohol do. In reaching this conclusion, however, the molecular weight was taken as 58.5, which implied the assumption that the dissolved salt consisted of molecules of the composition NaCl. If the salt is assumed to be completely dissociated into sodium and chloride ions, the number of particles is doubled, and the calculated freezing point depression for 58.5 g. of sodium chloride in 1000 g. of water is twice as large as the depression for one mole of sugar, alcohol or glycerine; that is, 2 × 1.86° or 3.72°. The actual depression for 58.5 g. of sodium chloride per 1000 g. is a little less than 3.72°, but much nearer to it than to 1.86°. Other salts behave similarly. The proposition that salts are in the dissociated condition in water solution is thus supported by the results of freezing point measurements.

The same conclusion can be drawn from the results of boiling point measurements. Salts raise the boiling point more than organic compounds when the number of moles[1] per 1000 g. of solvent is the same, but if the dissociation of the salt is assumed, and the comparison made on the basis of an equal number of particles, salts have nearly the same effect as organic compounds, though a little smaller, as is true also of the freezing point depression.

There are some salts that cause freezing-point depressions of more than twice what would be calculated on the basis of their molecular weights. The depressions for salts like sodium sulfate, Na_2SO_4, and calcium chloride, $CaCl_2$, approach three times the normal depression, and for salts like $FeCl_3$ or $Fe_2(SO_4)_3$ they are still larger. One mole of any of these salts gives more than two moles of particles in solution.

The value of *k* calculated from the freezing point equation for a salt solution varies somewhat with the concentration of the salt. It is smaller in the more concentrated solutions, and increases as the solution becomes more and more dilute. This means either that in the more concentrated solutions the particles are not as efficient in producing their effect on the freezing point as in the more dilute solutions, or that in the more concentrated solutions there are fewer particles per unit weight of solute.

78. Conduction of Electricity by Salt Solutions. There are two classes of materials that conduct electricity. To one class belong all metals and alloys, graphite (carbon) and a few compounds. These materials conduct electricity without themselves undergoing any change. The other class is composed of solutions of salts and salts in the molten (liquid) state. Conductors of the second class undergo decomposition, or *elec-*

---

[1] When the term mole is used in connection with salts, it should be understood in the sense explained on page 107.

trolysis, when they conduct a current of electricity. Conductors of the first class are called metallic conductors and conductors of the second class are called electrolytic conductors.

Conduction by metallic conductors may be considered to consist merely in a flow of electrons through the metal. The valence electrons of the atoms are so loosely attached that they flow through the metal when a difference of electrical potential is maintained between different parts. In electrolytic conduction, on the other hand, the current is carried by ions, not by free electrons.

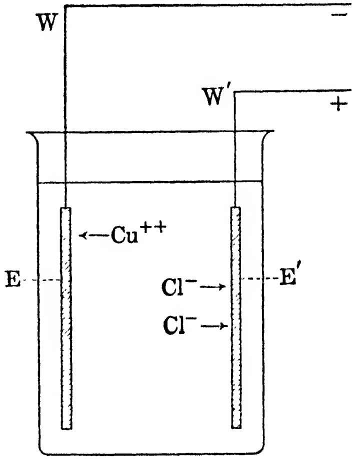


FIG. 7. Conduction of electricity by a copper chloride solution. E and E′ are the electrodes (cathode and anode, respectively) and W and W′ are the wires leading to the source of current. Cu^{++} is a copper ion and Cl^- is a chloride ion.

When a current is passed through a solution or a molten salt, the current must be passed into the liquid and out again by means of metallic conductors. The two metallic conductors that lead the current in and out of the liquid conductor are called the *electrodes.* When the liquid conductor is a salt solution, passage of the current causes the positively charged ion of the salt to travel toward the negative electrode, or *cathode,* and the negatively charged ion to travel toward the positive electrode, or *anode.* The behavior of a salt in solution when a current of electricity is passed through it is illustrated in Fig. 7.

Evidence in favor of this explanation of electrolytic conduction can be obtained by a simple experiment. The apparatus required is a U-shaped glass tube with an inlet tube at the lowest point of the U and a platinum electrode at the top of each branch of the U as shown in Fig. 8. A rubber tube is attached to the inlet tube, A, and at the other end to a glass vessel, B, that can serve as a reservoir and a funnel. The reservoir is lowered to a position slightly below the bottom of the U and filled with a solution of copper dichromate or of copper sulfate and potassium dichromate. Enough sodium or potassium sulfate solution is poured into the U-tube to fill the lower half, then the reservoir is carefully raised so that copper dichromate solution flows in at the bottom and elevates the other solution to the tops of the two branches of the U. The reservoir is then fixed in place. With sufficient care, the division between the colored copper dichromate solution and the colorless solution above it is sharp. Finally an electric current is passed between the platinum electrodes for a length of time that depends on the voltage and the size of the tube. After a time a blue band is seen between the two solutions on the side bearing the cathode, and an orange band on the side bearing the anode.

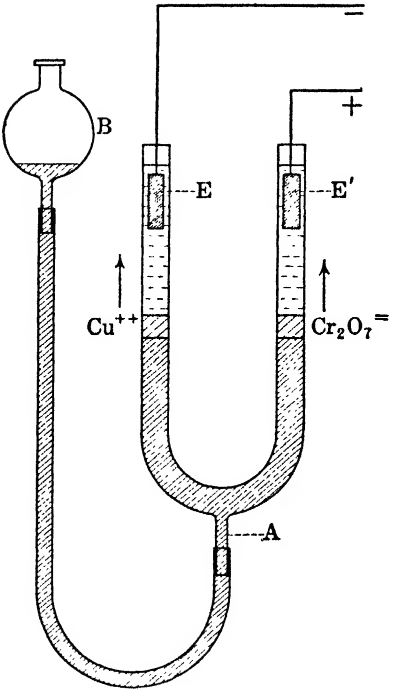


FIG. 8. Apparatus for showing the migration of ions.

A blue color is associated with the copper ion. Dilute solutions of copper sulfate, copper nitrate and copper chloride are all blue, since the solutions all contain the copper ion. The fact that solutions of sodium sulfate, sodium nitrate and sodium chloride are all colorless shows that the sulfate, nitrate and chloride ions are colorless. Potassium dichromate is orange, the orange color being associated with the dichromate ion. The color of copper dichromate is a combination of the blue of the copper ion and the orange of the dichromate ion. In the above experiment, the blue and orange bands are the result of the traveling, or *migration,* of the copper ion of the compound toward the cathode and the migration of the dichromate ion toward the anode.

In general, when an electric current passes through a solution of a salt or a strong acid, the metallic part of the salt, or the hydrogen of the acid, migrates toward the cathode, while the remainder of the compound migrates toward the anode. Compounds that conduct electricity in water solutions are called electrolytes.[1] Electrolytes conduct because they consist of two or more ions, which in solution (or in a liquid salt) are free to carry their charges to the electrodes. Ions that bear positive charges are called positive ions or *cations*, because they migrate to the cathode. Ions bearing negative charges are called negative ions or *anions*, because they migrate to the anode.

79. Electrolysis. When a current of electricity passes through a solution, or a molten salt, a chemical reaction takes place at each electrode. When the electrolyte in the solution is sulfuric acid or sodium hydroxide, for example, hydrogen and oxygen gases are evolved at the electrodes, and this process, called electrolysis, is a practical means of manufacturing these gases.

When copper chloride is electrolyzed, metallic copper is deposited on one electrode and chlorine is evolved at the other. Copper ions migrate to the cathode and are discharged there. The cathode contains an excess of electrons that are forced there by the electromotive force that drives the current through the circuit. At the same time the copper ions have fewer electrons than the number required for neutral atoms. When the copper ions come in contact with the negative electrode, electrons pass from the electrode to the ions and change the ions into neutral atoms of copper, which ordinarily stick to the electrode. If e represents an electron, the reaction may be represented by the following equation:

$$Cu^{++} + 2\,e \longrightarrow Cu$$

Simultaneously chloride ions migrate to the anode, and at the anode are relieved of their negative charges. The neutral atoms so formed unite in pairs to form chlorine molecules.

$$2\,Cl^- - 2\,e \longrightarrow Cl_2$$

If conditions are favorable when a solution of a copper salt is electrolyzed, the copper is deposited as a smooth layer on the

---

[1] The term electrolyte is also applied to the conducting solution in a voltaic cell, for example, the sulfuric acid in a lead storage cell.

cathode. Gold, silver, nickel, chromium and other metals are often deposited on the surfaces of metallic objects in this way, and the process is called electroplating.

The quantity of a metal deposited by electrolysis is exactly proportional to the quantity of electricity that flows through the solution, provided no other reaction takes place at the electrode. This is one of the laws of electrolysis discovered by Faraday. On this law is based the definition of the unit quantity of electricity; one coulomb of electricity is the quantity required to deposit 0.0011180 gram of silver. To deposit one gram-atom of silver or 107.88 g., the quantity of electricity required is 107.88 divided by 0.0011180 or approximately 96,500 coulombs. It is found that to deposit a gram-atom of other metals requires either exactly the same quantity of electricity as for silver, or a simple multiple of it. Thus, to deposit a gram-atom of copper, exactly twice 96,500 coulombs are required. Recalling that a gram-atom of copper contains the same number of atoms as a gram-atom of silver, it follows that a copper ion has twice the charge of a silver ion. Accordingly we write as the formula for silver ion Ag^+ and for copper ion Cu^{++}. Similarly the charges of other ions can be determined experimentally. It has been found that the number of unit charges on an ion is the same as the valence of the atom or radical in the compound of which the ion is a part. This is in accordance with the theory of electrovalence.

80. Ionization. If it is true, as postulated by the theory of electrolytic dissociation, or ionization, that electrolytes in solution are in the form of positive and negative ions, then transport experiments and experiments on electrolysis should show what the ions are and which kind of charge they bear.

Such experiments indicate that all acids are dissociated in such a way that the positive ion, or cation, is always the positively charged hydrogen atom, called the hydrogen ion, and the remainder of the molecule is the negative ion. It is very probable that the charged hydrogen atom is attached to a water molecule rather than free in solution. This picture of the hydrogen ion, however, is not a direct result of the experiments described, and it is only relatively recently that the concept of a hydrated hydrogen ion, $H_2O \cdot H^+$, has arisen. In writing equations involving the hydrogen ion it has been the custom in the past to neglect the water and to write the formula for the hydrogen ion H^+. In this book the formula H_3O^+ is used for the most part, but it is important to understand that at the present time both formulas (H^+ and H_3O^+) are used to represent the cation formed when an acid dissociates in water solution. The ionization of an acid such as hydrochloric acid may be considered to be a reaction with the water.

$$HCl + H_2O \longrightarrow H_3O^+ + Cl^-$$

The anions of various acids differ. The acid properties which are common to all acids are the properties of the hydrogen ion, and not connected with the anions of the acids.

Salts have no ion in common, and except for the conduction of electricity have no characteristic property common to all. Salts of a given metal, however, all have the same cation. Solutions of all sodium salts contain the sodium ion, Na^+. All copper salts contain the copper ion, and the blue color of dilute solutions of copper salts is the color of the copper ion. All silver salts contain the silver ion, and the reaction in solution with a chloride to precipitate silver chloride is a reaction of the silver ion. Similarly, all chlorides, including hydrochloric acid, give the chloride ion, Cl^-, in solution, and silver nitrate added to a solution of any chloride gives silver chloride. All sulfates contain the sulfate ion, $SO_4^=$, and barium chloride added to a solution of any sulfate gives a precipitate of barium sulfate, which is a test for the sulfate ion.

Ionization simplifies qualitative analysis, because it is necessary to test only for the various ions rather than for the much larger number of compounds that might be made by various combinations of the positive and negative ions. At the same time ionization imposes the limitation that when two or more salts are dissolved in a solution, the identities of the original salts disappear, and only uncombined ions remain. Thus, the actual salts composing a mixture of salts cannot be identified by a method in which the salts are brought into solution. Only the ions of which the salts are composed are identified in this way.

The ions formed by a number of representative compounds in solution are shown in Table 4. It will be noticed that polybasic acids can ionize in two or more ways. Phosphoric acid can ionize to give H_3O^+ and $H_2PO_4^-$. This anion ionizes less than the original phosphoric acid, but a small part of it ionizes to give another H_3O^+ and $HPO_4^{=}$, and a small part of the anion $HPO_4^{=}$ ionizes to give a third H_3O^+ and $PO_4^{\equiv}$.

TABLE 4

MANNER OF IONIZATION OF SOME COMMON ELECTROLYTES

Electrolyte	*Ions*	*Electrolyte*	*Ions*
HCl	$H_3O^+ + Cl^-$	NH_4OH	$NH_4^+ + OH^-$
HNO_3	$H_3O^+ + NO_3^-$	$Ba(OH)_2$	$Ba^{++} + 2\,OH^-$
H_2SO_4	$H_3O^+ + HSO_4^-$	$NaCl$	$Na^+ + Cl^-$
	$2\,H_3O^+ + SO_4^{=}$	Na_2SO_4	$2\,Na^+ + SO_4^{=}$
H_3PO_4	$H_3O^+ + H_2PO_4^-$	$ZnSO_4$	$Zn^{++} + SO_4^{=}$
	$2\,H_3O^+ + HPO_4^{=}$	Na_3PO_4	$3\,Na^+ + PO_4^{\equiv}$
	$3\,H_3O^+ + PO_4^{\equiv}$	$CuCl_2$	$Cu^{++} + 2\,Cl^-$
$NaOH$	$Na^+ + OH^-$	$PbCl_2$	$Pb^{++} + 2\,Cl^-$

EXERCISES

1. What evidence is there that the particles into which an electrolyte dissociates in solution bear electric charges?

2. What is the difference between a strong electrolyte and a weak electrolyte (*a*) experimentally and (*b*) from the point of view of the theory of ionization?

3. How do electrolytes differ from non-electrolytes with respect to (*a*) freezing points of their solutions and (*b*) conduction of electricity by their solutions? How are these facts interpreted in the theory of ionization?

4. Give the formulas for the ions furnished by the following electrolytes: KI, $MgBr_2$, K_2CrO_4, NH_4NO_3, $Ca_3(AsO_4)_2$, $(NH_4)_4Fe(CN)_6$, $Na_3Co(NO_2)_6$.

5. Explain why some of the reactions of sodium chloride in solution are identical with some of the reactions of ammonium chloride.

6. How could it be shown that the bismuth ion, Bi^{+++}, has a positive charge of three units?

7. Why do all soluble silver salts behave alike in solution in giving a precipitate of silver chloride when hydrochloric acid is added?

Chapter VIII

ELECTROLYTIC DISSOCIATION (PART II)

IT HAS been shown in Chapter VII that when salts are dissolved in water, the ions are separated or dissociated from each other and exist in solution as more or less independent, electrically charged particles. Certain other substances, such as acids, react with water to give ions. It may now be asked whether solutions of acids and salts are composed entirely of ions or whether neutral molecules are present in solution along with the ions.

81. Extent of Dissociation into Ions. It can be shown that some electrolytes conduct an electric current much better than others, when the molar concentration is the same. Thus, a 1 *M* hydrochloric acid solution is a much better conductor than a 1 *M* acetic acid solution, and a 1 *M* sodium hydroxide solution is a much better conductor than a 1 *M* ammonium hydroxide solution.

Quantitative data on the extent of dissociation can be obtained by means of electrical conductance measurements. The conductance, κ, of a solution is defined as the reciprocal of its electrical resistance, $\kappa = 1/R$, and conductance measurements are measurements of resistance. Suppose two platinum electrodes each 1 sq. cm. in area were placed 1 cm. apart, then 1 ml. of solution was placed in the cubical space so formed, and the resistance between the electrodes measured. The reciprocal of the resistance so found would be the specific conductance, κ, of the solution. The apparatus actually used does not have these exact dimensions, but a correction factor, the cell constant, is used to correct the measured conductance to give the specific conductance. Further details of such measurements need not be given here; they are given in books on physical chemistry.

By multiplying the specific conductance by the volume of solution in milliliters that contains a gram-equivalent,[1] the

---

[1] A gram-equivalent is equal to a mole for electrolytes giving only two ions of unit charge, such as NaCl, HCl and CH_3COOH. For electrolytes of the

equivalent conductance, Λ, is obtained. This calculation is equivalent to making the electrodes so large in area that the quantity of solution containing a gram-equivalent is held between them, but keeping them 1 cm. apart. Since the current that passes through a solution is carried by migration of the ions to the electrodes, the equivalent conductance represents the conducting action of all the ions in a gram-equivalent of solute.

The equivalent conductances of some typical electrolytes are given in Table 5. These figures were calculated from resistances expressed in ohms, and the corresponding conductance unit is called the reciprocal ohm. The values for the concentration $1/\infty$ were found by an extrapolation based on the other values, except for acetic acid for which an indirect method was used. The concentration $1/\infty$ should be taken to mean that one gram-equivalent of solute is dissolved in an infinite quantity of water.

TABLE 5

EQUIVALENT CONDUCTANCE IN RECIPROCAL OHMS OF SOME ELECTROLYTES IN WATER SOLUTION

Concentration	HCl	*Equivalent Conductance*, Λ		
N		NaCl	$BaCl_2$	Acetic Acid
0.1	391.2	106.7	90.8	5.20
.01	411.9	118.4	106.7	16.2
.001	421.2	123.7	115.6	48.6
.0001	424.5	125.6	—	133.3
$1/\infty$	426.0	126.4	120.9	390.6

It can be seen that the equivalent conductance in every case increases as the concentration decreases. There are two important factors that could cause this.

(1) If the electrolyte is only partially dissociated into ions, and the degree of dissociation increases as the solution is diluted, the equivalent conductance should also increase with dilution. In this case, the greater the dilution becomes, the more ions there will be in a gram-equivalent of the electrolyte.

type $BaCl_2$, Na_2SO_4 or $MgSO_4$ the gram-equivalent is equal to half of a mole, and for electrolytes of the type of $AlCl_3$ it is equal to one-third of a mole.

Increase in the degree of dissociation with dilution would be expected, at least for acids, from a consideration of the effect of dilution on an ionization reaction at equilibrium. Let us take as an example acetic acid in equilibrium with its ions in a dilute solution.

$$CH_3COOH + H_2O \rightleftarrows CH_3COO^- + H_3O^+ \qquad (1)$$

The velocity of the forward reaction depends on the concentration of acetic acid, and can be expected to decrease when the solution is diluted, since the concentration of water does not change much. The velocity of the reverse reaction, however, is dependent on the *product* of the concentrations of the two ions, and this velocity decreases faster as the solution is diluted than that of the forward reaction. Therefore, a partially ionized electrolyte should become ionized to a greater and greater extent as the solution is diluted. If the state of infinite dilution (concentration $1/\infty$) is imagined, it can be seen that in such a state the ions would be so far apart that they would never come together to form un-ionized molecules. At infinite dilution, therefore, electrolytes can be considered to be completely dissociated into ions, and the equivalent conductance at infinite dilution (Λ_0) is the conductance of one gram-equivalent of the anions and one gram-equivalent of the cations of the electrolyte.

If all this is true, and if there are no other complications, the fraction ionized should be given by Λ/Λ_0. It can be seen that for three of the electrolytes in the table the fraction ionized that would be calculated in this way is large, but for the fourth (acetic acid) it is much smaller. The first three are typical *strong* electrolytes while the fourth, acetic acid, is a typical *weak* one.

The fraction ionized calculated in this way is only approximately correct, however, and not as near the truth for strong electrolytes as for weak ones. This is the result of neglecting the second cause of the change of equivalent conductance with concentration.

(2) The conductance of a solution depends not only on the number of ions present, but also on how fast the ions travel, or migrate, through the solution. It has been found that the more dilute the solution the faster the ions move. The ions inter-

fere with each other in their migration, and the closer together they are the more they interfere. For many years after the theory of ionization was proposed, the change of speed of migration with dilution was not recognized. Eventually it was learned that this factor accounts for practically all of the change of equivalent conductance with concentration of strong electrolytes in dilute solutions.

82. Strong Electrolytes. Hydrochloric acid (in solution), sodium chloride and barium chloride are typical of the class of strong electrolytes, which includes nearly all salts and a number of acids. Nitric, sulfuric, and perchloric acids belong to this class. Electrolytes of this class are practically entirely ionized in dilute solutions.

It might seem that freezing point data are not in accord with the view that strong electrolytes are completely dissociated into ions in solution. The depression of the freezing point by a strong electrolyte that gives two ions is always somewhat less than twice the freezing point depression for a non-electrolyte at the same molar concentration. This could be interpreted as showing that the electrolyte is not completely dissociated. A better explanation is that every positive ion in the solution attracts every negative ion, and *vice versa*, and on this account the ions are less efficient at lowering the freezing point than the more nearly independent molecules of a non-electrolyte. Thus, it is consistent with known facts to assume that in a sodium chloride solution there are exactly twice as many ions as there are molecules in a sugar solution of the same volume and molar concentration.

83. The Calculation of Ion Concentrations. It has been shown in Chapter VI that the molar concentration of a salt in solution can be calculated without taking account of the ionization of the salt. It is sometimes necessary to calculate the concentrations of the ions of a salt from the molar concentration of the salt.

The calculation is very simple for dilute solutions of salts of the type of sodium chloride or magnesium sulfate, which ionize to give equal numbers of cations and anions. For such salts the concentration of each of the ions is equal to the molar concentration of the salt. Thus, in 0.25 M NaCl the concentration of the sodium ion is 0.25 M and the concentration of the chloride ion is 0.25 *M*. This follows from the fact that a mole of sodium chloride is made up of N sodium ions and N chloride ions, and consequently in a 0.25 *M* solution there are 0.25 N sodium ions and 0.25 N chloride ions per liter. Similarly in 0.42 *M* $MgSO_4$ the magnesium ion concentration is 0.42 *M* and the sulfate ion concentration is 0.42 *M*.

Salts of the type of barium chloride, $BaCl_2$, give two anions to each cation in solution. In 0.25 *M* $BaCl_2$ the barium ion concentration is 0.25 *M*, and since there are two chloride ions for each barium ion, the chloride ion concentration is 0.50 *M*. Similarly in 0.1 *M* Na_2SO_4 the sulfate ion concentration is 0.1 *M* and the sodium ion concentration is 0.2 *M*.

84. Weak Electrolytes. Because of the change in migration velocity of the ions with dilution, Λ/Λ_0 is not an accurate measure of the fraction of a weak electrolyte that is ionized. In the infinitely dilute solution the ions travel faster than in the solution in which Λ is measured. Instead of Λ_0, the denominator should be the equivalent conductance, Λ_e, that the electrolyte would have if it were completely ionized and the concentration were equal to the concentration of the *ions* in the solution in which Λ is measured. The quantity Λ_e for any concentration can be determined by an indirect method (which need not be described here), and consequently the fraction ionized can be calculated. Table 6 gives some of the values obtained in this way for acetic acid.

TABLE 6

IONIZATION OF ACETIC ACID

Moles per Liter	Λ	Λ_e	*Percentage Ionized*
0.1000	5.20	385.3	1.350
.00984	16.38	387.6	4.22
.001028	48.1	388.9	12.38
.0001114	127.7	389.7	32.8

85. Weak Acids. It has been mentioned that the cation of an acid is the hydrated hydrogen ion, H_3O^+. This ion is often called the hydronium ion, the term hydrogen ion being properly applied to the unhydrated hydrogen ion, which is a hydrogen nucleus, or proton.[1] When an acid ionizes in water solution, a proton is transferred from the acid molecule to a molecule of water. The ionization of a strong acid is practically complete in dilute solutions. An example is the ionization of hydrochloric acid.

$$HCl + H_2O \longrightarrow H_3O^+ + Cl^- \qquad (2)$$

The ionization of a weak acid is reversible and comes to equilibrium when only a small fraction of the acid has reacted with water.

The ionization of acetic acid is represented by Equation 1, page 129. The equation indicates that the three substances, acetic acid, hydronium ion and acetate ion, are all present in a water solution of acetic acid. The relative amounts vary with the conditions. When pure acetic acid is put into water, it reacts with water (ionizes) to form the acetate and hydronium ions, but the reaction is far from complete, as Table 6 shows. When hydronium ion and acetate ion are put together in solution, they react to form acetic acid molecules until the same equilibrium is reached as when an equivalent amount of acetic acid is added to water. Hydronium ion and acetate ion may be brought together by the addition of any acetate to a solution of a strong acid. Sodium acetate and hydrochloric acid may be used for illustration. Both of these compounds are strong electrolytes and are completely ionized in dilute solution. When the two solutions are mixed, the following reversible reaction takes place:

$$Na^+ + CH_3COO^- + H_3O^+ + Cl^- \rightleftarrows CH_3COOH + H_2O + Na^+ + Cl^- \qquad (3)$$

Equilibria between ions of weak electrolytes and the unionized molecules are of considerable importance in analytical chemistry. Other weak acids that are met in qualitative analysis are arsenic, arsenious, carbonic, nitrous, phosphoric, phosphorous, silicic, and sulfurous acids and hydrogen sulfide.

Phosphoric acid is a weak acid that ionizes in three different ways, as indicated in Table 4, page 126. A single proton can

---

[1] The names oxonium ion and hydroxonium ion are used for the hydrated hydrogen ion also. All of these names are new, and the ion is often given its older name hydrogen ion.

be removed from the phosphoric acid molecule according to the equation

$$H_3PO_4 + H_2O \rightleftharpoons H_3O^+ + H_2PO_4^- \qquad (4)$$

The ion $H_2PO_4^-$ is itself a weak acid, though weaker than H_3PO_4, and it can ionize to give a second hydronium ion.

$$H_2PO_4^- + H_2O \rightleftharpoons H_3O^+ + HPO_4^= \qquad (5)$$

Likewise the ion $HPO_4^=$, a weaker acid than $H_2PO_4^-$, can react to give a third hydronium ion.

$$HPO_4^= + H_2O \rightleftharpoons H_3O^+ + PO_4^{\equiv} \qquad (6)$$

A solution of phosphoric acid contains H_3PO_4 molecules and the ions H_3O^+, $H_2PO_4^-$, $HPO_4^=$, and $PO_4^{\equiv}$ all in equilibrium with each other. Phosphoric acid is typical of weak polybasic acids.

Sulfuric acid is a strong acid with respect to its first reaction with water to give hydronium ion and the ion HSO_4^-, but the latter is a weak acid and is only partially ionized in sulfuric acid solutions.

Hydrogen sulfide is a very weak acid, and ionizes to a small extent to give the hydronium ion and the hydrosulfide ion, HS^-. The latter ionizes to a still smaller extent to give another hydronium ion and the sulfide ion, $S^=$. The reactions can be represented by the following equations.

$$H_2S + H_2O \rightleftharpoons H_3O^+ + HS^- \qquad (7)$$

$$HS + H_2O \rightleftharpoons H_3O^+ + S^= \qquad (8)$$

These equations may be added together to give a single equation showing the ionization of hydrogen sulfide to give sulfide ion.

$$H_2S + 2\,H_2O \rightleftharpoons 2\,H_3O^+ + S^= \qquad (9)$$

Water is a very weak electrolyte. It reacts with itself to form a few hydronium and hydroxide ions.

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^- \qquad (10)$$

In pure water there are one hydronium ion and one hydroxide ion to about 550,000,000 undissociated water molecules.

When ammonia (NH_3) is dissolved in water, a reaction that bears a resemblance to the ionization of a weak acid takes place.

Protons from water molecules are transferred to some of the ammonia molecules, in accordance with the equation

$$H_2O + NH_3 \rightleftarrows NH_4^+ + OH^- \qquad (11)$$

This reaction is reversible and ordinarily only a small fraction of the ammonia reacts to give ions. Because solutions of ammonia contain ammonium ions and hydroxide ions, they are usually called ammonium hydroxide solutions. It has been thought in the past that considerable un-ionized ammonium hydroxide (NH_4OH) is present in ammonium hydroxide solutions, but definite experimental evidence on this point is hard to obtain. It is sufficient for all ordinary purposes to make the simpler assumption that only water, ammonia and the two ions are present, and that the reaction is correctly represented in Equation 11.

86. Reactions between Electrolytes. When a solution of hydrochloric acid is added to a solution of silver nitrate, a white precipitate of silver chloride is obtained and nitric acid remains in solution. The reaction can be represented by the equation

$$AgNO_3 + HCl \longrightarrow \underline{AgCl} + HNO_3 \qquad (12)$$

The formulas in this equation represent definite quantities of the various compounds, and the statement made by the equation is in accord with experience. The line under the formula AgCl indicates that the silver chloride is precipitated from the solution.

However, certain information is omitted. Two of the compounds are strong acids and two are salts, and all are ionized in solution. The formulas do not indicate ionization; they might even conceal the fact unless one has the theory of ionization constantly in mind. The above equation can be improved by writing the formulas in the ionic form. Instead of $AgNO_3$ we may write $Ag^+ + NO_3^-$ and instead of HCl we may write $H_3O^+ + Cl^-$. The next formula, AgCl, presents a difficulty. Practically all of the silver chloride is precipitated from the solution in the solid form. Although solid salts are composed of ions rather than molecules, the ions are not in the solution, and it is convenient to designate a solid salt, or precipitate, by a molecular formula rather than as a combination of two ions. In the present case, therefore, the formula AgCl for solid silver chloride is retained. The nitric acid that remains in solution is ionized and its formula may be written $H_3O^+ + NO_3^-$. The equation then becomes

$$Ag^+ + NO_3^- + H_3O^+ + Cl^- \longrightarrow \underline{AgCl} + H_3O^+ + NO_3^- \quad (13)$$

An equation of this type shall be called an ionic equation, and one of the type of Equation 12 a molecular equation.

The ionic equation can be further simplified if desired. The hydronium ion and the nitrate ion appear on both sides of the equation and apparently have undergone no change. It is permissible to omit these two ions, or to retain them, whichever best suits the purpose for which the equation is written. Omitted, the equation becomes

$$Ag^+ + Cl^- \longrightarrow \underline{AgCl} \quad (14)$$

This is an expression of the essential part of the reaction. It does not mean that silver ions alone can be added to a solution containing no other ions but chloride ions, because a solution containing only a single kind of ion is impossible. It rather means that it is immaterial what other ions are present as long as there are silver and chloride ions. Equation 14 emphasizes the fact that *any* substance giving chloride ions in solution when added to a solution of *any* substance giving silver ions produces a precipitate of silver chloride. Perchloric acid, $HClO_4$, though it contains chlorine, gives no chloride ions, and gives no precipitate of silver chloride when added to a silver salt.

If hydrochloric acid solution is added to sodium hydroxide in solution, sodium chloride and water are formed.

$$HCl + NaOH \longrightarrow NaCl + H_2O \quad (15)$$

In this reaction there are three strong electrolytes and the practically non-ionized water. Rewriting in the ionic form we have

$$H_3O^+ + Cl^- + Na^+ + OH^- \longrightarrow Na^+ + Cl^- + 2\,H_2O \quad (16a)$$

This can be simplified, if desired, by the omission of the two ions that appear on both sides of the equation.

$$H_3O^+ + OH^- \longrightarrow 2\,H_2O \quad (16b)$$

This equation represents the essential part of the reaction of any acid with any hydroxide; namely, the reaction of hydronium ion with the hydroxide ion to form water.

If the acid should be a weak one, such as acetic acid, another complication is involved. The molecular equation is

$$CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O \qquad (17)$$

Acetic acid exists in solution mostly in the molecular form, and it is a question whether we should write it in the molecular or the ionic form.

One way to avoid the difficulty is to write two equations.

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+ \qquad (18)$$

$$CH_3COO^- + H_3O^+ + Na^+ + OH^- \longrightarrow CH_3COO^- + Na^+ + 2\,H_2O \qquad (19)$$

Equation 18 indicates an equilibrium between acetic acid and its ions. If one of the ions is removed, the equilibrium is disturbed and more of the molecules dissociate to make up for the loss. Accordingly, as the hydronium ion is removed by reaction with hydroxide ion to form water, as in Equation 19, more and more of the acetic acid molecules dissociate into ions, until finally they are practically gone.

Equation 19 for the reaction of acetic acid and sodium hydroxide might be sufficient for some purposes; when simplified it becomes the same as Equation 16. On the other hand, if it is any advantage, the acetic acid may be written in the molecular form, keeping in mind the fact that it ionizes to a small degree.

$$CH_3COOH + OH^- \longrightarrow CH_3COO^- + H_2O \qquad (20)$$

This equation, taken as it stands, indicates the transfer of a proton directly from an un-ionized acetic acid molecule to a hydroxide ion. This can doubtless happen, and it may be that Equation 20 represents the greater part of the reaction of acetic acid with a hydroxide in solution.

The action of hydrogen sulfide on certain salts in solution is important in qualitative analysis. Hydrogen sulfide is a very weak acid, but in this case it is the sulfide ion rather than the hydrogen ion in which we are interested. Certain metallic ions, among them copper ion, unite with sulfide ion to form sulfide precipitates. The molecular equation is

$$CuCl_2 + H_2S \longrightarrow \underline{CuS} + 2\,HCl \qquad (21)$$

In applying the theory of ionization to this reaction, it is best to write two equations, unless the first, Equation 9, can be understood without being written.

$$H_2S + 2\,H_2O \rightleftarrows 2\,H_3O^+ + S^= \qquad (9)$$

$$Cu^{++} + S^= \longrightarrow \underline{CuS} \qquad (22)$$

When a weak acid is one of the products of a reaction, the necessity for writing its formula in the molecular form is often quite apparent. When hydrochloric acid reacts with sodium acetate, acetic acid is formed, as shown in Equation 3, which can be simplified by the omission of the chloride and sodium ions.

$$H_3O^+ + CH_3COO^- \rightleftarrows H_2O + CH_3COOH \qquad (23)$$

The reaction of hydrochloric acid and sodium acetate is similar to the reaction of hydrochloric acid and sodium hydroxide, the difference being that the acetic acid formed is ionized to a greater degree than water and consequently Reaction 23 is appreciably reversible.

EXERCISES

1. If the molar solubility of lead sulfate is 1.3×10^{-4}, what is the molar concentration of the lead ion and of the sulfate ion in a saturated solution? What is the concentration of each of the ions in grams per liter? *Ans.* 0.027 g. Pb^{++} and 0.012 g. $SO_4^=$.

2. The solubility of lead chloride is 10.8 g. per liter at 25°. Calculate the molar concentration of chloride ion in a saturated lead chloride solution at 25°. *Ans.* 0.078 *M.*

3. Calculate the chloride ion concentration of a solution containing 10 g. of sodium chloride and 10 g. of barium chloride per liter. *Ans.* 0.267 *M* Cl^-.

4. Write one or more ionic equations to show what changes take place in each of the following cases:

(*a*) Sulfuric acid (100%) added to water.

(*b*) Ammonia added to a solution of hydrochloric acid.

(*c*) Calcium hydroxide solution added to hydrochloric acid solution.

(*d*) Sodium hydroxide added to hydrogen sulfide solution.

(*e*) Hydrogen sulfide added to a solution of cadmium sulfate.

5. Benzoic acid, C_6H_5COOH, is a weak monobasic acid. The equivalent conductance of a 0.0144 *M* solution of benzoic acid is 24.9 and the equivalent conductance of the ions, Λ_e, is 378 reciprocal ohms. Calculate the percentage ionized and the concentration of the hydronium ion in 0.0144 *M* benzoic acid.

Ans. 6.59% ionized. 0.00095 *M*.

6. Write equations for the ionization in successive steps of (*a*) H_2CO_3, (*b*) H_2SO_4, (*c*) H_2CrO_4, (*d*) H_3AsO_4.

7. Write ionic equations for the reaction of phosphoric acid with (*a*) one and (*b*) two moles of ammonia (NH_3) per mole of acid, respectively.

8. Write equations in both the molecular and ionic forms for all of the reactions taking place in the analysis of the hydrochloric acid group, starting with $AgNO_3$, $Pb(NO_3)_2$ and $Hg_2(NO_3)_2$.

Chapter IX

A DISCUSSION OF SOME OF THE REACTIONS OF QUALITATIVE ANALYSIS

THE theory of electrolytic dissociation can be used to good advantage in connection with the reactions of qualitative analysis. A discussion of some of these reactions will serve for further illustration of the theory as well as to help in the understanding of the qualitative analysis procedure.

87. Classification of Reactions. The reactions of qualitative analysis considered from the point of view of the theory of electrolytic dissociation may be divided into three classes. The first consists of the addition of ions or molecules. In this class may be included decompositions, since these are the reverse of additions. An example of an addition reaction is the addition of silver and chloride ions to form solid silver chloride.

$$Ag^+ + Cl^- \longrightarrow \underline{AgCl} \qquad (1)$$

Another example is the formation of a complex ion, as when ammonia is added to a solution of a silver salt.

$$Ag^+ + 2\,NH_3 \longrightarrow Ag(NH_3)_2 \qquad (2)$$

The reverse of Reaction 2 is a decomposition.

The second class of reactions may be called protolytic reactions. These are reactions in which a hydrogen nucleus, or proton, is transferred from one group of atoms to another. When hydrogen chloride is dissolved in water, a protolytic reaction takes place, and hydronium ion and chloride ion are formed.

$$HCl + H_2O \longrightarrow H_3O^+ + Cl^- \qquad (3)$$

When ammonia is added to a hydrochloric acid solution, protons are transferred from the hydronium ions (H_3O^+) to the ammonia molecules. This is another protolytic reaction.

$$H_3O^+ + NH_3 \longrightarrow NH_4^+ + H_2O \qquad (4)$$

The third class of reactions is oxidation-reduction reactions. These are reactions in which valence changes take place. A simple example of an oxidation-reduction reaction is the reaction of ferrous chloride with chlorine, for which the molecular equation is

$$2\,FeCl_2 + Cl_2 \longrightarrow 2\,FeCl_3. \tag{5}$$

Written in the ionic form this reaction is

$$2\,Fe^{++} + Cl_2 \longrightarrow 2\,Fe^{+++} + 2\,Cl^{-}. \tag{6}$$

88. The Separation of the Cation Groups. The reactions involved in the separation of the cation groups are addition reactions and consist in the union of the anion of the group reagent with each of the cations of the group to form a precipitate. The following are typical reactions.

$$Ag^{+} + Cl^{-} \longrightarrow \underline{AgCl} \tag{7}$$

$$Cu^{++} + S^{=} \longrightarrow \underline{CuS} \tag{8}$$

$$Al^{+++} + 3\,OH^{-} \longrightarrow \underline{Al(OH)_3} \tag{9}$$

$$Zn^{++} + S^{=} \longrightarrow \underline{ZnS} \tag{10}$$

$$Ca^{++} + CO_3^{=} \longrightarrow \underline{CaCO_3} \tag{11}$$

There are two anions concerned in the precipitation of the ammonium sulfide group, sulfide ion and hydroxide ion. When both of these anions are present in sufficient quantity, aluminum and chromium ions unite with the hydroxide ion only, while nickel, cobalt, zinc, manganous and ferrous ions unite with the sulfide ion only.

Molecular equations for the above five typical reactions may be written as follows:

$$AgNO_3 + HCl \longrightarrow \underline{AgCl} + HNO_3 \tag{12}$$

$$Cu(NO_3)_2 + H_2S \longrightarrow \underline{CuS} + 2\,HNO_3 \tag{13}$$

$$Al(NO_3)_3 + 3\,NH_4OH \longrightarrow \underline{Al(OH)_3} + 3\,NH_4NO_3 \tag{14}$$

$$Zn(NO_3)_2 + (NH_4)_2S \longrightarrow \underline{ZnS} + 2\,NH_4NO_3 \tag{15}$$

$$Ca(NO_3)_2 + (NH_4)_2CO_3 \longrightarrow \underline{CaCO_3} + 2\,NH_4NO_3 \tag{16}$$

89. Writing Equations. It is presumed that the reader will be able to write the equations for the precipitation of the other cations after having studied the above typical equations. A list of the cations is given on page 21. In writing an equation it is necessary to know certain facts about the reaction and then to express those facts in the equation. Correct formulas for all reactants and products must be known, and often something of the conditions under which the reaction can take place. Much of the information needed for the reactions of qualitative analysis can be found in the outlines.

To illustrate the use of these sources of information let us write the equation for the precipitation of mercurous ion in the hydrochloric acid group. Consultation of Outline 3, page 34, shows that on the addition of hydrochloric acid to a solution containing a mercurous compound, a precipitate of mercurous chloride, Hg_2Cl_2, results. The doubling of the formula is unusual, but consultation of Table 1, page 21, shows that the formula for the mercurous ion is Hg_2^{++}. The ionic equation therefore is

$$Hg_2^{++} + 2\,Cl^- \longrightarrow \underline{Hg_2Cl_2} \qquad (17)$$

For the molecular equation we must know the anion present with the mercurous ion before precipitation. This again may be a question of fact, but in the absence of any information it is usually convenient to assume that the anion is either the nitrate or chloride ion. In this case the chloride ion is out of the question, and the nitrate ion may be assumed.

$$Hg_2(NO_3)_2 + 2\,HCl \longrightarrow \underline{Hg_2Cl_2} + 2\,HNO_4 \qquad (18)$$

It will be assumed that the reader can write equations for the other reactions of this type and that it is unnecessary to discuss other similar ones. There are a number of reactions that have unusual features, however, and these will be described.

90. Tests for Silver and Mercurous Ions. The dissolving of silver chloride when ammonium hydroxide is added to the mixture of mercurous and silver chlorides is an example of complex ion formation. It should be recalled that an ammonium hydroxide solution contains ammonia molecules (NH_3), as well as ammonium ions (NH_4^+) and hydroxide ions (OH^-), and that each of these is capable of reacting independently. Any water solution dissolves a small quantity of silver chloride when in contact with a silver chloride precipitate. In a solution containing ammonia, the silver ion of the small dissolved portion reacts with ammonia to form a complex cation.

$$Ag^+ + 2\,NH_3 \rightleftharpoons Ag(NH_3)_2^+ \qquad (19)$$

The chloride of the complex cation is soluble in water and is ionized like other salts. The reaction of the silver ion with ammonia is equivalent to removing the silver ion from the solution, and the solution is thereby made unsaturated with respect to silver chloride. More silver chloride dissolves, and the silver ion of the newly dissolved portion reacts with ammonia. This again leaves the solution unsaturated and the process continues until either the silver chloride is all dissolved or insufficient ammonia remains for reaction.

The formation of the complex ion is reversible, as indicated by the double arrow in Equation 19, and removal of the ammonia in equilibrium with the complex ion favors the decomposition of the complex ion. Ammonia can be removed by conversion to ammonium ion. Hydronium ion reacts with ammonia to give ammonium ion as shown in Equation 4. This equation may be combined with the equation for the decomposition of the complex ion and with an equation for the precipitation of silver chloride.

$$Ag(NH_3)_2^+ \rightleftarrows Ag^+ + 2\,NH_3 \qquad (20)$$

$$2\,NH_3 + 2\,H_3O \longrightarrow 2\,NH_4^+ + 2\,H_2O \qquad (4)$$

$$Ag^+ + Cl^- \longrightarrow \underline{AgCl} \qquad (7)$$

$$Ag(NH_3)_2 + 2\,H_3O^+ + Cl^- \longrightarrow 2\,NH_4^+ + \underline{AgCl} + 2\,H_2O \qquad (21)$$

This equation represents the decomposition of the complex ion in a solution containing chloride ion, and the consequent formation of a precipitate of silver chloride. The corresponding molecular equation, using nitric acid as the acid, is

$$Ag(NH_3)_2Cl + 2\,HNO_3 \longrightarrow \underline{AgCl} + 2\,NH_4NO_3 \qquad (22)$$

The black residue obtained when ammonium hydroxide solution is poured over the mercurous chloride precipitate is a mixture of finely divided metallic mercury and the white compound NH_2HgCl. Most metals in a finely divided state appear black in color. The compound NH_2HgCl is formed by a reaction that may be represented by the equation

$$Hg_2Cl_2 + 2\,NH_3 \longrightarrow Hg + NH_2HgCl + NH_4^+ + Cl^- \qquad (23)$$

91. The Hydrogen Sulfide Group. Precipitation. The precipitation of the hydrogen sulfide group results from the union of the various cations with the sulfide ion to form solid sulfides. The source of the sulfide ion is hydrogen sulfide, which is a very weak acid and is not very soluble in water. Therefore, the concentration of the sulfide ion in a hydrogen sulfide solution is small. The presence of hydrochloric acid (or any other strong acid) in the solution makes it still smaller. The reason why the addition of a strong acid decreases the concentration of sulfide ion in a solution can be seen by considering the ionization of hydrogen sulfide.

$$H_2S + H_2O \rightleftarrows H_3O^+ + HS^- \qquad (24)$$

$$HS^- + H_2O \rightleftarrows H_3O^+ + S^= \qquad (25)$$

If excess hydronium ion is added, the equilibrium is displaced in such a way that the concentration of sulfide ion decreases. When the acidity is adjusted as directed in the procedure for the precipitation of the hydrogen sulfide group (Section 14, page 38) the hydronium ion concentration is 0.3 *M*. With this hydronium ion concentration, the sulfide ion concentration is too small for the precipitation of the sulfides of the ammonium sulfide group, but large enough for practically complete precipitation of the hydrogen sulfide group.

92. Separation into Sub-groups. The dissolving of the tin-group sulfides by sodium polysulfide solution involves some relatively unusual reactions. These are analogous to the more familiar reaction of arsenic pentoxide, As_2O_5, with water to form arsenic acid:

$$As_2O_3 + 3\,H_2O \longrightarrow 2\,H_3AsO_4 \qquad (26)$$

This is an example of a general method of preparing acids. Oxygen is in the same group of the periodic table as sulfur, and sulfides are sometimes analogous to oxides. It might be expected that arsenic sulfide and hydrogen sulfide would react in a similar manner.

$$\underline{As_2S_5} + 3\,H_2S \rightleftarrows 2\,H_3AsS_4 \qquad (27)$$

This reaction, however, is reversible, and the equilibrium lies far to the side of the arsenic sulfide and hydrogen sulfide. With sodium (or ammonium) sulfide in place of hydrogen sulfide, however, the reaction goes practically to completion toward the right.

$$As_2S_5 + 3\,Na_2S \longrightarrow 2\,Na_3AsS_4 \qquad (28)$$

The compound formed is sodium thioarsenate, the prefix "thio" indicating that the oxygen of the ordinary arsenate radical has been replaced by sulfur. Sodium thioarsenate is soluble, and consequently arsenic sulfide is dissolved by sodium sulfide. Antimonic sulfide behaves like arsenic sulfide. Stannic and mercuric sulfides react in a similar manner. When the sulfides of arsenic, antimony and tin are in the lower state of oxidation, they must be oxidized before they can be dissolved by sodium sulfide. That is the reason why sodium disulfide, Na_2S_2, is included in the solution used for dissolving the tin group sulfides. Sodium disulfide is made by adding sulfur to sodium sulfide solution. The sulfur unites with some of the sulfide ion to form the disulfide ion.

$$S + S^{=} \longrightarrow S_2^{=} \qquad (29)$$

The prefix "poly" indicates that the average amount of sulfur per molecule is more than one atom and is somewhat indefinite. The formula may be written Na_2S_x. It may be considered that the disulfide ion oxidizes the sulfides of the tin group by giving sulfur to them.

$$As_2S_3 + 2\,S_2^{=} \longrightarrow As_2S_5 + 2\,S^{=} \qquad (30)$$

Equation 30 can be combined with the ionic form of Equation 28 to give an equation for the whole reaction of sodium polysulfide with arsenious sulfide.

$$\underline{As_2S_3} + 2\,S_2^{=} + S^{=} \longrightarrow 2\,AsS_4^{---} \qquad (31)$$

93. Copper Group. Lead, bismuth, copper and cadmium sulfides are dissolved by nitric acid, giving the corresponding nitrates. The reactions are oxidation-reduction reactions, as shown by the products. Sulfur is formed and nitric oxide is given off. The following equation is typical.

$$3\,CuS + 8\,H_3O^+ + 2\,NO_3^- \longrightarrow 3\,Cu^{++} + 4\,H_2O + 2\,NO + 3\,S \qquad (32)$$

The reaction taking place when the lead sulfate is dissolved by ammonium acetate solution deserves special notice.

$$\underline{PbSO_4} + 2\,NH_4OOCCH_3 \longrightarrow (NH_4)_2SO_4 + Pb(OOCCH_3)_2 \qquad (33)$$

It might be expected that Reaction 33 would go only from right to left rather than as shown, because lead sulfate is only slightly soluble. The reaction goes as shown, however, because lead acetate is very little ionized. Lead sulfate is soluble to a slight extent, giving lead ions and sulfate ions in solution, and the real reaction is

$$Pb^{++} + 2\,CH_3COO^- \longrightarrow Pb(OOCCH_3)_2 \qquad (34)$$

As the lead ion is removed from the solution, as indicated by Equation 34, more lead sulfate dissolves, until finally all of it is dissolved.

The test for bismuth involves oxidation and reduction, the bismuth hydroxide being reduced to the black, finely divided, metallic bismuth by the stannite ion, which is oxidized to stannate ion.

$$\underline{2\,Bi(OH)_3} + 3\,SnO_2^{=} \longrightarrow \underline{2\,Bi} + 3\,SnO_3^{=} + 3\,H_2O \qquad (35)$$

The preparation of the sodium stannite brings to notice a class of compounds called amphoteric hydroxides, of which stannous hydroxide is an example. When a small amount of sodium hydroxide is added to stannous chloride solution, stannous hydroxide is precipitated, as would be expected.

$$Sn^{++} + 2\,OH^- \longrightarrow \underline{Sn(OH)_2} \qquad (36)$$

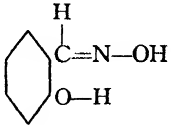
Stannous hydroxide reacts with acids in the same manner as other metallic hydroxides, and in addition it can act as a weak acid. When more sodium hydroxide is added, and the solution becomes alkaline, the stannous hydroxide acts as an acid (indicated by writing its formula H_2SnO_2) and is dissolved.

$$\underline{H_2SnO_2} + OH^- \longrightarrow HSnO_2^- + H_2O \qquad (37)$$

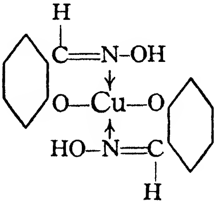
A hydroxide that can act either as an acid or in the manner of a metallic hydroxide is called an amphoteric hydroxide.

Some of the ammonia present when the bismuth hydroxide is precipitated unites with copper and cadmium ions to form the complex ions $Cu(NH_3)_4^{++}$ and $Cd(NH_3)_4^{++}$. A complex ion differs considerably in properties from the parent ion from which it was formed. For example, while copper ion unites with hydroxide ion to form a precipitate, the complex ion does not. The copper complex ion is darker blue in color than the ordinary copper ion. It is to be noticed that the number of ammonia molecules held by both copper and cadmium ions, as well as by silver ion, is twice the number of unit charges on the metallic ion.

The formation of the copper and cadmium complex ions prevents the precipitation of the hydroxides of copper and cadmium along with the bismuth hydroxide. Acetic acid is used to decompose the complex ions in order that no strong acid shall be present. The copper ion is then precipitated by means of an organic reagent called salicylaldoxime. This compound has the formula



the hexagon representing benzene, C_6H_6, in which, in this compound, two hydrogen atoms have been replaced by the groups shown. Two molecules of salicylaldoxime react with one copper ion to form the compound



which is only slightly soluble and precipitates.

94. Tin Group. The anions of the thio-salts, the thio-mercuriate, thio-arsenate, thio-antimonate and thio-stannate ions react with hydronium ion to form weak acids. For example,

$$AsS_4^{\equiv} + 3\,H_3O^+ \longrightarrow H_3AsS_4 + 3\,H_2O \qquad (38)$$

The weak acids formed are unstable and decompose, giving the sulfides of the tin group.

$$2\,H_3AsS_4 \longrightarrow 3\,H_2S + \underline{As_2S_5} \qquad (39)$$

On treatment with 12 *M* HCl under such conditions that the solution remains saturated with hydrogen sulfide, only antimony and tin sulfides react with the acid.

$$\underline{Sb_2S_5} + 6\,HCl \longrightarrow 2\,SbCl_3 + 3\,H_2S + \underline{2\,S} \qquad (40)$$

The precipitation of metallic antimony from the resulting solution by means of iron nails

$$2\,Sb^{+++} + \underline{3\,Fe} \longrightarrow 3\,Fe^{++} + \underline{2\,Sb} \qquad (41)$$

is an oxidation-reduction reaction in which iron is oxidized and antimony ion is reduced. As both tin and antimony are below iron in the electromotive series, one might expect the ions of both to react with iron. This would happen in a solution in which the only cations were tin and antimony. Antimony is lower in the series and so would be precipitated first. When the antimony was nearly all out of solution, the tin would begin to be precipitated. When a metal like iron is placed in a solution containing cations of two or more different metals lower in the series, only one kind of ion reacts at a time and the different ions react in the inverse order of their positions in the series, the lowest first. The separation of antimony from tin by the iron nails takes place in an acid solution containing much hydronium ion. In the electromotive series hydrogen comes between tin and antimony. Hence, in a solution containing tin, hydronium and antimony ions the order of displacement is antimony, hydrogen, tin. Tin is not displaced so long as there is a fairly large hydronium ion concentration. However, under these conditions the tin is reduced from stannic ion, with a valence of four, to stannous ion, with a valence of two.

$$Sn^{++++} + \underline{Fe} \longrightarrow Sn^{++} + Fe^{++} \qquad (42)$$

It is necessary that the tin be in the stannous condition for the final test, which consists in the reaction of stannous ion with mercuric ion to give mercurous ion. The latter unites with some of the chloride ion present to give a precipitate of mercurous chloride.

$$2\,Hg^{++} + Sn^{++} + 2\,Cl^{-} \longrightarrow \underline{Hg_2Cl_2} + Sn^{++++} \qquad (43)$$

Metallic antimony does not react with hydronium ion to give hydrogen gas and antimony ion. Antimony can be changed into the ionic form by oxidation by nitric acid in the presence of hydrochloric acid.[1]

$$\underline{Sb} + NO_3^{-} + 4\,H_3O^{+} \longrightarrow Sb^{+++} + NO + 6\,H_2O \qquad (44)$$

---

[1] Too much nitric acid in the mixture, or nitric acid alone, causes the formation of an insoluble antimonic acid.

The mixture of arsenic and mercuric sulfides remaining after the treatment with 12 M HCl is treated with ammonium hydroxide, which dissolves arsenic sulfide, forming a mixture of salts of such acids as H_3AsO_3S and $H_3AsO_2S_2$. Nitric acid oxidizes these compounds to arsenic acid, H_3AsO_4.

95. Removal of Phosphate Ion. If phosphate ion is present, it must be removed before the ammonium sulfide group is precipitated, if the separation of this group from the ammonium carbonate group is to be satisfactory. The phosphates of barium, strontium, calcium and magnesium are only slightly soluble, but cannot be precipitated from acid solutions. When the hydrochloric acid and hydrogen sulfide groups are precipitated, enough acid is present to prevent the precipitation of these phosphates. When the filtrate from the hydrogen sulfide group is neutralized in the precipitation of the ammonium sulfide group, the phosphates may be precipitated. Therefore phosphate ion is removed before the solution is neutralized.

In the procedure given on page 50 the phosphate ion is removed when metastannic acid is precipitated by the action of concentrated nitric acid on metallic tin. In the absence of chloride ion, the metastannic acid is practically insoluble and is removed from the solution, with all of the phosphate ion along with it. The tin used may contain small amounts of copper and lead, and it is necessary that these be removed by precipitation with hydrogen sulfide after the removal of the metastannic acid.

The test for phosphate ion consists in the addition of ammonium molybdate, $(NH_4)_2MoO_4$, in the presence of nitric acid. If phosphate ion is present, a yellow precipitate of ammonium phosphomolybdate, $(NH_4)_3PO_4 \cdot 12\,MoO_4$, is formed. Arsenate ion gives a similar precipitate with ammonium molybdate, but this ion will ordinarily have been removed before the test for phosphate ion is made.

96. Precipitation of the Ammonium Sulfide Group. In the filtrate from the precipitation of the hydrogen sulfide group, chromium, iron and manganese can be present only as chromic (Cr^{+++}), ferrous (Fe^{++}) and manganous (Mn^{++}) ions in the solution that is ready for the precipitation of the ammonium sulfide group. If these elements were present in the sample in a higher state of oxidation, they will have been reduced by hydrogen sulfide in the precipitation of the hydrogen sulfide group. Sulfur is precipitated when the reduction takes place.

When ammonium hydroxide is added, the acid present is neutralized. From the ionic point of view, the neutralization consists in the reaction of the hydronium ion of the acid solution with both the hydroxide ion and the ammonia furnished by the ammonium hydroxide solution.

$$H_3O^+ + OH^- \longrightarrow 2\,H_2O \tag{45}$$

$$H_3O^+ + NH_3 \longrightarrow H_2O + NH_4^+ \tag{46}$$

As the hydronium ion concentration is reduced, the hydroxide ion concentration increases, since water is always in equilibrium with its ions (Equation 47), and when a reaction is at equilibrium the reduction of the concentration of one of the reaction products causes an increase in the concentration of the other.

$$2\,H_2O \rightleftarrows H_3O^+ + OH^- \tag{47}$$

Before the hydroxide ion concentration becomes as large as the hydronium ion concentration, aluminum and chromium hydroxides begin to precipitate.

$$Al^{+++} + 3\,OH^- \rightleftarrows \underline{Al(OH)_3} \tag{48}$$

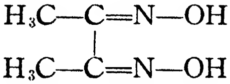
As more hydroxide ion is added, it is removed by union with aluminum and chromium ions until these ions are practically completely precipitated. The hydroxide ion can then increase further.

When hydrogen sulfide is added to this solution of small hydronium ion concentration, it ionizes to a greater extent than in the precipitation of the hydrogen sulfide group. The sulfide ion concentration is large enough for the precipitation of nickel, cobalt, zinc, manganous and ferrous sulfides.

It is important that the hydroxide ion concentration be kept as small as possible in the precipitation of the ammonium sulfide group. Large hydroxide ion concentrations favor the precipitation of the cations of the ammonium carbonate group along with aluminum and chromium hydroxides.

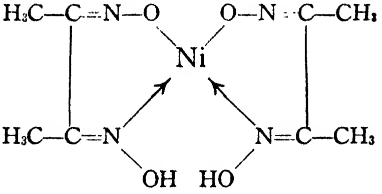
97. Nickel, Cobalt and Zinc Ions. The fact that nickel and cobalt sulfides are not dissolved to any great extent by a dilute hydrochloric acid solution is useful for the separation of nickel and cobalt ions from the others. The probable reason why these sulfides are not dissolved is that the rate of dissolving is slow, so that very little of the sulfides can be dissolved in the time allowed. Nickel and cobalt sulfides can be dissolved easily if an oxidizing agent, such as nitric acid, is present.

The test for nickel ion by means of dimethyl-glyoxime must be carried out in a solution of very small hydronium ion concentration. Therefore, the solution containing the nickel salt is made slightly alkaline with ammonium hydroxide before the dimethyl-glyoxime is added. Dimethyl-glyoxime has the following formula.



$$\begin{array}{l} H_3C-C=N-OH \\ \qquad\; | \\ H_3C-C=N-OH \end{array}$$

Nickel ion displaces a hydrogen atom of each of two molecules, and a non-ionized compound is formed having the following formula.



Dimethyl-glyoxime reacts with cobalt ion also, but the product is neither a precipitate nor highly colored, so the presence of cobalt ion does not interfere with the test for nickel ion, provided enough of the reagent is used.

Cobalt ion can be detected in the presence of nickel ion by the addition of another organic compound, nitroso-R-salt. The reaction of cobalt ion with this reagent to give the bright red compound is hindered by acids, so sodium acetate is added. The acidity of a solution of acetic acid is decreased by the addition of sodium acetate. Some other cations form colored compounds with nitroso-R-salt, but these colored compounds are destroyed by the addition of nitric acid, while the cobalt compound, once formed, is not affected by the acid.

The solution filtered from the cobalt and nickel sulfides contains the other ions of the group and small amounts of cobalt and nickel ions. The solution is boiled to remove the last traces of the hydrogen sulfide that is formed when the hydrochloric acid dissolves the sulfides.

$$\underline{ZnS} \longrightarrow Zn^{++} + S^{=} \tag{49}$$

$$S^{=} + H_3O^+ \longrightarrow HS^- + H_2O \tag{50}$$

$$HS^- + H_3O^+ \longrightarrow H_2O + H_2S \tag{51}$$

Bromine is added to oxidize the ferrous ion to ferric ion, because the next step is to precipitate all the ions except zinc ion by means of ammonium hydroxide and ammonium carbonate, and ferrous hydroxide would not be completely precipitated.

98. Separation of Aluminum and Chromium from Iron and Manganese. Aluminum hydroxide is amphoteric and, like stannous hydroxide, dissolves when an excess of sodium hydroxide is added. Aluminum hydroxide is slightly soluble in water. The small amount of aluminum hydroxide in solution consists at least partly of the ions Al^{+++} and OH^-. If an acid is added, the hydronium ion reacts with the hydroxide ion, and an aluminum salt is formed.

$$\underline{Al(OH)_3} \longrightarrow Al^{+++} + 3\,OH^- \tag{52}$$

$$Al^{+++} + 3\,OH^- + 3\,H_3O^+ + 3\,Cl \longrightarrow 6\,H_2O + Al^{+++} + 3\,Cl^- \tag{53}$$

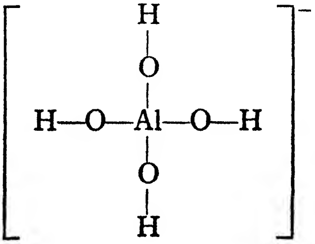
Two explanations may be given for the reaction of aluminum hydroxide with soluble hydroxides. (*1*) It may be considered that aluminum hydroxide ionizes as a monobasic acid.

$$\underline{Al(OH)_3} + H_2O \rightleftarrows H_3O^+ + H_2AlO_3^- \tag{54}$$

The ion $H_2AlO_3^-$ is often written $AlO_2^- + H_2O$. (2) Aluminum hydroxide may be considered to add a hydroxide ion to give the ion $Al(OH)_4^-$.

$$Na^+ + OH^- + \underline{Al(OH)_3} \longrightarrow Na^+ + Al(OH)_4^- \tag{55}$$

The structure of the ion $Al(OH)_4^-$ might be as follows, in which each line between atoms represents a pair of electrons:



$$\left[\begin{array}{c} H \\ | \\ O \\ | \\ H{-}O{-}Al{-}O{-}H \\ | \\ O \\ | \\ H \end{array}\right]^-$$

Chromium hydroxide is oxidized to chromate ion, $CrO_4^{=}$, by means of sodium peroxide, Na_2O_2, which may be considered a salt giving the anion $O_2^{=}$.

$$\underline{2\,Cr(OH)_3} + 3\,O_2^{=} \longrightarrow 2\,CrO_4^{=} + 2\,OH^- + 2\,H_2O \quad (56)$$

At the same time manganese carbonate is oxidized to manganese dioxide, MnO_2.

$$\underline{MnCO_3} + O_2^{=} \longrightarrow \underline{MnO_2} + CO_3^{=} \quad (57)$$

The manganese dioxide and the ferric hydroxide (which is unchanged by the sodium peroxide) are only very slightly soluble and so can be separated by filtration from the sodium aluminate and the sodium chromate in the solution.

99. Test for Manganese. When the manganese dioxide has been separated from the solution containing ferric ion, it is dissolved by means of hydrogen peroxide and nitric acid. Hydrogen peroxide is both an oxidizing agent and a reducing agent. It acts as a reducing agent toward manganese dioxide and is itself oxidized to oxygen.

$$MnO_2 + H_2O_2 + 2\,H_3O^+ \longrightarrow Mn^{++} + O_2 + 4\,H_2O \quad (58)$$

Sodium bismuthate, in the final test for manganese, oxidizes the manganous ion to permanganate ion, MnO_4^-, which when present even in very small concentration gives a pink or purple color to the solution.

$$2\,Mn^{++} + 5\,BiO_3^- + 14\,H_3O^+ \longrightarrow 2\,MnO_4^- + 21\,H_2O + 5\,Bi^{+++} \quad (59)$$

EXERCISES

1. Make outlines showing the steps necessary for the analysis of the hydrochloric acid group (*a*) if only lead ion were present, (*b*) if only mercurous ion were present.

2. Could a solution of copper chloride be used to precipitate the hydrochloric acid group? Is there any objection to its use?

3. Can lead chloride be more completely precipitated from a hot or from a cold solution? Why?

4. Write a molecular equation showing the use of potassium chromate to confirm the presence of lead ion. Could sodium or ammonium chromate probably be used in place of potassium chromate?

5. Write molecular and ionic equations illustrating the dissolving of silver chloride by ammonium hydroxide.

6. Make an outline showing a simple method of separating one of each of the following pairs of ions from the other:

(*a*) Cu^{++} and Pb^{++}
(*b*) Pb^{++} and Cd^{++}
(*c*) Bi^{+++} and Sn^{++}
(*d*) Cu^{++} and As^{+++}
(*e*) As^{+++} and Sn^{++}
(*f*) Hg_2^{++} and Cd^{++}

7. Complete and balance the following equations in the molecular form, underlining all precipitates:

$Pb(NO_3)_2 + H_2SO_4 \longrightarrow$
$Bi(NO_3)_3 + H_2SO_4 \longrightarrow$
$Cu(NO_3)_2 + H_2SO_4 \longrightarrow$
$Pb(C_2H_3O_2)_2 + K_2CrO_4 \longrightarrow$
$Bi_2(SO_4)_3 + NH_4OH \longrightarrow$
$CuSO_4 + NH_4OH \longrightarrow$
$Na_3AsS_4 + HCl \longrightarrow$
$Na_3SnS_3 + HCl \longrightarrow$
$CuSO_4 + H_2S \longrightarrow$
$Sb_2S_5 + Na_2S \longrightarrow$
$SnS_2 + Na_2S \longrightarrow$
$Cu(NH_3)_4SO_4 + H_2SO_4 \longrightarrow$

8. Complete and balance each of the equations of Exercise 7 in the ionic form, writing the formulas for solid substances in the molecular form.

9. Complete and balance the following equations for oxidation-reduction reactions in the ionic form:

$CuSO_4 + Fe \longrightarrow$
$SnCl_2 + HgCl_2 \longrightarrow$
$SbCl_3 + Fe \longrightarrow$
$Bi(OH)_3 + Na_2SnO_2 \longrightarrow$
$SnCl_4 + Fe \longrightarrow$
$FeCl_3 + H_2S \longrightarrow$

10. Write equations for the dissolving of antimonous and stannous sulfides (Sb_2S_3 and SnS) by sodium polysulfide.

11. Make an outline showing a simple method of separating one ion of each of the following pairs from the other:

(*a*) Al^{+++} and Cr^{+++}
(*b*) Al^{+++} and Zn^{++}
(*c*) Cr^{+++} and Mn^{++}
(*d*) Ni^{++} and Fe^{++}
(*e*) Cr^{+++} and Fe^{++}
(*f*) Ba^{++} and Zn^{++}
(*g*) Ba^{++} and Ca^{++}
(*h*) Sr^{++} and Mg^{++}

12. Write equations in both the ionic and the molecular form for the reactions taking place when 1 *M* hydrochloric acid is added to the ammonium sulfide group precipitate.

13. Write equations in both the ionic and the molecular form for the reactions taking place when ammonium hydroxide is added to the solution containing aluminum, chromium, ferric, manganese and zinc ions.

14. Write ionic equations showing the changes that take place when a solution containing aluminate ion is made acidic by adding hydrochloric acid and then is made alkaline with ammonium hydroxide.

15. What would happen to copper ion if it were present in the filtrate from the hydrogen sulfide group when the ammonium sulfide group was being precipitated?

16. If the ammonium sulfide group precipitate consisted of 0.5 g. of zinc sulfide and nothing else, how much 1 *M* hydrochloric acid would be required to dissolve it? *Ans.* 10.2 ml.

Chapter X

CHEMICAL EQUILIBRIUM (PART I)

An understanding of the principles of chemical equilibrium is necessary for an understanding of analytical processes and also of many other chemical phenomena. It is the purpose of this and the next chapter to make some applications of the principles of chemical equilibrium to qualitative analysis.

100. Reversible Reactions. Most chemical reactions are reversible; that is, the products are capable of reacting to produce the original reactants again. If methyl alcohol and acetic acid are mixed, they react to form methyl acetate and water.

$$CH_3OH + CH_3COOH \rightleftarrows CH_3COOCH_3 + H_2O. \qquad (1)$$

But, if the latter two are mixed, they react to form methyl alcohol and acetic acid. The reversibility is indicated in the equation by the double arrow.

When alcohol and acetic acid are mixed, the forward reaction to form methyl acetate and water starts immediately. As soon as these products are formed, the reverse reaction given by Equation 1 when read from right to left begins. Since the speed of a reaction is governed by the concentrations of the reactants, the speed of the forward reaction is fast at first while that of the reverse reaction is slow; the alcohol and acetic acid react faster than they are produced by the reverse reaction. The result is that these compounds decrease in concentration as time goes on, and the products increase. But these concentration changes cause a slowing of the forward reaction and an acceleration of the reverse, and eventually the rate at which the alcohol and acetic acid react becomes equal to the rate at which they are formed. At this point the reaction *seems* to stop; no further change in the concentrations of any of the four substances takes place, and the reaction is said to have come to equilibrium.

101. The Law of Chemical Equilibrium. Many years ago it was found that the velocity of a chemical reaction is proportional to the "active masses" of the reactants, and the statement to this effect is known as the law of mass action. For a gas, either the partial pressure or the concentration can be used as a measure of the "active mass," and for a substance in solution the concentration can be used, at least as an approximate measure.

That the law of mass action is reasonable, should be apparent from the following considerations. Imagine a number of molecules of the substance A distributed throughout a given volume and in motion. Let us introduce a single molecule of the substance B which can react with A. The molecule of B can react with a molecule of A only when the two collide. If there are only a few molecules of A per unit volume, a long time may elapse before the collision. If there are many molecules of A per unit volume, the chances for a collision are much better. If instead of one molecule of B, many are introduced, the chances of collision between molecules of A and B are increased in proportion to the increase in the concentration of B. Not every collision between two molecules that can react actually results in a reaction, but the number of molecules that react is proportional to the number of collisions, and this in turn is proportional to the concentrations of the reactants.

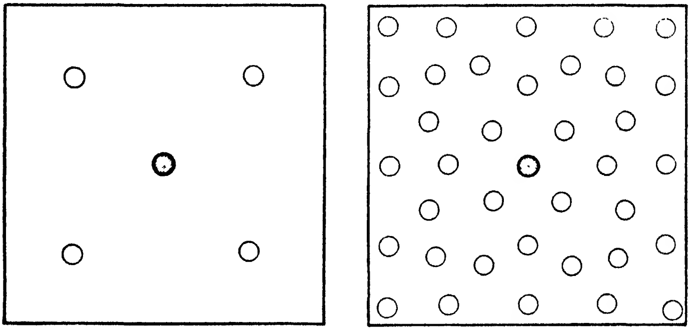


FIG. 9. Illustration of the relation between the probability of collision and the concentration of molecules. If the molecules are all in random motion (rebounding from the walls of the container when they strike them), collisions between the shaded molecule and a white molecule will be much more frequent in the system represented by the right-hand diagram than in that represented by the left-hand diagram.

For the reaction

$$A + B \rightleftarrows C + D \qquad (2)$$

which is similar to Reaction 1, the velocity, v_1, with which A and B react is proportional to the concentrations of both A and B. Since v_1 is proportional to both concentrations, it is proportional to their product, and is equal to a fixed number, or constant, times their product. This can be expressed as an equation. Let $[A]$ and $[B]$ represent the concentrations of A and B, respectively, and let k_1 represent a constant.

$$v_1 = k_1[A][B]. \tag{I}$$

If the reaction is reversible, C and D react to form A and B with velocity v_2; and the velocity is proportional to the concentrations of C and D.

$$v_2 = k_2[C][D]. \tag{II}$$

At equilibrium the two velocities are equal; $v_1 = v_2$. Then

$$k_1[A][B] = k_2[C][D]$$

$$\frac{[C][D]}{[A][B]} = \frac{k_1}{k_2} = K. \tag{III}$$

In this equation k_1/k_2 represents one constant divided by another constant and can be set equal to a third constant, K, which is called the equilibrium constant. Equation III means that when a reaction has come to equilibrium, the product of the concentrations of the products of the reaction divided by the product of the concentrations of the reactants is equal to a constant.

As an example of the application of Equation III, which may be called the equilibrium equation, some data for the reaction

$$CO_2 + H_2 \rightleftarrows CO + H_2O \tag{3}$$

are given in Table 7. This reaction takes place at high temperatures, with the reactants in the gaseous state, and is of interest in connection with water gas manufacture and use. In the table, concentrations in moles per liter are used to measure the "active masses" in the equation

$$\frac{[CO][H_2O]}{[CO_2][H_2]} = K. \tag{IV}$$

In the first four experiments shown in the table, carbon dioxide and hydrogen were mixed and heated to 986° and the reaction allowed to go as far as it would. In the last four, carbon monoxide and water were mixed and treated similarly. A catalyst consisting of cobalt or iron oxide with certain impurities was necessary to make the reaction go. When the mixture had come to equilibrium, it could be removed from the catalyst and cooled without any further reaction taking place when the temperature was changed. The mixture was then analyzed quantitatively and the concentrations of CO_2, H_2, CO and H_2O calculated. The values for the concentrations are given in the table.

TABLE 7

EQUILIBRIUM DATA AT 986° C. FOR THE REACTION

$$CO_2 + H_2 \rightleftarrows CO + H_2O$$

Expt.	$[CO_2]$	$[H_2]$	[CO]	$[H_2O]$	*K*
1	0.007876	0.01204	0.01134	0.01336	1.60
2	.007884	.01189	.01106	.01378	1.63
3	.006205	.01440	.01292	.01110	1.60
4	.006447	.01393	.01311	.01113	1.63
5	.00994	.00886	.01775	.00808	1.59
6	.00942	.00932	.01776	.00813	1.64
7	.01078	.00889	.00902	.01691	1.59
8	0.00880	0.00843	0.00553	0.02186	1.63

Allowing for some experimental error, the table shows that when equilibrium was reached, the proportions of the four substances present were in accordance with the equilibrium law. This is shown by the fact that K is as nearly constant as can be expected.

The equilibrium constant is a constant only at a single temperature. Thus, the value $K = 1.61$ for Reaction 3 holds only at 986°. The values of the constant for other temperatures are as follows:

T, °C	515	702	860	986
K	0.243	0.66	1.13	1.61

Whether or not pressure has any effect on an equilibrium constant depends on whether or not the volume of the reaction mixture changes as the reaction proceeds. The effect of pressure can be predicted from Le Chatelier's principle. In the reaction just considered, the volume does not change, and pressure has no effect. Pressure has little effect on equilibria in solution, unless one of the substances involved is a gas, since the volume of a solution does not change appreciably as a reaction proceeds in it.

It sometimes happens that there is only one reactant, for example, in a reaction like $A \rightleftarrows C + D$. In this case the velocity of the forward reaction is proportional to the concentration of A alone, and the concentration of B drops out of the equilibrium equation.

The ionization of a weak acid is of the type of Reactions 1 and 2. The ionization of acetic acid is represented by the equation

$$CH_3COOH + H_2O \rightleftarrows H_3O^+ + CH_3COO^- \qquad (4)$$

Applying the equilibrium equation,

$$\frac{[H_3O^+][CH_3COO^-]}{[H_2O][CH_3COOH]} = K'. \qquad (V)$$

In dilute solutions the concentration of water is practically constant and nearly equal to its concentration in pure water. Pure water at 25° can be considered a 55.4 molar solution, because at 25° a liter of water weighs 997 g. and this is 55.4 moles. When about 0.1 mole of water is removed and replaced by a solute, the water concentration is still 55.3 molar. For present purposes this change may be considered too small to be taken into account. When the solute is acetic acid, its ionization removes a further small quantity of water, according to Equation 4, but this quantity is much less than 0.1 mole.

If we multiply both sides of Equation V by $[H_2O]$ and write $K'[H_2O] = K$ and also employ the simpler formula H^+ for the hydronium ion, the equation becomes

$$\frac{[H^+][CH_3COO^-]}{[CH_3COOH]} = K'[H_2O] = K \qquad (VI)$$

The constant K in Equation VI is usually called the ionization constant of acetic acid.

In order to calculate K we must know the total concentration, C, of acetic acid and the fraction, α, that is ionized. Then αC is the concentration of each of the ions, if the solution does not contain other acids or other acetates.

It has been shown in Chapter VIII how the fraction ionized in an acetic acid solution can be calculated from measured values of the electrical conductance, with the help of some conductance data for certain other electrolytes. The values for the fraction ionized can be used for the calculation of the equilibrium constant. For example, the fraction ionized in 0.001028 M acetic acid is 0.1238. Then the concentration of the hydrogen and acetate ions is

$$0.1238 \times 0.001028 = 0.0001273\ M$$

and the concentration of non-ionized acetic acid is

$$0.001028 - 0.0001273 = 0.0009007\ M$$

Therefore,

$$K = \frac{(0.0001273)^2}{0.0009007} = 0.00001798 = 1.798 \times 10^{-5}$$

Table 8 gives the conductance data for acetic acid at several concentrations, the values of the fraction ionized and the values of K calculated as illustrated above.

TABLE 8

Ionization Constant of Acetic Acid

M	Λ	Λ_e	α	$K \times 10^5$
0.0001114	127.7	389.7	0.3277	1.779
.0002184	96.5	389.5	.2478	1.782
.001028	48.13	388.9	.1238	1.798
.003441	27.19	388.3	.07002	1.814
.009842	16.37	387.6	.04224	1.833
.05000	7.356	386.2	.01905	1.849
.1000	5.200	385.3	.01350	1.846
0.2308	3.391	384.2	.00883	1.814

In view of the wide range of concentrations involved, the last being two thousand times the first, the small variation in the value of K cannot be taken as a serious objection to the proposition that the law of chemical equilibrium applies to this case. If a high degree of precision is not required, the constant $K = 1.8 \times 10^{-5}$ can be quite useful in a practical way. It allows one to calculate the approximate ion concentrations in any dilute acetic acid solution, and takes the place of a large table of experimental results that might give the same information. For example, let us calculate the hydrogen-ion (strictly, hydronium-ion) concentration in a 0.02 *M* acetic acid solution. Let x equal the desired concentration. Then x also represents the acetate ion concentration, because when acetic acid ionizes, one acetate ion is formed for each hydrogen ion. The concentration of un-ionized acetic acid will be $0.02 - x$, because x mole of the original 0.02 mole has ionized. Substituting in Equation VI,

$$\frac{x^2}{0.02 - x} = 0.000018$$

$$x^2 = 0.00000036 - 0.000018\,x$$

$$x^2 + 0.000018\,x - 0.00000036 = 0.$$

This is a quadratic equation and can be solved by the use of the formula

$$x = -b \pm \frac{\sqrt{b^2 - 4\,ac}}{2\,a}$$

giving two roots,

$$x = 0.00059 \text{ or } -0.00061.$$

The negative concentration has no physical significance and is therefore discarded and the positive result retained.

The equation can be solved more simply by a method that gives only an approximate solution. Since we know that acetic acid is a weak acid, and ionized to only a small extent, the concentration of non-ionized acetic acid is nearly as large as the total concentration. In terms of the symbols, $0.02 - x$ is nearly equal to 0.02. If the error is allowable, we may use 0.02 in place of $0.02 - x$. The advantage of this is that the equation is more easily solved.

$$\frac{x^2}{0.02} = 0.000018$$

$$x^2 = 0.00000036 = 36 \times 10^{-8}$$

$$x = 6.0 \times 10^{-4} = 0.00060.$$

If after such an approximate solution it is desired to estimate the error involved, the hydronium-ion concentration found can be subtracted from the total concentration to give an approximate value of the concentration that should have been used for the non-ionized acid.

$$0.02 - 0.0006 = 0.0194.$$

The error made was the error of using the number 0.02 in the denominator when 0.0194 should have been used. If desired, the better value for the non-ionized acid, 0.0194, can be substituted in the equilibrium equation, and the equation solved again, giving a closer approximation to the true hydrogen-ion concentration.

The fact that K in Table 9 is not entirely constant needs explaining. One of the more important of the causes of this variation is the use of the concentration as a measure of the active mass. It has been found that concentration is only an approximate measure of the tendency to react, especially for ions. It is possible to introduce a correction factor by which the concentration can be multiplied to give a better measure of active mass, but we need not consider that here. The concentration will do well enough for present purposes, since a qualitative understanding of the equilibrium law is of much more importance at present than its precise application.

102. The Common-Ion Effect. When sodium acetate is added to a solution of acetic acid, the acetate-ion concentration of the solution is increased. Sodium acetate is a salt, and we may assume it completely dissociated into ions in dilute solution. If the ions of acetic acid are in equilibrium with the non-ionized molecules just before the sodium acetate is added, the following relationship holds.

$$\frac{[H^+][CH_3COO^-]}{[CH_3COOH]} = 1.8 \times 10^{-5} \qquad \text{(VII)}$$

When the sodium acetate is added, the acetate-ion concentration is greatly increased, making the numerator of the left-hand term of the equation too large. The substances in solution are consequently not in equilibrium with each other, and a reaction must take place. The only reaction possible is the following:

$$H_3O^+ + CH_3COO^- \longrightarrow CH_3COOH + H_2O. \qquad (5)$$

This takes place, causing a decrease in the hydronium- and acetate-ion concentrations and an increase in the concentration of un-ionized acetic acid. These changes decrease the value of the left-hand term of Equation VII. Soon a new equilibrium is established in which the hydronium-ion concentration is much less than before. The concentration of un-ionized acetic acid is now a little larger than before. This result of the addition of a salt with an ion like one of the ions of the weak electrolyte is called the *common-ion effect.*

To calculate the hydronium-ion concentration in a solution of a weak acid in the presence of one of its salts, we must know the ionization constant of the acid, the total concentration of the acid, and the concentration of the salt.

All of the anion present (including that supplied by the salt) is involved in the ionization equilibrium of the acid. Often the total anion concentration can be taken as equal to that supplied by the salt, because the quantity supplied by the acid in the presence of the salt is small enough to be neglected. It is so in the following problem.

Let us calculate the hydronium-ion concentration of a 0.020 molar acetic acid solution to which 0.01 mole per liter of sodium acetate has been added. Let y be the hydronium-ion concentration. For every hydronium ion, one acetate ion has been formed by ionization of acetic acid. The total acetate ion concentration is $0.01 + y$, or approximately 0.01 M, and the concentration of un-ionized acetic acid is approximately 0.02 M.

$$\frac{[\mathrm{H^+}][\mathrm{Ac^-}]}{[\mathrm{HAc}]} = \frac{0.01\,y}{0.02} = 1.8 \times 10^{-5}$$

$$y = 3.6 \times 10^{-5}\,M$$

The hydronium-ion concentration of pure 0.02 M acetic acid was shown above to be $5.9 \times 10^{-4}\,M$ which is over ten times as large as $3.6 \times 10^{-5}\,M$. This calculation illustrates the principle of the common-ion effect, which can be shown experimentally to take place as predicted by the theory.

103. General Form of the Equilibrium Equation. The above applications of the equilibrium equation have been confined to some of the simplest reactions. For a reaction of the type

$$mA + nB \rightleftarrows pC + qD \tag{6}$$

where m, n, p, and q are the relative numbers of moles reacting, the equilibrium equation is

$$\frac{[C]^p[D]^q}{[A]^m[B]^n} = K \tag{VIII}$$

in which $[C]$, $[D]$, $[A]$, and $[B]$ represent the *total* concentrations of the substances *C, D, A,* and *B,* respectively.

For the reaction $2\ HI \rightleftarrows H_2 + I_2$, which takes place in the gaseous state at high temperatures, the concentration [HI] must be squared in the denominator of the equilibrium expression. The reason for this may be seen if the reaction is written

$$HI + HI \rightleftarrows H_2 + I_2 \tag{7}$$

and the equilibrium equation written

$$\frac{[H_2][I_2]}{[HI][HI]} = K \tag{IX}$$

It might at first be thought that half of the hydrogen iodide concentration should be used for each [HI], but this is wrong. *Any* hydrogen iodide molecule present might act as the first one in Equation 7, and *any other* might act as the second. The concentration of molecules that can act as the first hydrogen iodide molecule is expressed by the total hydrogen iodide concentration, and the concentration of molecules that can act as the second is given by the same total concentration. Therefore, the velocity with which the hydrogen iodide can react with itself is proportional to the square of its concentration, and the square of the concentration appears in the denominator of the equilibrium equation.

EXERCISES

1. Calculate the ionization constants for acetic acid from some of the figures in Table 8 for the fraction ionized and check the figures for the constants that are given in the table.

2. Calculate the hydronium-ion concentration of a solution containing 0.01 mole per liter of acetic acid and 0.05 mole per liter of potassium acetate. *Ans.* 3.6×10^{-6} *M.*

3. Calculate the approximate hydronium-ion concentration of a solution 0.1 *M* with respect to acetic acid and 0.1 *M* with respect to sodium acetate. *Ans.* 1.8×10^{-5} *M.*

4. Calculate the hydronium-ion concentration of 0.1 *M* benzoic acid solution. Benzoic acid, C_6H_5COOH, is a monobasic acid having an ionization constant of 6.3×10^{-5}. *Ans.* 2.5×10^{-3} *M.*

5. Calculate the hydronium-ion concentration of a solution prepared by the addition of 14.4 g. of sodium benzoate, C_6H_5COONa, to 2000 ml. of 0.1 *M* benzoic acid solution. Assume that the final volume is practically 2000 ml. *Ans.* 1.26×10^{-5} *M.*

Chapter XI

CHEMICAL EQUILIBRIUM (PART II)

In Chapter X the equilibrium equation was derived and applied to the ionization of acetic acid, a typical weak electrolyte. In this chapter some equilibria of more immediate interest in qualitative analysis are discussed.

104. The Ionization of Hydrogen Sulfide. When a dibasic acid ionizes, one of the protons comes off more easily than the other, and two chemical equations are needed to express the ionization as it actually occurs. For hydrogen sulfide the ionization is expressed by the following equations:

$$H_2S + H_2O \longrightarrow H_3O^+ + HS^- \tag{1}$$

$$HS^- + H_2O \longrightarrow H_3O^+ + S^=. \tag{2}$$

Application of the equilibrium equation to these two reactions gives two equations.

$$\frac{[H_3O^+][HS^-]}{[H_2S]} = K_1 = 1 \times 10^{-7} \tag{I}$$

$$\frac{[H_3O^+][S^=]}{[HS^-]} = K_2 = 1 \times 10^{-15} \tag{II}$$

The constant K_1 which has the numerical value 1×10^{-7} is called the first ionization constant of hydrogen sulfide, and the constant K_2, or 1×10^{-15}, is called the second. The numerical values of these constants show that hydrogen sulfide is a much weaker acid than acetic acid, since even the first ionization constant is much smaller than the constant for acetic acid.

Multiplication of Equations I and II together gives an equation that is more useful for some calculations. The advantage is that the concentration of the hydrosulfide ion (HS^-) cancels and the result is a fairly simple single equation.

$$\frac{[H_3O^+]^2\,[S^=]}{[H_2S]} = 1 \times 10^{-22} \tag{III}$$

The numerical values of the constants given for Equations I, II and III are for temperatures of 20 to 25°, and are only approximate. They are good enough for present purposes, however.

One precaution in the use of Equation III, or other similar equations, should be mentioned. It is not correct to consider that the hydronium-ion concentration of a pure hydrogen sulfide solution is equal to twice the sulfide-ion concentration, as one might incorrectly assume on the basis of the equation

$$H_2S + 2\,H_2O \longrightarrow 2\,H_3O^+ + S^= \qquad (3)$$

which is the sum of Equations 1 and 2. Since the ionization takes place in two steps, and the second ionization is much less extensive than the first, the correct relation is

$$[H_3O^+] = [HS^-] + 2[S^=]. \qquad (IV)$$

In the precipitation of the hydrogen sulfide group of qualitative analysis, hydrogen sulfide is passed into a solution that is 0.3 *M* with respect to hydrochloric acid. The large hydronium-ion concentration causes the sulfide-ion concentration to be extremely small, because of the common-ion effect. It is for the purpose of keeping the hydronium-ion concentration extremely small that the acid is added.

The sulfide-ion concentration when the hydrogen sulfide group is precipitated can be calculated by means of Equation III. The hydronium-ion concentration is 0.3 *M*. In a solution of this concentration, however, the hydronium ion acts as if its concentration were 0.23 *M*, or even less, depending on the total concentration of electrolytes present. We need not inquire why this is so, or how it is determined. In fact it would make little difference if this fact were overlooked, but for the sake of precision in the calculation it is taken into account. If the solution is saturated with hydrogen sulfide at 25°, the concentration of un-ionized hydrogen sulfide, which can be taken as practically equal to the total hydrogen sulfide concentration, is equal to 0.1 *M*.

$$\frac{(0.23)^2\,[S^=]}{0.1} = 1 \times 10^{-22}$$

$$[S^=] = 2 \times 10^{-22} \text{ (approximately)}$$

If a solution containing ammonium chloride and hydrochloric acid is neutralized by the addition of ammonium hydroxide until litmus paper is turned to a violet color, the hydronium-ion concentration is about 10^{-7}. This is approximately the condition in the precipitation of the ammonium sulfide group. If the solution is then saturated with hydrogen sulfide, the sulfide-ion concentration is much larger than when 0.3 *M* hydrochloric acid is present.

$$\frac{(10^{-7})^2\,[S^{=}]}{0.1} = 1 \times 10^{-22}$$

$$[S^{=}] = 1 \times 10^{-9}$$

The sulfide-ion concentrations in other solutions can be calculated in a similar manner. Also, the hydrosulfide-ion (HS^-) concentration can be calculated by means of Equation I, when the hydrogen sulfide and hydronium-ion concentrations are known. The results of a few such calculations are given in Table 9.

TABLE 9

SULFIDE, HYDROSULFIDE AND HYDRONIUM ION CONCENTRATIONS IN SULFIDE SOLUTIONS

Solution	*Molar Concentration at 25°*		
	H_3O^+	HS^-	$S^{=}$
Na_2S, 1 *M*	1×10^{-14}	0.91	0.09
$(NH_4)_2S$, 1 *M*	5×10^{-10}	1	2×10^{-6}
H_2S, saturated, when $[H_3O^+] = 10^{-7}$	1×10^{-7}	0.1	1×10^{-9}
H_2S, saturated in water	1×10^{-4}	1×10^{-4}	1×10^{-15}
H_2S, saturated + 2 *M* acetic acid	6×10^{-3}	2×10^{-6}	3×10^{-19}
H_2S, saturated + 0.3 *M* HCl	0.3[a]	4×10^{-8}	2×10^{-22}

[a] The hydronium ion in a solution of this concentration acts as if its concentration were 0.23 *M*.

105. Acids and Bases. An acid may be defined as a compound that can part with a proton under suitable conditions. Hydrogen chloride is a typical strong acid and can part with a proton (H^+) in accordance with the equation

$$HCl \qquad H^+ + Cl^-. \tag{4}$$

This reaction goes forward to only a minute extent unless the proton is removed by combination with some other ion or molecule. If water is present, the proton combines with a water molecule to give the hydronium ion.

$$H^+ + H_2O \rightleftharpoons H_3O^+. \tag{5}$$

This allows Reaction 4 to proceed practically to completion. Equations 4 and 5 may be combined to give

$$HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-. \tag{6}$$

In dilute solutions Reaction 6 is practically complete, and the acid properties of a dilute hydrochloric acid solution are the properties of the hydronium ion. This ion is itself an acid as indicated by the reverse arrow in Equation 5. If a compound giving the hydroxide ion is added to a solution containing hydronium ion, Reaction 5 is reversed because the hydroxide ion adds a proton to form water.

$$H^+ + OH^- \longrightarrow H_2O \tag{7}$$

Acids are classified by the extent to which they react with water. Some acids, such as hydrochloric, nitric, sulfuric and perchloric, react practically completely with water in dilute solutions.[1] These acids are called strong acids. All strong acids are alike in water solution as far as acid properties are concerned, because the acid properties of all of them are the properties of the hydronium ion. It is necessary to keep in mind, however, that each different anion has a set of properties of its own, and differences in the reactions of various strong acids are to be ascribed to differences in the properties of the anions.

Acids that react to only a small extent with water are called weak acids. Acetic acid is a typical weak acid. In dilute solutions its reaction with water comes to equilibrium when only a small fraction of the acid has ionized. The strength of a weak acid is ordinarily measured by its ionization constant, the smaller the ionization constant the weaker the acid.

---

[1] Sulfuric acid reacts with water to form the acid sulfate ion, HSO_4^-, and this reaction goes to completion. Part of the resulting acid-sulfate ion reacts further with water to form the sulfate ion and a second hydronium ion, but this "second ionization" is incomplete.

The term base has been used in the past to mean a compound that can react with an acid to form a salt, and it has also been used to mean a compound that gives the hydroxide ion in water solution. These two meanings are not inconsistent with each other, because compounds that react with acids to form salts ordinarily give more or less hydroxide ion in water solution. A newer definition of base that is preferable to either of these older ones is coming into use at the present time. According to the newer definition, a base is any molecular or ionic species that can unite with a proton. This definition was proposed by the English chemist Lowry and the Danish chemist Bronsted, and is frequently called the Lowry-Bronsted, or sometimes the Bronsted, definition. Along with the Bronsted definition of base goes the definition of acid given above.

According to the Lowry-Bronsted definition, water is a base because it can unite with a proton to form the hydronium ion, H_3O^+. The hydroxide ion is also a base because it unites with a proton to form water.[1] The hydroxide ion is a stronger base than water, because when protons are added to a solution containing water and hydroxide ion, they unite with the hydroxide ion in preference to the water.

In general, anions are bases, because they can unite with protons to form acids. Anions of strong acids are weak bases, because they hold the protons weakly and easily surrender them to other bases. Anions of weak acids are fairly strong bases, and the weaker the acid the stronger is the base that is formed when it ionizes. Acetate, carbonate and sulfide ions are moderately strong bases.

$$CH_3COO^- + H^+ \longrightarrow CH_3COOH \tag{8}$$

$$CO_3^= + H^+ \longrightarrow HCO_3^- \tag{9}$$

$$S^= + H^+ \longrightarrow HS^- \tag{10}$$

Not all bases are anions. **Water and ammonia are examples** of bases that are neutral molecules. When such a base unites with a proton, an acid is formed that is also a cation. Thus,

---

[1] According to the older definition, sodium hydroxide would be called a base, while according to the newer, the hydroxide ion is the base. Sodium hydroxide may be called a salt.

ammonia unites with a proton to form the weakly acid ammonium ion.

$$NH_3 + H^+ \longrightarrow NH_4^+ \qquad (11)$$

Ammonia is a somewhat stronger base than water, but not as strong as the hydroxide ion. Accordingly, the ammonium ion is a weaker acid than the hydronium ion, but a stronger one than water. When ammonia is dissolved in water, it reacts with water to form a small amount of hydroxide ion, and the reaction then comes to equilibrium.

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^- \qquad (12)$$

If we designate a base by B^-, the union of B^- with a proton, H^+, gives the acid HB. This reaction is reversible, and when a proton separates from the acid HB, the base B^- is left.

$$HB \rightleftharpoons H^+ + B^- \qquad (13)$$

It should be remembered that only very few protons can exist in the free state at any one time, and if an acid is to dissociate appreciably to give protons and a base, there must be another base present to unite with the protons as fast as they are liberated by the acid. Similarly, if a base adds protons there must be an acid present to supply the protons.

Water is much stronger as a base than some of the anions. When hydrochloric acid is brought in contact with water, the proton is transferred from the acid to the water, forming the hydronium ion, because water is a much stronger base than the chloride ion

$$HCl + H_2O \longrightarrow H_3O^+ + Cl^- \qquad (14)$$

The acetate ion is also much stronger as a base than the chloride ion, which means that the acetate ion combines with a proton (forming acetic acid) and holds it more tightly than the chloride ion does. Accordingly, acetic acid in water reacts to only a small extent with the water. It can be considered that in an acetic acid solution there are two bases (water and the acetate ion) competing for the same limited quantity of protons. In such a case the stronger base gets most of the protons, provided that its concentration is not too small.

There are some compounds that are weaker acids than water. Ammonia, NH_3, and alcohol, C_2H_5OH, are two such compounds.

Metallic sodium displaces hydrogen from each of these compounds in the pure state, giving salts analogous to sodium hydroxide in which the anions are strong bases.

$$2\,Na + 2\,NH_3 \longrightarrow 2\,Na^+ + 2\,NH_2^- + H_2 \qquad (15)$$

$$2\,Na + 2\,C_2H_5OH \longrightarrow 2\,Na^+ + 2\,C_2H_5O^- + H_2 \qquad (16)$$

When the ions NH_2^- and $C_2H_5O^-$ are brought into water, they react practically completely with the water, which acts as an acid in the presence of the very strong bases.

$$\underset{\text{Acid}}{H_2O} + \underset{\text{Base}}{NH_2^-} \longrightarrow \underset{\text{Acid}}{NH_3} + \underset{\text{Base}}{OH^-} \qquad (17)$$

$$\underset{\text{Acid}}{H_2O} + \underset{\text{Base}}{C_2H_5O^-} \longrightarrow \underset{\text{Acid}}{C_2H_5OH} + \underset{\text{Base}}{OH^-} \qquad (18)$$

Bases considerably stronger than the hydroxide ion cannot exist in water solution in any appreciable concentration.

A similar relationship holds for acids. Acids considerably stronger than the hydronium ion cannot exist undissociated in water solution. Hydrochloric acid can be taken as an example. It reacts with water in accordance with Equation 14 to give the hydronium ion. Perchloric acid has been found to be a stronger acid than hydrochloric, but in water solution the two have the same strength, if the concentrations are equal. The reason, as explained previously, is that both react to form the hydronium ion and both solutions really contain the same acid.

106. Ammonia and Ammonium Hydroxide. There are two ways of accounting for the behavior of ammonia when dissolved in water. The facts on which the explanation may be based are that ammonia is very soluble in water, that even fairly dilute solutions smell strongly of ammonia and that ammonium and hydroxide ions are present in the solution. We may, if we like, assume that part of the ammonia reacts with water to give the compound ammonium hydroxide, NH_4OH, and that this compound is partially ionized.

$$NH_3 + H_2O \rightleftharpoons NH_4OH \qquad (19)$$

$$NH_4OH \rightleftharpoons NH_4^+ + OH^- \qquad (20)$$

Only part of the ammonia could be combined with water to form ammonium hydroxide, because otherwise the solution would not smell so strongly of ammonia; ammonia in the gas above the solution must be in equilibrium with ammonia in the solution.

$$NH_3 \text{ (gas)} \rightleftharpoons NH_3 \text{ (dissolved)} \qquad (21)$$

The dissolved ammonia according to this view enters into a reversible reaction with water to give un-ionized ammonium hydroxide, but at equilibrium there is some ammonia present. The un-ionized ammonium hydroxide is in equilibrium with the ions, of which there are relatively few present. Ammonium hydroxide is thus a weak base, in the sense of the older definition of base.

The concept of an ammonia solution is made simpler if we overlook any un-ionized compound between water and ammonia that may be present. This makes little difference with the practical conclusions to be drawn and has the advantage of simplicity.

Neglecting any un-ionized compound between water and ammonia that may be present, we may consider that ammonia is a moderately strong base, and that when it dissolves in water the water acts as a very weak acid.

$$\underset{\text{Acid}}{H_2O} + \underset{\text{Base}}{NH_3} \rightleftharpoons \underset{\text{Acid}}{NH_4^+} + \underset{\text{Base}}{OH^-} \qquad (22)$$

This reaction comes to equilibrium when only a small fraction of the ammonia has reacted with water. The equilibrium equation can be applied as follows.

$$\frac{[NH_4^+][OH^-]}{[H_2O][NH_3]} = K' \qquad (V)$$

In dilute solutions the concentration of water is practically constant, and the equation can be transformed into a simpler form:

$$\frac{[NH_4^+][OH^-]}{[NH_3]} = K'(H_2O) = K. \qquad (VI)$$

The value of K for this equilibrium happens to be very nearly equal to that for the ionization of acetic acid, and can be taken as 1.8×10^{-5}.

There is a common-ion effect in a solution containing ammonia when an ammonium salt is added. Increasing the ammonium-ion concentration increases the numerator of the left-hand term of Equation VI, which means that the system is no longer in equilibrium. A reaction then takes place that reduces the product of the ammonium- and hydroxide-ion concentrations and restores equilibrium. The reaction that does this is the formation of ammonia and water from the two ions.

$$NH_4^+ + OH^- \longrightarrow NH_3 + H_2O \tag{23}$$

The result of this reaction is that the hydroxide-ion concentration becomes less than before. An ammonia solution containing ammonium chloride has a smaller hydroxide-ion concentration than a pure ammonia solution of the same concentration. This is the reason for the addition of ammonium chloride before the precipitation of the ammonium sulfide group. It is desired to add ammonia, but ammonia alone gives too much hydroxide ion, and there is danger of precipitation of magnesium hydroxide. The presence of ammonium chloride keeps the hydroxide-ion concentration too small to precipitate magnesium hydroxide.

107. The Ionization of Water. Water ionizes slightly in accordance with the equation

$$2\,H_2O \rightleftarrows H_3O^+ + OH^-. \tag{24}$$

In pure water or in any water solution the water is in equilibrium with hydronium and hydroxide ions. It follows that both hydronium and hydroxide ions are present in *all* water solutions; acid solutions contain a trace of hydroxide ion and solutions of hydroxides, which are strongly basic, contain a trace of hydronium ion. Because water solutions are used so much, the equilibrium of water with its ions is of special importance.

The equilibrium equation can be applied to the ionization of water.

$$\frac{[H_3O^+][OH^-]}{[H_2O]} = K' \tag{VII}$$

We can consider the concentration of water constant in dilute solutions, or in pure water. Letting $K'(H_2O) = K$, the equation becomes

$$[H^+][OH^-] = K = 1 \times 10^{-14}. \tag{VIII}$$

The K of this equation is often called the ion product of water. It has a value very close to 1×10^{-14} at 25° and somewhat different values at other temperatures. At temperatures from

20 to 30° we may take its value to be near enough to 1×10^{-14} for many purposes.

The use of this equation and also of the ionization constant for ammonia is illustrated by the following problem. Let us calculate the *hydronium-ion* concentration of a solution containing 0.01 mole per liter of ammonia and 0.05 mole per liter of ammonium chloride. It may be assumed that the concentration of ammonia (NH_3) is 0.01 *M* without much error, and also that the concentration of ammonium ion is 0.05 *M*. Substituting in Equation VI we have:

$$\frac{0.05[OH^-]}{0.01} = 1.8 \times 10^{-5}$$

$$[OH^-] = 0.36 \times 10^{-5}.$$

Knowing the hydroxide-ion concentration of the solution, we can calculate the hydronium-ion concentration from Equation VIII.

$$[H_3O^+] \times 0.36 \times 10^{-5} = 1 \times 10^{-14}$$

$$[H_3O^+] = \frac{1 \times 10^{-14}}{0.36 \times 10^{-5}} = 2.8 \times 10^{-9}$$

The hydronium-ion concentration is 2.8×10^{-9} mole per liter.

EXERCISES

1. What tests might be made to show that a solution of ammonia contains ammonium ions and hydroxide ions?

2. Calculate the hydroxide-ion concentration in a 0.02 *M* NH_3 solution. *Ans.* 0.0006 *M*.

3. Calculate the hydroxide-ion concentration of a 0.02 *M* NH_3 solution to which has been added 0.01 mole per liter of ammonium sulfate, $(NH_4)_2SO_4$. Compare with problem 2. *Ans.* 0.000018 *M*.

4. Calculate the hydrosulfide-ion concentration of a solution that is saturated with hydrogen sulfide and has a hydronium-ion concentration of 1×10^{-7} *M*.

5. Calculate the sulfide-ion concentration of a solution 2 *M* with respect to acetic acid and saturated with hydrogen sulfide.

6. Calculate the hydronium-ion concentration of 0.01 *M* NaOH. *Ans.* 1×10^{-12} *M*.

7. Why is the concentration of water omitted from the denominators of the left-hand terms of Equations I and II, page 164? Multiply these equations together and derive from them Equation III.

8. Calculate the hydrosulfide ion concentration of a saturated solution of hydrogen sulfide in pure water, assuming that $[HS^-] = [H_3O^+]$ and that $[H_2S] = 0.1$. Calculate also the sulfide-ion concentration on the basis of the same assumptions. Is it approximately correct to assume that the hydronium-ion concentration is equal to the hydrosulfide-ion concentration? See Equation IV.

9. Which has the larger sulfide-ion concentration, (*a*) a solution containing 0.1 mole of H_2S and 0.3 mole of HCl per liter, or (*b*) a solution containing 0.1 mole of H_2S and 0.3 mole of acetic acid per liter? Give reasons in detail.

10. Calculate the *hydronium*-ion concentration of a solution containing 0.03 mole of NH_3 and 0.01 mole of NH_4Cl per liter.

Ans. 1.3×10^{-9} *M*.

Chapter XII

THEORY OF PRECIPITATION (PART I)

For convenience the theory of precipitation may be divided into two parts, (1) the general conditions under which the formation of a precipitate is possible and (2) the mechanism of precipitate formation.

The basis of the first part is the solubility product principle. This can be considered as a definition of a saturated solution in terms of ion concentrations. Like many scientific laws, the solubility product principle as usually stated is not exact. It can be made so at the expense of making it more complicated, but for many purposes this is undesirable. A simple but approximate law is often more desirable for giving a general idea of a process, and for rough calculations, than a more complicated exact one.

For the formation of a precipitate a solution must be supersaturated. A supersaturated solution is one that holds more solute per unit quantity of solution than a saturated solution at the same temperature. A saturated solution can be defined, if desired as a solution that can exist in equilibrium with the solid solute. This definition is correct, but not very useful for present purposes, because it gives no information as to the concentration of the solution. If the solute is an electrolyte, the presence of certain other electrolytes has considerable effect on the concentration of a saturated solution. This is illustrated in Table 10, which gives the concentrations of some saturated solutions of thallous chloride, as determined by analysis. The solubility product principle can be used satisfactorily to define a saturated solution of an electrolyte in terms of the composition of the solution.

108. Derivation of the Solubility Product Principle. In order to understand the solubility product principle it is desirable to understand its derivation. The derivation to be given is valuable because it gives a kinetic picture of the equilibrium of a salt with its saturated solution.

TABLE 10

SOLUBILITY OF THALLOUS CHLORIDE IN SOLUTIONS OF OTHER SALTS

(Solubilities are given in moles per liter at 25°)

Conc'n of other salt, M	0	0.05	0.1
In KCl solution	0.0161	0.0059	0.0040
In $TlNO_3$ solution	.0161	.0062	.0042
In KNO_3 solution	.0161	.0183	.0196

In the derivation and the discussion immediately following, electrolytes are considered completely dissociated into ions in very dilute solutions. Also, the electrical attraction of the ions for oppositely charged ions is considered negligible, for simplicity. This would be strictly true only if the ions were an infinite distance apart.

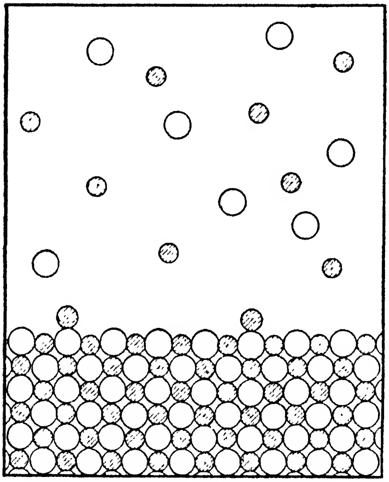


FIG. 10. Diagram of a portion of a crystal of silver chloride in equilibrium with a saturated solution. The smaller, shaded circles represent silver ions and the white circles represent chloride ions; the water molecules and other ions that might be present in the solution are not shown. The concentration in the solution is exaggerated.

Fig. 10 represents a portion of a crystal of silver chloride in equilibrium with its saturated solution. The crystal is considered to be made up of the ions of the salt arranged in an orderly pattern. This is in accord with the results of the analysis of crystal structures by means of X-rays, the particular pattern chosen for illustration being the cubic. If silver chloride is taken as the salt, the black dots can be assumed to represent silver ions and the circles chloride ions.

The state of equilibrium is not to be considered a state in which no further change takes place, but rather as a state in which the effects of all changes are compensated by other equal and opposite changes. Silver and chloride ions are continually dissolving from the crystal, but no change in concentration of the solution results, because at the same time an equal number of ions are deposited on the crystal. This picture of the process forms the basis of the derivation.

First, the factors determining the rate at which the ions leave the crystal will be considered. The rate, v_1, at which the silver ion leaves the surface of the crystal is proportional to the concentration of silver ions in the surface layer of the crystal. This concentration may or may not be equal to the concentration of chloride ions in the surface layer. An examination of Fig. 10 will doubtless make this evident. Let us designate the concentration of silver ions in the surface of the crystal by $[Ag^+]_s$, the brackets signifying concentration of whatever is included within them. Similarly, the rate, v_2, at which the chloride ions leave the crystal is proportional to the concentration of the chloride ions, $[Cl^-]_s$, in the surface layer. Putting these statements into equations,

$$v_1 = k_1[Ag^+]_s$$
$$v_2 = k_2[Cl^-]_s$$

The symbols k_1 and k_2 stand for numbers (constants) that make the proportionality between rate and concentration into an equality.

If numbers were to be substituted in the above equations, the rate, v, might be given by the number of ions leaving a unit area of surface in unit time, and the concentration by the number of ions in a unit area of surface. The equation would say that the number of ions leaving a unit area in unit time is proportional to the number present in the unit area. If the number present in the area decreases, the rate decreases.

The rate, v_3, at which silver ions are *deposited* on the surface of the crystal is proportional to two things. First, it is proportional to the concentration of silver ions in the solution, $[Ag^+]$. This concentration may or may not be equal to the chloride-ion concentration in the solution. For example, consider a dilute solution of silver nitrate that has been saturated with silver chloride. Here, the concentration of silver ions might be many times as large as the concentration of chloride ions. Second, the rate of deposition of silver ions is proportional to the concentration of chloride ions in the surface of the crystal, because each silver ion deposits on top of a chloride ion.

$$v_3 = k_3[\mathrm{Ag}^+][Cl^-]_S$$

The rate, v_4, at which chloride ions deposit on the crystal can be expressed similarly,

$$v_4 = k_4[\mathrm{Cl}^-][Ag^+]_s$$

When equilibrium is established between solution and crystal, both of the ions are being deposited at a rate equal to that at which they leave. Expressing this algebraically,

$$v_1 = v_3 \text{ and } v_2 = v_4.$$

Since things equal to the same thing are equal to each other,

$$k_1[Ag^+]_S = k_3[\mathrm{Ag}^+][Cl^-]_S$$

$$k_2[Cl^-]_S = k_4[\mathrm{Cl}^-][Ag^+]_S$$

These two simultaneous equations constitute the desired definition of a saturated solution. They can be simplified, however, by multiplying them together and cancelling the concentrations in the crystal surface from both sides, giving

$$[\mathrm{Ag}^+][\mathrm{Cl}^-] = \frac{k_1k_2}{k_3k_4} = K_{\mathrm{S.P.}} \qquad \text{(I)}$$

$K_{\mathrm{S.P.}}$ is a number made up of the small k's as indicated, and is called the solubility product constant, or merely the solubility product. Stated in words, the final equation tells us that in a saturated solution of an electrolyte (of the type of silver chloride) the *product* of the concentrations of the ions in the solution is a constant.

109. Calculation of the Solubility Product from the Solubility. The numerical value of the constant $K_{\mathrm{S.P.}}$ can only be found experimentally. There are several different methods, but it will be sufficient to consider only one of them. If the solubility in pure water can be determined, the solubility product can be calculated from it. For example, the concentration of silver chloride in a saturated solution in pure water at 25° is 1.86 mg. per liter. In this solution the number of silver ions must be equal to the number of chloride ions, since no other electrolytes are present. If we arbitrarily define a molecule of silver chloride as a unit composed of one silver ion and one chloride ion, or a mole as composed of a mole of silver ions plus a mole of chloride ions, the molecular weight is 143.5, and a mole is 143.5 g. The quantity dissolved in a liter of saturated solution is

$$\frac{0.00186}{143.5} = 1.3 \times 10^{-5} \text{ mole of AgCl.}$$

Since by definition a mole of silver chloride consists of one mole of each of the ions,

$$[Ag^+] = [Cl^-] = 1.3 \times 10^{-5}$$

and

$$[Ag^+][Cl^-] = (1.3 \times 10^{-5})^2 = 1.7 \times 10^{-10}.$$

Solid silver chloride can exist in equilibrium with a solution if in the solution the product of the concentrations of the silver and chloride ions is equal to 1.7×10^{-10}.

110. More General Solubility Product Equation. The solubility product principle as stated above applies only to electrolytes having equal numbers of positive and negative ions, such as AgCl, $CaSO_4$, or $FePO_4$. For electrolytes like Ag_2CrO_4, $PbCl_2$, Bi_2S_3, and $Ca_3(PO_4)_2$, or in general M_mX_n where M and X are the positive and negative ions, repectively, and m and n are the numbers of atoms in the molecule, the equation takes the form

$$[M]^m[X]^n = K_{S.P.} \qquad \text{(II)}$$

in which each concentration is raised to a power equal to the number of moles of the ionic species in question given by a mole of the solute.

The solubility products for a number of salts are given in Table 11.

111. Rule for Precipitation. When the product of the concentrations of the ions of a salt (each concentration raised to the proper power, in accordance with Equation II) is larger than the solubility product of the salt, the solution is supersaturated. If the degree of supersaturation is sufficiently large, precipitation results. Though the solubility principle itself does not promise precipitation, experience shows that we may expect it when the solubility product is exceeded, and the more it is exceeded, the more likely is precipitation. Likewise, when the product of the concentrations of the ions of

TABLE 11

SOLUBILITY PRODUCTS[1]

Salt	*Ions*		*Solubility Product*
$AgBr$	Ag^+	Br^-	3×10^{-13}
$AgCl$	Ag^+	Cl^-	2×10^{-10}
Ag_2CrO_4	$2\ Ag^+$	$CrO_4^{=}$	2×10^{-12}
AgI	Ag^+	I^-	1×10^{-16}
Ag_2S	$2\ Ag^+$	$S^{=}$	10^{-52}
$AgSCN$	Ag^+	SCN^-	6×10^{-13}
$BaCO_3$	Ba^{++}	$CO_3^{=}$	8×10^{-9}
$BaCrO_4$	Ba^{++}	$CrO_4^{=}$	2×10^{-10}
$BaSO_4$	Ba^{++}	$SO_4^{=}$	4×10^{-10}
$Bi(OH)_3$	Bi^{+++}	$3\ OH^-$	10^{-31}
$CaCO_3$	Ca^{++}	$CO_3^{=}$	5×10^{-9}
CaC_2O_4	Ca^{++}	$C_2O_4^{=}$	2×10^{-9}
$CaSO_4$	Ca^{++}	$SO_4^{=}$	10^{-4}
$Cd(OH)_2$	Cd^{++}	$2\ OH^-$	10^{-14}
CdS	Cd^{++}	$S^{=}$	10^{-28}
CuS	Cu^{++}	$S^{=}$	10^{-38}
$Fe(OH)_2$	Fe^{++}	$2\ OH^-$	10^{-14}
$Fe(OH)_3$	Fe^{+++}	$3\ OH^-$	10^{-38}
FeS	Fe^{++}	$S^{=}$	10^{-19}
Hg_2Cl_2	Hg_2^{++}	$2\ Cl^-$	1×10^{-18}
HgS	Hg^{++}	$S^{=}$	10^{-50}
$MgCO_3$	Mg^{++}	$CO_3^{=}$	1×10^{-5}
$Mg(OH)_2$	Mg^{++}	$2\ OH^-$	5×10^{-12}
$Mn(OH)_2$	Mn^{++}	$2\ OH^-$	10^{-14}
MnS	Mn^{++}	$S^{=}$	10^{-15}
$Ni(OH)_2$	Ni^{++}	$2\ OH^-$	10^{-14}
$PbCl_2$	Pb^{++}	$2\ Cl^-$	10^{-4}
$PbCrO_4$	Pb^{++}	$CrO_4^{=}$	2×10^{-14}
PbS	Pb^{++}	$S^{=}$	10^{-29}
$PbSO_4$	Pb^{++}	$SO_4^{=}$	1×10^{-8}
$SrCO_3$	Sr^{++}	$CO_3^{=}$	2×10^{-9}
$SrCrO_4$	Sr^{++}	$CrO_4^{=}$	8×10^{-6}
$SrSO_4$	Sr^{++}	$SO_4^{=}$	2×10^{-7}
$Zn(OH)_2$	Zn^{++}	$2\ OH^-$	3×10^{-17}
ZnS	Zn^{++}	$S^{=}$	10^{-26}

---

[1] Many of the solubility products given in this table are uncertain. Those that are the least certain are given only as an even power of ten, the digit term being omitted, as for example in the solubility product for silver sulfide. For purposes of calculation such solubility products may be taken as one times the value given. For most calculations of qualitative analysis approximate values of the solubility products are sufficient.

a salt in solution is less than the solubility product, the solution is unsaturated. The solid salt, if present, should dissolve until equilibrium conditions are again attained.

The rule for precipitation may be illustrated by a problem. Suppose that one liter of a $2 \times 10^{-4}\ M$ solution of silver nitrate is added to one liter of a $2 \times 10^{-3}\ M$ solution of sodium chloride. Is the solution supersaturated with respect to silver chloride?

In the first place, each solution is diluted to two liters when the two are mixed, and so the two concentrations are reduced to half their former values. A solution containing 1×10^{-4} mole per liter of silver nitrate is $1 \times 10^{-4}\ M$ with respect to silver ion. Likewise, the concentration of the chloride ion in the mixed solution is $1 \times 10^{-3}\ M$. The product of the concentrations of the silver and chloride ions is

$$[Ag^+][Cl^-] = 1 \times 10^{-4} \times 1 \times 10^{-3} = 1 \times 10^{-7}.$$

Since the solubility product of silver chloride is 1.7×10^{-10}, the ion product in the solution is about 600 times the solubility product. The solution is therefore greatly supersaturated and precipitation should take place.

112. The Common-Ion Effect. The solubility product for silver chloride should have the same value for all saturated solutions of silver chloride whether or not other silver or chloride salts are present. If the value of the solubility product is known, some useful calculations can be made.

Let us calculate the silver-ion concentration in a saturated solution of silver chloride containing enough hydrochloric acid to give a total chloride-ion concentration of 0.01 M. Let x be the silver-ion concentration.

$$0.01\,x = 1.7 \times 10^{-10}$$

$$x = 1.7\,\frac{10^{-10}}{10^{-2}} = 1.7 \times 10^{-8} M.$$

The silver-ion concentration in this case is much smaller than in the absence of the acid, 1.7×10^{-8} as compared with 1.3×10^{-5}.

Let us calculate the solubility of silver chloride, in grams per liter, in a 0.001 M silver nitrate solution. The solubility of silver chloride in moles per liter is equal to the chloride-ion concentration in the saturated solution, but not to the total silver-ion concentration, because part of the silver ion has been added as silver nitrate. Let x equal the chloride-ion concentration in the saturated solution. The silver-ion concentration is $(0.001 + x)$ molar, the sum of the silver-nitrate concentration and the silver-chloride concentration. A little reflection will show that x can be disregarded in this case, and the silver-ion concentration taken as approximately 0.001 *M*. This is true because the silver-chloride concentration must be less than 1.3×10^{-5}, or 0.000013 *M*, which is the solubility in pure water. The addition of this relatively small value to 0.001 *M* would give a number that would be rounded off to 0.001 *M* in any but a very exact calculation. The desirability of neglecting x when added to 0.001 can be shown by attempting to solve the problem without doing so, the equation being

$$(0.001 + x)x = 1.7 \times 10^{-10}$$

This is a quadratic equation. If 0.001 is substituted for $(0.001 + x)$ the equation is no longer a quadratic and is solved more easily and with results that are just as satisfactory for present purposes.

$$\begin{aligned} 0.001\,x &= 1.7 \times 10^{-10} \\ x &= 1.7 \times 10^{-7} \text{ mole of Cl}^- \text{ per liter} \end{aligned}$$

The chloride-ion concentration is equal to the number of moles of silver chloride dissolved in a liter. Converting to grams,

$$1.7 \times 10^{-7} \times 143.5 = 2.4 \times 10^{-5} \text{ g. AgCl per liter}$$

The addition of 0.001 mole of silver nitrate per liter reduces the solubility of silver chloride from 1.86 mg. per liter, its value in pure water, to 0.024 mg. per liter.

The predictions of the solubility product principle are found to be at least qualitatively true in practice. The addition of an electrolyte with an ion in common reduces the solubility of the precipitate. In making a precipitation, an excess of the precipitating reagent is usually added for two reasons. It insures the addition of enough, and it furnishes an excess of the common ion to reduce the solubility of the precipitate. For the more soluble precipitates, such as calcium oxalate or lead sulfate, the latter effect is of considerable importance.

EXERCISES

1. The solubility product of thallous chloride (TlCl) is 0.0003. Show by means of a calculation based on the solubility-product principle that the addition of 3.73 g. of KCl (molecular weight 74.6) to one liter of 0.01 *M* thallous nitrate ($TlNO_3$) solution should give either a supersaturated solution of thallous chloride or a precipitate.

2. The solubility of silver iodate, $AgIO_3$, in water is 4×10^{-8} mole per liter. What would be the result of adding 0.17 milligram of $AgNO_3$ (mol. wt. = 170) to one liter of 0.0001 *M* $NaIO_3$ solution?

3. Calculate the molar solubility of barium sulfate in 0.02 *M* barium chloride solution. *Ans.* 2×10^{-8} *M*.

4. A solution that is saturated with lead sulfate has a total lead ion concentration of 0.01 *M*. Calculate the sulfate-ion concentration. *Ans.* 1×10^{-6} *M*.

5. The solubility of calcium sulfate ($CaSO_4.2\,H_2O$) is 0.015 mole per liter at 25°. If 1 ml. of 0.2 *M* $BaCl_2$ were added to one liter of saturated calcium sulfate solution, would the solution be supersaturated with respect to barium sulfate?

6. If silver nitrate were added a very small portion at a time to a large volume of a solution containing 0.01 mole per liter each of chloride, bromide and iodide ions, with which of the three silver salts would the solution become saturated first? What concentration of silver ion in moles per liter would be required to saturate the solution with the least soluble of the silver halides? *Ans.* AgI, 1×10^{-14} *M*.

7. Taking the solubility of magnesium hydroxide in water as 0.0063 g. per liter, calculate the solubility product and also the solubility of magnesium hydroxide in a 0.01 *M* NaOH solution. In the latter calculation the hydroxide ion contributed by the dissolved magnesium hydroxide can be neglected. *Ans.* $K_{S.P.} = 5.2 \times 10^{-12}$; 5.2×10^{-8}.

8. Sodium hydroxide is added to a 0.01 *M* $MgCl_2$ solution until the solution is saturated with magnesium hydroxide. What is the hydronium-ion concentration? *Ans.* 2.3×10^{-8} *M*.

9. Explain with the help of calculations based on the solubility product principle why silver ion would be precipitated in the hydrogen sulfide group if it had not already been previously precipitated as silver chloride and removed.

Chapter XIII

THEORY OF PRECIPITATION (PART II)

Many of the precipitation processes of qualitative analysis are complicated by participation of one of the ions of the precipitate in a reversible reaction with one or more of the components of the solution. Thus, in sulfide precipitations the reagent, hydrogen sulfide, is a very weak electrolyte, and gives only a small concentration of sulfide ion when it ionizes in an acid solution.

$$H_2S + H_2O \rightleftarrows H_3O^+ + HS^-$$
$$HS^- + H_2O \rightleftarrows H_3O^+ + S^=$$

Since the sulfide ion and hydronium ion are in equilibrium with hydrosulfide ion and hydrogen sulfide, the sulfide-ion concentration is dependent on the hydronium-ion concentration of the solution, as shown in Table 9 on page 166. Whether or not a metal sulfide will be precipitated when hydrogen sulfide is added and the cation in question is present in appreciable concentration, depends on the sulfide-ion concentration. Therefore, by regulation of the hydronium-ion concentration one may determine what sulfides are to be precipitated.

113. Precipitation of Lead and Manganese Sulfides. The precipitation of lead sulfide may be considered typical of the precipitation of the hydrogen sulfide group. In the precipitation of the hydrogen sulfide group it is desired that all but a negligible quantity of lead ion shall be precipitated. For illustration, 1 mg. of lead ion may be considered negligible when the total volume of solution is 100 ml., or on the semimicro scale 0.05 mg. in 5 ml. of solution. A concentration of 1 mg. in 100 ml. is 0.01 g. per liter, or approximately 5×10^{-5} *M*. If the hydronium-ion concentration is 0.3 *M* as usual in the precipitation of the hydrogen sulfide group, and the solution is saturated with hydrogen sulfide, the sulfide-ion concentration is 2×10^{-22} *M* according to Table 9.

$$[Pb^{++}][S^=] = 5 \times 10^{-5} \times 2 \times 10^{-22} = 1 \times 10^{-26}$$

Since the solubility product of lead sulfide is about 10^{-29} the solution is still supersaturated with respect to lead sulfide, and still further precipitation of lead ion is to be expected.

If the above solution contained manganese ion at the large concentration of 0.22 g. in 100 ml., or 4×10^{-2} *M*, the product of the manganous- and sulfide-ion concentrations would be

$$[Mn^{++}][S^{=}] = 4 \times 10^{-2} \times 2 \times 10^{-22} = 8 \times 10^{-24}$$

Since the solubility product of manganous sulfide is about 10^{-15}, the solution would be unsaturated with respect to manganous sulfide. The solution was assumed to contain nearly the maximum amount of manganous ion that could be present if the directions as to the size of samples on page 92 were followed. The calculation shows why manganous sulfide is not precipitated in the hydrogen sulfide group.

Manganous sulfide is precipitated practically completely in the ammonium sulfide group, and it remains to show that the theory predicts this. A concentration of 1×10^{-4} *M* manganous ion may be considered negligible. If such a solution is saturated with hydrogen sulfide when the hydronium-ion concentration is 10^{-7} *M*,

$$[Mn^{++}][S^{=}] = 1 \times 10^{-4} \times 1 \times 10^{-9} = 1 \times 10^{-13}$$

Since the ion product is about one hundred times as large as the solubility product (10^{-15}), the solution is still considerably supersaturated with respect to manganous sulfide, and still further precipitation is to be expected. It may be concluded, therefore, that manganous ion will be practically completely precipitated in the ammonium sulfide group.

The theory of the precipitation of nickel, cobalt and zinc sulfides is not so clear. The solubility products of these sulfides are somewhat uncertain, but are considerably smaller than that of manganous sulfide. It would seem that these solubility products must necessarily be large enough so that they are not exceeded in the precipitation of the hydrogen sulfide group. On the other hand, it is known that a solution may sometimes be supersaturated without a precipitate appearing. Nickel and cobalt sulfides form slowly, as shown in connection with the final precipitation of zinc ion as zinc sulfide in the analysis of the ammonium sulfide group. In this precipitation, even though nickel and cobalt ions are present in small amounts, the white zinc sulfide can be precipitated in the $2\,M$ acetic acid solution without contamination with the black nickel and cobalt sulfides. In a short time, however, the black sulfides begin to appear, and if the zinc sulfide is to be separated from nickel and cobalt ions, it must be removed from the solution as soon as formed. This is an example of slow formation of a precipitate, and because of this possibility the reason why nickel and cobalt sulfides are not precipitated in the hydrogen sulfide group must be considered not clear.

Zinc sulfide when present alone is not precipitated under the conditions of the hydrogen sulfide group precipitation. However, when some of the members of the hydrogen sulfide group are present and have been precipitated, more or less zinc sulfide is precipitated on the surface of the sulfide precipitate already present. This is undesirable, and can be prevented by separation of the precipitate from the solution as soon as possible. This is effective because the precipitation of the zinc sulfide on the surface is a relatively slow process.

114. Precipitation by Ammonium Hydroxide. In the ammonium sulfide group of qualitative analysis, aluminum and chromium hydroxides are precipitated by the addition of ammonium hydroxide or ammonium sulfide. In the latter case, hydroxide ion is present as well as sulfide and hydrosulfide ions. It is desired that the ions of the carbonate group should stay in solution when the ammonium sulfide group is precipitated. Magnesium hydroxide has the smallest solubility product of the hydroxides of the carbonate group metals, and there is danger of its being precipitated with the ammonium sulfide group. There is no danger of the precipitation of the sulfides of the carbonate group metals.

Let us first inquire whether or not ammonium hydroxide can precipitate magnesium hydroxide from a solution of a magnesium salt. This inquiry may well consist in the calculation of the concentration of ammonia (NH_3) required for saturating the solution with magnesium hydroxide. We may take the magnesium-ion concentration as $0.2\,M$. This is the largest concentration likely to be met in practice and requires the least hydroxide ion. The solubility product of magnesium hydroxide is

$$[\mathrm{Mg^{++}}][\mathrm{OH^-}]^2 = 5 \times 10^{-12}$$
$$0.2[\mathrm{OH^-}]^2 = 5 \times 10^{-12}$$
$$[\mathrm{OH^-}]^2 = 2.5 \times 10^{-11}$$

If the hydroxide ion is furnished by a pure ammonium hydroxide solution and no extra ammonium ion is present, the ammonium-ion concentration is equal to the hydroxide-ion concentration.

$$[\mathrm{NH_4^+}][\mathrm{OH^-}] = [\mathrm{OH^-}]^2 = 2.5 \times 10^{-11}$$
$$\frac{[\mathrm{NH_4^+}][\mathrm{OH^-}]}{[\mathrm{NH_3}]} = \frac{2.5 \times 10^{-11}}{[\mathrm{NH_3}]} = 1.8 \times 10^{-5}$$
$$[\mathrm{NH_3}] = \frac{2.5 \times 10^{-11}}{1.8 \times 10^{-5}} = 1.4 \times 10^{-6}\,M$$

The hydroxide ion in equilibrium with this very small concentration of ammonia (NH_3) in the solution is enough to saturate the solution with magnesium hydroxide.

The total ammonium hydroxide to be added to the solution is the sum of the NH_3 concentration and the NH_4^+ (or OH^-) concentration, the latter being equal to the square root of 2.5×10^{-11} or 5×10^{-6}.

$$(5 \times 10^{-6}) + (1.4 \times 10^{-6}) = 6.4 \times 10^{-6}\,M$$

According to this calculation, the addition of 0.64 ml. of 0.01 *M* NH_4OH to a liter of the solution which is 0.2 *M* with respect to magnesium ion gives enough hydroxide ion to saturate the solution with magnesium hydroxide. More, of course, would be required to supersaturate the solution sufficiently to give a visible precipitate.

The correctness of the conclusion that magnesium hydroxide is easily precipitated by ammonium hydroxide can be confirmed experimentally by adding some ammonium hydroxide solution to a magnesium salt solution. It may be asked why we should bother with the calculation when the fact of the precipitation of magnesium hydroxide can be so easily ascertained experimentally. The answer is that if we can draw a conclusion from theoretical considerations and confirm the conclusion experimentally we feel that we have some understanding of the process concerned. Oftentimes, as in the above case, an understanding of the process is of much more importance than a knowledge of the fact.

Let us now inquire as to how much ammonium hydroxide would be required if the solution containing the magnesium ion should contain one mole of ammonium chloride per liter. It has been found above that to saturate the solution with magnesium hydroxide the hydroxide-ion concentration must be $5 \times 10^{-6}\,M$. The ammonium-ion concentration is $1\,M$ this time.

$$\frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{1 \times 5 \times 10^{-6}}{[NH_3]} = 1.8 \times 10^{-5}$$

$$[NH_3] = \frac{5 \times 10^{-6}}{1.8 \times 10^{-5}} = 0.3\,M$$

An ammonia concentration of $0.3\,M$ is required to saturate the solution with magnesium hydroxide in the presence of the ammonium chloride.

A much smaller concentration of ammonia than $0.3\,M$ gives enough hydroxide ion to precipitate aluminum and chromium hydroxides, because these hydroxides have extremely small solubility products. Therefore, it should be possible to separate magnesium ion from aluminum and chromium ions by precipitation of the latter two as hydroxides in the presence of considerable ammonium ion. Here again the calculations are in accord with experience.

The theory overlooks one important fact, however. When aluminum or chromium hydroxide is precipitated under conditions that should allow magnesium ion to remain in solution, the precipitate is often badly contaminated with magnesium hydroxide. The clean-cut separation that one would expect from the solubility-product theory is not realized in practice. Furthermore, unless conditions are favorable, the other ions of the carbonate group are apt to contaminate the precipitate. The inclusion within a precipitate of material that should remain in solution is often called *co-precipitation.*

Experiments have shown that the best separation of the hydroxides of the ammonium-sulfide group from the ions of the carbonate group is made when the hydroxides are precipitated with the smallest possible hydroxide ion concentration. This is accomplished by adding the ammonium hydroxide solution a little at a time with thorough mixing and stopping before an appreciable excess has been added. The reason why this procedure gives good results is not well understood.

115. The Dissolving of Slightly Soluble Salts. To dissolve a solid, a solvent or solution that is unsaturated with the solid must be brought in contact with it. If the solubility of the solid is large, all that is necessary is to provide enough of the dissolving liquid and allow sufficient time, or provide stirring or heat, or both, to hasten the process. If the solubility of the solid is small, it may be a practical impossibility to provide enough of the liquid to dissolve it, but when the solid is a salt it is often possible by other means to keep a dissolving liquid unsaturated in spite of the small solubility.

The solubility-product principle helps in understanding how this can be done. Let us consider the dissolving of manganese sulfide by 1 *M* hydrochloric acid solution. It will simplify the calculation if we assume the solution to be saturated with hydrogen sulfide. The sulfide ion concentration in such a solution can be calculated. The hydronium-ion concentration is 1 *M* and the concentration of un-ionized hydrogen sulfide is 0.1 *M*.

$$\frac{[H_3O^+]^2[S^=]}{[H_2S]} = \frac{1 \times [S^=]}{0.1} = 1 \times 10^{-22}$$

$$[S^=] = 1 \times 10^{-23}$$

If another sulfide is added to such a solution, increasing the sulfide-ion concentration, the system reacts in such a way as to bring the sulfide-ion concentration back to $1 \times 10^{-23}\ M$ and form more hydrogen sulfide, provided that the hydronium-ion concentration remains 1 *M*. Manganese sulfide can dissolve in this solution as long as the product of the concentration of its ions is less than the solubility product, which is about 10^{-15}. The product of the concentrations of the ions will become equal to the solubility product when the manganese-ion concentration attains some value which we may designate by x, while the sulfide-ion concentration, let us assume, remains practically equal to 1×10^{-23}.

$$(1 \times 10^{-23})x = 10^{-15}$$

$$x = 10^{8}\ M$$

If the manganese-ion concentration in the solution is less than the impossibly high concentration of $10^8\,M$, the product of the concentrations of the ions is less than the solubility product, and the solution is unsaturated. Therefore, a solution $1\,M$ with respect to hydronium ion and saturated with hydrogen sulfide can dissolve manganese sulfide. If the solution were not saturated with hydrogen sulfide, the sulfide-ion concentration would be still less than the above value, and manganese sulfide would dissolve still more easily.

The dissolving of manganese sulfide by an acid is a special case of a general phenomenon. It is often possible to cause one of the ions furnished by a precipitate to react to form a little-ionized compound. If this reduces the concentration of the ion in question to such an extent that the ion product (in the solution) of the precipitate is less than the solubility product, the solution becomes unsaturated with respect to the precipitate. The precipitate then continues to dissolve as long as the ion concentration is kept small enough.

Many of the sulfide precipitates can be dissolved by hydrochloric acid because the sulfide ion reacts with the hydronium ion to form hydrogen sulfide.

$$S^{=} + H_3O^+ \longrightarrow HS^- + H_2O$$

$$HS^- + H_3O^+ \longrightarrow H_2S + H_2O$$

The sulfides that have extremely small solubility products, however, do not dissolve, because the sulfide-ion concentration is not made small enough. Nitric acid is more effective than hydrochloric acid in dissolving sulfides, because it oxidizes the sulfide ion to sulfur and reduces its concentration more than hydrochloric acid does.

Hydroxides that are not soluble in water can generally be dissolved by acids, because of the reaction of hydroxide and hydronium ions to form water. Carbonates are dissolved by acids because of the reaction of the carbonate and hydronium ions to form carbonic acid, part of which decomposes to carbon dioxide and water.

$$2\,H_3O^+ + CO_3^{=} \longrightarrow H_2CO_3 + 2\,H_2O \longrightarrow CO_2 + 3\,H_2O$$

Similarly, most other slightly soluble salts of *weak* acids can be dissolved by strong acids. Slightly soluble salts of strong acids are not dissolved by strong acids. Examples of the latter are silver chloride and lead and barium sulfates.

Some salts of strong acids are dissolved by reagents other than acids. Silver chloride, for example, is dissolved when ammonia is added, because the ammonia unites with the silver ion to form a complex ion, and the consequent reduction of the silver-ion concentration makes the solution unsaturated.

116. Hydrolysis. The term *hydrolysis* is applied to reactions of the type represented by the molecular equation

$$AB + H_2O \longrightarrow AOH + HB$$

The compound AB may be a salt or a compound composed of two organic radicals, such as an ester. This representation of hydrolysis takes no account of the theory of ionization.

Hydrolysis reactions are quite important in organic chemistry. An example is the hydrolysis of an ester.

$$\underset{\text{Ethyl acetate}}{C_2H_5OOCCH_3} + H_2O \longrightarrow \underset{\text{Ethyl alcohol}}{C_2H_5OH} + \underset{\text{Acetic acid}}{CH_3COOH}$$

Hydrolysis reactions in which AB, the compound hydrolyzed, is a salt are of more importance for inorganic analytical chemistry, but the example of ester hydrolysis serves to emphasize the broadness of the term hydrolysis.

Sodium carbonate is an example of a soluble salt that is hydrolyzed. The carbonate ion reacts with water according to the following equation:

$$CO_3^{=} + H_2O \rightleftarrows HCO_3^- + OH^-$$

The reaction is reversible and comes to equilibrium when only a small fraction of the carbonate ion has reacted; in 0.01 M sodium carbonate solution about 5% of the carbonate ion is hydrolyzed to bicarbonate ion. The presence of the resulting hydroxide ion in a sodium carbonate solution accounts for the precipitation of aluminum, ferric and chromic hydroxides when sodium carbonate is added to solutions of aluminum, ferric and chromic salts.

Sodium carbonate can be taken as more or less typical of salts that hydrolyze. In terms of the Lowry-Bronsted definitions of acid and base, the carbonate ion is a strong enough base to react appreciably with the very weak acid water. All bases that are comparable in strength with the hydroxide ion react appreciably with water. Some other examples are the cyanide ion, the sulfide ion, the acetate ion and ammonia. All of these are weaker than the hydroxide ion, and their reactions with water do not go far before equilibrium is attained.

$$CN^- + H_2O \rightleftharpoons HCN + OH^-$$

$$S^= + H_2O \rightleftharpoons HS^- + OH^-$$

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$$

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

The extent to which sodium and ammonium sulfide solutions are hydrolyzed can be seen by an examination of Table 9 on page 166. Ammonium sulfide gives only a very small concentration of sulfide ion, and is practically all ammonium hydrosulfide, NH_4HS. However, it is customary to consider it ammonium sulfide and write its formula $(NH_4)_2S$, since it is the sulfide ion in which we are interested.

Another type of hydrolysis occurs when salts of bismuth, antimony and tin are brought in contact with water or when the excess acid that must be added in making clear solutions of these salts is partly neutralized. When the hydroxide-ion concentration in a solution of bismuth chloride is large enough, the solubility product of bismuth oxychloride, BiOCl, is exceeded, and this compound precipitates.

$$Bi^{+++} + Cl^- + 2\,OH^- \longrightarrow \underline{BiOCl} + H_2O$$

The hydroxide-ion concentration required depends on the bismuth and chloride-ion concentrations, but is usually very small and is attained in solutions that are still acid.

Antimony oxychloride, SbOCl, and bismuth oxychloride are precipitated when solutions of antimony and bismuth chlorides are diluted. The hydrolysis of bismuth, antimony and tin chlorides is often observed when solutions are being prepared for the precipitation of the hydrogen sulfide group. The oxychlorides can be dissolved by the addition of acid, because this reduces the hydroxide-ion concentration of the solution. However, it is not necessary to dissolve the oxychlorides, if present, before the precipitation of the hydrogen-sulfide group. The precipitation of the sulfides reduces the concentrations of the cations so much that the oxychlorides dissolve and are completely converted to sulfides

$$2\,\underline{\mathrm{BiOCl}} + 3\,\mathrm{H_2S} \longrightarrow \underline{\mathrm{Bi_2S_3}} + 2\,\mathrm{H_2O} + 2\,\mathrm{H^+} + 2\,\mathrm{Cl^-}$$

There are salts that cannot be formed in the presence of water. Such salts are completely hydrolyzed when brought in contact with water. Aluminum sulfide is an example. Aluminum sulfide can be made by direct combination of aluminum and sulfur at high temperatures. When brought in contact with water, aluminum sulfide is completely hydrolyzed.

$$\mathrm{Al_2S_3} + 6\,\mathrm{H_2O} \longrightarrow \underline{\mathrm{Al(OH)_3}} + 6\,\mathrm{H_2S}$$

The mechanism of the reaction is as follows. A little of the aluminum sulfide dissolves, and the product of the aluminum-ion concentration and the cube of the concentration of the hydroxide ion present in the water exceeds the solubility product of aluminum hydroxide. The precipitation of aluminum hydroxide keeps the aluminum-ion concentration so small that the aluminum sulfide continues to dissolve. Also the reaction of the sulfide ion with the hydronium ion of the water to form hydrosulfide ion and non-ionized hydrogen sulfide keeps the sulfide ion small, and this also helps the aluminum sulfide to dissolve. The hydronium-ion concentration is kept small because this ion reacts with the sulfide ion. Since any pronounced increase in hydronium ion is prevented, the hydroxide ion concentration is not suppressed as it would be if the hydronium ion accumulated in the solution. There is thus a large total quantity of hydroxide ion available from the water at a concentration large enough for the precipitation of aluminum hydroxide.

Salts of acids that are considerably weaker than water are practically completely hydrolyzed by water. The anion of such a salt is a considerably stronger base than the hydroxide ion, and it always removes a proton from a water molecule when it comes in contact with one. Two examples of such salts have already been mentioned, sodium amide, $\mathrm{NaNH_2}$, and sodium ethylate, $\mathrm{NaOC_2H_5}$, and equations for their reaction with water are to be found on page 170, Equations 17 and 18.

EXERCISES

1. Suppose that a solution contains 0.01 mole per liter of silver nitrate and 0.1 mole per liter of benzoic acid, the ionization constant of which is 6.6×10^{-5}; would silver benzoate be precipitated? The solubility product of silver benzoate is 1.2×10^{-4}. Make the appropriate calculation and state the conclusion to be drawn from it and the reason.

2. The value 4.5×10^{-23} is given for the solubility product of thallium sulfide, Tl_2S. Would you expect thallium sulfide to be precipitated from a solution 0.1 molar with respect to hydrogen sulfide and containing 0.2 mole per liter of hydronium ion and 0.01 mole per liter of thallous ion?

3. Explain in detail why dilute hydrochloric acid dissolves calcium carbonate, using the solubility product principle and the law of chemical equilibrium.

4. Explain in detail why calcium phosphate is not precipitated from an acid solution containing phosphoric acid and calcium ion, but is precipitated when the acid is neutralized by ammonia.

5. Write ionic equations for all of the changes that take place when aluminum sulfide reacts with water.

6. The following compounds are only slightly soluble in water. Predict what treatment would be the easiest way of getting each one into solution. Write an ionic equation for the reaction involved and give the reason why the treatment in question should dissolve the compound: $BaCrO_4$, $CuHAsO_3$, $Ag_3Fe(CN)_6$, $Ca(PO_4)_2$.

7. Write ionic equations for the reaction of sodium amide and the reaction of sodium ethylate with water.

8. Taking the solubility product of zinc sulfide as 1×10^{-23}, calculate the concentration of zinc ion in a solution saturated with both hydrogen sulfide and zinc sulfide and containing 0.1 mole of hydrochloric acid per liter. *Ans.* 0.01 *M*.

9. A solution of one liter volume contains 7 g. of lead nitrate, 0.01 mole of hydrochloric acid and 0.1 mole of hydrogen sulfide. Is the solution supersaturated with lead sulfide? *Ans.* Yes.

10. Would cadmium sulfide be dissolved by a solution 0.5 *M* with respect to hydronium ion, 0.1 *M* with respect to hydrogen sulfide and 0.01 *M* with respect to cadmium ion, or would the solution be already supersaturated with cadmium sulfide? *Ans.* Supersaturated.

11. Explain in detail why barium carbonate can be dissolved by acetic acid. Carbonic acid is weaker than acetic acid and decomposes partially to carbon dioxide and water; carbon dioxide is only slightly soluble in water.

12. Chromic acid, H_2CrO_4, is a strong acid in its reaction with water to form H_3O^+ and $HCrO_4^-$, but the ion $HCrO_4^-$ is weak, its ionization constant being 3.2×10^{-7}. The ion $HCrO_4^-$ reacts partially to form $Cr_2O_7^{=}$ and H_2O. Explain why barium chromate cannot be precipitated in a solution containing nitric acid, but can be precipitated when acetic acid and sodium acetate are present. Explain why strontium chromate is not precipitated under the latter condition but is precipitated when ammonium hydroxide and alcohol are added.

13. To a solution containing barium ion and also 0.1 mole per liter of acetate ion and 0.1 mole per liter of un-ionized acetic acid was added enough K_2CrO_4 to give a precipitate of barium chromate and make the concentration of the ion $HCrO_4^-$ in the solution 0.01 mole per liter. Calculate the concentration of barium ion remaining in the solution. See Exercise 12. *Ans.* 0.9×10^{-6} *M.*

14. Lead chromate can be precipitated in the presence of nitric acid, while barium chromate cannot. Is the solubility product of lead chromate larger or smaller than that of barium chromate. Explain.

Chapter XIV

OXIDATION AND REDUCTION

REACTIONS in which oxidation and reduction occur are sometimes more complicated than reactions involving only the combination of ions or the transfer of protons from one group of atoms to another. It is desirable to understand something of the mechanism of oxidation-reduction reactions and to be able to write equations for them. These two objectives are related, because an understanding of the mechanism leads to a method of writing the equations, and practice in writing the equations brings about a more thorough understanding of the reactions.

117. Simple Oxidation-Reduction Reactions. It will be recalled that ferric ion reacts with hydrogen sulfide with the precipitation of sulfur and the reduction of the ferric ion to ferrous ion. This reaction occurs in the precipitation of the hydrogen sulfide group (or in connection with the test for this group if it is absent) whenever ferric ion is present in the solution.

Ferric ion, Fe^{+++}, may be considered to have been formed from an iron atom by the removal of three valence electrons, and ferrous ion, Fe^{++}, by the removal of two electrons. To convert a ferric ion into a ferrous ion, one of the missing electrons must be replaced. If *e* is used as the symbol for an electron, an equation can be written for the conversion of ferric ion to ferrous ion.

$$Fe^{+++} + e \longrightarrow Fe^{++} \qquad (1)$$

The ferric ion is said to be *reduced* to ferrous ion.

The precipitate of sulfur when sulfide ion reacts with ferric ion is the result of the removal of electrons from the sulfide ion.

$$S^{=} - 2\,e \longrightarrow \underline{S} \qquad (2)$$

The sulfide ion is said to be *oxidized* to sulfur. The electrons that are removed from the sulfide ions are taken up by ferric ions. An equation for the complete reaction may be obtained by the addition of Equations 1 and 2, which may be called partial equations. Two partial equations may be added much as two algebraic equations are added, with cancellation of the electrons. On addition of two partial equations, the electrons must be made to cancel exactly. Therefore, Equation 1 must be multiplied through by two.

$$2\,Fe^{+++} + 2\,e \longrightarrow 2\,Fe^{++} \tag{1}$$

$$S^{=} - 2\,e \longrightarrow \underline{S} \tag{2}$$

$$2\,Fe^{+++} + S^{=} \longrightarrow 2\,Fe^{++} + \underline{S} \tag{3}$$

Equation 3 is an ionic equation for the oxidation of sulfide ion to sulfur by ferric ion. Equation 3 could be made into a molecular equation by the addition of six chloride ions and two hydronium ions to each side of the equation.

Equation 1 is easily reversible, and ferrous ion can be oxidized to ferric ion by any substance that is able to remove electrons from ferrous ions. In the ammonium sulfide group, bromine is used for this purpose. Bromine, Br_2, adds electrons to form bromide ions, Br^-.

$$Br_2 + 2\,e \longrightarrow 2\,Br^- \tag{4}$$

$$2\,Fe^{++} - 2\,e \longrightarrow 2\,Fe^{+++} \tag{5}$$

$$2\,Fe^{++} + Br_2 \longrightarrow 2\,Fe^{+++} + 2\,Br^- \tag{6}$$

Most of the metals are easily oxidized to cations and this change consists merely in the removal of electrons from the metal.

$$Fe - 2\,e \longrightarrow Fe^{++} \tag{7}$$

A substance from which electrons can be removed is called a *reducing agent*, because such a substance can reduce certain other substances. The removal of electrons from most of the metals is relatively easy and the metals are good reducing agents. Bismuth, for example, can reduce chlorine to chloride ion.

$$2\,Bi - 6\,e \longrightarrow 2\,Bi^{+++} \tag{8}$$

$$3\,Cl_2 + 6\,e \longrightarrow 6\,Cl^- \tag{9}$$

$$2\,Bi + 3\,Cl_2 \longrightarrow 2\,Bi^{+++} + 6\,Cl^- \tag{10}$$

118. The Electromotive Series. The oxidation of a metal to a cation is a reversible reaction; cations can add electrons and become reduced to the metallic state. Cations are therefore *oxidizing agents.* Most of them are poor oxidizing agents, and not many reducing agents are strong enough to reduce them. Certain of the metals, however, are capable of reducing certain of the cations to the metallic state. Zinc, for example, reduces copper ion to copper.

$$Cu^{++} + 2\,e \longrightarrow \underline{Cu} \tag{11}$$

$$\underline{Zn} \quad - 2\,e \longrightarrow Zn^{++} \tag{12}$$

$$Cu^{++} + \underline{Zn} \longrightarrow Zn^{++} + \underline{Cu} \tag{13}$$

This reaction is the basis of the Daniell cell, illustrated in Fig. 11, by which a current of electricity can be generated. Zinc, copper and solutions of their sulfates are arranged so that when the reaction takes place the electrons in passing from the zinc to the copper ion must pass through an external metallic circuit.

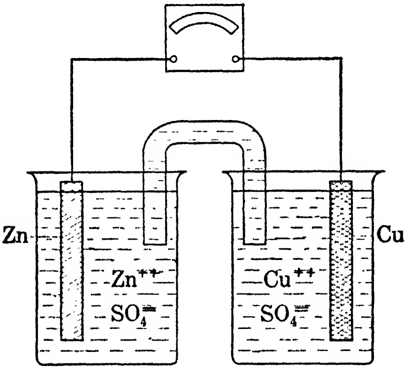


FIG. 11. Daniell cell.

The electromotive series tells which of the metals can reduce a given cation. The electromotive series is a list of the metals in order of their respective abilities as reducing agents. In the list that follows, the best reducing agent is at the top and the others follow in the order of decreasing reducing ability.

The cation of any metal can be reduced to the metallic state by any of the metals higher in the electromotive series. Thus, zinc is higher in the electromotive series than copper, and zinc reduces copper ion. To reduce antimony ion, any of the metals above antimony might be chosen. In general, the higher in the series the metal stands, the more vigorously it reacts with a given cation. In the test for antimony ion, in the tin group, iron is used to reduce the antimony ion. At the same time the iron reduces stannic tin to stannous ion, Sn^{++}, but does not reduce the stannous ion to metallic tin. The reason for this is that hydronium ion is present. When a metal is added to a solution containing two or more cations of metals lower in the series, the cation of the metal lowest in the series is reduced first. When the lowest is practically completely reduced, the cation of the next higher metal in the electromotive series starts to be reduced. In the antimony test, the cation of the next higher "metal" is the hydronium ion (H_3O^+) which is reduced to hydrogen (and water) by iron.

Electromotive Series

Potassium
Barium
Calcium
Sodium
Magnesium
Aluminum
Manganese
Zinc
Iron
Cadmium
Nickel
Tin
Lead
Hydrogen
Bismuth
Antimony
Copper
Mercury
Silver
Platinum
Gold

$$2\,H_3O^+ + 2\,e \longrightarrow 2\,H_2O + H_2 \quad (14)$$

If the reaction were continued until only a very small hydrogen-ion concentration was left, the stannous ion would be reduced next. When the test is carried out correctly, the reaction is interrupted before this takes place.

It will be apparent from the above discussion that it is easier to reduce stannic tin to stannous ion than to reduce stannous ion to metallic tin. Likewise it is easier to reduce ferric ion to ferrous ion than to reduce ferrous ion to metallic iron. Cupric ion, Cu^{++}, is exceptional in that under ordinary conditions it is as easily reduced to metallic copper as to cuprous ion, Cu^+. When metallic tin or iron is oxidized, the ion of lower valence is formed first and only in the presence of an excess of the oxidizing agent is the ion of higher valence formed. When copper is oxidized, on the other hand, the cupric ion is usually formed. Most of the other metals that have more than one valence react like iron and tin rather than like copper.

Hydrogen is included in the electromotive series, because it is a reducing agent like the metals, and hydronium ion is a very weak oxidizing agent like other cations. Hydrogen does not act on the cations below it as a true metal would, but the reason for this is not that such a reaction is impossible, but that a catalyst is necessary. Hydronium ion reacts with the metals above hydrogen in the electromotive series about as would be expected from the position of hydrogen.

119. Oxygen Acids as Oxidizing Agents. The anions of some of the oxygen acids can act as fairly strong oxidizing agents in acid solutions, and a few are oxidizing agents in neutral or alkaline solutions. Nitric acid, which is frequently used as an oxidizing agent, may be taken as an example.

To write a partial equation, it is necessary to know the products of the partial reaction. The manner of decomposition of an anion on reduction is an experimental fact and cannot be deduced from the formula. It is therefore necessary to know the facts before proceeding.

The manner in which nitrate ion acts when reduced in an acid solution depends on the concentrations. In concentrated nitric acid solution, nitrogen dioxide and water are the chief products. It may be considered that one of the oxygen atoms of the ion NO_3^- unites with two protons to form water, leaving NO_2. The first step in writing the partial equation is to set down these facts in equation form.

$$NO_3^- + 2\,H^+ \longrightarrow NO_2 + H_2O$$

This is not a completely balanced partial equation, because it is not balanced electrically. The algebraic sum of the charges on the left-hand side is $-1 + 2 = +1$ and since there are no charges on the right-hand side, one electron must be added to the left-hand side.

$$NO_3^- + 2\,H^+ + e \longrightarrow NO_2 + H_2O \qquad (15)$$

In Equation 15 the algebraic sum of the charges on the left-hand side is zero, since the electron is to be counted as a unit negative charge.

To write an equation for the action of concentrated nitric acid on copper, Equation 15 may be combined with the reverse of Equation 11 to give the ionic equation.

$$\underline{Cu} + 2\,NO_3^- + 4\,H^+ \longrightarrow Cu^{++} + 2\,NO_2 + 2\,H_2O \qquad (16)$$

Dilute nitric acid on reduction decomposes to give chiefly nitric oxide, NO, and water.

$$NO_3^- + 4\,H^+ + 3\,e \longrightarrow NO + 2\,H_2O \qquad (17)$$

In equations like this the symbol H^+ denoting a proton may be replaced by H_3O^+, indicating the source of the protons. This is an added complication, however, and since many oxidation-reduction equations are rather complicated at best, it is well to retain the simpler symbol H^+.

In the analysis of the copper group, dilute nitric acid is employed to dissolve the sulfides. It acts by oxidizing the sulfides with the formation of the various cations and sulfur. Copper sulfide, for example, is oxidized to cupric ion and sulfur.

$$\underline{CuS} \longrightarrow Cu^{++} + \underline{S} + 2\,e \qquad (18)$$

Multiplication of Equation 17 by two and Equation 18 by three allows these two equations to be added with exact cancellation of the electrons to give Equation 32 of Chapter IX.

Dichromate ion, $Cr_2O_7^{=}$, is reduced in acid solution by hydrogen sulfide to chromic ion, Cr^{+++}. This occurs in the precipitation of the hydrogen sulfide group if dichromate ion is present. To write a partial equation for this reaction it is necessary to add 14 protons to unite with the seven oxygen atoms in the dichromate ion.

$$Cr_2O_7^{=} + 14\,H^+ \longrightarrow 2\,Cr^{+++} + 7\,H_2O$$

To balance this equation electrically, six electrons must be added on the left-hand side. This may be determined by the algebraic addition of the charges on the left-hand side and subtraction of those on the right-hand side; $-2 + 14 - 6 = +6$. The addition of 6 electrons to the left-hand side makes the algebraic sum of the charges on each side equal to $+6$, and the equation is then balanced.

$$Cr_2O_7^{=} + 14\,H^+ + 6\,e \longrightarrow Cr^{+++} + 7\,H_2O \qquad (19)$$

Combination of this partial equation with Equation 2 gives the equation for the reduction of dichromate ion by hydrogen sulfide.

The final test for manganese ion is an example of the formation of an anion of an oxygen acid. Manganous ion, Mn^{++}, is oxidized to permanganate ion, MnO_4^-, by means of bismuthate ion, BiO_3^-. The bismuthate ion is reduced to bismuth ion, Bi^{+++}. The oxygen atoms needed for the formation of the permanganate ion might be considered to be obtained either from bismuthate ions or from water molecules. In the absence of information as to the facts in the case, we may assume either source, and for purposes of balancing the equation the final result will be the same in either case. It will be more convenient to consider that the water molecules are the source. The partial equation for the oxidation of the manganous ion may then be set down as follows.

$$Mn^{++} + 4\,H_2O \longrightarrow MnO_4^- + 8\,H^+ + 5\,e \qquad (20)$$

When the water molecules are broken up to furnish oxygen for the permanganate ions, they must be considered decomposed into oxide ions, $[:\ddot{\underset{\cdot\cdot}{O}}:]^=$, and protons, H^+. Comparison of the charges on the two sides of the equation shows that five electrons must be added to the right-hand side.

Bismuthate ion reacts with protons and electrons to give bismuth ions and water.

$$BiO_3^- + 6\,H^+ + 2\,e \longrightarrow Bi^{+++} + 3\,H_2O \qquad (21)$$

Two electrons on the left-hand side are required to balance the equation.

In order to add Equations 20 and 21, they must be multiplied by two and five respectively. Addition then gives

$$2\,Mn^{++} + 5\,BiO_3^- + 30\,H^+ + 8\,H_2O \longrightarrow$$
$$2\,MnO_4^- + 5\,Bi^{+++} + 16\,H^+ + 15\,H_2O \qquad (22)$$

This equation can be simplified, because both water and protons appear on both sides. The 16 protons on the right may be subtracted from the 30 on the left, leaving 14 on the left and none on the right. The water molecules on the two sides may be treated similarly.

Sometimes oxidation-reduction reactions take place in alkaline solutions. Writing equations for such reactions is little different from writing them for reactions in acid solution, if it is remembered that hydronium ions are practically absent and that water may be taken as the source of any protons needed. Care should be taken also to see that equations do not indicate the presence of both protons (or hydronium ions) and hydroxide ions in the same solution.

As an example of a reaction occurring in alkaline solution, the oxidation of chromium hydroxide to chromate ion may be taken. This reaction takes place in the analysis of the ammonium sulfide group. Water may be taken as the source of oxygen atoms.

$$\underline{Cr(OH)_3} + H_2O \longrightarrow CrO_4^{=} + 5\,H^+ + 3\,e \qquad (23)$$

Since the solution is alkaline, protons if formed in accordance with Equation 23 would unite with hydroxide ions to form water.

$$5\,H^+ + 5\,OH^- \longrightarrow 5\,H_2O$$

Addition of this equation to Equation 23 gives a better partial equation.

$$\underline{Cr(OH)_3} + 5\,OH^- \longrightarrow CrO_4^{=} + 4\,H_2O + 3\,e \qquad (23a)$$

The oxidizing agent is sodium peroxide, Na_2O_2, of which the peroxide ion, $O_2^{=}$, may be considered to be the active part.

$$O_2^{=} + 2\,H_2O + 2\,e \longrightarrow 4\,OH^- \qquad (24)$$

Combination of 23 *a* and 24 gives

$$2\,\underline{Cr(OH)_3} + 3\,O_2^{=} \longrightarrow 2\,CrO_4^{=} + 2\,OH^- + 2\,H_2O \quad (25)$$

EXERCISES

1. Add Equations 17 and 18 and also Equations 2 and 19.

2. Write partial ionic equations for the reduction of bromine and the oxidation of zinc, and add them to obtain the ionic equation for the action of bromine on zinc to give zinc bromide.

3. Simplify Equation 22 and show that it balances.

4. Write an ionic equation for the oxidation of ferrous ion by dilute nitric acid.

5. Convert Equations 3 and 16 into molecular equations.

6. Write an equation for the preparation of sulfur dioxide by the reaction of sulfuric acid and copper.

7. Write electronic formulas for all of the substances in Equation 20.

8. Write ionic equations for each of the following oxidation-reduction reactions. Although some of the equations can be written by inspection it is suggested that all be worked out by means of partial equations.

$BiCl_3 + Zn \longrightarrow$
$SbCl_3 + Fe \longrightarrow$
$Bi_2S_3 + HNO_3 \longrightarrow$
$Bi(OH)_3 + Na_2SnO_2 \longrightarrow$
$SnCl_4 + Fe \longrightarrow$
$MnO_4^- + H_2S + HCl \longrightarrow$
$MnCO_3 + Na_2O_2 \longrightarrow$
$HNO_3 + H_2S \longrightarrow$

9. What is an oxidizing agent? What is a reducing agent? Illustrate both.

APPENDIX

Appendix

I. APPARATUS AND MATERIALS

1. APPARATUS AND MATERIALS NEEDED FOR GENERAL LABORATORY USE, OR FOR OCCASIONAL USE ONLY

Distilled water.

Ring stands.

Tripods, six inches high (*for semi-micro work*).

A balance or scale that will weigh from 0.1 to 50 g., preferably without the use of brass weights.

A balance (*for semi-micro work*) that will weigh quantities as small as 0.01 g.

Paper for weighing powders. A roll of paper 4 inches wide is convenient.

Waste jars.

Centrifuges (*for semi-micro work*). Hand centrifuges available from apparatus dealers can be used. Some of these, however, are not sufficiently rugged for the use of undergraduates. A home-made type of air-driven centrifuge built for semi-micro work and described by Vosburgh and Saylor in the *Journal of Chemical Education*, Vol. 14, No. 3, page 142 (March, 1937), has been in successful use in the laboratory at Duke University for over four years.

A low-priced electrically driven centrifuge designed for semi-micro work is manufactured by Phipps and Bird, Inc., Richmond, Virginia.

Crucibles, nickel or iron, for carbonate fusions. Nickel crucibles are more satisfactory, as less metal disintegrates during fusion than with iron. Iron crucibles are cheaper, but withstand fewer fusions. "Domes of Silence," hemispherical vessels of sheet-iron which may be purchased at furniture stores can be used for fusions.

Nickel crucibles of 1 or 2 ml. capacity (*for semi-micro work*) can be made from sheet nickel.

Meker burners, or blast lamps, for carbonate fusions. Blast lamps if improperly regulated may destroy iron or nickel crucibles.

Clay crucibles, bottomless, surrounding flame and crucible are helpful in lessening the time required for fusions. (These are unnecessary in semi-micro work.) Secure clay assay crucibles, about three inches in diameter at the larger end and about five inches in height. To make them bottomless requires two persons. One holds the crucible in an upright position. The other places the cutting edge of a cold-chisel against the inside bottom of the crucible and strikes the cold-chisel a vigorous blow with a hammer.

Hydrogen sulfide gas. The most nearly satisfactory source is the compressed gas in cylinders. The gas may be transferred from the cylinder to a floating gas holder, and from the holder conducted to suitable outlets in the laboratory. The gas may also be conducted from the cylinder to the pipe leading to the laboratory outlets through a reducing valve. A reducing valve made for hydrogen sulfide should be used.

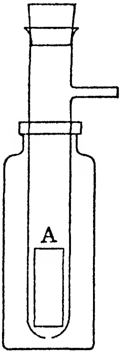


FIG. 12. Diagram of a simple hydrogen sulfide generator that is satisfactory for semi-micro work. Glass wool is placed in the bottom of the bottle and a slice of a two-hole rubber stopper at A. Ferrous sulfide rests above the rubber disc at A. The bottle is nearly filled with 6 *M* hydrochloric acid solution.

For semi-micro work a small generator is more satisfactory. The smaller the generator the less the gas that escapes into the laboratory, as a rule. Figure 12 represents a generator made from a 250-ml. wide-mouthed bottle, a 25 × 200 mm. test tube, a small piece of glass tubing of 18 to 20 mm. outside diameter, a rubber stopper and some glass wool. A side-arm may be sealed to the test tube as an exit tube, or a one-hole rubber stopper may be used. The former is preferable. A rubber tube attached to the exit tube, with a glass bead in it for a valve, completes the apparatus.

2. APPARATUS NEEDED FOR EACH STUDENT DESK

(*a*) Ordinary-scale Qualitative Analysis

Glassware

3 Beakers, each 250 ml.
12 Reagent bottles
4 Erlenmeyer flasks, each 250 ml.

2 Funnels, each about 6.5 cm. in diameter
1 Graduated cylinder, 10 ml.
1 Graduated cylinder, 50 ml.
1 Florence flask, 500 or 1000 ml.
1 Filter flask, side-arm, 250 ml.
12 Test tubes, 18 × 150 mm.
1 Test tube, 10 × 75 mm., or 1 centrifuge tube, 3 ml.
1 Watch glass, 100 mm. diameter

Porcelain Ware

1 Casserole, 75 ml.
1 Funnel, Hirsch No. 00
1 Mortar, 70 mm., and pestle

Other Apparatus

1 Burner and connection
1 Fishtail burner tip
1 Suction pump (unless vacuum is available otherwise)
1 Triangle, nichrome or clay
1 Iron ring, 3 in. outside diameter
1 Test-tube stand
1 Test-tube holder, wire
1 Funnel support. (If the funnels can be supported in 250-ml. Erlenmeyer flasks, the funnel support is not necessary.)
1 Iron tongs
1 Triangular file
1 Package filter paper, 10 cm. diameter
1 Package filter paper, 5 cm. diameter, to fit Hirsch funnel No. 00. Hardened filter paper to fit the Hirsch funnel should be available also.
5 ft. glass tubing, 6 mm. outside diameter
6 inches pure gum tubing, $\frac{3}{16}$ inch inside diameter
1 Sponge
Red and blue litmus paper in glass containers
1 Test-tube brush
1 Towel
1 Wire gauze
1 Piece of rubber tubing, $\frac{3}{16}$ inch inside diameter, 30 inches long, to connect filter flask with suction
1 Rubber stopper, 1 hole, to fit a 250-ml. Erlenmeyer flask
1 Rubber stopper, 2 hole, to fit a 250-ml. Erlenmeyer flask
1 Rubber stopper, 2 hole, to fit Florence flask

(*b*) Semi-Micro Qualitative Analysis

Articles That May Be Returned to the Stockroom[1]

1	Beaker, 100 ml.
1	Beaker cover, aluminum, for supporting centrifuge tubes inside a beaker.* (Fig. 13, page 211)
9	Bottles, cork stopper, 30 ml.
3	Bottles, cork stopper, 60 ml.
1	Burner, micro
12	Centrifuge tubes, 3 ml., Pyrex
1	Clamp holder
1	Flask, Erlenmeyer, 50 ml.
1	Flask, Erlenmeyer, 250 ml.
1	Funnel, glass, Büchner, small* (Fig. 5, page 18)
12	Medicine droppers (without bulb). At least three of these should be long enough to reach to the bottom of a 60-ml. bottle when mounted in the stopper of the bottle.
1	Graduated cylinder, 25 ml.
1	Test-tube rack, small
6	Test tubes, 10 × 75 mm.
2	Test tubes, 18 × 150 mm., Pyrex
1	Test tube, side-arm, 12 × 100 mm.
1	Wing top for burner
1	Pipette, Mohr, 1 ml. in tenths
1	Tube-holder, Iron.* (Fig. 14, page 212)

Articles Not Returnable to the Stockroom

1	Brush, test-tube, to fit centrifuge tubes and 10 × 75 mm. test tubes
15	Corks, No. 1
3	Corks, No. 2
2	Corks, No. 3
15	Medicine-dropper bulbs
1	File, triangular
1 ft.	glass rod, 3 mm.
5 ft.	glass tubing, 5 mm. outside diameter
2.5 ft.	glass tubing, 7 mm. outside diameter
1	Box of labels
1	Vial red litmus paper
1	Vial blue litmus paper

---

[1] The articles marked with an asterisk are described in more detail below.

1 Vial methyl orange paper
2 Sheets of parchment powder paper, for weighing
1 Rubber stopper, 1-hole, No. 1
1 Rubber stopper, 2-hole, No. 1
1 Rubber stopper, 2-hole, No. 5
2 ft. rubber tubing
9 Pieces of rubber tubing about 1 cm. long for use as one-hole rubber stoppers in 30-ml. bottles
1 Sponge
1 Crucible, porcelain
1 Wire gauze

II. SPECIAL APPARATUS FOR SEMI-MICRO QUALITATIVE ANALYSIS

Some of the articles listed above for use in semi-micro qualitative analysis need further description.

The aluminum beaker cover shown in Fig. 13 is made from a piece of thin aluminum sheet 6.5 cm. square by drilling three 0.5 inch holes as shown and turning down the four corners. A 0.5 inch hole allows a centrifuge tube made from 11 mm. (outside diameter) glass tubing to pass through all except the rim. If centrifuge tubes of any other size are used, the holes in the aluminum covers should be adjusted accordingly. The beaker cover is used in heating centrifuge tubes by immersion in hot water. The tubes are hung by their rims from the cover and project down into hot water in the beaker.

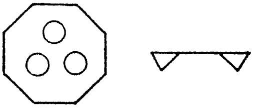


FIG. 13. Aluminum beaker cover for holding centrifuge tubes in hot water.

The small glass Büchner funnel (together with a side-arm test tube) is shown in Fig. 5, page 18. It is made somewhat the shape of a thistle tube, but with a constriction at the point where the stem joins the upper portion. The bottom of the upper portion should be nearly flat. The diameter of the upper portion is 15 mm., and the stem is made from 4 mm. (outside diameter) tubing. The funnel is used in connection with a 12 × 100 mm. side-arm test tube for suction filtration. The hole leading down into the stem of the funnel is covered with a small disc of filter paper, and the side-arm of the test tube connected to a moderate suction.

A test-tube rack to hold 10 × 75 mm. test tubes and centrifuge tubes of about the same size can be made by boring 0.5 inch holes part way through a piece of 2 × 4 inch lumber.

A holder that will hold one or more centrifuge tubes and an 18 × 150 mm. test tube and which can be clamped to a ring stand is a convenience. Such a holder is shown in Fig. 14. It is made of a piece of 0.5 inch iron rod 7 inches long fastened to a piece of sheet iron 1.75 × 3.5 inches. In the sheet iron are drilled a 0.75 inch hole and two 0.5 inch holes. In these holes an 18 × 150 mm. test tube and a centrifuge tube made from 11 mm. tubing will hang by their rims.

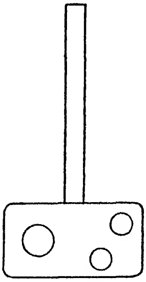


FIG. 14. Iron holder that can be clamped to a ring stand, for holding one 18 × 150 mm. test tube and two centrifuge tubes.

III. REAGENTS AND SOLUTIONS

1. REAGENTS FOR STUDENT DESK SETS[1]

Solutions

Acetic acid, CH_3COOH, 6 *M*. Dilute 370 ml. of 99% acetic acid to one liter.

Ammonium hydroxide, NH_4OH, 6 *M*. Dilute 400 ml. of concentrated ammonium hydroxide (14 *M*) to one liter. (Some of this is needed in the preparation of ammonium carbonate and other solutions.) *For semi-micro work, 3 M; 200 ml. of 14 M NH_4OH diluted to one liter.*

Ammonium acetate, CH_3COONH_4, 3 *M*; 231 g. per liter.

Ammonium carbonate, $(NH_4)_2CO_3$, 3 *M*. Dissolve 250 g. of ammonium carbonate in 600 ml. of 3 *M* NH_4OH and dilute to one liter.

Hydrochloric acid, HCl, 6 *M*. Dilute 500 ml. of 12 *M* HCl (concentrated acid) to one liter. *For semi-micro work, 3 M; 250 ml. of 12 M HCl diluted to one liter.*

Hydrochloric acid, HCl, 12 *M* (concentrated).

Nitric acid, HNO_3, 6 *M*. Dilute 380 ml. of 16 *M* HNO_3 (concentrated acid) to one liter.

Potassium chromate, K_2CrO_4, 1 *M*; 194 g. per liter.

Silver nitrate, $AgNO_3$, 0.2 *M*; 34 g. per liter.

---

[1] These are the most frequently used reagents.

Sodium hydroxide, NaOH, 6 *M*. Dissolve 250 g. in 500 ml. of water in a covered porcelain dish, cool and dilute to one liter. *For semi-micro work 3 M. Dissolve 125 g. of NaOH in 200 ml. of water and dilute to 1 liter.*

Sodium polysulfide, Na_2S_x, 2.5 *M* with respect to Na_2S and Na_2S_2 and 1 *M* with respect to NaOH. *First Method.* Dissolve 600 g. of $Na_2S \cdot 9\,H_2O$ and 40 g. of NaOH in water, dilute to one liter and dissolve in the resulting solution 10 g. of flowers of sulfur. *Second Method.* Prepare a solution of 100 g. of NaOH in 500 ml. of water and saturate it with hydrogen sulfide. Add to this solution another sodium hydroxide solution containing 140 g. of NaOH in 500 ml. of water and dissolve in the resulting solution 10 g. of flowers of sulfur.

Sulfuric acid, H_2SO_4, 3 *M*. *Carefully* add 167 ml. of 18 *M* H_2SO_4 (concentrated acid) to 800 ml. of water and dilute to one liter.

Solids[1]

Ammonium chloride, NH_4Cl, 50 g. (*5 g.*)
Aluminum turnings, 20 g. (*1 g.*)
Asbestos, for filtering. (*None for semi-micro work.*)
Iron nails, 5. (*For semi-micro work, very small nails.*)
Potassium chlorate, $KClO_3$, 20 g. (*2 g.*)
Potassium carbonate, K_2CO_3 (anhydrous), 10 g. (*2 g.*)
Sodium bismuthate, $NaBiO_3$, 5 g. (*1 g.*)
Sodium carbonate, Na_2CO_3 (anhydrous), 10 g. (*2 g.*)
Sodium cobaltinitrite, $Na_3Co(NO_2)_6$, 10 g. (*1 g.*)
Sodium peroxide, Na_2O_2, 20 g. (*3 g.*)
Tin foil, Sn, 5 g. (*1 g.*)
Zinc, Zn, granulated, 2 g. (*2 g.*)

2. SIDE-SHELF REAGENTS

Liquids and Solutions

1. **Alcohol,** denatured.
2. **Aluminon, 0.1% solution.** To a mixture of 1 g. of aurin tricarboxylic acid and 1 liter of water add small quantities of 6 *M* NH_4OH with stirring until the acid is dissolved.
3. **Aluminum nitrate, $Al(NO_3)_3$, 1 *M*;** 375 g. of $Al(NO_3)_3 \cdot 9\,H_2O$ per liter.

---

[1] The quantities in parentheses are the quantities required for semi-micro work.

4. **Ammonium hydroxide, NH_4OH, 15 *M*;** (concentrated).
5. **Ammonium mercuric thiocyanate, $(NH_4)_2Hg(SCN)_4$, 0.5 *M*.** Dissolve 170 g. of NH_4SCN in one liter of water, add 135 g. of $HgCl_2$ and stir to dissolve.
6. **Ammonium molybdate, $(NH_4)_2MoO_4$, 0.5 *M*.** Dissolve 90 g. of ammonium molybdate in 100 ml. of 6 *M* NH_4OH (or 200 ml. of 3 *M* NH_4OH) add 240 g. of NH_4NO_3 and dilute to one liter.
7. **Ammonium thiocyanate, NH_4SCN, 0.2 *M*;** 15 g. per liter.
8. **Antimony chloride, $SbCl_3$, 0.2 *M*.** Dissolve 46 g. in 250 ml. of 6 *M* HCl (or 500 ml. of 3 *M* HCl) and dilute to one liter.
9. **Arsenic chloride, $AsCl_3$, 0.2 *M*.** Dissolve 24 g. of As_2O_3 in 200 ml. of 12 *M* HCl and dilute to one liter.
10. **Barium chloride, $BaCl_2$, 0.2 *M*;** 49 g. of $BaCl_2 \cdot 2\,H_2O$ per liter.
11. **Barium hydroxide, $Ba(OH)_2$, 0.2 *M*;** 65 g. of $Ba(OH)_2 \cdot 8\,H_2O$ per liter. Filter.
12. **Bismuth nitrate, $Bi(NO_3)_3$, 0.1 *M*.** Dissolve 49 g. of $Bi(NO_3)_3 \cdot 5\,H_2O$ or 31 g. of $BiONO_3 \cdot H_2O$ in 250 ml. of 6 *M* HNO_3 and dilute to 1 liter.
13. **Bromine water, saturated;** add enough liquid bromine to water so that after thorough mixing a little remains undissolved.
14. **Cadmium nitrate, $Cd(NO_3)_2$; 0.2 *M*;** 62 g. of $Cd(NO_3)_2 \cdot 4\,H_2O$ per liter.
15. **Calcium nitrate, $Ca(NO_3)_2$, 0.5 *M*;** 118 g. of $Ca(NO_3)_2 \cdot 4\,H_2O$ per liter.
16. **Carbon tetrachloride.**
17. **Chromium nitrate, $Cr(NO_3)_3$, 0.5 *M*;** 200 g. of $Cr(NO_3)_3 \cdot 9\,H_2O$ per liter.
18. **Cobalt chloride, $CoCl_2$, 0.5 *M*;** 119 g. of $CoCl_2 \cdot 6\,H_2O$ per liter.
19. **Copper nitrate, $Cu(NO_3)_2$, 0.5 *M*;** 120 g. of $Cu(NO_3)_2 \cdot 3\,H_2O$ per liter.
20. **Copper sulfate, $CuSO_4$, 0.01 *M*;** 2.5 g. of $CuSO_4 \cdot 5\,H_2O$ per liter.
21. **Dimethyl glyoxime, 10 g. per liter,** in 95 per cent alcohol.
22. **Ferric chloride, $FeCl_3$, 0.5 *M*.** Dissolve 135 g. of $FeCl_3 \cdot 6\,H_2O$ in a mixture of 25 ml. of 6 *M* HCl (or 50 ml. of 3 *M* HCl) and 500 to 800 ml. of water and dilute to one liter.
23. **Ferric nitrate, $Fe(NO_3)_3$, 0.2 *M*.** Dissolve 81 g. of $Fe(NO_3)_3 \cdot 9\,H_2O$ in a mixture of 25 ml. of 6 *M* HNO_3 and 500 to 800 ml. of water and dilute to one liter.

24. **Ferrous sulfate, $FeSO_4$, 0.5 *M*.** Dissolve 138 g. of $FeSO_4 \cdot 7\,H_2O$ in a mixture of 50 ml. of 3 *M* H_2SO_4 and 500 to 800 ml. of water and dilute to one liter.
25. **Lead nitrate, $Pb(NO_3)_2$, 0.1 *M*;** 33 g. per liter.
26. **Magnesium nitrate, $Mg(NO_3)_2$, 1 *M*;** 256 g. of $Mg(NO_3)_2 \cdot 6\,H_2O$ per liter.
27. **Magnesia mixture.** Dissolve 130 g. of $Mg(NO_3)_2 \cdot 6\,H_2O$ and 240 g. of NH_4NO_3 in water, add 35 ml. of 6 *M* NH_4OH and dilute to one liter.
28. **Manganese chloride, $MnCl_2$, 0.5 *M*;** 99 g. of $MnCl_2 \cdot 4\,H_2O$ per liter.
29. **Mercuric chloride, $HgCl_2$; 0.1 *M*;** 27 g. per liter.
30. **Mercurous nitrate, $Hg_2(NO_3)_2$, 0.05 *M*.** Dissolve 30 g. of $Hg_2(NO_3)_2 \cdot 4\,H_2O$ in 150 ml. of 6 *M* HNO_3 and dilute to one liter.
31. **Methyl orange;** 0.5 g. per liter.
32. **Nessler's reagent.** Dissolve 22.5 g. of iodine in a solution of 30 g. of potassium iodide in enough water to make 20 ml. Add 30 g. of mercury, and shake the mixture well, keeping it from becoming hot by cooling with tap water. Continue until the liquid has lost all the yellow color of iodine. Decant the solution and test by adding a few drops of it to 1 ml. of a 1 per cent starch solution. If the starch test for iodine is not obtained, the solution may contain mercurous compounds. In this case add an iodine solution, of the same concentration as employed above, drop by drop until a faint excess of free iodine can be detected by adding a few drops of the solution to 1 ml. of the starch solution. When a slight excess of iodine has been assured, dilute to 200 ml. and mix well.
33. **Nickel nitrate, $Ni(NO_3)_2$, 0.5 *M*;** 145 g. of $Ni(NO_3)_2 \cdot 6\,H_2O$ per liter.
34. **Nitric acid, HNO_3, 16 *M*;** concentrated nitric acid; keep in a glass-stoppered bottle.
35. **Nitroso-R-salt;** 5 g. per liter.
36. **Perchloric acid, $HClO_4$, 6 *M*.** Dilute 667 ml. of 60% acid to one liter.
37. **Potassium bromide, KBr, 0.5 *M*;** 60 g. per liter.
38. **Potassium chloride, KCl, 1 *M*;** 75 g. per liter.
39. **Potassium ferricyanide, $K_3Fe(CN)_6$, 0.1 *M*;** 33 g. per liter.
40. **Potassium ferrocyanide, $K_4Fe(CN)_6$, 0.1 *M*;** 42 g. of $K_4Fe(CN)_6 \cdot 3\,H_2O$ per liter.
41. **Potassium fluoride, KF, 1 *M*;** 58 g. per liter.
42. **Potassium iodide, KI, 0.2 *M*;** 33 g. per liter.

43. **Potassium nitrate, KNO_3, 1 *M*;** 100 g. per liter.
44. **Potassium oxalate, $K_2C_2O_4$, 1 *M*;** 184 g. of $K_2C_2O_4 \cdot H_2O$ per liter.
45. **Potassium permanganate, $KMnO_4$, 0.02 *M*;** 3.2 g. per liter.
46. **Salicyl-aldoxime, sodium salt (copper reagent), 0.2 *M*.** Dissolve 9 g. of sodium hydroxide in 100 ml. of water and add 12.3 g. of salicylaldehyde and 7.0 g. of hydroxylamine hydrochloride, stirring until dissolved. Allow to stand over night, then add 5 ml. of 6 *M* acetic acid and dilute to 500 ml.
47. **Sodium arsenate, Na_2HAsO_4, about 0.2 *M*;** 60 g. of $Na_2HAsO_4 \cdot 7\,H_2O$ per liter.
48. **Sodium arsenite, $NaAsO_2$, about 0.2 *M*;** 26 g. per liter.
49. **Sodium carbonate, Na_2CO_3, 1.5 *M*;** 160 g. of the anhydrous salt, or 186 g. of $Na_2CO_3 \cdot H_2O$, per liter.
50. **Sodium chloride, NaCl, 1 *M*;** 58 g. per liter.
51. **Sodium nitrite, $NaNO_2$, 0.2 *M*;** 69 g. per liter.
52. **Sodium phosphate, Na_2HPO_4, 0.3 *M*;** 107 g. of $Na_2HPO_4 \cdot 12\,H_2O$ per liter.
53. **Sodium sulfate, Na_2SO_4, 0.2 *M*;** 64 g. of $Na_2SO_4 \cdot 10\,H_2O$ per liter, or 28 g. of Na_2SO_4, per liter.
54. **Stannic chloride, $SnCl_4$, 0.2 *M*.** Dissolve 70 g. of $SnCl_4 \cdot 5\,H_2O$ or 52 g. (or 23.3 ml.) of $SnCl_4$ in 250 ml. of 6 *M* HCl and dilute to one liter.
55. **Stannous chloride, $SnCl_2$, 0.5 *M*.** Dissolve 56 g. of $SnCl_2 \cdot 2\,H_2O$ in 50 ml. of 6 *M* HCl and dilute to 500 ml.
56. **Starch.** Mix 3 g. of soluble starch with enough water to make a paste that will pour, and pour it into 500 ml. of boiling water, boil for a minute or two, add 5 g. of $ZnCl_2$ and dilute to about 600 ml.
57. **Strontium chloride, $SrCl_2$, 0.2 *M*;** 53 g. of $SrCl_2 \cdot 6\,H_2O$ per liter.
58. **Thio-urea, 1 *M*;** 38 g. of thio-urea (also called thiocarbamide) in 500 ml.
59. **Zinc nitrate, $Zn(NO_3)_2$, 0.5 *M*;** 150 g. of $Zn(NO_3)_2 \cdot 6\,H_2O$ per liter.
60. **Zinc uranyl acetate (sodium reagent).** Prepare two solutions: (*a*) 100 g. of uranyl acetate, $UO_2(C_2H_3O_2)_2 \cdot 2\,H_2O$, 18 ml. of 99% acetic acid, and 500 ml. of water, and (*b*) 300 g. of zinc acetate ($Zn(C_2H_3O_2)_2 \cdot 3\,H_2O$), 10 ml. of 99% acetic acid and 500 ml. of water; warm to dissolve and then mix the two solutions. Filter if necessary. Keep in pyrex glass vessels.

Solids

Silver carbonate, Ag_2CO_3.
Iodine, I_2.
Antimony sulfide, Sb_2S_3.

IV. MATERIALS FOR ANALYSIS

Certain limitations with respect to materials given for analysis by the methods of this book should be recognized.

1. Alloys should be such as are attacked reasonably rapidly by acids. Silver should not be present along with antimony or tin, but lead and mercury may be present.

2. Small amounts of certain of the metallic elements may be missed, for example, small amounts of tin, zinc, magnesium and the alkali metals.

3. In general, organic matter, including oxalates and tartrates, should be absent, and also fluorides, silicates, cyanides, ferrocyanides and ferricyanides should not be present in materials that do not require carbonate fusion.

4. If materials for analysis are given in solution, either the approximate concentration of the solution in total solids or directions as to the volume to be taken for a sample should be given.

5. Materials for anion analysis should not contain both oxidizing and reducing ions (see page 72), except such combinations as arsenate and arsenite, or ferricyanide and ferrocyanide; in other words, combinations of two ions that cannot react with each other. The combination of nitrate and nitrite should not be given.

6. Silver compounds should not be present along with halides, and silver halides should not be included in materials for analysis.

7. The cations and anions included should be restricted to the lists on pages 21 and 72.

8. For the preparation of materials for anion analysis (Exercise 14), sodium and potassium salts are satisfactory.

9. In the preparation of salt mixtures for analysis, certain combinations must be avoided. These can best be learned by experience. In general, deliquescent salts should not be mixed with other salts containing much water of crystallization. Salts that would react with each other or with water to form a volatile compound should not be mixed. Whether or not salts that react to form a precipitate are to be mixed, may be left to the judgment of the instructor, with the limitation of item 6 above.

INDEX